DEVELOPMENT OF NOVEL POLYMERIC CROSS-LINKERS FOR WRINKLE-RESISTANT FINISHING OF CELLULOSIC FABRICS

TSOI WING YU IRIS

Ph.D

The Hong Kong Polytechnic University
2016

The Hong Kong Polytechnic University
Institute of Textiles and Clothing

Development of Novel Polymeric Cross-linkers for Wrinkle-resistant Finishing of Cellulosic Fabrics

TSOI Wing Yu Iris

A thesis submitted in partial fulfilment of the requirements for
the degree of Doctor of Philosophy

June 2015

CERTIFICATE OF ORIGINALITY

I hereby declare that this thesis is my own work and that, to the best of my knowledge and belief, it reproduces no material previously published or written, nor material that has been accepted for the award of any other degree or diploma, except where due acknowledgement has been made in the text.

TSOI WING YU IRIS

Abstract

The present work lays down some new ways, by which promising cellulose reactive cross-linkers can be developed based on utilising naturally available acids as the building blocks. Citric acid (CA) and malic acid (MA) have been focused. Two approaches, i.e., azeotropic polycondensation and bulk polycondensation, have been adopted and studied to synthesise the corresponding well-defined polymers from them with a series of co-reactants such as multifunctional alcohols, poly(ethylene glycol)s (PEG)s, and itaconic acid (IA). It was found that when the multifunctional alcohols were used, dendritic polymers with different numbers of polyacid arm segments can sucessfully be produced in reasonably high yields. In case of (PEG)s, polyacids with linear-dendritic structures were yielded. The way involving IA can enable the formation of linear polyacids with additional functionality. FTIR and NMR analyses have been conducted to verify the polymer composition and architecture.

A comprehensive wrinkle-resistant finishing study was carried out to evaluate the cross-linking performance of the newly developed polymers comprised of various compositions and architectures. The resultant performance of dendritic polyacids with various numbers of reactive CA and MA moieties were evaluated in term of wrinkle recovery performance of the modified cotton substrates. Meanwhile, linear-dendritic structure was capable of furnishing strength retention of the modified substrate. In particular, poly(malic acid) capped with IA (PMA-IA) has a strong cross-linking effect to cellulose chains. Upon impregnation of PMA-IA, cellulosic fabric improves substantially in wrinkle-recovery performance. The vinyl moiety on the polymer is polymerisable, which can give hand to building higher network density under a condition with potassium persulfate ($K_2S_2O_8$). The combined effect proved to promote better wrinkle-resistant performance along with an improved retention in mechanical properties for the cross-linked system. The effects of finishing variables such as polymer concentration, catalyst concentration, pH, and treatment temperature and time have been deeply studied in connection to the FTIR-ATR analysis on the modified materials. The findings in this study could help alleviate the drawbacks of conventional wrinkle-resistant treatment used in the industry.

Publication

Conference presentation

TSOI I.W.Y., Cheuk, K.K.L., Xin, J.H., Yao, Z., Modification of cellulosic fabric using a novel malic-acid based polymeric cross-linker, The 2nd International Conference on Bio-Based Polymers and Composites, Visegrád, Hungary, August 24-28, 2014, 233

Acknowledgements

I would like to express my deepest gratitude to my chief supervisor, Dr. K. K. L. Cheuk, Assistant Professor of Institute of Textiles & Clothing at The Hong Kong Polytechnic University, for providing the opportunity of undertaking this project, and for his constant guidance, encouragement, and invaluable advice throughout the study.

I would like to express my sincere thanks to my co-supervisors, Prof. J. H. Xin, Professor of Institute of Textiles & Clothing at The Hong Kong Polytechnic University, and Dr. Z. Yao, Associate Professor of Department of Applied Biology & Chemical Technology at The Hong Kong Polytechnic University, for providing his invaluable advice and consecutive support in carrying out this research.

My thanks are also extended to all the staff members and technicians in the textile laboratories of Institute of Textiles and Clothing at the Hong Kong Polytechnic University. I would also like to express my thanks to the members in the Open Laboratory of Chirotechnology of Department of Applied Biology & Chemical Technology at The Hong Kong Polytechnic University for the technical support in Nuclear Magnetic Resonance Spectroscopy.

Last but not least, special thanks are dedicated to my parents and family for giving their encouragement and spiritual support during this endeavour.

Table of Contents

Page

Chapter One –

Chapter Two –

Chapter Seven –
Conclusion and Recommendation 226

List of Figures

List of Tables

List of Abbreviations

f	Branching factor / no. of branches of polyols
Ft	Breaking force of tested fabric determined based on ASTM D5034-2009
BTCA	1,2,3,4-butanetetracarboxylic acid
CA	Citric acid
A_{1720}	Peak height of absorbance at carbonyls at 1720 cm^{-1} in FTIR-ATR
A_{1585}	Peak height of absorbance at carboxylates at 1585 cm^{-1} in FTIR-ATR
DMSO-d_6	Deuterated dimethyl sulfoxide
D	Dipentaerythritol
FTIR-ATR	Fourier Transform Infrared Spectroscopy in attenuated total internal reflectance mode
G	Glycerol
GPC	Gel Permeation Chromatography
IA	Itaconic acid
MA	D,L-malic acid
NMR	Nuclear Magnetic Resonance
MWCO	Molecular weight cut off
M_n	Number average molecular weight
n	Number of repeating unit of polyethylene glycols
H_3PO_4	*Ortho*- phosphoric acid
P	Pentaerythritol
PCA	Polycitric acid-based polymer
PCA-T	Polycitric acid-1,1,1-tris(hydroxymethyl)ethane polymer
PCA-P	Polycitric acid-pentaerythritol dendritic polymer
PCA-D	Polycitric -dipentaerythritol dendritic polymer
PCA-PEG	Polycitric acid-polyethylene glycol linear-dendritic polymer
PCA-PEG2	Polycitric acid-polyethylene glycol 200 linear-dendritic polymer
PCA-PEG6	Polycitric acid-polyethylene glycol 600 linear-dendritic polymer
PCA-PEG10	Polycitric acid-polyethylene glycol 1000 linear-dendritic polymer
PDI	Polydispersity index

PEG	Polyethylene glycol
AB_m	Polyfunctional monomer with two types of different functional groups
B_f	Polyfunctional core molecule
PMA	Polymalic acid-based polymer
PMA-G	Polymalic acid-glycerol dendritic polymer
PMA-IA	Polymalic acid- itaconic acid polymer
PMA-T	Polymalic acid-1,1,1-tris(hydroxymethyl)ethane dendritic polymer
PMA-P	Polymalic acid-pentaerythritol dendritic polymer
PMA-D	Polymalic acid-dipentaerythritol dendritic polymer
PS	Polystyrene standard
$K_2S_2O_8$	Potassium persulfate
δ	Chemical shift in NMR
NaOH	Sodium hydroxide
$NaH_2PO_2 \cdot H_2O$	Sodium hypophosphite monohydrate
ν	Vibrational stretching of bonding in FTIR
Fb	Tearing force of tested fabric determined based on ASTM D1424-2009
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TMS	Tetramethylsilane
T	1,1,1-tris(hydroxymethyl)ethane
M_w	Weight average molecular weight
WRA	Wrinkle recovery angle of tested fabric determined based on AATCC 66-2008
WI	Whiteness Index of tested fabric determined based on AATCC 110-2005
YI	Yellowness Index of tested fabric determined based on ASTM E313-2010

Chapter One –

General Introduction

1.1 Introduction

The aim of this study is to develop novel cross-linkers for cotton cellulose based on polymer chemistry. This chapter begins with the research background of the issue of concern. Objectives, significance and values, and research methodology are then addressed. Finally, this chapter is rounded up with the organisation of the thesis.

1.2 Research Background

1.2.1 Wrinkle-resistant Finishing in Textile Industry

Wrinkle-resistant finishing plays an essential role in the field of textile processing, especially for cellulosic materials. However, most of the prior technologies developed to date suffer from various key deficiencies included severe loss in strength, release of toxic substances and of exceedingly high cost for commercialisation [1]–[13]. Considerable interests are aroused, focused on non-toxic remedies in the last few decades. Elimination of incorporating carcinogenic formaldehyde, formaldehyde derivatives and other short chain aldehydes in the textile production and manufacturing processes is indispensable in the twenty-first century [4], [14]–[24]. In this vein, using naturally available organic acids as alternatives cellulosic cross-linkers are desirable [11],

[25], [26]**.** However, some drawbacks of utilising polycarboxylic acids as cellulose cross-linkers have not yet been solved. Nevertheless, fabric discoloration and fabric strength deterioration are always the associated issues of concern upon such finishing treatment.

Albeit synthetic fibres are one of the easy care textile materials starting from the mid-twentieth century, the dwindling of finite petrochemical resources leads to the resurgence of the utility of naturally available textile fibres [27]–[30]**.** The reviving demand of natural fibres, especially the use of cellulose expedites in recent decades. Cotton is one of the candidates. With respect to the inherently attractive properties of cotton, such as soft hand, comfort, and durability to abrasion; a wide range of wearing apparels and home fashion made of cotton are popular. However, cotton textiles require intensive care as they are prone to shrinkage and wrinkling, especially after laundry. Cellulose cross-linking remains as an important chemical finishing process to produce easy-care cotton products. Easy-care cotton products hitherto are still of great interest giving researchers and technologists continual impetus to look for better cellulose cross-linkers.

1.2.2 Alternative Polymeric Cross-linking Agents

The exponential growth of interest in macromolecules among both scientific and industrial communities has engendered remarkable development since 1920s. After decades of extensive studies of polymers, scientists and technologists shift the interest in polymer chemistry from pursuing material strength to functionality in recent years. Highly functionalised macromolecules are of great interest. This family of polymers is thriving and prosperous with respect to their unique properties over the conventional linear polymers. Dendritic polymers not only possess low processing temperature and low viscosity, but also allow processability of such highly functionalised materials [31]–[37]. Dendritic macromolecules comprised of successive branching are classified into dendrimers and hyperbranched polymers. Preparations of hyperbranched polymers are much more efficient and cost-effective compared to dendrimer syntheses. This arouses tremendous interest to pursue this particular subclass of dendritic polymers for industrial applications. Their chemical flexibility permits tailor-made performance catering to an ever-expanding multitude of applications. Today, polymer science paradigm transits from theoretical-based to application-driven research. The application of this class of dendritic macromolecules in textile industry is emerging [38]–[46]. Hitherto, limited researches of developing polymeric cross-linkers have been devoted for wrinkle-resistant purpose.

The approach of utilising carboxyl-functionalised dendritic polymer as cellulose cross-linkers furnishing cotton with winkle-resistant property is promising. In recent years, polymer scientists pay more attention of building hyperbranched polymers via polycondensation of AB_m monomers with B_f as the core or branch point. It is notable that various available A_mB monomers present in nature could be utilised. One of the purposes of this study is to explore the development of novel polymers, included synthesis and characterisation, utilising natural hydroxylcarboxylic acids, A_3B and A_2B, and polyols, B_f, as cross-linkers for cotton cellulose. Polymers of various molecular architectures, molecular weights and functionalities are examined accordingly aiming of alleviating the drawbacks of conventional finishing systems. Another purpose is to investigate the cross-linking behaviour of the newly developed with cotton cellulose and the effectiveness in terms of wrinkle-resistant performance of the modified cotton fabrics.

1.3 Objectives

1. To synthesise novel wrinkle-resistant finishing agents utilising naturally available monomers based on the chemistry of polymers.
2. To study the finishing process of cotton substrates with the proposed polymeric agents.
3. To characterise the synthesised polymers and modified fabric substrates by means of advanced analytical characterisation techniques and standard assessment tests.
4. To study the effects of the novel polymers on modified fabric substrates with respect to wrinkle-resistant performance and the alteration of other fabric properties.
5. To study the wrinkle-resistant performance of modified substrates in relation to structural characteristics of novel polymers.

1.4 Significance and Values of Research

Although a considerable number of studies have been devoted for finding robust solutions to the issue of concern, novel approaches based on polymers are rarely reported. This study will afford important insights into the key impacts of the new approach as well as the understanding of complex processes and mechanisms involved. The findings and new knowledge generated are of great scientific and technological values that would help open up a new platform for better improvement on the relevant finishing treatment.

Despite the great interest and extensive research in this stream of finishing, hitherto only limited attention devoted to exploitation of polymer chemistry as an approach to improve wrinkle-resistant performance of textile materials. In this project, a range of novel water-soluble polymers was synthesised and sequentially applied in the modification of cotton substrates. The current study of this project would look at another aspect compared to ones before, which lies in the use of a special kind of macromolecules as the core technology. The approach allows several remarkable advantages such as 1) a vast number of functional groups per molecules promoting reactivity; 2) relatively low melting point and 3) solution viscosity allowing processability**.**

This would be the cardinal attempt to synthesise low molecular weight polymeric wrinkle-resistant finishing agents. In addition, this is the attempt to look into and reveal the effectiveness of this class of macromolecules for the purpose of wrinkle-resistant finishing on textile substrates. It is believed that this pioneer work would afford a valuable template which helps expanding the scope of using such polymeric compounds in this field application.

1.5 Research Methodology

Development of the novel polymeric cross-linkers for cotton cellulose was based on azeotropic polycondensation and bulk polycondensation approaches. The newly developed cross-linkers were characterised with advanced analytical techniques such as Fourier Transform Infrared Spectroscopy (FTIR), Nuclear Magnetic Resonance Spectroscopy (NMR), Gel Permeation Chromatography (GPC) and Thermogravimetric analysis (TGA).

Sequentially, newly developed polymeric cross-linkers were subjected to wrinkle-resistant finishing study. Semi-bleached cotton fabrics were used as the substrate. Cotton fabrics were impregnated with the aqueous finishing bathes comprised of selected cross-linker via conventional pad-dry-cure method. Formation of ester cross-links on the modified cotton fabrics was revealed by Fourier Transform Infrared Spectroscopy coupled with a universal attenuated total internal reflectance sampler (FTIR-ATR). Wrinkle-resistant performance and other fabric properties of the modified cotton fabrics were evaluated based on AATCC and ASTM assessment methods.

1.6 Organisation of thesis

The thesis consists of seven chapters which are outline as follows.

Chapter 1 introduces the general background, objectives, methodology and outline of this study.

Chapter 2 is a comprehensive review comprised of literatures included problems and deficiencies of the present wrinkle-resistant finishing in the industry, and hence the development of polymer chemistry in relation to the finishing, and as well as the application of polymeric compounds as cellulose cross-linkers.

Chapter 3 presents the development of series of dendritic polymeric cross-linkers with the use of citric acid and various branched polyols. The sequential application of the newly developed cross-linkers for the wrinkle-resistant finishing study of cotton fabrics was explored and evaluated.

Chapter 4 explores the attempt to develop linear-dendritic polymeric cross-linkers with the use of citric acid and various polymeric glycols. The sequential application the newly developed cross-linkers for the wrinkle-resistant finishing study of cotton fabrics were explored and evaluated.

Chapter 5 illustrates the attempt to develop series of dendritic polymeric cross-linkers with the use of malic acid and various branched polyols. Sequentially, this chapter describes the application of the newly developed cross-linkers for wrinkle-resistant purpose.

Chapter 6 explores the incorporation and utility of the vinyl group in the polymalic acid cross-linkers. The approach for the development and application of the polymeric cross-linkers is demonstrated in this chapter.

Chapter 7 states a general conclusion of the major results and findings achieved the present project. Recommendations for further study on the associated deficiencies and limitations in the present work are also proposed in this chapter.

1.7 Bibliography

[1] B. A. K. Andrews, "Wrinkle-resistant cotton and formaldehyde release," *Colourage*, vol. 41, no. 10, pp. 87–93, 1995.

[2] T. F. Cooke and H. D. Weigmann, "The chemistry of formaldehyde release from durable press fabrics," *Text. Chem. Color*., vol. 14, no. 5, pp. 100/25–106/31, 1982.

[3] T. F. Cooke and H. D. Weigmann, "The chemistry of formaldehyde release from durable press fabrics-part 2," *Text. Chem. Color*., vol. 14, no. 6, pp. 136/33–144/41, 1982.

[4] A. C. De Groot and H. I. Maibach, "Does allergic contact dermatitis from formaldehyde in clothes treated with durable-press chemical finishes exist in the USA?," *Contact Dermatitis*, vol. 62, pp. 127–136, 2010.

[5] S. Varadarajan and N. Bhattacharyya, "Eco-textiles regulations, labels, processing, and testing," 1996.

[6] B. A. K. Andrews and B. J. Collier, "Finishing additives in treatments of cotton fabrics for durable press with polycarboxylic acids," *Ind. Eng. Chem. Res*., vol. 31, no. 8, pp. 1981–1984, 1992.

[7] C. E. Morris, N. M. Morris, and B. J. Trask-morrell, “Interaction of meso-1,2,3,4-butanetetracarboxylic acid with phosphorus-containing catalysts for esterification cross-linking of cellulose,” *Ind. Eng. Chem. Res.*, vol. 35, no. 3, pp. 950–953, 1996.

[8] C. M. Welch, “Tetracarboxylic acids as formaldehyde-free durable press finishing agents,” *Text. Res. J.*, vol. 58, no. 8, pp. 480–486, 1988.

[9] C. M. Welch and B. A. K. Andrews, “Ester crosslinks: a route to high performance non-formaldehyde finishing of cotton,” *Text. Chem. Color.*, vol. 21, no. 2, pp. 13–17, 1989.

[10] C. M. Welch and G. J. Peters, “Mixed polycarboxylic acids and mixed catalyst in formaldehyde-free durable press finishing,” *Text. Chem. Color.*, vol. 29, no. 3, pp. 22–27, 1997.

[11] C. Q. Yang, X. Wang, and I.-S. Kang, “Ester crosslinking of cotton fabric by polymeric carboxylic acids and citric acid,” *Text. Res. J.*, vol. 67, no. 5, pp. 334–342, 1997.

[12] C. Q. Yang, X. Wang, and Y. Lu, “Infrared spectroscopy studies of cyclic anhydrides as intermediates for ester crosslinking of cotton cellulose by polycarboxylic acids. IV. In situ free radical copolymerization of maleic acid and itaconic acid on cotton,” *J. Appl. Polym. Sci.*, vol. 75, no. 2, pp. 327–336, Jan. 2000.

[13] C. Q. Yang and Y. Lu, “In-situ polymerization of maleic acid and itaconic acid on cotton: MALDI/TOF mass spectroscopy and light-scattering study,” *Text. Res. J.*, vol. 70, no. 4, pp. 359–362, 2000.

[14] K. L. Hatch and H. I. Maibach, “Textile dermatitis: an update (I) Resins, additives and fibers,” *Contact Dermatitis*, vol. 32, pp. 319–326, 1995.

[15] IARC, *Formaldehyde, 2-butoxyethanol and 1-tert-butoxypropan-2-ol*. Lyon, France: International Agency for Research on Cancer, 2006.

[16] A. J. Scheman, P. A. Carroll, K. H. Brown, and A. H. Osburn, “Formaldehyde-related textile allergy: an update,” *Contact Dermatitis*, vol. 38, no. 6, pp. 332–336, 1998.

[17] C. Bosetti, J. K. McLaughlin, R. E. Tarone, E. Pira, and C. La Vecchia, “Formaldehyde and cancer risk: A quantitative review of cohort studies through 2006,” *Ann. Oncol.*, vol. 19, pp. 29–43, 2008.

[18] M. Hauptmann, P. A. Stewart, J. H. Lubin, L. E. Beane Freeman, R. W. Hornung, R. F. Herrick, R. N. Hoover, J. F. Fraumeni, A. Blair, and R. B. Hayes, “Mortality from lymphohematopoietic malignancies and brain cancer among embalmers exposed to formaldehyde,” *J. Natl. Cancer Inst.*, vol. 101, no. 24, pp. 1696–1708, 2009.

[19] M. Hauptmann, J. H. Lubin, P. A. Stewart, R. B. Hayes, and A. Blair, “Mortality from solid cancers among workers in formaldehyde industries,” *Am. J. Epidemiol*., vol. 159, no. 12, pp. 1117–1130, 2004.

[20] M. Hauptmann, J. H. Lubin, P. A. Stewart, R. B. Hayes, and A. Blair, “Mortality from lymphohematopoietic malignancies among workers in formaldehyde industries,” *J. Natl. Cancer Inst.,* vol. 95, no. 21, pp. 1615–1623, 2003.

[21] A. Wilson and J. Mowbray, *Eco-textile labelling-a guide for manufacturers, retailers and brands*. West Yorkshire, UK: Mowbray Communications Ltd., 2008.

[22] NICNAS, “Priority Existing Chemical Assessment Report No. 28-Formaldehyde,” Sydney, Australia, 2006.

[23] NICNAS, “Formaldehyde in clothing and textiles factsheet,” Australian National Industrial Chemicals Notification and Assessment Scheme, 2013. [Online]. Available: http://www.nicnas.gov.au/chemical-information/information-sheets/existing-chemical-info-sheets/formaldehyde-in-clothing-and-textiles-factsheet. [Accessed: 24-Nov-2013].

[24] EPA, “Technical Support Document : Printing, Coating, and Dyeing of Fabrics and Other Textiles Proposed NESHAP (Publication No. EPA 453/R-02-010),” North Carolina, 2002.

[25] B. A. K. Andrews, E. J. Blanchard, and R. M. Reinhardt, “Fabric whiteness retention in durable press finishing with citric acid,” *Text. Chem. Color*., vol. 25, no. 3, pp. 52–54, 1993.

[26] B.-H. Kim, J. Jang, and S.-W. Ko, “Durable press finish of cotton fabric using malic acid as a crosslinker,” *Fibers Polym*., vol. 1, no. 2, pp. 116–121, 2000.

[27] M. Hoel and S. Kverndokk, “Depletion of fossil fuels and the impacts of global warming,” *Resour. Energy Econ*., vol. 18, no. 2, pp. 115–136, Jun. 1996.

[28] D. Nabi Saheb and J. P. Jog, “Natural fiber polymer composites: a review,” *Adv. Polym. Technol.,* vol. 18, no. 4, pp. 351–363, 1999.

[29] S. Shafiee and E. Topal, “When will fossil fuel reserves be diminished?,” *Energy Policy*, vol. 37, pp. 181–189, 2009.

[30] P. J. Wakelyn, “The evolution of durable press and flame retardant cotton,” *American Chemical Society National Historic Chemical Landmarks*. Cotton Products, 2004. [Online]. Available: http://portal.acs.org/portal/PublicWebSite/education/whatischemistry/landmarks/cottonproducts/index.htm. [Accessed: 01-Nov-2014].

[31] C. Gao and D. Yan, “Hyperbranched polymers: from synthesis to applications,” *Prog. Polym. Sci.*, vol. 29, pp. 183–275, 2004.

[32] B. Helms and E. W. Meijer, “Dendrimers at work,” *Sci. New Ser*., vol. 313, no. 5789, pp. 929–930, 2006.

[33] Y. H. Kim, “Hyperbranched polymers 10 years after,” *J. Polym. Sci. Part A Polym. Chem*., vol. 96, pp. 1685–1698, 1998.

[34] B. I. Voit, “Hyperbranched polymers: a chance and a challenge,” *Comptes Rendus Chim*., vol. 6, no. 8–10, pp. 821–832, Aug. 2003.

[35] K. Inoue, “Functional dendrimers, hyperbranched and star polymers,” *Prog. Polym. Sci.,* vol. 25, pp. 453–571, 2000.

[36] M. Jikei and M. Kakimoto, “Hyperbranched polymers: a promising new class of materials,” *Prog. Polym. Sci.,* vol. 26, pp. 1233–1285, 2001.

[37] X. Zhu, Y. Zhou, and D. Yan, “Influence of branching architecture on polymer properties,” in *Hyperbranched Polymers: Synthesis, Properties, and Applications*, D. Yan, C. Gao, and H. Frey, Eds. New Jersey: John Wiley & Sons, Inc., 2011, pp. 317–332.

[38] F. Zhang, X. Wu, Y. Chen, and H. Lin, “Application of silver nanoparticles to cotton fabric as an antibacterial textile finish,” *Fibers Polym*., vol. 10, no. 4, pp. 496–501, 2009.

[39] F. Zhang, D. Zhang, Y. Chen, and H. Lin, “The antimicrobial activity of the cotton fabric grafted with an amino-terminated hyperbranched polymer,” *Cellulose*, vol. 16, pp. 281–288, 2009.

[40] D. Zhang, L. Chen, D. Fang, Gg. W. Toh, X. Yue, Y. Chen, and H. Lin, “In situ generation and deposition of nano-ZnO on cotton fabric by hyperbranched polymer for its functional finishing,” *Text. Res. J.,* 2013. DOI: 10.1177/0040517512474362

[41] N. A. Ibrahim, H. M. Fahmy, M. A. Rehim, S. S. Sharaf, and M. H. Abo-Shosha, “Finishing of cotton fabrics with hyperbranched poly(ester-amine) to enhance their antibacterial properties and UV protection,” *Polym. Plast. Technol. Eng*., vol. 49, no. 13, pp. 1297–1304, 2010.

[42] N. A. Ibrahim, B. M. Eid, and H. El-Batal, “A novel approach for adding smart functionalities to cellulosic fabrics,” *Carbohydr. Polym*., vol. 87, pp. 744–751, 2012.

[43] G. Wang, L. Zhuang, J. Sun, and C.-L. Zheng, “Salt-free dyeing of ramie fabric with an amino-terminated hyperbranched polymer,” *Cellulose*, vol. 21, pp. 3725–3736, 2014.

[44] S. M. Burkinshaw, P. E. Froehling, and M. Mignanelli, “The effect of hyperbranched polymers on the dyeing of polypropylene fibres,” *Dye. Pigment*., vol. 53, pp. 229–235, 2002.

[45] F. Zhang, Y. Chen, H. Lin, and Y. Lu, “Synthesis of an amino-terminated hyperbranched polymer and its application in reactive dyeing on cotton as a salt-free dyeing auxiliary,” *Color. Technol.*, vol. 123, pp. 351–357, 2007.

[46] P. Froehling, “Development of DSM’s hybrane hyperbranched polyesteramides,” *J. Polym. Sci. Part A Polym. Chem*., vol. 42, no. 13, pp. 3110–3115, 2004.

Chapter Two –

Literature Review

2.1 Introduction

This chapter comprised of a comprehensive review of literature focuses on two major aspects of this project. One aspect concerns about the development of the wrinkle-resistant finishing in textile industry. Nature of the textile materials, background, current development and limitations of the finishing system are reviewed. Another aspect is related to the potentials of developing novel polymeric cross-linkers. Background, recent development and applications of carboxyl-functionalised polymers as wrinkle-resistant finishing agents are discussed.

2.2 Background and Current Development of Textile Wrinkle-resistant Finishing

2.2.1 History of Wrinkle-resistant Finishing in Cotton Industry

Tootal Broadhurst Lee Co. Ltd. firstly established and patented wrinkle-resistant cellulosic fabrics using simple urea-formaldehyde resin in 1926 [1]–[3]. Wrinkle-resistant finishing becomes a crucial finishing in textile industry since after. This noteworthy benefit revolutionised our lifestyle towards easy-care clothing. In the gestation period of the wrinkle-resistant finishing, formaldehyde-based N-methylol compounds were adopted as the principal cross-linkers [4]–[11]. However, the adverse effect of liberation of toxic formaldehyde from the textile materials and during production was revealed [12], [13]. Meanwhile, synthetic polyester fibres and polyester/cotton blend fabrics were gaining popularity as the predominant textile materials starting from 1970s. Interest towards this finishing began to decline.

Though synthetic fibres have usurped natural fibres as the dominant textiles materials by the mid twentieth century, the depletion of finite petrochemical resources leads to the resurgence of interest in naturally available materials [14]–[17]**.** Cellulose is one of the most abundant natural materials. Seed hairs of cotton is one of the candidates extensively utilised as textile materials among a wide scope of botanic fibres, for example, jute, kenaf, flax, ramie, sisal, bamboo, and etc. This natural polymer possesses fascinating properties manifested by its distinctive structure. Easy-care cotton products hitherto are still of great interest, especially in apparel industry. Cotton inherently possesses attractive properties, included high moisture absorbance and durability to abrasion, affording cotton as a comfortable apparel material. However, cotton textiles need intensive care as they are prone to shrinkage and wrinkling, especially after laundry. The wrinkle formation of cotton textiles originates from the inherent physicochemical characteristic of cotton cellulose.

2.2.2 Structure and Properties of Cotton Cellulose

Cotton fibre is structurally distinctive. Figure 2-1 illustrates the morphological structure of cotton fibres. Unlike other natural and man-made fibres, cotton is inherently comprised of hollow fibres. With a lumen at the centre of the fibre, air effectively trapped enables warmth retention of garments. Cotton fibre is a flat, twisted ribbon consists of multiple walls. These walls comprise of spiral fibrils hierarchically oriented give convolutions to the fibre. The micro-fibril orientation denotes the mechanical strength of respective cellulosic fibres [18]. For example, cotton fibres are of lower strength with the helix angle larger than that of other bast fibres [19]. In particular, the outer primary wall with criss-cross morphology which facilitates yarn spinning as cotton yarns and threads. Surface convolutions scatter incident light, thus cotton fabric usually exhibits poor lustre.

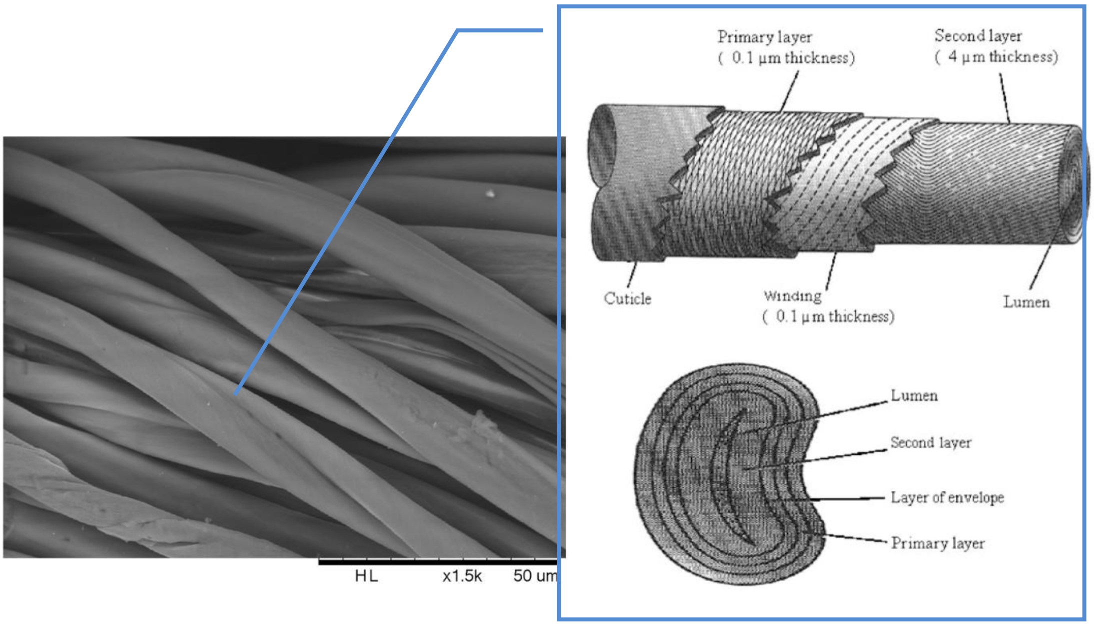


Figure 2-1 Morphology of cotton fibres [20], [21]

Cotton being a botanic fibre is the purest natural form of cellulose of over 90% in content. Cellulose molecule is a linear homo-polysaccharide of D-glucopyranose linked by β-1,4-glycosidic acetal bonds as illustrated in Figure 2-2. This linear biopolymer usually extends from 1000 to 1500 of β-D-glucose units [19]. Linearity enables close proximity between cellulose molecules. Looking into this β-1,4-glucan, individual glucose unit contains three hydroxyls, two secondary hydroxyls (2° OH) at the C2 and the C3 positions and one primary hydroxyl (1° OH) at the C6 position. Extensive intramolecular and intermolecular hydrogen bonding as shown in Figure 2-3 is the prime factor imposing profound effect on the intrinsic properties to cellulose fibres. For native cellulose, intramolecular hydrogen bonding mainly forms in between C3 hydroxyl with oxygen atom in the glucose ring. Another possible intramolecular bonding involves C2 hydroxyls and C6 hydroxyls between the adjacent glucose units. Intermolecularly, C6 hydroxyl forms hydrogen bonding with C3 hydroxyls of glucose on the same plane [22]**.** Such bonding offers high cohesive force between chains and within chains to afford cellulose fibrils and fibres high stiffness and crystallinity. The degree of internal cohesion renders the randomness of molecular arrangement. The superamolecule of cotton cellulose is made up of amorphous and crystalline regions. The randomness controls the accessibility and transport of moisture and external reagents interacting with reactive hydroxyls of cellulose [22]–[25].

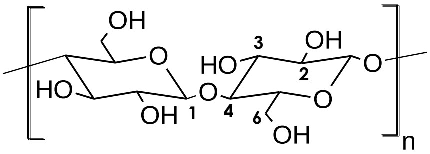


Figure 2-2 Chemical structure of cellulose

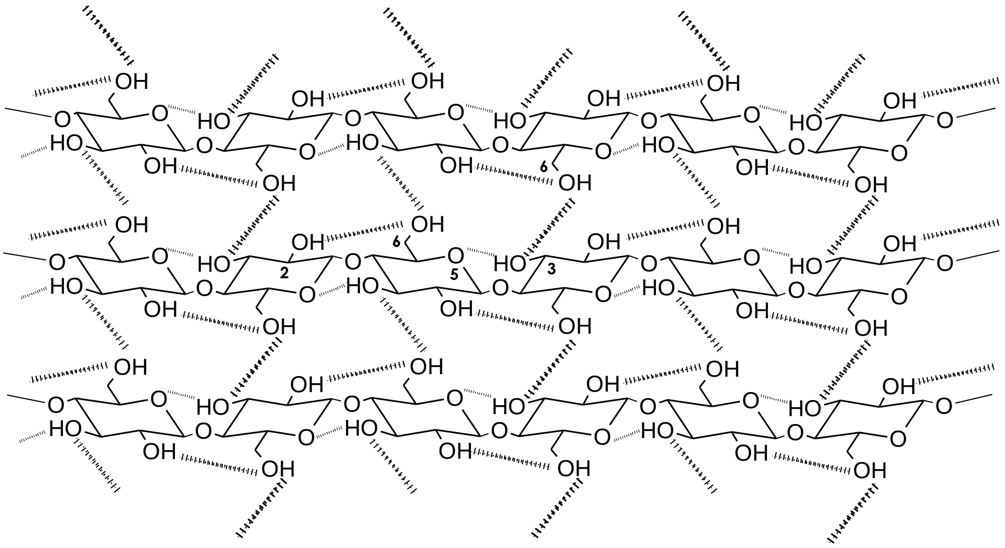


Figure 2-3 Intramolecular and intermolecular hydrogen bonding of native cellulose

2.2.3 Wrinkling of Cellulosic Fabrics

Wrinkle-resistance of fabrics is measured by the ease of resilience upon folding deformation, in terms of speed and completeness of the recovery from deformation. Wrinkling phenomenon of textile materials is a complex result of physicochemical properties of the substrates and diverse factors. Buck & McCord and Gagliardi & Gruntfest have delivered comprehensive discussions about wrinkling of cellulosic textiles materials**.** When folding deformation applied exceeds the elastic limit of a material, wrinkling would be occurred. Considering textile materials, fibre, yarn and fabric characteristics and constructions are the attributes for the formation of wrinkles. Among those attributes, fibre characteristic is the prime element [18], [26]**.**

Cellulose molecule being a linear β-1,4-glucan restricted molecular movement in the fibres elicits high crystallinity. Stiff cotton fibres limit extensibility upon deformation.

Intermolecular interaction between fibres impacts the degree of resilience of the material. β-1,4-glucan is highly functionalised with hydroxyls. Extensive non-permanent hydrogen bonding is weak and easily cleaved upon applying forces. When distortion forces such as stress or strain impose, intermolecular hydrogen bonds break leading to molecular or fibrous chain slippage. Hydrogen bonds reformed on the displaced molecules inhibits recovery of the fabric to its original state. Thus, cotton fabrics inherently possess low resilience and prone to form wrinkles.

Moisture content of textile fibres is another influential factor rendering wrinkles. Moisture essentially acts as the lubricant between fibres and hence promotes extensibility of the fibres. Cotton fibres inherently hydrophilic have prevalent interaction with moisture. Wrinkle resistance of cotton fabrics is principally affected by humidity of the environment. In significance, complementary interaction with water and forces during laundry and sequential drying processes fundamentally impart wrinkles along with daily wear and usage.

Cotton possesses attractive properties engendering it to be the ubiquitous material in the textile field. Its high moisture absorbance, in particular, is important in apparel industry, to endow garment with comfort. Despite cotton textiles need intensive care as they are prone to shrink and wrinkle, especially after laundry; obsession with the use of cotton or other cellulosic fibres as textile commodities never halts. Chemical modification is adapted as the core methodology to alleviate the inherent drawbacks of cellulose while conferring additional functionalities to cellulosic materials. Cellulose, functionalised with extensive primary and secondary hydroxyls, is intrinsically reactive. Reactive hydroxyls afford affinity to interact with wetting agents and reactions with chemical finishing agents. For example, hydroxyls in native cellulose serve as dye sites for reactive dyes imparting dyeability to cotton fibres [27]–[29]. Modified cellulose becomes dyeable with direct dyes [28], [30]. Cotton is an organic material with low resistance to fire and susceptible microbial attack. Scientists constantly focus on chemical modifications of cellulose to accomplish improved functionalities, included flame retardancy [31], [32], anti-microbial activity [33]–[35], water repellence [32], [36], [37], and etc.

Strategies to alleviate wrinkling of cellulosic textile materials are classified into non-crosslinking and cross-linking approaches. Non-crosslinking approach is to relief wrinkling without chemically altered the cellulose. Manipulating fabric and garment construction, mercerisation with caustic soda or application of silicone finishes are some of the methods [38]–[41]. For instance, mercerisation using swelling agents, such as caustic soda or liquid ammonium, alters the lattice structure of cellulose temporarily to improve chain alignment and fibre interaction [19], [24]. Silicone finishing is another non-crosslinking method. Silicone finishes formed around fibres reduce bonding activity of cellulose. Wrinkle formation is inhibited by preventing new hydrogen bonding formed at new positions after stress [42]–[44]. Another approach is to cross-link molecules of cellulose with chemical compounds to inhibit chain slippage.

2.2.4 Fundamentals of Cellulose Cross-linking

Cross-linking approach is dependent on the physicochemical characteristic of the textile fibres [45]. The strategy for chemical modification of cellulose is principally based on the formation of cross-links with hydroxyls to inhibit mobility of cellulose chains and hence reduce wrinkling of cellulosic textile materials. Cross-links not only limit stress-induced chain displacement, but also afford restoring force to recover from deformation. To impregnate the cross-linking agents, the treatment methods include pre-curing and post curing, garment dip treatment, vapour phase treatment, kiss roll technique and spray application. Pad-Dry-Cure is the most common procedures in the treatment [42], [46].

In general, cross-links are formed when cross-linkers react with hydroxyls of cellulose in the curing step under elevated temperature in the finishing treatment. Typical cross-links are ether or ester linkages between chains of cellulose. With the presence of cross-links, chain slippage is inhibited and hence wrinkle-resistance could achieve. On one hand, cross-links help relieve wrinkling of cellulosic textile materials. One the other hand, the cross-links reduce flexibility and extensibility of fibres leading to deterioration in mechanical properties included increased brittleness, loss of tensile strength, tearing strength and abrasion resistance. Incorporation of cross-links is one of the factors contributed to the deterioration in mechanical strength. Finishing environment is another attribute which impinges the strength included pH of the finishing bath, treatment time and temperature, use of catalysts, presence of additives and etc.

Technologists and researchers are endlessly in pursuit of the balance between the wrinkle-resistance performance and physical properties of textile materials.

2.2.5 Formaldehyde based Cellulose Cross-linkers

2.2.5.1 Early Generations of Wrinkle-resistant Finishing

In the early twentieth century, resins of formaldehyde with phenol, urea and melamine were introduced as the wrinkle-resistant finishing agents. The first generation of bi- and tri-functional compounds which were urea-formaldehyde and melamine-formaldehyde pre-condensates, herein laid down the principle strategy for cross-linking cellulose [1]–[3]. Figure 2-4 describes the reaction of reactive resins formed serving as cellulose cross-linkers. These resins consist of the N-methylol functionalities which are highly reactive. These resins are inexpensive and very reactive. However, cross-linked cotton substrates are very stiff and firm in handle while are of high propensity of liberating formaldehyde subsequently.

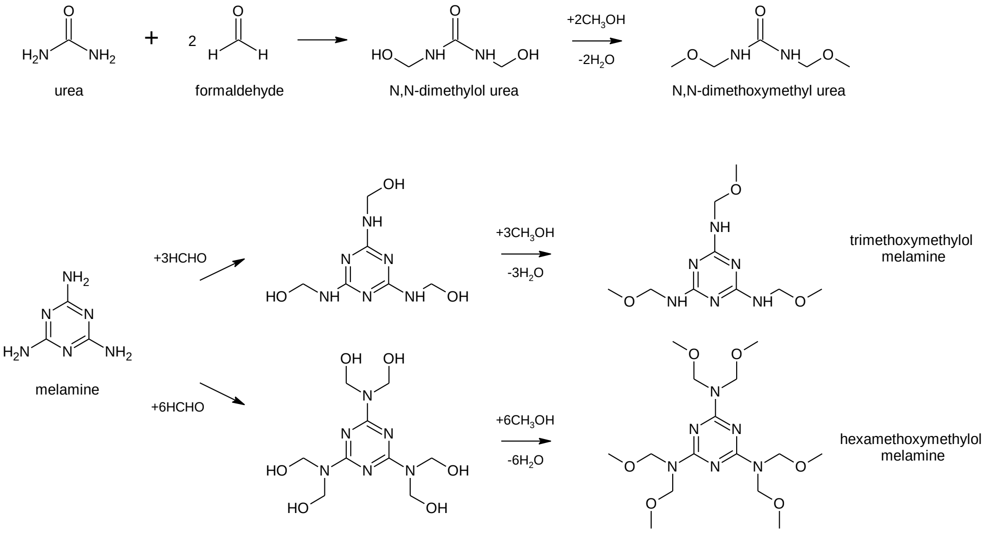


Figure 2-4 Reactions of urea-formaldehyde and melamine-formaldehyde derivatives

With respect to the drawbacks of the previous generation of cross-linkers, dimethylolethylene urea (DMEU) compounds were then introduced in 1947 and began to adopt as the predominant cross-linkers for cellulose in the textile industry. Benerito and her colleagues extensively studied the interaction, kinetics and finishing conditions of DMEU and the derivatives with cotton cellulose [4]–[11]. In particular, N,N'-dimethylol-4,5-dihydroxyethlene urea (DMDHEU) is most successful finishing agent produced by BASF [3], [15], [47]**.** Figure 2-5 illustrates the preparation of DMDHEU. DMDHEU is capable of forming methylene ether bridges effectively with cellulose chains to inhibit cotton wrinkling as illustrated in Figure 2-6.

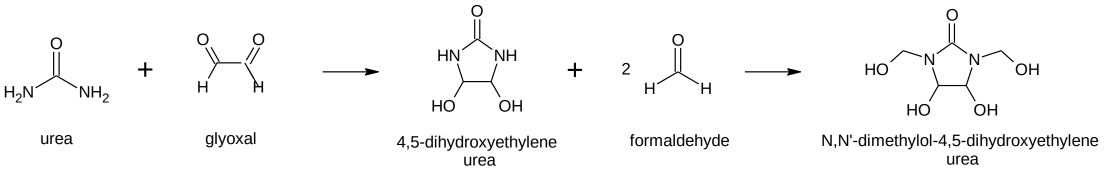


Figure 2-5 Preparation of N,N’-dinethylol-4,5-dihydroxyethylene urea (DMDHEU)

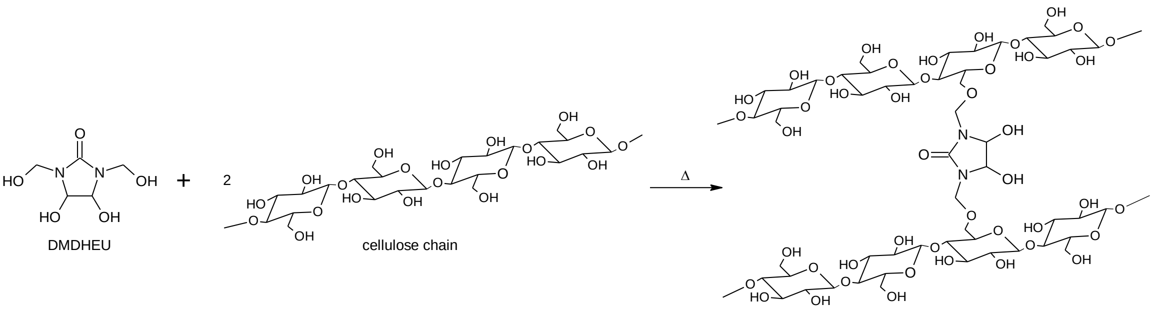


Figure 2-6 Cross-linking of cellulose with DMDHEU

Later generations of N-methylol cross-linkers are less susceptible to liberate formaldehyde with respect to the alkylation and cyclisation [12], [13]. Figure 2-7 shows the equilibrium of released formaldehyde from N-methylol compounds of various chemical structures. Yet, the possibility of releasing toxic formaldehyde still exists. Consumers and the industry have the continuous quest to pursue zero formaldehyde based cross-linkers. The ultimate strategy to tackle the release is to employ formaldehyde free cross-linkers in the finishing. Regarding to the success of DMDHEU, N,N'-Dimethyl-4,5-dihydroxyethylene urea (DMeDHEU) could be prepared without formaldehyde as illustrated in Figure 2-8**.** DMeDHEU is one of the potential substitutes for cellulose cross-linkers. Despite the fact that DMeDHEU retards the liberation of formaldehyde more effectively than DMDMEU regarding to the chemistry of the cross-linkers as shown in the Figure 2-9, the effectiveness of DMeDHEU is only one fourth of that of DMDHEU retarding the industrialisation of DMeDHEU [48].

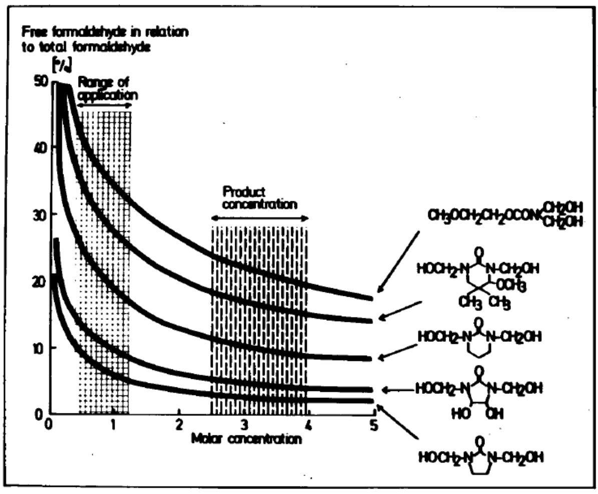


Figure 2-7 Equilibrium of formaldehyde release from various N-methylol cross-linkers [13]

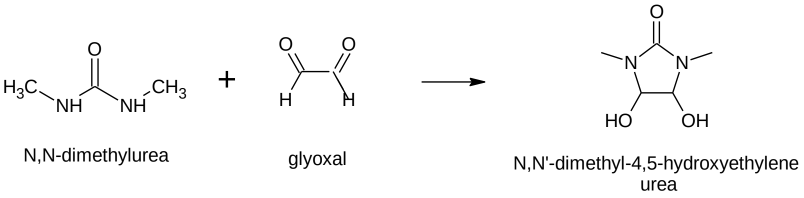


Figure 2-8 Preparation of N,N’-dimethyl-4,5-dihydroxyethylene urea (DMeDHEU)

2.2.5.2 Impacts of Formaldehyde Release

N-methylol compounds are capable of imparting superior wrinkle-resistant performance to cotton substrates. Meanwhile, loss of mechanical strength is still subjected to further research on the cross-linkers [11], [26], [49]–[51]. Another drawback associated is the susceptibility of formaldehyde release driving the industry to look for remedies thereafter [52]–[56]. Since after, the utilisation of formaldehyde-based cross-linkers trims down in the textile industry**.**

The release mechanism was initially revealed in the 1980s. Early generations fo wrinkle-resistant finishing agents are N-methylol or N-alkoxylmethyl compounds. These cross-linkers are susceptible to liberate formaldehyde during finishing process and subsequently from the finished textile materials. Reactions occurred not only involves the desirable cross-linking reaction with cellulose(1), but also undergoes self-condensation (2) and cleavage (3 & 4) of the finishing compounds as presented in Figure 2-9 [12], [13], [57].

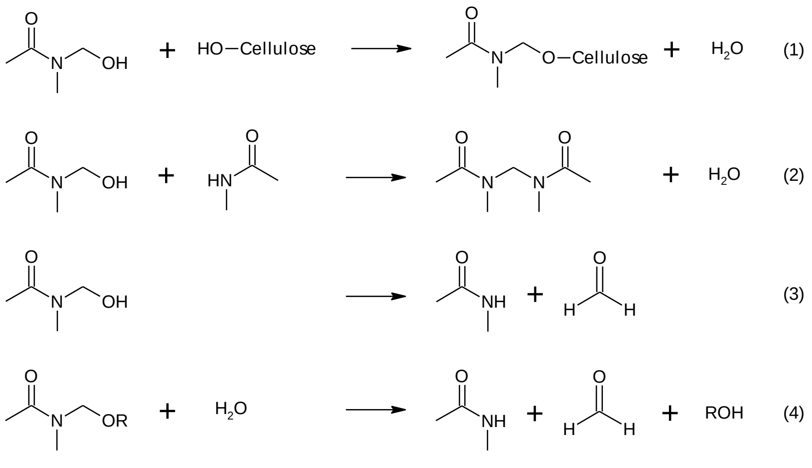


Figure 2-9 Reactions schemes of N-methylol and N-alkoxylmethyl compounds

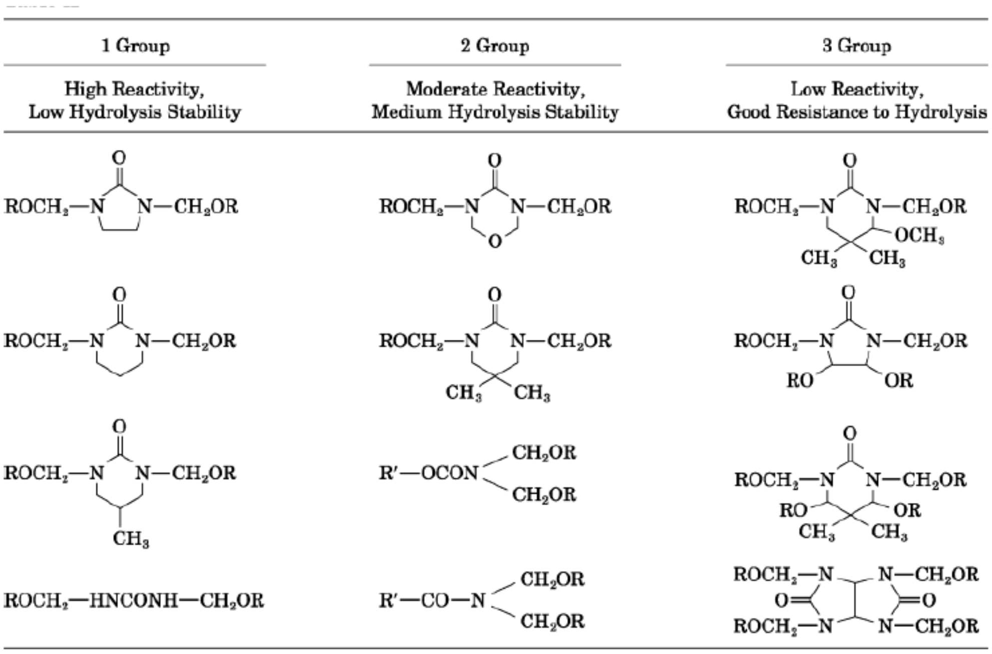
Formaldehyde not only irritates and sensitises skin, but also is categorised as "carcinogenic to humans" (Group 1). International Agency for Research on Cancer (IARC) of World Health Organisation (WHO) concludes the carcinogenicity of formaldehyde based on sufficient evidence and studies [55], [56], [58]–[63]. Worldwide concern over the safety, health and environmental impacts has been raised [64]–[67]. Formaldehyde is a widely used resin in the textile industry. Various studies indicated that exposure to formaldehyde would cause occupational mortality of workers from nasopharyngeal cancer, leukaemia and lymphohematopoietic malignancies [57], [68]–[70]. The adverse effect alarms the industry to trims down the use of formaldehyde based chemicals for textiles. Regulations and legislation of the release of formaldehyde during production processes, and toxic vapour liberated from textile materials.

In 2002, the Intercot conference in Dusseldorf made a clear move in harmonising international standards for organic textile materials as the Global Organic Textile Standard (GOTS). This voluntary standard was firstly developed in 2005 and revised in 2008 covering all processes included production, processing, manufacturing, labelling, transport and distribution of all natural fibres. In particular, GOTS prohibits the use of formaldehyde and other short-chains of aldehydes in all production stages and lowers the acceptable level of released formaldehyde from 20mg/kg to 16mg/kg. Eco-textile standards are gaining more attention in the industry to guarantee safe textile products for consumers and during production processes. In significance, the Öko-Tex Standard 100 is the most widely adopted. It stresses the permissible level of free formaldehyde in textile products. The acceptable limits ranging from 20ppm to 300ppm for various products included infant clothing, clothes in direct skin contact and outer apparel [46], [64], [71]–[73].

To inhibit of subsequent release of formaldehyde from the cross-linked substrates and at the workplace during the finishing treatment, a number of measures has been suggested by researchers and technologists. One approach is to derive various derivatives of N-methylol-based cross-linkers to reduce hydrolysis of the cross-links. Petersen reviewed the detail chemistry of N-methylol derivatives. The susceptibility of formaldehyde release is closely related to the chemical structures of the N-methylol compounds [12], [13], [42]. However, derivatisation of cross-linkers would diminish the reactivity of the cross-linkers and hence the effectiveness of wrinkle-resistant accordingly as illustrate in Table 2-1. Another measure is to add formaldehyde scavengers in the finish bath. Some other tactics to limit the release is to modify the N-methylol compounds with alcohols or polyols [74], [75].

The quest for completely formaldehyde free wrinkle-resistant finishing never halts. Consumer demand on the eco- and organic textile materials galvanizes the industry to pursue superior wrinkle-resistant finishing anew. The ultimate strategy to tackle the release is to employ formaldehyde free and environmentally friendly cross-linkers in the finishing.

Table 2-1 Reactivity and stability of various groups of N-methylol cross-linkers [42]



2.2.6 Non-formaldehyde based Cellulose Cross-linkers

Though formaldehyde based cellulose cross-linkers are capable of imparting brilliant wrinkle-resistance to cellulosic fabrics; severe strength loss, offensive odour and toxicity are unfavourable properties for cotton apparel in the textile industry. Moreover, concerning health hazard and toxicity of formaldehyde release, scientists and technologists shifted to explore the use of non-formaldehyde based cross-linker for cellulose. Glyoxal and some short chain dialdehyde could be considered as cellulose cross-linkers [48], [76]–[78]. Regarding to the success of DMDHEU in the wrinkle-resistant finishing, an analogous formaldehyde-free compound was developed by glyoxal with glutaraldehyde in replacement of urea as shown in Figure 2-10 [6], [46], [48],

[79]. Hereinto, this group of cross-linkers remains with adverse effect on fabric strength and fabric discolouration.

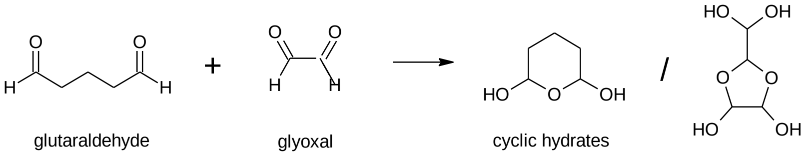


Figure 2-10 Adduct formation of glyoxal with glutaraldehyde

Isocynates, epoxides, divinylsulfones, chlorohydrins and polycarboxylic acids are also doable non-formaldehyde cellulose cross-linkers [9], [34], [76]–[78], [80]–[85]. Notably, polycarboxylic acids have been employed in research with certain degree of success [11], [33], [86]–[120]. Another approach is to create ionic cross-links rather than covalent linkages. Ionic celluloses are initially produced via reactions with a variety of reagents, anionisation reagents and cationisation reagents. Ionic celluloses are then capable of absorbing polyelectrolyte to form ionic cross-links [23], [121]–[123].

2.2.6.1 Utility of Polycarboxylic Acids as Cellulose Cross-linkers

The effectiveness of non-formaldehyde cross-linking utilising polycarboxylic acids as cellulose cross-linkers is prominent [81], [85]**.** Polycarboxylic acids form ester cross-links between cellulose chains to impart wrinkle-resistance to cellulosic textile materials. The use of polycarboxylic acid was firstly documented by Rowland [106]**.** A wide scope of polycarboxylic acids has been investigated. In 1988, meso-1,2,3,4-butanetetracarboxylic acid (BTCA) was introduced to cotton research and well documented by Welch [100], [101]. Among the acid cross-linkers, BTCA is capable of furnishing cotton and other cellulosic textile materials with the most brilliant wrinkle-resistance and initiates extensive studies afterwards [97], [99], [111], [124]–[128].

Detailed study of cross-linking mechanism of BTCA lays the milestone of utilising polycarboxylic acid as the non-formaldehyde based cross-linkers for cellulosic textile materials [100], [101], [125], [127]–[131]. Yang's group extensively studied the cross-linking mechanism of polycarboxylic acids with cellulose. An acid cross-linker undergoes intramolecular dehydration to form reactive cyclic anhydride as the intermediate prior to reacting with cellulose hydroxyls. Possession of at least three carboxyls in an acid cross-linker is the prerequisite to form the reactive intermediate and hence achieve effective cross-linking.

Formation of diester bridges between cellulose chains is crucial to impart wrinkle-resistance to cellulosic textile materials. Reaction mechanism of BTCA with cellulose is illustrated in Figure 2-11 as the typical example. Cellulose esterification involves two steps. Firstly, two hydroxyls of polycarboxylic acid react to form a 5 or 6 member cyclic anhydride. Sequentially, the anhydride intermediate interacts with cellulose hydroxyls to form an ester. Esterification of cellulose hydroxyls with polycarboxylic acid is essentially catalysed by sodium salts of phosphoric acid, such as sodium hypophosphite (NaH_2PO_2), monosodium phosphate (NaH_2PO_4), disodium phosphate (Na_2HPO_4) and trisodium phosphate (Na_3PO_4). NaH_2PO_2 is found to be the most effective one [99], [101], [106], [124], [125], [132]–[137]. NaH_2PO_2 facilitates carboxyls to form of the cyclic anhydride intermediate reducing acid-catalysed depolymerisation of cotton cellulose [98], [100]. Utilising NaH_2PO_2 for cellulose cross-linking not only reduces curing temperature, but also assists strength retention and whiteness retention.

BTCA is an outstanding cellulose cross-linker. However, high capital cost and severe strength loss preclude the commercialisation of BTCA as a wrinkle-resistant finishing agent in the industry [104], [137]. Yang's group has conducted a comprehensive study on various kinds of polycarboxylic acids and hydroxylcarboxylic acids for cross-linking cellulosic textile materials [88]. To reduce the production cost for the manufacturing of easy-care cellulosic textile materials, technologists shift their investigations to natural alternatives included, **citric acid (CA), malic acid (MA)** and **tartaric acid** [98], [112], [120], [138], [139]. These natural acids are economical to be utilised as industrial finishing agents.

CA is one of the most extensively studied natural polycarboxylic acids [88], [102], [119], [138], [139]. CA with 3 carboxyl groups is a promising cellulose cross-linker. CA is not only inexpensive but also non-toxic. However, fabrics modified with CA always suffer from intense yellowing. CA consisted of tertiary hydroxyl is susceptible to undergo intramolecular dehydration. The formation of aconitic acid and other unsaturated compounds from CA under elevated temperatures imparting yellowing to the substrate materials [120], [139]–[143]. Figure 2-12 illustrates the reactions occurred during the curing process. Fabric yellowing is the biggest obstacle of utilising CA as the cellulose cross-linkers in wrinkle-resistant finishing. Contributions of researches are devoted to mitigate fabric discoloration [87], [120], [140], [144], [145].

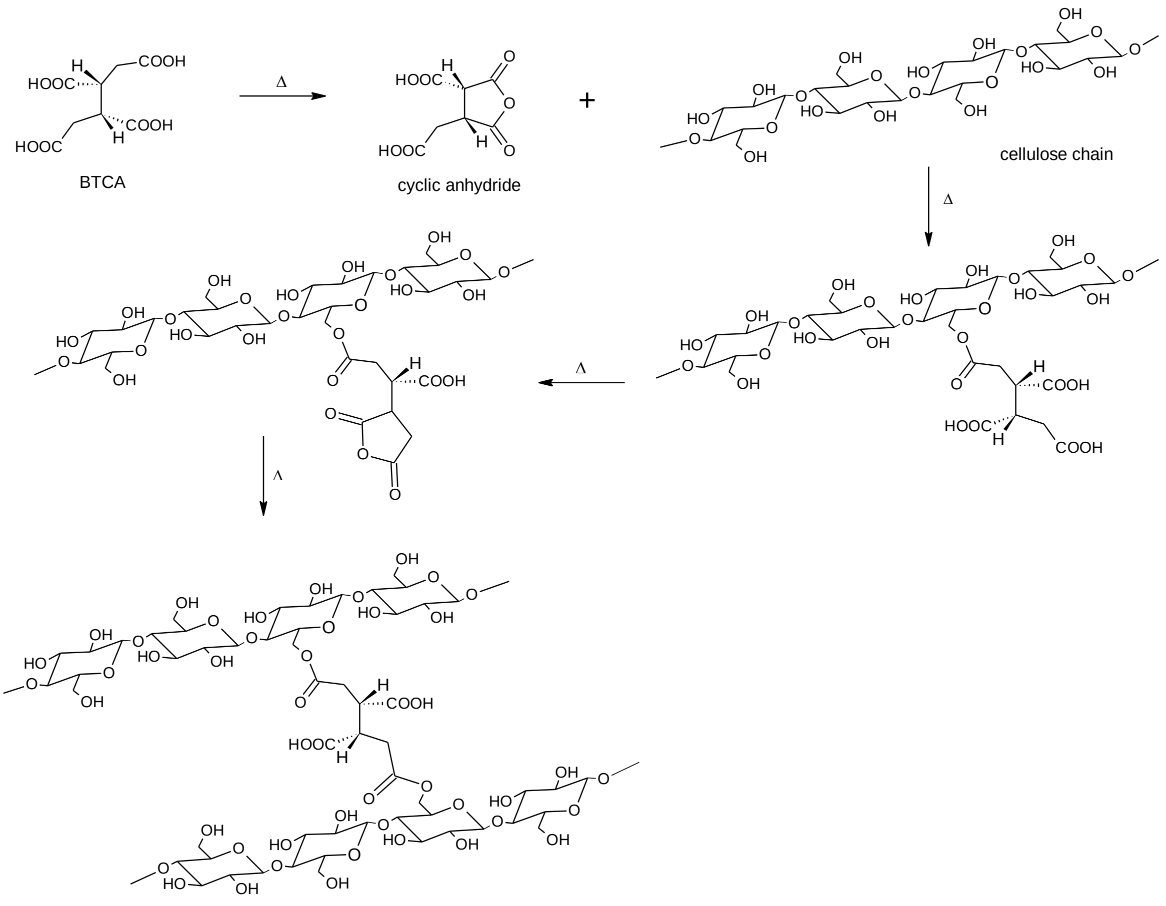


Figure 2-11 Cross-linking mechanism of BTCA with cellulose via cyclic anhydride intermediate

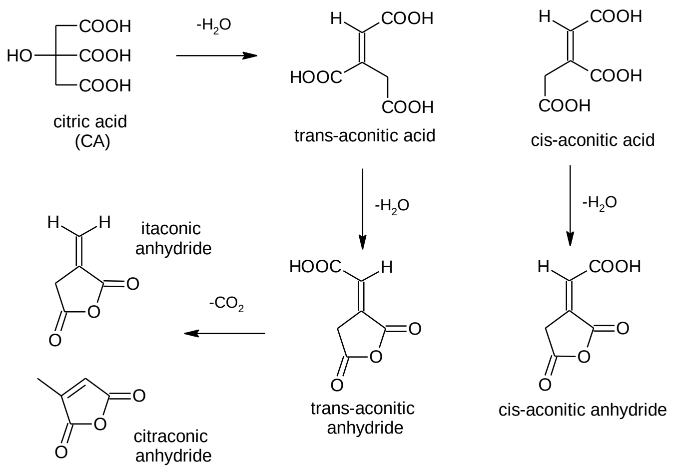


Figure 2-12 Thermal transformation of CA

2.2.6.2 Recent Development of Cellulose Cross-linking Systems

Decades ago, researches suggested that three being the minimum number of carboxyls in an acid cross-linker is the prerequisite to proceed to effective esterification of cellulose via the formation of reactive anhydride intermediate. The cross-linking mechanism has been investigated and verified [127]–[131]. Recent researches revealed that polycarboxylic acids consisted of less than three carboxyls are also able to furnish textile materials with wrinkle-resistance property. Peng proposed that unsaturated dicarboxylic acid, such as IA or MeA is capable of cross-linking cotton cellulose in the combination of NaH_2PO_2. The proposed mechanism using IA and NaH_2PO_2 is illustrated in Figure 2-13. NaH_2PO_2 might serve as a part of the IA- NaH_2PO_2-IA cross-links [146].

Other than utilisation of typical phosphorus based catalysts, cross-linking reaction between acid cross-linkers and cellulose could be induced by photo-catalysts, for example, titanium dioxide (TiO_2) nano-particles. This metal oxide is served as the radical initiator. In an aqueous finishing medium, it enables photoreduction of water molecules for further radical propagation or photoreduction of adsorbed acid cross-linkers directly at the surface of TiO_2 particles. Cross-linking of cellulose was found to be feasible under the ultraviolet irradiation using BTCA, CA, MeA and SA with TiO_2. Photocatalysis not only helps retaining fabric strength upon lowering curing temperature in the finishing treatment, but also offers an alternative catalytic system in mitigating water pollution for the industry [111], [147]–[151].

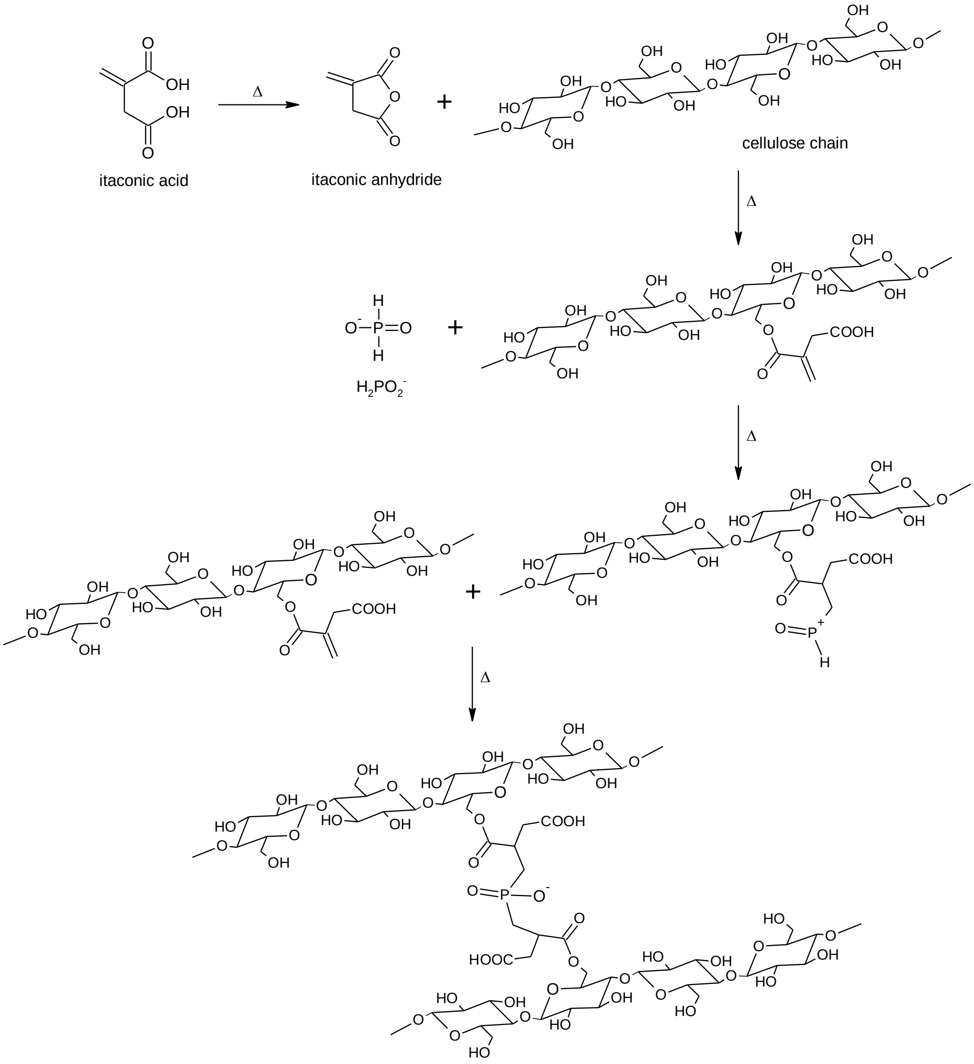


Figure 2-13 Proposed mechanism of cross-linking of cotton cellulose by IA in the combination of NaH_2PO_2 [146]

2.3 Potentials, Development and Synthesis of Polymeric Cellulose Cross-linkers

The success of BTCA lays the milestone of utilising polycarboxylic acids as the formaldehyde free cross-linkers for cellulosic textile materials [100], [101], [125]. In the past, monomeric polycarboxylic acids adopted in the finishing systems confine to tricarboxylic acids or tetracarboxylic acids. They are effective cross-linkers. However, significant loss in fabric strengths remains the disadvantage of this group of systems. With the continual exploration and understanding of the interaction between the cross-linkers and cellulose, cross-linking cellulose no longer confines monomeric cellulose cross-linkers. With the knowledge in macromolecules blooming in the early twentieth century, researchers and scientists reveal the promising properties of polymeric materials which could cater to versatile applications [152]–[154]. Polymeric structures of cross-linkers have illustrated its attractiveness to the issue of concern.

2.3.1 Potentials of Carboxyl-functionalised Polymers

In the past, dicarboyxlic acids are not considered as viable cellulose cross-linkers. They are only capable of affording monoester with cellulose. Cellulose chains are not cross-linked. In recent times, utilisation of dicarboxylic acid as cellulose cross-linker is found to be feasible. With the continual exploit and understanding of the interaction between the cross-linkers and cellulose, cross-linking cellulose no longer confines to tricarboxylic acids or tetracarboxylic acids. Dicarboyxlic acids are also potential and usable to develop as carboxyl-based cross-linkers.

Unsaturated dicarboxylic acids such as **acrylic acid (AA), maleic acid (MeA), itaconic acid (IA),** have been subjected to investigations [89]–[93], [109], [114], [116], [127], [146], [155]–[157]**.** These unsaturated acids are able to undergo free radical polymerisation similar as other vinyl monomers in the presence of radical initiators. Polymeric carboxylic acids with multiple carboxyl groups formed sequentially are able to participate in cellulose cross-linking. In the presence of NaH_2PO_2 and $K_2S_2O_8$ in aqueous medium, researchers suggested the *in-situ* polymerisation of vinyl moieties forming poly(acrylic acid), poly(maleic acid) and poly(itaconic acid). On one hand, the polymeric structure of the carboxyl-based cross-linkers enables retention in fabric strengths of the modified cellulosic fabrics [89]–[91], [93], [109], [116], [127], [156], [158]–[160]. On the other hand, oxidative effect of the radical initiator (e.g. $K_2S_2O_8$) in the system would impose detrimental effect on mechanical properties of the cellulosic materials [91], [160].

Another potential candidate is MA, a hydroxylcarboxylic acid which is capable of self-polymerising under elevated temperatures. Kim reported that MA is competent to form a functional oligomeric compound as the cellulose cross-linker. The resultant trimer of higher order functionality allows esterification of cellulose via the formation of cyclic anhydride intermediate [112]. MA could also serve as an additive in the formulation with BTCA to reduce material cost in the finishing. MA is able to condensate with BTCA as a pentacarboxylic acid [98], [161]. Simultaneously, MA has been suggested to be competent to retain fabric whiteness of modified fabric substrates [98], [99]. Bifunctional acids capable of undergoing polycondensation give insight of another category of carboxyl-functionalised macromolecules as cellulose cross-linkers.

One of the feasible approaches is to develop linear polymeric cross-linkers with reactive carboxyl pendants. Another approach is to furnish macromolecules with cross-linking capability through building highly functionalised dendritic architectures. The latter approach is also a green perspective for cellulose cross-linking. Naturally available hydroxylcarboxylic acids such as CA and MA are potential candidates for developing formaldehyde free polymeric cross-linkers.

2.3.2 Background and Development of Polycondensates

Naturally available hydroxylcarboxylic acids are potential to undergo self-condensation reaction to form condensation polymers (i.e. polycondensates) with elimination of water molecules upon heating. This type of macromolecules essentially present in versatile forms of biopolymers on earth. The first synthesis of polycondensate was obtained by heating lactic acid as poly(D,L-lactic acid) polyester in 1833 [162]. Molecular composition and structures were still controversial in past times. Wait until a century later, Wallace Hume Carothers elaborated the step-growth polymerisation reaction occurred in the synthesis of linear polycondensates, included polyesters and polyamides.

In the early growth of polymer science and chemistry, linear architecture is the main focus [163]. Linear condensation polymers and addition polymers are the main stream to develop macromolecules with superior mechanical properties. The most prominent linear polycondensate is nylon-6,6 launched out to the commercial markets in 1938. Such synthetic polycondensate spun into fibres with high-melting point and brilliant mechanical properties. Conventional linear polycondensates are water insoluble and essentially chemically inert which are not applicable as reactive cellulose cross-linkers. Cellulose cross-linkers shall be water soluble and possess sufficient number of reactive carboxyls groups for cross-linking. A new stream of polycondensates with dendritic architectures is of great potential as wrinkle-resistant finishing agents for cellulosic textiles. Dendritic architecture furnished the macromolecules with unique physicochemical properties lays down the enthralling vein to utilising natural hydroxylcarboxylic acids to develop as polymeric cellulose cross-linkers.

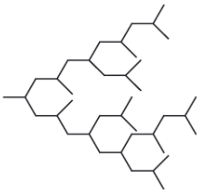
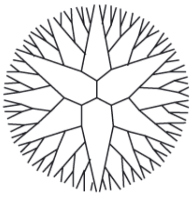
2.3.3 Background of Dendritic Polymers

The term "**Dendritic**", means "tree-like" in Greek. Dendritic architecture is a pervasive pattern in nature, as tiny as neurons in our brain to as huge as tree roots, from abiotic snowflakes to biotic vasculatory system of mammals. Nature manifests the advantageous of such architectures for optimising energy transfer and nutrient extraction, and information storage and retrieval. Scientists exploit the possibility of synthetic mimics. Preeminent pioneers, Fréchet and Tomalia, initially built perfectly branched macromolecules, namely the **dendrimers** [164]–[167]. Simultaneously, another group of researchers, Kim and Webster, prepared randomly branched macromolecules, coined the term as **hyperbranched polymers** [168], [169]. Such breakthrough spurs a novel and innovative stream of polymer chemistry ever since. Dendritic polymers begin to bloom.

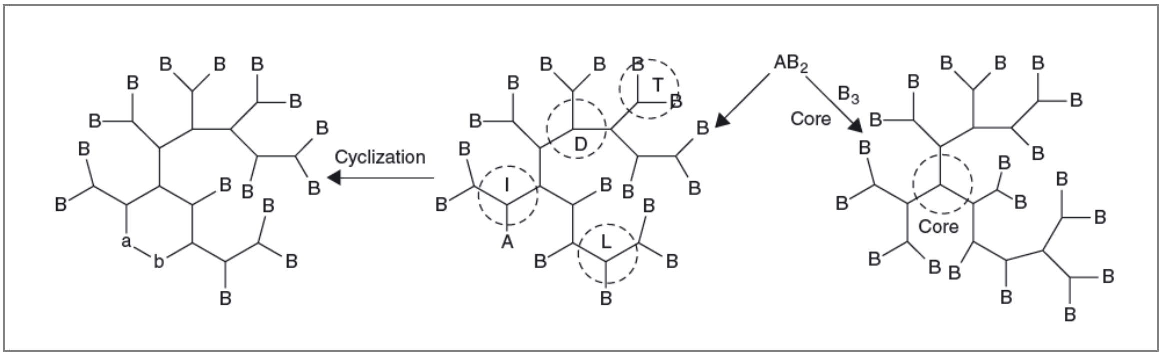
The gestation of dendritic architecture dates back to the early 19th century. Berzelius reported the first formulation using glycerol and tartaric acid to produce polyester resin in 1847 [170]. Sequentially, further investigations explored the reaction kinetics and the interesting properties of the highly branched macromolecules of glycerol with phthalic acid and anhydride. Resinous products were obtained with a three dimensional complexity as reported [170]–[173]. Not until 1940, Flory established the theory and concepts of molecular size distribution and the degree of branching, laying the theoretical foundation of schematic preparations of highly branched polycondensates [174]–[178].

Dendritic family comprised of successive branching are mainly classified into two main classes, dendrimers and hyperbranched polymers. Dendrimers are defined as three-dimensional macromolecules which are symmetrically branched in the form of globular geometry. Layers and layers of regular branching units are emanating from a focal point at the core. Hyperbranched polymers are also composed of highly branched architecture. However, their branching is asymmetric and irregular. This family of polymers is thriving and prosperous with respect to their unique characteristics over the conventional linear polymers. Dendritic polymers possessing compact morphology hampered chain entanglement affords low melting temperature and low viscosity. Such characteristic allows processability of the polymers. These polymers with multiple functional groups at linear and/or terminal units per molecules are highly functionalised. In contrast to linear family, they are endowed with superior reactivity and hence broadened the scope of applications. Characteristics and general properties of the two main families of polymers are summarised in Table 2-2.

Table 2-2 Comparison between characteristics of linear and dendritic polymers [179]

Characteristics	Linear polymers	Dendritic polymers	
		Hyperbranched polymers	Dendrimers
Architecture	 One dimensional, linear	 Three dimensional, irregular	 Three dimensional, globular
Synthesis approach	One step	One step or multi-steps	Multi-steps, laborious
Molecular size and distribution	Mixed MWs, PDI >1.1, DB = 0	Mixed MWs, PDI >3, DB = 0.4-0.6	Single MW, PDI =1/<1.05, DB = 1.0
Physical properties	Viscosity: high solubility: low	Viscosity: low solubility: high	Viscosity: very low solubility: very high
Functional terminals	At two ends	Multiple at linear and terminal units	Multiple, at terminal and peripheral

In general, dendritic macromolecules comprise of various units, namely initial (I), linear (L), dendritic (D) and terminal (T) units. A schematic illustration of the typical structure of hyperbranched polymer is presented in Figure 2-14. A and B represent two different functional groups of a monomer. A being retained un-reacted in the synthesis is defined as the focal point of a hyperbranched polymer. This is the initial unit. B is defined as the counterpart which reacts with A constantly. In some cases, A in the initial unit is reacted with B of another monomer. The initial unit is then transformed into a core unit, i.e. a dendritic unit. There is a possibility for A to react with adjacent B to form a cyclic moiety or macrocycle.



* I is the initial unit. L is the linear unit. D is the dendritic unit. T is the terminal unit.

Figure 2-14 Schematic configuration of a dendritic polymer of AB_2 monomer [179]

The typical strategy to build a hyperbranched polymer is to use a polyfunctional AB_m monomer, where $m \geq 2$ is the prerequisite when considering a single monomer polycondensation [166], [174]. With the exploration of dendritic macromolecules, the concept of the degree of branching (DB) introduced. DB of the polymerisation of an AB_2 monomer could be estimated based on equation 1 as follows. For linear polymers, DB equals to zero as there is no dendritic and terminal units. For dendrimers, DB equals to one as there is no linear units. DB of hyperbranched polymers typically lies between 0.4 to 0.6. DB tends to be close to 0.5 for the random one-pot polymerisation of AB_2 [180].

$$\mathrm{DB} = \frac{\mathrm{D} + \mathrm{T}}{\mathrm{D} + \mathrm{T} + \mathrm{L}} \qquad \text{equation 1}$$

The above equation is valid for AB_2 monomers. Flory did not account for the semi-dendritic units (sD) possibly present in highly branched architectures. Frey and his fellowmen further studied the factors influencing DB of using AB_m monomers. For AB_m where m>3, another possible, sD units, could be present in a hyperbranched macromolecule. The postulation of polymerisation phenomenon has altered due to the unequal reactivity of B_m in the L (or sD) and T units. Equation for estimation of DB is modified accordingly as depicted in equation 2. Another terminology introduced by Frey, the average number of branches (ANB), helps speculate the branching phenomenon based on equation 3 [180].

$$\mathrm{DB} = \frac{\mathrm{m}}{2\mathrm{m} + 1} \qquad \text{equation 2}$$

$$\mathrm{ANB} = \frac{\mathrm{D}}{\mathrm{D} + \mathrm{L}} \qquad \text{equation 3}$$

Frey suggested several approaches to enhance DB of dendritic macromolecules. One of the routes is to incorporation of core molecules (B_f) [181]–[185]. Incorporation of core molecules not only alters DB, but also changes the polydispersity of the macromolecules. Statistical postulation for polydispersity of typical AB_m hyperbranched polymers could be extremely large. The growth in polydispersity is due to the difference in reactivity of the propagating molecules of various sizes. Bigger molecules with more B functional groups are able to grow faster and coupled each other. With the presence of polyfunctional B_f core molecules, polydispersity would be reduced. The greater number of functional groups in the core moiety retenders narrower polydispersity. Another route to achieve narrow polydispersity is by slow addition technique [184], [186]. Notwithstanding DB of hyperbranched macromolecules could achieve 1; the DB value does not imply that a highly branched macromolecule is in globular shape approaching as a dendrimer. There is the possibility of irregularity in structures with the presence of isomeric macromolecules in a system.

The polycondensation phenomenon no longer simply adheres to Flory's classical theory and concept with the fast growing dendritic polymer chemistry. Complexity is growing with the advance in synthesis avenues in the dendritic polymer chemistry. More new findings depict the discrepancy and deviation of statistical postulations suggested in the 1950s. Mechanistic understanding for the polymerisation of hyperbranched polymers still is emerging [181], [187]. Over twenty years of intended development of hyperbranched polymers, characterisations of hyperbranched polymers remain challenging in the dendritic polymer science. Many facets of factors of the polymer involved, such as the diversity of functionality, branching density and polydispersity, would affect behaviour, structural dimensions, aggregation, and interactions in solution [188], [189] .

A kind of AB_m monomer could be incited a diversity of structural architectures and functionalities as exemplified in Figure 2-15. This example demonstrated that full characterisation of property profile of hyperbranched polymers remains a challenge [190]. Regarding the molecular weight determination by GPC, several factors contribute to inaccuracy in determination. The choice of standards for calibration and solvent interaction during elution are strongly governed by the polarity of the end groups of the dendritic analytes. The hydrodynamic radius and solution viscosity would lead to false determination by detection based on light scattering or refractive index. Considerable discrepancy in rheology of dendritic analytes and the linear standards lead to deviation from the actual molecular weight. Recently, attempts have contributed to prepare dendrimers as calibration standards for better correlation to rheology during chromatographic analysis. Other than molecular weight determination, characterisations of other properties such as mechanical and thermal properties still require further research. Lack of appropriate analogues for comparison makes the characterisation of physiochemical properties of dendritic macromolecule not an easy task.

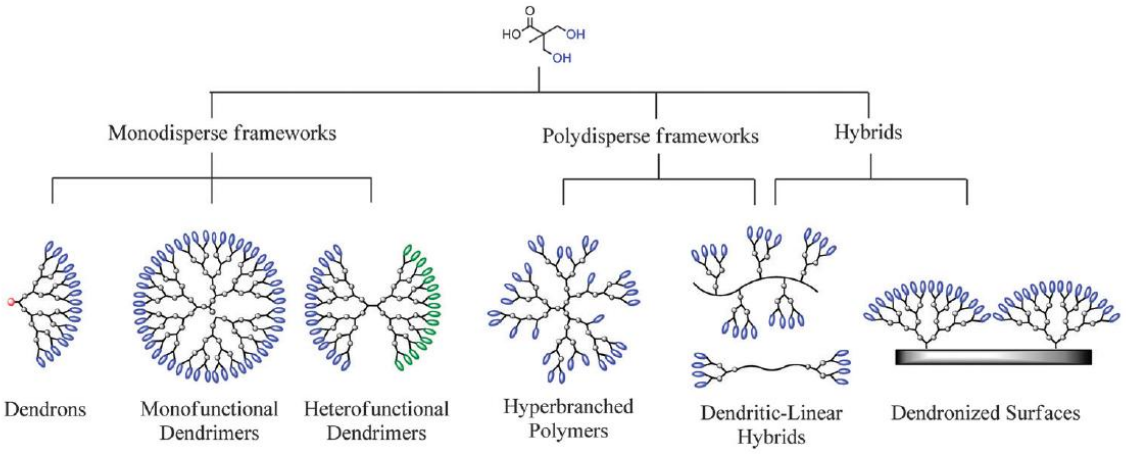


Figure 2-15 Possible dendritic architectures generated from of AB_2 monomer [191]

2.3.4 Synthesis and Applications of Dendritic Polymers

2.3.4.1 Syntheses of Dendrimers

There are three main routes to build dendrimers. The conventional methodology is adopting convergent or divergent approaches as illustrated in Figure 2-16 [164], [165], [167], [192]. Dendrimers could be built by attachment of dendrons to a central core inwardly or growth from the central core outwardly. In general, both approaches involve iterative processes of protection and deprotection reactions, isolation and purification in order to build individual generation with precisely defined bonding and structure. In the early twenty-first century, click chemistry is introduced into the realm of dendritic polymer chemistry [193]–[195]. Iterative synthesis could revamp to be more efficient with specificity without involving tedious protection-deprotection reactions and chromatographic purifications. However, this approach limits the varieties and structures of the dendrimers. Stringent criteria have to be complied in the pursuit of feasible click chemistry.

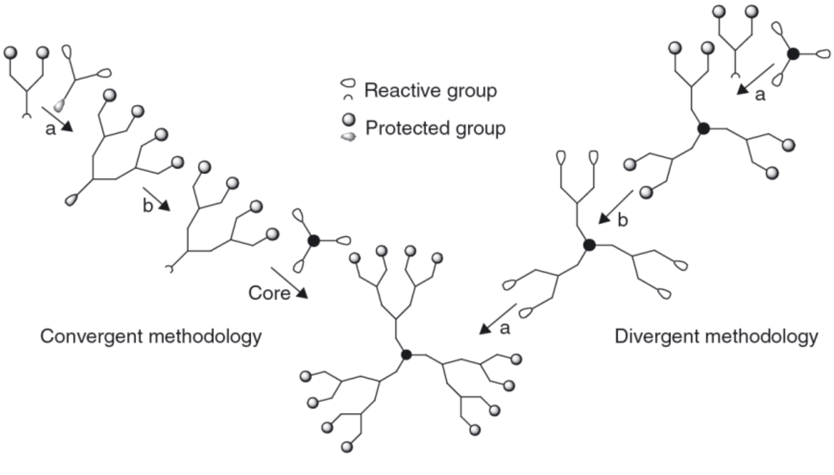


Figure 2-16 Convergent and divergent synthesis approaches for dendrimers [179]

Though dendrimers with well-defined architecture possess attractive properties, syntheses of dendrimers are tedious. Nowadays, the focus switches to develop hyperbranched polymers which are more cost-effective for mass production and sequential applications [196], [197]. With respect to the randomness in configuration, hyperbranched polymers permit versatile and relatively simpler synthesis strategy. The strategy for building hyperbranched polymers usually adopts single-step polymerisation in contrast to iterative preparation of dendrimers.

2.3.4.2 Syntheses of Hyperbranched Polymers

The attempt to prepare synthetic hyperbranched polymers traces back to the end of nineteenth century. Primitive exploration utilised polyfunctional monomers to prepare resins. The primordial formulations were based on glycerol (B_3 monomer) with tartaric acid (A_2B_2 monomer), phthalic acid (A_2 monomer) and anhydride (latent A_2 monomer) [170]–[173]. Until 1940s, the classical theory of polycondensation and concepts of DB and molecular weight distributions of highly branched macromolecules were established [174]–[178]. The polycondensation without gelation using polyfunctional AB_2 monomer was postulated. The theory lays the fundamentals for dendritic polymers. Realisation of the polymerisation of AB_2 monomers was published three decades later. The first hyperbranched polyphenylene was reported [169], [198].

Three pathways to achieve hyperbranched macromolecules are schematically depicted in Figure 2-17. Polymerisation of monomer(s), i.e. the bottom-up ideology is the most prevailing pathway to prepare hyperbranched polymers. Versatile methodologies could be applied to access this novel class of dendritic polymers included homopolymerisation of AB_m, copolymerisation of symmetric monomer pairs of A_x and B_y, copolymerisation of asymmetric monomer pairs, self-condensing vinyl polymerisation of AB*, self-condensing ring-opening polymerisation of latent AB_m and proton-transfer polymerisation [179], [190], [199]–[206]. Conventionally, polyfunctional AB_m monomers are competent to develop hyperbanched polymers without the occurrence of gelation via polycondensation [200], [207], [208]. However, the source of most of AB_m monomers are not commercially available impedes large-scale productions. One remedy is to utilise symmetric monomer pairs (A_x and B_y) for polycondensation. This would be a promising route to realise commercialisation of hyperbranched polymers. Meanwhile appropriate control of the reaction is required to avoid gelation [205]. Starting from 2000s onwards, polycondensation using asymmetric monomer pairs was introduced to the dendritic polymer arena [209]–[212]. With respect to the rule of non-equal reactivity, gelation could be essentially ruled out. And hence this basis facilitates industrialisation of hyperbranched polymer production.

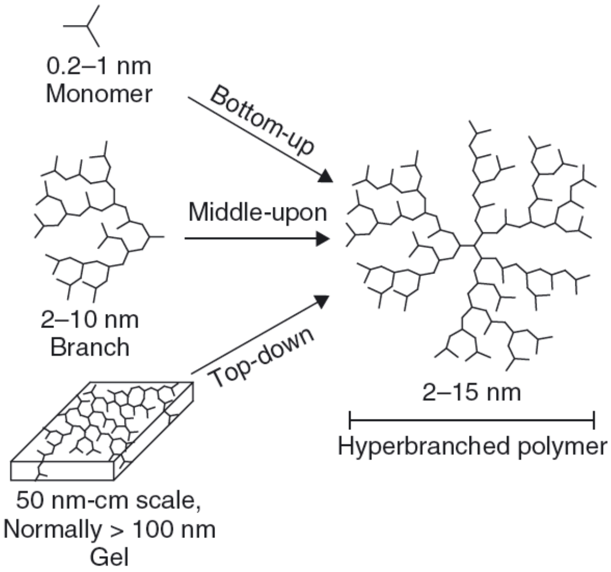


Figure 2-17 Synthesis pathways for hyperbranched polymers [179]

Other than the aforementioned reactions, recent researches utilised B_f-type molecules as the core unit in combination with AB_2 or AB_3 monomers in the preparation of hyperbranched polyesters [213]–[216]. More reviews about the polymerisation mechanism, kinetics and thermodynamics are ongoing in recent years, from non-stoichiometric polycondensation to hyperbranched polycondensates of high molecular weights and narrow polydispersity. Some approaches developed hyperbranched polymers via ”core-first” or “ arm-first” strategy using AB_x and B_f [181], [217]. Alternative routes such as “graft onto” and “graft from” methodologies allowed to form new architectures like comb and star shaped hyperbranched polymers [199]. The spectrum of synthesis methodologies and approaches to build hyperbranched is still expanding.

With better understanding of the polymerisation philosophy of dendritic polymer chemistry, the classical theory developed by Flory more than 50 years ago is subjected to literacy criticism [181], [187]. Flory's classical step-growth polymerisation assumed that intramolecular or intermolecular cyclisation is negligible. However, experimental reality deviates from theoretical assumptions. Convincing premises for molecular weight distribution and polydispersity still requires further scientific research. Several attempts have been exploited to manipulate polydispersity, whether the rapid syntheses for develop hyperbranched polymers could achieve monodispersity like dendrimers [181]–[186].

Highly functionalised, low solution viscosity and low melting point are the prosperous potentials for exploring diverse applications of dendritic polymers. Novel interfaces of polymer chemistry and different streams of sciences are inexhaustible. Dendritic macromolecules designed with special functionalities could serve as novel optical, electronic, magnetic and stimuli-responsive materials [200], [218]–[220]. Recently, enormous effort put on polymer therapeutics for drug and DNA delivery, bio-sensing, and tissue engineering [200], [221]–[234].

2.3.4.3 Applications of Hyperbranched Polymers in Textiles

Preparations of hyperbranched polymers are much rapid and economical compared to dendrimer syntheses arousing tremendous interest for researchers to pursue this particular subclass of dendritic polymers for industrial applications. Their chemical flexibility permits tailor-made performance catering to an ever-expanding multitude of applications. Today, polymer science transits from theoretical-based to application-driven research.

The preparation of dendrimers is labour and resource driven. With respect to the tedious syntheses of dendrimers, this subclass of dendritic polymers is relatively suitable for applications such as for pharmaceuticals and biomedical sectors. When considering finishing applications in textile industry, dendrimers are out of the option. The synthesis approach for hyperbranched polymers is versatile and relatively simpler, usually single-step polymerisation. Hyperbranched polymers which are promising candidates for industrial production and sequential applications [196], [197]. Commercial hyperbranched polymers have been launched out to the market, for examples, polyester (Boltorn^{TM}), hyperbranched poly(ester-amide) (Hybrane^{TM}) and hyperbranched poly(ethyleneimine) (Lupasol^{TM}) with speciality functions mushroomed in a variety of industries, included coatings & adhesives industry, fibre manufacturing, paper manufacturing, oil refinery, drug developments and etc. [189], [205], [235]–[240]. This class of dendritic polymers as functional polymers with improved reactivity permits further modifications catering to inexhaustible applications.

The application of this class of dendritic macromolecules in textile industry is emerging. In view of resurgence of the demand in natural cellulosic fibres and fabrics in the textile fields, antimicrobial performance of the substrate materials is always of high values. Hyperbranched poly(amide amine) and poly(ester amine) could cope with such deficiency of cellulosic materials. This group of antimicrobial agents furnishes antimicrobial property and UV protection to the substrate with the impregnation of transition metal particles [241]–[245]. Amino terminated hyperbranched polyester could serve as receptor sites to improve dyeability of textile materials. For examples, amino functionalities assist reactive dyeing of cotton and ramin fabrics while hydroxyl functionalities afford dyeability of polypropylene fibres towards disperse dye. Hyperbranched polymers possessing compact structures would hardly alter the mechanical properties [239], [246]–[248]. Other than incorporating additional functional properties into the textile materials, hyperbranched poly(ester amide) or poly(propylene imine) could help tackle problems associated with the effluent treatment [144], [239], [249]–[251]. For example, hyperbranched poly(esteramide) based resin interacted and removed the dyestuff in the effluent.

2.4 Potentials and Rationales of Carboxyl-functionalised Polymer as Cellulose Cross-linkers

Despite attempts to reduce health hazard and environmental impacts of the current fishing systems and the modified products, non-toxic and formaldehyde free while being cost-effective is still the goal to be achieved. Elimination of incorporating formaldehyde and other short chain aldehydes in the whole production and manufacturing processes is indispensable in the twenty-first century. Scientific efforts towards the utility of non-toxic reactants and finishing agents in the modification processes have expanded tremendously in the last two decades. Exploitation of naturally available organic acids as cross-linkers for cotton textiles is burgeoning as the remedy to eliminate potential toxicity and to reduce production cost.

The effectiveness of wrinkle-resistance is proportional to the number of cross-links formed between cellulose molecules and fibres. However, not all natural organic acids consist of sufficient number of carboxyls to proceed to cellulose esterification [88], [102], [119], [138], [139]. Thus, developing carboxyl-functionalised dendritic polymers as cellulose cross-linkers would be a promising strategy to increase reactivity. The number of reactive groups per molecule of cross-linker in a dendritic polymer is greater than the conventional monomeric counterparts. Dendritic polymers not only furnish the cross-linker with reactivity, but also could be the possible amelioration to abate strength loss of the cross-linked substrate. Polymeric structure of the cross-linkers could afford additional strength and flexibility to the cross-linked cellulosic fibres. Polymeric cross-linkers would help alleviate the drawbacks of strength loss [89]–[91], [109], [116], [156].

Hitherto, limited researches of developing dendritic polymeric cross-linkers have been devoted for wrinkle-resistant purpose. Understanding and utility of dendritic polymers as cellulose cross-linkers in wrinkle-resistant finishing in the textile industry is still in infancy. Polymer scientists have paid much attention of building dendritic polymers via polycondensation of AB_m monomers with B_f as the core or branch points.

Most AB_m monomers are not commercially available. It is notable that various A_mB monomers present in nature could be potential building blocks for developing carboxyl-functionalised dendritic polymers with appreciable reactivity for cross-linking or further modification. This would be the promising attempt to look into and reveal the effectiveness of dendritic macromolecules for the purpose of wrinkle-resistant finishing on textile substrates. This work would afford a valuable template which helps expanding the scope of using polymeric carboxyl-functionalised polymers and the derivates in this field application.

2.5 Conclusion

This chapter provides a comprehensive review of literature focused on the two main aspects of this project. One aspect related to the fundamentals, development and limitations of the wrinkle-resistant finishing for textiles are presented. Concerns over health hazard and environmental impacts are the impetus for researchers and technologists to look for superior substitutes as cellulose cross-linkers. Another aspect is related to the development of the polymeric cross-linkers. Background, synthesis strategies and development of carboxyl-functional polymers, in particular, hyperbranched polymers have been discussed. Enthusiasm for this sub-class of dendritic macromolecules has been rising steadily with respect to their accessibility in a single synthesis. In the last past of this chapter, the rationale for this study is based on the development of carboxyl-functionalised polymers as wrinkle-resistant finishing agents using naturally available hydroxylcarboxylic acids has been reviewed.

2.6 Bibliography

[1] R. P. Foulds, J. T. Masrh, F. C. Wood, H. Boffey, and J. Tankard, “Forming synthetic resins within textile materials,” GB 291473, 1926.

[2] R. P. Foulds, J. T. Marsh, and F. C. Wood, “Impregnating textile materials with condensation products of phenols and formaldehyde,” GB 291474, 1926.

[3] D. W. Heywood, “Easy Care,” in *Chemistry of the Textiles Industry*, C. M. Carr, Ed. Cambridge: Blackie Academic & Professional, 1995, pp. 173–186.

[4] E. J. Gonzales, R. R. Benerito, and R. J. Berni, “Kinetics of the reactions of ethyleneurea derivatives with cotton cellulose: part I: the cellulose-dihydroxyethyleneurea reaction,” *Text. Res. J.*, vol. 36, no. 6, pp. 565–571, 1966.

[5] E. J. Gonzales, R. R. Benerito, R. J. Berni, and H. M. Zacharis, “Kinetics of the reactions of ethyleneurea derivatives with cotton cellulose: Part II: the cellulose-dimethyldihydroxyethyleneurea reaction,” *Text. Res. J.*, vol. 36, no. 6, pp. 571–578, 1996.

[6] E. J. Gonzales and R. R. Benerito, “Effect of catalyst upon the physical and chemical properties of cotton finished with derivatives of ethyleneurea,” *Text. Res. J.*, vol. 35, no. 2, pp. 168–178, 1965.

[7] H. M. Ziifle, R. R. Berni, and R. R. Benerito, “Investigation of the catalyst in the cellulose-DMEU reaction: part I: effect of catalyst upon the Physical and chemical properties of the finished cottons,” *Text. Res. J.*, vol. 31, no. 4, pp. 349–365, 1961.

[8] E. J. Gonzales, R. R. Benerito, and L. G. Spears, “Effect of catalyst upon the physical and chemical properties of cotton finished with derivatives of ethylenethiourea,” *Text. Res. J.*, vol. 35, no. 2, pp. 192–193, 1965.

[9] R. J. Berni, R. R. Benerito, and D. M. Soignet, “Sodium cellulosate and diethylaminoethlcellulose as substrates for modification of cotton with epoxides,” *Text. Res. J.*, vol. 42, no. 11, pp. 667–675, 1972.

[10] E. J. Gonzales, H. M. Ziifle, R. J. Berni, and R. R. Benerito, “Physicochemical study of the cotton cellulose- dimethylolpropyleneurea reaction,” *Text. Res. J.*, vol. 37, no. 9, pp. 726–735, 1967.

[11] S. P. Rowland, N. R. Bertoniere, and L. F. Martin, “The development of abrasion resistance and breaking strength in durable-press cotton fabrics,” *Text. Res. J.*, vol. 44, no. 8, pp. 595–599, 1974.

[12] H. Petersen, “Advances in the chemistry of N-containing cross-linking agents,” *Text. Res. J.*, vol. 41, no. 3, pp. 239–254, 1971.

[13] H. Petersen and P. S. Pai, “Reagents for low-formaldehyde finishing of textiles,” *Text. Res. J.*, vol. 51, no. 4, pp. 282–302, 1981.

[14] S. Shafiee and E. Topal, “When will fossil fuel reserves be diminished?,” *Energy Policy*, vol. 37, pp. 181–189, 2009.

[15] P. J. Wakelyn, “The evolution of durable press and flame retardant cotton,” American Chemical Society National Historic Chemical Landmarks. Cotton Products, 2004. [Online]. Available: http://portal.acs.org/portal/PublicWebSite/education/whatischemistry/landmarks/cottonproducts/index.htm. [Accessed: 01-Nov-2014].

[16] M. Hoel and S. Kverndokk, “Depletion of fossil fuels and the impacts of global warming,” *Resour. Energy Econ*., vol. 18, no. 2, pp. 115–136, Jun. 1996.

[17] D. Nabi Saheb and J. P. Jog, “Natural fiber polymer composites: a review,” *Adv. Polym. Technol*., vol. 18, no. 4, pp. 351–363, 1999.

[18] G. S. Buck and F. A. McCord, “Crease-resistance and cotton,” *Text. Res. J.,* vol. 19, no. 4, pp. 216–247, 1949.

[19] D. Klemm, B. Heublein, H.-P. Fink, and A. Bohn, “Cellulose: fascinating biopolymer and sustainable raw material,” *Angew. Chemie (International Ed. English)*, vol. 44, no. 22, pp. 3358–3393, 2005.

[20] K. L. Hatch, *Textile Science*. Minneapolis/Saint Paul: West Publishing, 1993.

[21] N. Rjiba, M. Nardin, J.-Y. Drean, and R. Frydrych, “Comparison of surfaces properties of different types of cotton fibers by inverse gas chromatography,” *J. Polym. Res*., vol. 17, no. 1, pp. 25–32, 2009.

[22] H. A. Krassgi, *Cellulose-Structure, Accessibility and Reactivity*. Yverdon: Gordon and Breach Science Publisher, 1993.

[23] J.-L. Wertz, O. Bedue, and J. P. Mercier, *Cellulose science and Technology*. Switzerland: EPFL Press, 2010.

[24] A. C. O' Sullivan, "Cellulose: the structure slowly unravels," *Cellulose*, vol. 4, pp. 173–207, 1997.

[25] H. A. Krassgi, *Cellulose and its derivatives: chemistry, biochemistry, and applications*. Chichester: Ellis Horwood Limited, 1985.

[26] D. D. Gagliardi and I. J. Gruntfest, "Creasing and creaseproofing of textiles," *Text. Res. J.*, vol. 20, no. 3, pp. 180–188, 1950.

[27] S. Houshyar and S. H. Amirshahi, "Treatment of cotton with chitosan and its effect on dyeability with reactive dyes," *Iran. Polym. J.,* vol. 11, no. 5, pp. 295–301, 2002.

[28] A. Hebeish, A. Z. Moursi, M. I. Khalil, and F. A. Abdel-Mohdy, "Dyeing of chemically modified celluloses. II. Effect of chemical modification of cellulose on the dyeing properties of some direct dyes," *J. Appl. Polym. Sci*., vol. 21, no. 8, pp. 2191–2199, 1977.

[29] H. Wang and D. M. Lewis, "Chemical modification of cotton to improve fibre dyeability," *Color. Technol.*, vol. 118, pp. 159–168, 2002.

[30] M. Raheel and G. Chen, "Single-step dyeing and formaldehyde-free durable press finishing of cotton fabric," *Text. Res. J*., vol. 68, no. 8, pp. 571–577, 1998.

[31] D. Roy, M. Semsarilar, J. T. Guthrie, and S. Perrier, "Cellulose modification by polymer grafting: a review," *Chem. Soc. Rev*., vol. 38, no. 7, pp. 2046–2064, 2009.

[32] W. A. Reeves, O. J. McMillan, and J. D. Guthrie, "Chemical and physical properties of aminized cotton," *Text. Res. J*., vol. 23, no. 8, pp. 527–532, 1953.

[33] Y.-S. Chung, K.-K. Lee, and J.-W. Kim, "Durable press and antimicrobial finishing of cotton fabrics with a citric acid and chitosan treatment," *Text. Res. J*., vol. 68, no. 10, pp. 772–775, 1998.

[34] Y.-L. Lam, C.-W. Kan, and C.-W. M. Yuen, "Developments in functional finishing of cotton fibres- wrinkle-resistant, flame-retardant and antimicrobial treatments," *Text. Prog*., vol. 44, no. 3–4, pp. 175–249, 2012.

[35] S. Kittinaovarat, P. Kantuptim, and T. Singhaboonponp, "Wrinkle resistant properties and antibacterial efficacy of cotton fabrics treated with glyoxal system and with combination of glyoxal and chitosan system," *J. Appl. Polym. Sci*., vol. 100, no. 2, pp. 1372–1377, 2006.

[36] C. Sawatari, Y. Sekiguchi, and T. Yagi, "Durable water-repellent cotton fabrics prepared by low-degree substitution of long chain alkyl groups," *Text. Res. J*., vol. 68, no. 7, pp. 508–514, 1998.

[37] J. W. Gilkey, "Durable water repellency by chemical bonding of silicones," *Text. Res. J*., vol. 33, no. 2, pp. 129–137, 1963.

[38] F. Robers, “Wrinkle-free technology for shirting materials,” *New Cloth Mark*., vol. 14, no. 4, pp. 19–22, 2000.

[39] F. Robers, “Wrinkle-free shirtings in Europe,” *World Cloth. Manuf*., vol. 80, no. 5, pp. 21–25, 1999.

[40] J. D. Tuner, “Durable press finishing without formaldehyde,” in *Wrinkle-Free Finishing of Cotton and Cotton Blends*, 1994.

[41] R. M. Tynadall and J. D. Tuner, “Wrinkle-resistant finishing of cotton fabrics and garments,” in *AATCC Garment Wet Processing Technique Manual,* American Association of Textile Chemists and Colorists, 1994, pp. 155–168.

[42] P. Bajaj, “Finishing of textile materials,” *J. Appl. Polym. Sci*., vol. 83, no. 3, pp. 631–659, 2002.

[43] B. G. Simpson, “The effect of silicone softeners on resin treated cottons,” *Text. Res. J*., vol. 28, no. 2, pp. 170–179, 1958.

[44] F. Fortess, “Silicone resins in textiles,” *Ind. Eng. Chem*., vol. 46, no. 11, pp. 2325–2331, 1954.

[45] S. L. Vail, “Cross-linking of cellulose,” in *Cellulose Chemistry and its Applications*, T. P. Nevell and S. H. Zeronian, Eds. Chichester, West Sussex, England: Ellis Horwood, 1985, pp. 384–422.

[46] W. D. Schindler and P. J. Hauser, “Easy-care and durable press finishes of cellulosics,” in *Chemical Finishing of Textiles*, Woodhead Publishing, 2004, pp. 51–72.

[47] B. V. Reibnitz, A. Woerner, and H. Scheuermann, “Condensation products of glyoxal monourein and aldehydes,” US 2764573, 1956.

[48] J. G. Frick and R. J. Harper, “Investigations toward formaldehyde-free finishes,” *Text. Res. J*., vol. 52, no. 2, pp. 141–148, 1982.

[49] N. R. S. Hollies and N. F. Getchell, “Wet-fixation process for improved durable-press cotton,” *Text. Res. J.*, vol. 37, no. 2, pp. 70–76, 1967.

[50] W. D. Hurwitz, “The evolution of permanent press,” *Text. Chem. Color*., vol. 19, no. 2, pp. 13–23, 1987.

[51] S. P. Rowland, F. A. Blouin, and J. S. Mason, “Polymerization-crosslinking of N-methylolacrylamide in cotton fabric,” *Text. Res. J*., vol. 48, no. 2, pp. 73–80, 1978.

[52] B. A. K. Andrews, “Wrinkle-resistant cotton and formaldehyde release,” *Colourage*, vol. 41, no. 10, pp. 87–93, 1995.

[53] T. F. Cooke and H. D. Weigmann, “The chemistry of formaldehyde release from durable press fabrics,” *Text. Chem. Color*., vol. 14, no. 5, pp. 100/25–106/31, 1982.

[54] T. F. Cooke and H. D. Weigmann, “The chemistry of formaldehyde release from durable press fabrics-part 2,” *Text. Chem. Color*., vol. 14, no. 6, pp. 136/33–144/41, 1982.

[55] K. L. Hatch and H. I. Maibach, “Textile dermatitis: an update (I) Resins, additives and fibers,” *Contact Dermatitis*, vol. 32, pp. 319–326, 1995.

[56] A. J. Scheman, P. A. Carroll, K. H. Brown, and A. H. Osburn, “Formaldehyde-related textile allergy: an update,” *Contact Dermatitis*, vol. 38, no. 6, pp. 332–336, 1998.

[57] R. Griesemer, “Report of the federal panel formaldehyde,” *Environ. Health Perspect*., vol. 43, pp. 139–168, 1982.

[58] A. C. De Groot and H. I. Maibach, “Does allergic contact dermatitis from formaldehyde in clothes treated with durable-press chemical finishes exist in the USA?,” *Contact Dermatitis*, vol. 62, pp. 127–136, 2010.

[59] IARC, *Formaldehyde, 2-butoxyethanol and 1-tert-butoxypropan-2-ol*. Lyon, France: International Agency for Research on Cancer, 2006.

[60] C. Bosetti, J. K. McLaughlin, R. E. Tarone, E. Pira, and C. La Vecchia, “Formaldehyde and cancer risk: A quantitative review of cohort studies through 2006,” *Ann. Oncol*., vol. 19, pp. 29–43, 2008.

[61] M. Hauptmann, P. A. Stewart, J. H. Lubin, L. E. Beane Freeman, R. W. Hornung, R. F. Herrick, R. N. Hoover, J. F. Fraumeni, A. Blair, and R. B. Hayes, “Mortality from lymphohematopoietic malignancies and brain cancer among embalmers exposed to formaldehyde,” *J. Natl. Cancer Inst.*, vol. 101, no. 24, pp. 1696–1708, 2009.

[62] M. Hauptmann, J. H. Lubin, P. A. Stewart, R. B. Hayes, and A. Blair, “Mortality from solid cancers among workers in formaldehyde industries,” *Am. J. Epidemiol*., vol. 159, no. 12, pp. 1117–1130, 2004.

[63] M. Hauptmann, J. H. Lubin, P. A. Stewart, R. B. Hayes, and A. Blair, “Mortality from lymphohematopoietic malignancies among workers in formaldehyde industries,” *J. Natl. Cancer Inst.*, vol. 95, no. 21, pp. 1615–1623, 2003.

[64] A. Wilson and J. Mowbray, *Eco-textile labelling-a guide for manufacturers, retailers and brands*. West Yorkshire, UK: Mowbray Communications Ltd., 2008.

[65] NICNAS, “Priority Existing Chemical Assessment Report No. 28-Formaldehyde,” Sydney, Australia, 2006.

[66] NICNAS, “Formaldehyde in clothing and textiles factsheet,” Australian National Industrial Chemicals Notification and Assessment Scheme, 2013. [Online]. Available:

http://www.nicnas.gov.au/chemical-information/information-sheets/existing-chemical-info-sheets/formaldehyde-in-clothing-and-textiles-factsheet. [Accessed: 24-Nov-2013].

[67] EPA, “Technical Support Document : Printing, Coating, and Dyeing of Fabrics and Other Textiles Proposed NESHAP (Publication No. EPA 453/R-02-010),” North Carolina, 2002.

[68] L. E. Pinkerton, M. J. Hein, and L. T. Stayner, “Mortality among a cohort of garment workers exposed to formaldehyde: an update,” *Occup. Environ. Med*., vol. 61, no. 3, pp. 193–200, 2004.

[69] L. E. Beane Freeman, A. Blair, J. H. Lubin, P. A. Stewart, R. B. Hayes, R. N. Hoover, and M. Hauptmann, “Mortality from lymphohematopoietic malignancies among workers in formaldehyde industries: the national cancer institute cohort,” *J. Natl. Cancer Inst*., vol. 101, no. 10, pp. 751–761, 2009.

[70] V. Cogliano, Y. Grosse, R. Baan, K. Straif, B. Secretan, and F. El Ghissassi, “Advice on formaldehyde and glycol ethers,” *Lancelet Oncol.,* vol. 5, no. 9, p. 528, 2004.

[71] U. Sewekow, “How to meet the requirements for eco-textiles,” *Text. Chem. Color*., vol. 28, pp. 21–28, 1996.

[72] M. und Herausgeber, “Oeko-Tex Standard 100,” Zurich, 2015.

[73] S. Varadarajan and N. Bhattacharyya, “Eco-textiles regulations, labels, processing, and testing,” 1996.

[74] I. Holme, “New developments in the chemical finishing of textiles,” *J. Text. Inst*., vol. 84, no. 4, pp. 520–533, 1993.

[75] I. Holme, “Recent advances in chemical processing,” *Colour. Annu*., pp. 41–56, 1998.

[76] K. Yamamoto, “Crease-resistance treatments of cotton fabrics with non-formaldehyde crosslinking agents,” *Text. Res. J*., vol. 52, no. 6, pp. 357–362, 1982.

[77] C. M. Welch and J. G. Peters, “Low, medium, and high temperature catalysts for formaldehyde-free durable press finishing by the glyoxal-glycol process,” *Text. Res. J*., vol. 57, no. 6, pp. 351–356, 1987.

[78] C. M. Welch, “Glyoxal as a formaldehyde-free durable press reagent for mild curing applications,” *Text. Res. J.*, vol. 53, no. 3, pp. 181–186, 1983.

[79] D. Lämmermann, “New possibilities for non-formaldehyde finishing for cellulosic fibers,” *Melliand Textilberichte*, vol. 73, no. 3, pp. 274–379, 1992.

[80] J. G. Frick and R. J. Happer, “Acetals as crosslinking reagents for cotton,” *J. Appl. Polym. Sci*., vol. 29, pp. 1433–1447, 1984.

[81] T. Harifi and M. Montazer, “Past, present and future prospects of cotton cross-linking: new insight into nano particles,” *Carbohydr. Polym.*, vol. 88, no. 4, pp. 1125–1140, 2012.

[82] D. Kut, C. Gunesoglu, and M. Orhan, “Crease-resistant finish of linen / viscose blend fabrics,” *Fibres Text. East. Eur.*, vol. 20, no. 5, pp. 91–93, 2010.

[83] D. M. Lewis and B. Voncina, “Durable press finishing of cotton with polycarboxylic acids. II. ester crosslinking of cotton with dithiosuccinic acid derivative of S-triazine,” J*. Appl. Polym. Sci.*, vol. 66, pp. 171–177, 1997.

[84] D. M. Lewis and B. Voncina, “Durable press finishing of cotton with polycarboxylic acids. I. Preparation of thiosuccinyl-s-triazine,” *J. Appl. Polym. Sci.*, vol. 66, pp. 1465–1474, 1997.

[85] V. Ameri Dehabadi, H.-J. Buschmann, and J. S. Gutmann, “Durable press finishing of cotton fabrics: an overview,” *Text. Res. J.,* vol. 83, no. 18, pp. 1974–1995, 2013.

[86] Y. Yang and S. Li, “Silk fabric non-formaldehyde crease-resistant finishing using citric acid,” *J. Text. Inst.,* vol. 84, no. 4, pp. 638–644, 1993.

[87] W. Yao, B. Wang, T. Ye, and Y. Yang, “Durable press finishing of cotton fabrics with citric acid: enhancement of whiteness and wrinkle recovery by polyol extenders,” *Ind. Eng. Chem. Res.*, vol. 52, pp. 16118–16127, 2013.

[88] C. Q. Yang, X. Wang, and I.-S. Kang, “Ester crosslinking of cotton fabric by polymeric carboxylic acids and citric acid,” *Text. Res. J.*, vol. 67, no. 5, pp. 334–342, 1997.

[89] C. Q. Yang and Y. Lu, “In-situ polymerization of maleic acid and itaconic acid and crosslinking of cotton fabric,” *Text. Res. J.*, vol. 69, no. 10, pp. 782–789, 1999.

[90] C. Q. Yang and Y. Lu, “In-situ polymerization of maleic acid and itaconic acid on cotton: MALDI/TOF mass spectroscopy and light-scattering study,” *Text. Res. J.*, vol. 70, no. 4, pp. 359–362, 2000.

[91] C. Q. Yang, C. Hu, and G. C. Lickfield, “Crosslinking cotton with poly(itaconic acid) and in situ polymerization of itaconic acid : fabric mechanical strength retention,” *J. Appl. Polym. Sci.,* vol. 87, pp. 2023–2030, 2003.

[92] C. Q. Yang, Q. He, and B. Voncina, “Cross-linking cotton cellulose by the combination of maleic acid and sodium hypophosphite. 2. fabric fire performance,” *Ind. Eng. Chem. Res.*, vol. 50, no. 10, pp. 5889–5897, 2011.

[93] C. Q. Yang and X. Gu, “Polymerization of maleic acid and itaconic acid studied by FT-Raman spectroscopy,” *J. Appl. Polym. Sci.*, vol. 81, pp. 223–228, 2001.

[94] C. Q. Yang, D. Chen, J. Guan, and Q. He, “Cross-linking cotton cellulose by the combination of maleic scid and sodium hypophosphite. 1. fabric wrinkle resistance,” *Ind. Eng. Chem. Res*., vol. 49, pp. 8325–8332, 2010.

[95] C. Q. Yang, “Evaluating ester crosslinking of cotton fabric by a polycarboxylic acid using acid-base titration,” *Text. Res. J*., vol. 70, no. 7, pp. 615–620, 2000.

[96] C. Q. Yang, W. Wei, and G. C. Lickfield, “Mechanical strength of durable press finished cotton fabric: part II: comparison of crosslinking agents with different molecular structures and reactivity,” *Text. Res. J.*, vol. 70, no. 2, pp. 143–147, 2000.

[97] W. Xu and Y. Li, “Crosslinking analysis of polycarboxylic acid durable press finishing of cotton fabrics and strength retention improvement,” *Text. Res. J.*, vol. 70, no. 7, pp. 588–592, 2000.

[98] C. M. Welch and G. J. Peters, “Malic acid as a nonformaldehyde DP finishing agent activated by BTCA and polymer additives,” *Text. Chem. Color*., vol. 29, no. 10, pp. 33–37, 1997.

[99] C. M. Welch and G. J. Peters, “Mixed polycarboxylic acids and mixed catalyst in formaldehyde-free durable press finishing,” *Text. Chem. Color*., vol. 29, no. 3, pp. 22–27, 1997.

[100] C. M. Welch and B. A. K. Andrews, “Ester crosslinks: a route to high performance non-formaldehyde finishing of cotton,” *Text. Chem. Color*., vol. 21, no. 2, pp. 13–17, 1989.

[101] C. M. Welch, “Tetracarboxylic acids as formaldehyde-free durable press finishing agents,” *Text. Res. J.*, vol. 58, no. 8, pp. 480–486, 1988.

[102] W. Wei and C. Q. Yang, “Polymeric carboxylic acid and citric acid as a nonformaldehyde DP finish,” *Text. Chem. Color*., vol. 32, no. 2, pp. 53–57, 2000.

[103] W. Udomkichdecha, S. Kittinaovarat, U. Thanasoonthornroek, P. Potiyaraj, and P. Likitbanakorn, “Acrylic and maleic acids in nonformaldehyde durable press finishing of cotton fabric,” *Text. Res. J.,* vol. 73, no. 5, pp. 401–406, 2003.

[104] W. Sricharussin, W. Ryo-Aree, W. Intasen, and S. Poungraksakirt, “Effect of boric acid and BTCA on tensile strength loss of finished cotton fabrics,” *Text. Res. J*., vol. 74, no. 6, pp. 475–480, 2004.

[105] C. Schramm, S. B. Vukušic, and D. Katovic, “Non-formaldehyde durable press finishing of dyed fabrics: evaluation of cotton-bound polycarboxylic acids,” *Color. Technol.,* vol. 118, pp. 244–249, 2002.

[106] S. P. Rowland, C. M. Welch, M. A. F. Brannan, and D. M. Gallagher, “Introduction of ester cross links into cotton cellulose by a rapid curing process,” *Text. Res. J*., vol. 37, no. 11, pp. 933–941, 1967.

[107] C. Schramm, B. Rinderer, and O. Bobleter, “Kinetic data for the crosslinking reaction of polycarboxylic acids with cellulose,” *J. Soc. Dye. Color.,* vol. 113, pp. 346–349, 1997.

[108] B. Martel, M. Weltrowski, D. Ruffin, and M. Morcellet, “Polycarboxylic acids as crosslinking agents for grafting cyclodextrins onto cotton and wool fabrics: Study of the process parameters,” *J. Appl. Polym. Sci.*, vol. 83, no. 7, pp. 1449–1456, 2002.

[109] Z. Mao and C. Q. Yang, “Polymeric multifunctional carboxylic acids as crosslinking agents for cotton cellulose: poly(itaconic acid) andin situ polymerization of itaconic acid,” *J. Appl. Polym. Sci*., vol. 79, no. 2, pp. 319–326, 2001.

[110] M. J. Lees, “Formaldehyde-free durable press finishing based on polymaleic acid chemistry,” *J. Text. Inst.*, vol. 90, no. 3, pp. 42–49, 1999.

[111] Y. Lam, C. Kan, and C. Yuen, “Wrinkle-resistant finishing of cotton fabric with BTCA - the effect of co-catalyst,” *Text. Res. J.,* vol. 81, no. 5, pp. 482–493, 2010.

[112] B.-H. Kim, J. Jang, and S.-W. Ko, “Durable press finish of cotton fabric using malic acid as a crosslinker,” *Fibers Polym*., vol. 1, no. 2, pp. 116–121, 2000.

[113] I. S. Kang, C. Q. Yang, and G. C. Lickfield, “Mechanical strength of durable press finished cotton fabrics: part I: effects of acid degradation and crosslinking of cellulose by polycarboxylic acids,” *Text. Res. J.,* vol. 68, no. 11, pp. 865–870, 1998.

[114] H. Choi, “Nonformaldehyde polymerization-crosslinking treatment of cotton fabrics for improved strength retention,” *Text. Res. J.,* vol. 62, no. 10, pp. 614–618, 1992.

[115] H.-M. Choi and Y. M. Kim, “Performance improvement of nonformaldehyde wrinkle resistant finished cotton fabrics treated with dialdehydes,” *Fibers Polym*., vol. 2, no. 4, pp. 190–195, 2001.

[116] D. Chen, C. Q. Yang, and X. Qiu, “Aqueous polymerization of maleic acid and cross-linking of cotton cellulose by poly(maleic acid),” *Ind. Eng. Chem. Res*., vol. 44, pp. 7921–7927, 2005.

[117] A. Bagchi and S. G. Saha, “Crease-resistant finishing of jute fabric using polycarboxylic acids,” *Indian J. Fibre Text. Res*., vol. 27, no. 6, pp. 166–170, 2002.

[118] B. A. K. Andrews and B. J. Collier, “Finishing additives in treatments of cotton fabrics for durable press with polycarboxylic acids,” *Ind. Eng. Chem. Res.,* vol. 31, no. 8, pp. 1981–1984, 1992.

[119] B. A. K. Andrews, “Nonformaldehyde DP finishing of cotton with citric acid,” *Text. Chem. Color*., vol. 22, no. 9, pp. 63–67, 1990.

[120] B. A. K. Andrews, E. J. Blanchard, and R. M. Reinhardt, “Fabric whiteness retention in durable press finishing with citric acid,” *Text. Chem. Color*., vol. 25, no. 3, pp. 52–54, 1993.

[121] U. K. Sahin, N. C. Gursoy, O. Hauser, and B. Smith, “Optimization of ionic crosslinking process: an alternative to conventional durable press finishing,” *Text. Res. J.*, vol. 79, no. 8, pp. 744–752, 2009.

[122] M. Hashem, M. H. Elshakankery, S. M. Abd El-Aziz, M. M. G. Fouda, and H. M. Fahmy, “Improving easy care properties of cotton fabric via dual effect of ester and ionic crosslinking,” *Carbohydr. Polym.*, vol. 86, no. 4, pp. 1692–1698, 2011.

[123] M. Hashem, P. Hauser, and B. Simth, “Wrinkle recovery for cellulosic fabric by means of ionic crosslinking,” *Text. Res. J.*, vol. 73, no. 9, pp. 762–766, 2003.

[124] N. R. Bertoniere, W. D. King, and C. M. Welch, “Effect of catalyst on the pore structure and performance of cotton cellulose crosslinked with butanetetracarboxylic acid,” *Text. Res. J.*, vol. 64, no. 5, pp. 247–255, 1994.

[125] C. E. Morris, N. M. Morris, and B. J. Trask-morrell, “Interaction of meso-1,2,3,4-butanetetracarboxylic acid with phosphorus-containing catalysts for esterification cross-linking of cellulose,” *Ind. Eng. Chem. Res.*, vol. 35, no. 3, pp. 950–953, 1996.

[126] A. Nazari, M. Montazer, A. Rashidi, M. Yazdanshenas, and M. Anary-Abbasinejad, “Nano TiO2 photo-catalyst and sodium hypophosphite for cross-linking cotton with poly carboxylic acids under UV and high temperature,” *Appl. Catal. A Gen.*, vol. 371, no. 1 – 2, pp. 10–16, 2009.

[127] C. Q. Yang, X. Wang, and Y. Lu, “Infrared spectroscopy studies of cyclic anhydrides as intermediates for ester crosslinking of cotton cellulose by polycarboxylic acids. IV. In situ free radical copolymerization of maleic acid and itaconic acid on cotton,” *J. Appl. Polym. Sci.*, vol. 75, no. 2, pp. 327–336, Jan. 2000.

[128] C. Q. Yang and X. Wang, “Infrared spectroscopy studies of the cyclic anhydride as the intermediate for the ester crosslinking of cotton cellulose by polycarboxylic acids. III. molecular weight of a crosslinking agent,” *J. Polym. Sci. Part A Polym. Chem.*, vol. 35, no. 3, pp. 557–564, 1997.

[129] X. Gu and C. Q. Yang, “FT-IR and FT-Raman spectroscopy study of the cyclic anhydride intermediates for esterification of cellulose: I. formation of anhydrides without a catalyst,” *Res. Chem. Intermed.*, vol. 24, no. 9, pp. 979–996, 1998.

[130] C. Q. Yang and X. Wang, “Formation of cyclic anhydride intermediates and esterification of cotton cellulose by multifunctional carboxylic acids: an infrared spectroscopy study,” *Text. Res. J.,* vol. 66, no. 9, pp. 595–603, 1996.

[131] C. Q. Yang, “FTIR spectroscopy study of the formation of cyclic anhydride intermediates of polycarboxylic acids catalyzed by sodium hypophosphite,” *Text. Res. J.,* vol. 70, no. 1, pp. 64–70, 2000.

[132] C. M. Welch, “Durable press finishing without formaldehyde,” *Text. Chem. Color.*, vol. 22, no. 5, pp. 13–16, 1990.

[133] C. Q. Yang, “FTIR spectroscopy study of ester crosslinking of cotton cellulose catalyzed by sodium hypophosphite,” *Text. Res. J.,* vol. 71, no. 3, pp. 201–206, 2001.

[134] C. Q. Yang, “FT-IR spectroscopy study of the ester crosslinking mechanism of cotton cellulose,” *Text. Res. J.,* vol. 61, no. 8, pp. 433–440, 1991.

[135] B. J. Trask-morrell and B. A. K. Andrews, “Effect of catalysts on the thermal characteristics of cotton citric acid DP finishes,” *Text. Res. J.,* vol. 67, pp. 846–853, 1997.

[136] O. Šauperl, K. Stana-Kleinschek, B. Voncina, M. Sfiligoj-Smole, and A. Majcen-Le Marechal, “Application of spectrophotometric methods in assessing the influence of alkaline treatment on the degree of crosslinking of cotton cellulose with BTCA,” *Croat. Chem. Acta*, vol. 76, no. 4, pp. 293–298, 2003.

[137] N. Bhattacharya, B. A. Doshi, and A. S. Sahasrabudhe, “Cost effective catalyst for polycarboxylic acid finishing,” *Text. Chem. Color.*, vol. 31, no. 6, pp. 33–37, 1999.

[138] N. A. Ibrahim, M. H. Abo-Shosha, E. I. Elnagdy, and M. A. Gaffar, “Eco-friendly durable press finishing of cellulose-containing fabrics,” *J. Appl. Polym. Sci.*, vol. 84, no. 12, pp. 2243–2253, 2002.

[139] Y. Lu and C. Q. Yang, “Fabric yellowing caused by citric acid as a crosslinking agent for cotton,” *Text. Res. J.*, vol. 69, no. 9, pp. 685–690, 1999.

[140] C. Schramm and B. Rinderer, “Influence of additives on the formation of unsaturated PCAs produced during durable-press curing with citric acid,” *Color. Technol.*, vol. 115, no. 10, pp. 306–311, 1999.

[141] M. M. Barbooti and D. A. Al-Sammerrai, “Thermal decomposition of citric acid,” *Thermochim. Acta,* vol. 98, pp. 119–126, 1986.

[142] J. W. Fischer, L. H. Merwin, and R. A. Nissan, “NMR investigation of the thermolysis of citric acid,” *Appl. Spectrosc.,* vol. 49, no. 1, pp. 120–126, 1995.

[143] D. Wyrzykowski, E. Hebanowska, G. Nowak-Wiczk, M. Makowski, and L. Chmurzyński, “Thermal behaviour of citric acid and isomeric aconitic acids,” *J. Therm. Anal. Calorim.*, vol. 104, no. 2, pp. 731–735, 2010.

[144] R. Allabashi, M. Arkas, G. Hörmann, and D. Tsiourvas, “Removal of some organic pollutants in water employing ceramic membranes impregnated with cross-linked silylated dendritic and cyclodextrin polymers,” *Water Res.*, vol. 41, pp. 476–486, 2007.

[145] T. Karthik, R. Rathinamoorthy, and R. Murugan, “Enhancement of wrinkle recovery angle of cotton fabric using citric acid cross-linking agent with nano-TiO2 as a co-catalyst,” *J. Ind. Text.*, vol. 42, no. 2, pp. 99–117, 2011.

[146] H. Peng, C. Q. Yang, X. Wang, and S. Wang, “The combination of itaconic acid and sodium hypophosphite as a new cross-linking system for cotton,” *Ind. Eng. Chem. Res.*, vol. 51, no. 35, pp. 11301–11311, 2012.

[147] C. C. Wang and C. C. Chen, “Physical properties of crosslinked cellulose catalyzed with nano titanium dioxide,” *J. Appl. Polym. Sci.*, vol. 97, no. 6, pp. 2450–2456, 2005.

[148] C.-C. Chen and C.-C. Wang, “Crosslinking of cotton cellulose with succinic acid in the presence of titanium dioxide nano-catalyst under UV irradiation,” *J. Sol-Gel Sci. Technol.*, vol. 40, no. 1, pp. 31–38, 2006.

[149] A. Nazari, M. Montazer, A. Rashidi, M. Yazdanshenas, and M. B. Moghadam, “Optimization of cotton crosslinking with polycarboxylic acids and nano TiO2 using central composite design,” *J. Appl. Polym. Sci.*, vol. 117, pp. 2740–2748, 2010.

[150] C. C. Wang and C. C. Chen, “Physical properties of the crosslinked cellulose catalyzed with nanotitanium dioxide under UV irradiation and electronic field,” *Appl. Catal. A Gen.*, vol. 293, no. 1–2, pp. 171–179, 2005.

[151] Y. L. Lam, C. W. Kan, C. W. M. Yuen, and C. H. Au, “Fabric objective measurement of the plasma-treated cotton fabric subjected to wrinkle-resistant finishing with BTCA and TiO_2 system,” *Fibers Polym.*, vol. 12, no. 5, pp. 626–634, 2011.

[152] L. Karimi, M. Mirjalili, M. E. Yazdanshenas, and A. Nazari, “Effect of nano TiO2 on self-cleaning property of cross-linking cotton fabric with succinic acid under UV irradiation,” *Photochem. Photobiol.*, vol. 86, no. 5, pp. 1030–1037, 2010.

[153] A. Hebeish, F. A. Abdel-Mohdy, M. M. G. Fouda, Z. Elsaid, S. Essam, G. H. Tammam, and E. A. Drees, “Green synthesis of easy care and antimicrobial cotton fabrics,” *Carbohydr. Polym.,* vol. 86, no. 4, pp. 1684–1691, 2011.

[154] M. Nazi, R. M. A. Malek, and R. Kotek, “Modification of ß-cyclodextrin with itaconic acid and application of the new derivative to cotton fabrics,” *Carbohydr. Polym.*, vol. 88, no. 3, pp. 950–958, 2012.

[155] J. Szejtli, “Cyclodextrins in the textile industry,” *Starch*, vol. 55, no. 5, pp. 191–196, 2003.

[156] D. H. Keifer, “Foundations of Polymer Science: Wallace Carothers and the Development of Nylon,” *American Chemical Society National Historic Chemical Landmarks*, 2000. [Online]. Available:

http://www.acs.org/content/acs/en/education/whatischemistry/landmarks/carotherspolymers.html. [Accessed: 10-Aug-2013].

[157] “Hermann Staudinger and the Foundation of Polymer Science,” *American Chemical Society National Historic Chemical Landmarks,* 1999. [Online]. Available: http://www.acs.org/content/acs/en/education/whatischemistry/landmarks/staudingerpolymerscience.html. [Accessed: 10-Aug-2013].

[158] J. Ginsberg, “Herman Mark and the Polymer Research Institute,” *American Chemical Society National Historic Chemical Landmarks*, 2003. [Online]. Available: http://www.acs.org/content/acs/en/education/whatischemistry/landmarks/polymerresearchinstitute.html. [Accessed: 10-Aug-2013].

[159] L. Wei, J. Wang, H. Zhou, W. Jin, Z. Hu, and J. Ni, “Directional breeding of high itaconic acid yielding strain of Aspergillus terreus with a new plate technique,” *Adv. Microbiol*., vol. 3, pp. 376–381, 2013.

[160] K. J. Yoon, J. H. Woo, and Y. S. Seo, “Formaldehyde free cross-linking agents based on maleic anhydride copolymers,” *Fibers Polym*., vol. 4, no. 4, pp. 182–187, 2003.

[161] H. Peng, C. Q. Yang, and S. Wang, “Nonformaldehyde durable press finishing of cotton fabrics using the combination of maleic acid and sodium hypophosphite,” *Carbohydr. Polym*., vol. 87, no. 1, pp. 491–499, 2012.

[162] P. Ghosh and D. Das, “Modification of cotton by acrylic acid (AA) in the presence of NaH_2O_4 and $K_2S_2O_8$ as catalysts under thermal treatment,” *Eur. Polym. J.,* vol. 36, pp. 2505–2511, 2000.

[163] S. Kittinaovarut, “Acrylic and citric acid in nonformaldehyde durable press finishing on cotton fabric,” *AATCC Rev*., vol. 3, no. 8, pp. 62–64, 2003.

[164] W. Udomkichdecha, S. Kittinaovarat, U. Thanasoonthornroek, P. Potiyaraj, and P. Likitbanakorn, “Acrylic and Maleic Acids in Nonformaldehyde Durable Press Finishing of Cotton Fabric,” *Text. Res. J.,* vol. 73, no. 5, pp. 401–406, May 2003.

[165] C. M. Welch, “Improved strength and flex abrasion resistance in durable press finishing with BTCA,” *Text. Chem. Color*., vol. 29, no. 2, pp. 21–24, 1997.

[166] H. Kricheldorf, “Experiments Before World War I,” in *Polycondensation: History and New Results*, Heidelberg: Springer-Verlag, 2014, pp. 7–25.

[167] R. Mülhaupt, “Hermann staudinger and the origin of macromolecular chemistry,” *Angew. Chemie Int. Ed*., vol. 43, no. 9, pp. 1054–1063, 2004.

[168] D. A. Tomalia, H. Baker, J. Dewald, M. Hall, G. Kallos, J. Roeck, J. Ryder, and P. Smith, "A new class of polymers: starburst-dendritic macromolecules," *Polym. J.,* vol. 17, no. 1, pp. 117–132, 1985.

[169] D. A. Tomalia, H. Baker, J. Dewald, M. Hall, G. Kallos, S. Martin, J. Roeck, J. Ryder, and P. Smith, "Dendritic macromolecule: synthesis of starburst dendrimers," *Macromolecules*, vol. 19, pp. 2466–2468, 1986.

[170] C. J. Hawker, R. Lee, and J. M. J. Frechet, "One-step synthesis of hyperbranched dendritic polyesters*," J. Am. Chem. Soc.,* vol. 113, no. 12, pp. 4583–4588, 1991.

[171] C. J. Hawker and J. M. J. Fréchet, "Preparation of polymers with controlled molecular architecture. A new convergent approach to dendritic macromolecules," *J. Am. Chem. Soc*., vol. 112, no. 8, pp. 7638–7647, 1990.

[172] Y. H. Kim and O. W. Webster, "Hyperbranched polyphenylenes," *Macromolecules*, vol. 25, no. 21, pp. 5561–5572, 1992.

[173] Y. H. Kim and O. W. Webster, "Water-soluble hyperbranched polyphenylene: 'a unimolecular micelle'?," *J. Am. Chem. Soc*., vol. 112, no. 11, pp. 4592–4593, 1990.

[174] R. H. Kienle and A. G. Hovey, "The polyhydric alcohol-polybasic acid reaction. I. Glycerol-phthalic anhydride," *J. Am. Chem. Soc*., vol. 51, pp. 509–519, 1929.

[175] R. H. Kienle, P. A. Van der Meulen, and F. E. Petke, "The polyhydric alcohol-polybasic acid reaction. III. Further studies of the glycerol-phthalic anhydride reaction*," J. Am. Chem. Soc*., vol. 61, pp. 2258–2268, 1939.

[176] R. H. Kienle, P. A. Van der Meulen, and F. E. Petke, "The polyhydric alcohol-polybasic acid reaction. IV. glyceryl phthalate from phthalic acid," *J. Am. Chem. Soc*., vol. 61, pp. 2268–2271, 1939.

[177] W. Smith, "A new glyceride: glycerine phthalate," *J. Soc. Chem. Ind*., vol. 20, pp. 1075–1076, 1901.

[178] P. J. Flory, "Molecular size distribution in three dimensional polymers. VI. Branched polymers containing A-R-Bf-1 type units," *J. Am. Chem. Soc*., vol. 74, pp. 2718–2723, 1951.

[179] P. J. Flory, "Molecular size distribution in three dimensional polymers. II. Trifunctional branching units*," J. Am. Chem. Soc*., vol. 63, pp. 3091–3096, 1941.

[180] P. J. Flory, "Molecular size distribution in three dimensional polymers. I. Gelation," *J. Am. Chem. Soc.*, vol. 63, pp. 3083–3090, 1941.

[181] P. J. Flory, "Molecular size distribution in three dimensional polymers. V. Post-gelation relationships," *J. Am. Chem. Soc*., vol. 69, pp. 30–35, 1947.

[182] P. J. Flory, “Molecular size distribution in three dimensional polymers. III. Tetrafunctional branching units,” *J. Am. Chem. Soc*., vol. 64, pp. 3096–3100, 1941.

[183] C. Gao, D. Yan, and H. Frey, “Promising dendritic materials : an introduction to hyperbranched polymers,” in *Hyperbranched Polymers: Synthesis, Properties, and Applications*, D. Yan, C. Gao, and H. Frey, Eds. New Jersey: John Wiley & Sons, Inc, 2011, pp. 1–26.

[184] D. Hölter, A. Burgath, and H. Frey, “Degree of branching in hyperbranched polymers,” *Acta Polym.*, vol. 48, no. 1–2, pp. 30–35, 1997.

[185] H. R. Kricheldorf*, Polycondensation*. Heidelberg: Springer-Verlag, 2014.

[186] H. R. Kricheldorf, M. G. Zolotukhin, and J. Cárdenas, “Non-stoichiometric polycondensations and the synthesis of high molar mass polycondensates,” *Macromol. Rapid Commun*., vol. 33, pp. 1814–1832, 2012.

[187] H. Frey and D. Hölter, “Degree of branching in hyperbranched polymers. 3 Copolymerization of ABm-monomers with AB and ABn-monomers,” *Acta Polym*., vol. 50, no. 2–3, pp. 67–76, 1999.

[188] D. Hölter and H. Frey, “Degree of branching in hyperbranched polymers. 2. Enhancement of the DB: scope and limitations,” *Acta Polym*., vol. 48, no. 8, pp. 298–309, 1997.

[189] D. Yan and Z. Zhou, “Molecular weight distribution of hyperbranched polymers generated from polycondensation of AB_2 type monomers in the presence of multifunctional core moieties,” *Macromolecules*, vol. 32, no. 3, pp. 819–824, 1999.

[190] R. Hanselmann, D. Hölter, and H. Frey, “Hyperbranched polymers prepared via the core-dilution/slow addition technique: computer simulation of molecular weight distribution and degree of branching,” *Macromolecules*, vol. 31, no. 12, pp. 3790–3801, 1998.

[191] S. Kuchanov, H. Slot, and A. Stroeks, “Development of a quantitative theory of polycondensation,” *Prog. Polym. Sci.,* vol. 29, no. 6, pp. 563–633, 2004.

[192] C. Gao, H. Frey, and D. Yan, “Conclusions and perspective: toward hyperbranched/dendritic states,” in *Hyperbranched Polymers: Synthesis, Properties, and Applications*, D. Yan, C. Gao, and H. Frey, Eds. New Jersey: John Wiley & Sons, Inc., 2011, pp. 441–454.

[193] B. Voit, “Hyperbranched polymers—all problems solved after 15 years of research?,” *J. Polym. Sci.,* vol. 43, pp. 2679–2699, 2005.

[194] B. I. Voit, “Hyperbranched polymers: a chance and a challenge,” *Comptes Rendus Chim*., vol. 6, no. 8–10, pp. 821–832, Aug. 2003.

[195] A. Carlmark, E. Malmström, and M. Malkoch, “Dendritic architectures based on bis-MPA: functional polymeric scaffolds for application-driven research.,” *Chem. Soc. Rev.,* vol. 42, pp. 5858–5879, 2013.

[196] J. M. J. Fréchet, “Functional molecular dendrimers: reactivity, molecular architecture, interfacial energy,” *Sci. New Ser*., vol. 263, no. 5154, pp. 1710–1715, 1994.

[197] H. C. Kolb, M. G. Finn, and K. B. Sharpless, “Click chemistry: diverse chemical function from a few good reactions,” *Angew. Chemie Int. Ed*., vol. 40, no. 11, pp. 2004–2021, 2001.

[198] K. L. Killops, L. M. Campos, and C. J. Hawker, “Robust, efficient, and orthogonal synthesis of dendrimers via thiol-ene ‘click’ chemistry*,” J. Am. Chem. Soc.,* vol. 130, no. 15, pp. 5062–5064, 2008.

[199] G. Franc and A. K. Kakkar, “Diels-alder ‘click’ chemistry in designing dendritic macromolecules,” *Chem. Eur. J.,* vol. 15, pp. 5630–5639, 2009.

[200] B. Helms and E. W. Meijer, “Dendrimers at work,” *Sci. New Ser*., vol. 313, no. 5789, pp. 929–930, 2006.

[201] J. Alper, “Rising chemical ‘stars’ could play many roles,” *Sci. New Ser*., vol. 251, no. 5001, pp. 1562–1564, 1991.

[202] H. R. Kricheldorf, Q.-Z. Zang, and G. Schwarz, “New polymer syntheses: 6. Linear and branched poly(3-hydroxy-benzoates),” *Polymer (Guildf).*, vol. 23, no. 12, pp. 1821–1829, 1982.

[203] C. R. Yates and W. Hayes, “Synthesis and applications of hyperbranched polymers,” *Eur. Polym. J.*, vol. 40, pp. 1257–1281, 2004.

[204] C. Gao and D. Yan, “Hyperbranched polymers: from synthesis to applications,” *Prog. Polym. Sci.*, vol. 29, pp. 183–275, 2004.

[205] M. Jikei and M. Kakimoto, “Hyperbranched polymers: a promising new class of materials,” *Prog. Polym. Sci.*, vol. 26, pp. 1233–1285, 2001.

[206] H. Mori, A. H. E. Muller, and P. F. W. Simon, “Self-condensing vinyl polymerization,” in *Hyperbranched Polymers: Synthesis, Properties, and Applications*, D. Yan, C. Gao, and H. Frey, Eds. New Jersey: John Wiley & Sons, Inc., 2011, pp. 139–174.

[207] S. Unal, G. I. Ozturk, and T. E. Long, “Synthesis of hyperbranched polymers via polymerization of functionally symmetric monomer pairs,” in *Hyperbranched Polymers: Synthesis, Properties, and Applications*, D. Yan, C. Gao, and H. Frey, Eds. New Jersey: John Wiley & Sons, Inc., 2011, pp. 79–106.

[208] D. Wilms and H. Frey, “Ring-opening multibranching polymerization,” in *Hyperbranched Polymers: Synthesis, Properties, and Applications*, D. Yan, C. Gao, and H. Frey, Eds. New Jersey: John Wiley & Sons, Inc., 2011, pp. 175–202.

[209] R. A. T. M. Van Benthem, “Novel hyperbranched resins for coating applications,” *Prog. Org. Coatings*, vol. 40, no. 1–4, pp. 203–214, 2000.

[210] J. M. J. Fréchet, M. Henmi, I. Gitsov, S. Aoshima, M. R. Leduc, R. B. Grubbs, and J. M. J. Frechet, “Self-condensing vinyl polymerization : an approach to dendritic materials,” *Sci. New Ser.*, vol. 269, no. 5227, pp. 1080–1083, 1995.

[211] L. J. Hobson, A. M. Kenwright, and W. J. Feast, “A simple ‘one pot’ route to the hyperbranched analogues of Tomalia’s poly(amidoamine) dendrimers,” *Chem. Commun.*, pp. 1877–1878, 1997.

[212] L. J. Hobson and W. J. Feast, “Poly(amidoamine) hyperbranched systems: synthesis, structure and characterization*,” Polymer (Guildf).,* vol. 40, pp. 1279–1297, 1999.

[213] C. Gao and D. Yan, “Synthesis of hyperbranched polymers from commercially available A2 and BB’2 type monomers,” *Chem. Commun.*, pp. 107–108, 2001.

[214] C. Gao and D. Yan, “Polyaddition of B2 and BB’2 type monomers to A2 type monomer. 1.Synthesis of highly branched copoly(sulfone-amine)s,” *Macromolecules*, vol. 34, pp. 156–161, 2001.

[215] C. Gao and D. Yan, “Hyperbranched polymers made from A2, BB’2 type monomers. 1. Polyaddition of 1-(2-aminoethyl)piperazine to divinyl sulfone,” *Macromolecules*, vol. 33, pp. 7693–7699, 2000.

[216] Z. Zhou and D. Yan, “Kinetic treatment for the copolycondensation of A_2 and CB_2 monomers with non-equal reactivity,” *Polymer (Guildf).*, vol. 52, pp. 5387–5392, 2011.

[217] W. J. Feast and N. M. Stainton, “Synthesis, structure and properties of some hyperbranched polyesters,” J*. Mater. Chem.*, vol. 5, no. 3, pp. 405–411, 1995.

[218] E. Malmström and A. Hult, “Hyperbranched polymers: a review,” J*. Macromol. Sci. Part C*, vol. 37, no. 3, pp. 555–579, 1997.

[219] E. Malmström and A. Hult, “Kinetics of formation of hyperbranched polyesters based on 2,2-bis(methylol)propionic acid,” *Macromolecules*, vol. 29, pp. 1222–1228, 1996.

[220] A. Burgath, A. Sunder, and H. Frey, “Role of cyclization in the synthesis of hyperbranched aliphatic polyesters*,” Macromol. Chem. Phys.*, vol. 201, pp. 782–791, 2000.

[221] R. Knischka, P. J. Lutz, A. Sunder, R. Mülhaupt, and H. Frey, “Functional poly(ethylene oxide) multiarm star polymers: core-first synthesis using hyperbranched polyglycerol initiators,” *Macromolecules*, vol. 33, pp. 315–320, 2000.

[222] G. Jiang, X. Sun, Y. Wang, and M. Ding, “Synthesis and fluorescence properties of hyperbranched poly(amidoamine)s with high density tertiary nitrogen*,” Polym. Chem.*, vol. 1, no. 10, pp. 1644–1649, 2010.

[223] H. Gao, D. Yorifuji, J. Wakita, Z. Jiang, and S. Ando, "In situ preparation of nano ZnO/hyperbranched polyimide hybrid film and their optical properties," *Polymer (Guildf).*, vol. 51, no. 14, pp. 3173–3180, 2010.

[224] B. Yu, X. Jiang, G. Yin, and J. Yin, "Multistimuli-responsive hyperbranched poly(ether amine)s," *J. Polym. Sci. Part A Polym. Chem*., vol. 48, no. 19, pp. 4252–4261, 2010.

[225] A. D'Emanuele and D. Attwood, "Dendrimer-drug interactions," *Adv. Drug Deliv. Rev*., vol. 57, no. 15, pp. 2147–2162, 2005.

[226] A. Duda and S. Penczek, "Mechanisms of aliphatic polyester formation," in *Biopolymers 3: Polyesters II : properties and chemical synthesis*, A. Steinbüchel and Y. Doi, Eds. New York: Wiley-VCH, 2002, pp. 371–383.

[227] M. W. Grinstaff, "Biodendrimers: new polymeric biomaterials for tissue engineering," *Chem. - A Eur. J.*, vol. 8, no. 13, pp. 2838–2846, 2002.

[228] A. Tiwari, S. Aryal, S. Pilla, and S. Gong, "An amperometric urea biosensor based on covalently immobilized urease on an electrode made of hyperbranched polyester functionalized gold nanoparticles.," *Talanta*, vol. 78, no. 4–5, pp. 1401–1407, 2009.

[229] C. Kontoyianni, Z. Sideratou, T. Theodossiou, L.-A. Tziveleka, D. Tsiourvas, and C. M. Paleos, "A novel micellar PEGylated hyperbranched polyester as a prospective drug delivery system for paclitaxel," *Macromol. Biosci*., vol. 8, no. 9, pp. 871–881, 2008.

[230] C. M. Paleos, D. Tsiourvas, and Z. Sideratou, "Molecular Engineering of Dendritic Polymers and Their Application as Drug and Gene Delivery Systems," *Mol. Pharm*., vol. 4, no. 2, pp. 169–188, 2006.

[231] O. L. Padilla De Jesús, H. R. Ihre, L. Gagne, J. M. J. Fréhet, and F. C. Szoka, "Polyester dendritic systems for drug delivery applications: in vitro and In vivo Evaluation," *Bioconjug. Chem*., vol. 13, pp. 453–461, 2002.

[232] C. Xia, X. Ding, Y. Sun, H. Liu, and Y. Li, "Hyperbranched-upon-dendritic macromolecules as unimolecular hosts for controlled release," *J. Polym. Sci. Part A Polym. Chem*., vol. 48, no. 18, pp. 4013–4019, 2010.

[233] B. K. Nanjwade, H. M. Bechra, G. K. Derkar, F. V. Manvi, and V. K. Nanjwade, "Dendrimers: emerging polymers for drug-delivery systems," *Eur. J. Pharm. Sci*., vol. 38, pp. 185–196, 2009.

[234] R. Esfand and D. A. Tomalia, "Poly(amidoamine) (PAMAM) dendrimers: from biomimicry to drug delivery and biomedical applications," *Drug Discov. Today*, vol. 6, no. 8, pp. 427–436, 2001.

[235] E. R. Gillies and J. M. J. Fréchet, “Dendrimers and dendritic polymers in drug delivery,” *Drug Discov. Today,* vol. 10, no. 1, pp. 35–43, 2005.

[236] S. Svenson and D. A. Tomalia, “Dendrimers in biomedical applications - Reflections on the field,” *Adv. Drug Deliv. Rev*., vol. 57, pp. 2106–2129, 2005.

[237] H. Namazi and M. Adeli, “Dendrimers of citric acid and poly (ethylene glycol) as the new drug-delivery agents,” *Biomaterials*, vol. 26, no. 10, pp. 1175–1183, 2005.

[238] P. Kolhe, “Drug complexation, in vitro release and cellular entry of dendrimers and hyperbranched polymers,” *Int. J. Pharm*., vol. 259, no. 1–2, pp. 143–160, 2003.

[239] E. Zagar, M. Zigon, and S. Podzimek, “Characterization of commercial aliphatic hyperbranched polyesters,” *Polymer (Guildf)*., vol. 47, no. 1, pp. 166–175, 2006.

[240] N. J. Mount Oliver, “BASF increases production of Lupasol[TM] polyethyleneimine,” *Adhes. Sealants Ind.*, vol. 5, no. 9, p. 18, 1998.

[241] “Hpyerbranched polymers,” *Polymer Factory Sweden AB*, 2014. [Online]. Available: http://www.polymerfactory.com/hyperbranched-polymers. [Accessed: 31-Aug-2014].

[242] B. Editors, “ChemPoint.com expands relationship with BASF for larostat and lupasol specialty additives,” *Business Wire*, 2003. [Online]. Available: http://search.proquest.com/docview/446326306?accountid=16210. [Accessed: 31-Oct-2013].

[243] P. Froehling, “Development of DSM’s hybrane hyperbranched polyesteramides,” *J. Polym. Sci. Part A Polym. Chem.*, vol. 42, no. 13, pp. 3110–3115, 2004.

[244] H. Bergenudd, P. Eriksson, C. Dearmitt, B. Stenberg, and M. E. Jonsson, “Synthesis and evaluation of hyperbranched phenolic antioxidants of three different generations,” *Polym. Degrad. Stab.*, vol. 76, pp. 503–509, 2002.

[245] F. Zhang, X. Wu, Y. Chen, and H. Lin, “Application of silver nanoparticles to cotton fabric as an antibacterial textile finish,” *Fibers Polym*., vol. 10, no. 4, pp. 496–501, 2009.

[246] F. Zhang, D. Zhang, Y. Chen, and H. Lin, “The antimicrobial activity of the cotton fabric grafted with an amino-terminated hyperbranched polymer,” Cellulose, vol. 16, pp. 281–288, 2009.

[247] D. Zhang, L. Chen, D. Fang, G. W. Toh, X. Yue, Y. Chen, and H. Lin, “In situ generation and deposition of nano-ZnO on cotton fabric by hyperbranched polymer for its functional finishing,” *Text. Res. J*., 2013., DOI: 10.1177/0040517512474362

[248] N. A. Ibrahim, H. M. Fahmy, M. A. Rehim, S. S. Sharaf, and M. H. Abo-Shosha, “Finishing of cotton fabrics with hyperbranched poly(ester-amine) to enhance their antibacterial properties and UV protection,” *Polym. Plast. Technol. Eng*., vol. 49, no. 13, pp. 1297–1304, 2010.

[249] N. A. Ibrahim, B. M. Eid, and H. El-Batal, “A novel approach for adding smart functionalities to cellulosic fabrics*,” Carbohydr. Polym.*, vol. 87, pp. 744–751, 2012.

[250] G. Wang, L. Zhuang, J. Sun, and C.-L. Zheng, “Salt-free dyeing of ramie fabric with an amino-terminated hyperbranched polymer,” *Cellulose*, vol. 21, pp. 3725–3736, 2014.

[251] S. M. Burkinshaw, P. E. Froehling, and M. Mignanelli, “The effect of hyperbranched polymers on the dyeing of polypropylene fibres,” *Dye. Pigment.*, vol. 53, pp. 229–235, 2002.

[252] F. Zhang, Y. Chen, H. Lin, and Y. Lu, “Synthesis of an amino-terminated hyperbranched polymer and its application in reactive dyeing on cotton as a salt-free dyeing auxiliary,” *Color. Technol*., vol. 123, pp. 351–357, 2007.

[253] N. M. Mahmoodi, B. Hayati, M. Arami, and F. Mazaheri, “Single and binary system dye removal from colored textile wastewater by a dendrimer as a polymeric nanoarchitecture: equilibrium and kinetics*,” J. Chem. Eng*., vol. 55, pp. 4660–4668, 2010.

[254] B. Hayati, A. Mokhtar, A. Maleki, and E. Pajootan, “Desalination and water Treatment thermodynamic properties of dye removal from colored textile wastewater by poly(propylene imine) dendrimer,” *Desalin. Water Treat*., pp. 1–10, 2014.

[255] M. Abdel Rehim, H. M. Fahmy, M. H. Abo-Shosha, and N. A. Ibrahim, “Synthesis, characterisation and utilisation of hyperbranched poly(ester-amide) for the removal of some anionic dyestuffs from their aqueous solutions,” *Pigment Resin Technol*., vol. 39, no. 3, pp. 149–155, 2010.

Chapter Three –

Development and Application of Dendritic Polycitric Acid Cross-linker

3.1 Introduction

In view of attractive potentials of polymeric cross-linkers, CA, a naturally available α-hydroxylcarboxylic acid, was coupled with various polyols to develop carboxyl-based cross-linkers as wrinkle-resistant finishing agents for cotton textiles in the first stage of this study.

CA is an A_3B building block. Theoretically, CA is capable of self-polymerising as dendritic macromolecules. The dual functionality of hydroxylcarboxylic acids is distinguishing. They could undergo mutual esterification to form polyester. However, undesirable reaction is encountered due to their dual functionality. CA consists of tertiary hydroxyl which is susceptible to undergo internal dehydration reduced the capability of further polymerisation and imparting colour to the products [1]–[3]. To suppress the suggested side reaction, several polyols with primary hydroxyls were selected as the core molecules with more than two active functional groups (B_f) to build dendritic CA cross-linkers in this part of the study. CA is vulnerable to form unsaturated polycarboxylic acids, acontic acids, imparting severe fabric yellowing. In spite of such deficiency, naturally available CA with 3 carboxyls is a non-toxic, low-cost, and effective cross-linker [1]–[6].

In this chapter, a series of polycitric acid (PCA) polymers coupled with various polyols were prepared. Chemical structures of individual reactants are illustrated in Figure 3-1. Sequential application of the newly developed PCA polymers was subjected to wrinkle-resistant finishing study. Evaluations of the wrinkling phenomenon and other properties of the modified cotton textiles were studied.

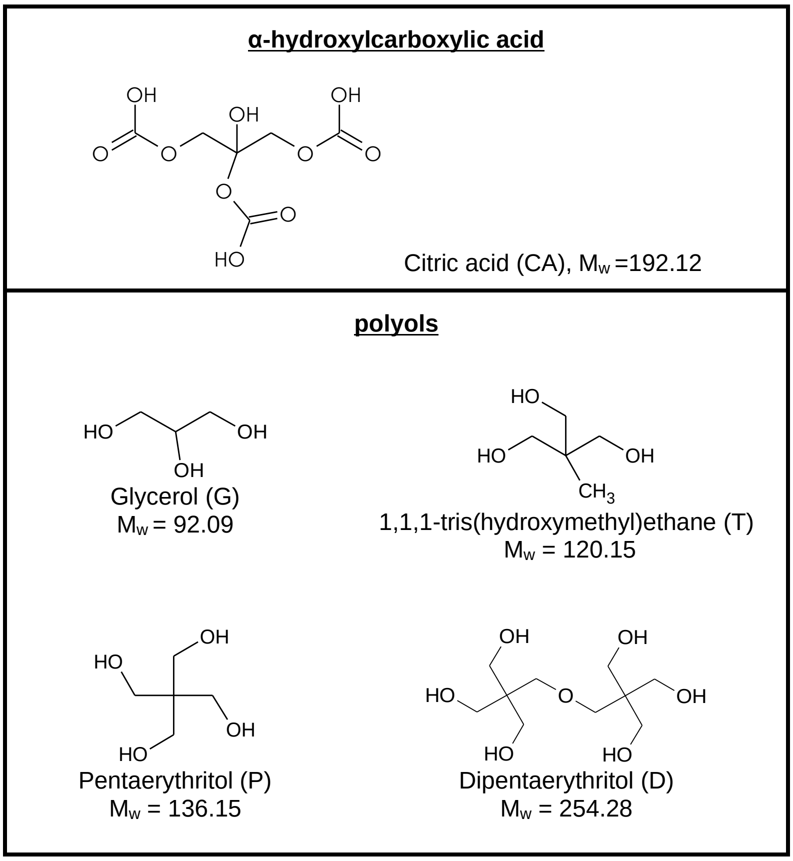


Figure 3-1 CA and core molecules used in the preparation of dendritic PCA cross-linkers

3.2 Experimental

3.2.1 Materials

Anhydrous CA was purchased from Acros Organics. Glycerol (G) was obtained from Fisher Scientific. 1,1,1-tris(hydroxymethyl)ethane (T) and pentaerythritol (P) obtained were from Sigma-Aldrich Co. Dipentaerythritol (D) and sulfolane were supplied by AccuChem Co. while mesitylene and sodium hydroxide (NaOH) were supplied by International Laboratory. *Ortho*-phosphoric acid (H_3PO_4) was purchased from Rankem Chemical. Chloroform, diethyl ether and tetrahydrofuran (THF) were purchased from Duskan Pure Chemicals. Sodium hypophosphite monohydrate ($NaH_2PO_2{\cdot}H_2O$) and absolute ethanol were supplied by International Laboratory and VWR respectively. Dimethyl sulfoxide-d_6 (DMSO-d_6) was obtained from Acros Organics. All chemicals were used as received. 100% plain woven semi-bleached cotton fabric (160 x 72, 127g/m^2) was used for the wrinkle-resistant finishing study.

3.2.2 Synthesis of Polymeric Cross-linker

α-hydroxylcarboxylic acid, CA in a combination with various polyols were mixed and reacted to form dendritic polymers via azeotropic polycondensation as shown in Scheme 3-1. General procedures are summarised as below.

In a 250ml round bottom flask, a suspension of CA (0.26mol), the designated polyol of various molar ratios (G of 0.009mol to 0.022mol; T of 0.009mol to 0.029mol; P of 0.008mol to 0.033mol; D of 0.007mol to 0.022mol), and H_3PO_4 (0.013mol) in the solvent mixture of sulfolane and mesitylene (100ml in total) was refluxed under nitrogen atmosphere at 175°C. Water generated in the reaction was continuously removed from the system using a Dean–Stark trap with a reflux condenser. The reaction was conducted for 4 hours. Crude product was firstly dissolved in minimum amount of ethanol and sequentially precipitated in diethyl ether or chloroform. The purified product was dried under reduced pressure. Purified products were clear yellowish pastes. The yield obtained by precipitation of crude products ranging from 42% to 87% by weight.

Several purified PCAs were subjected to study of the feasibility of this series of dendritic polymers serving as the wrinkle-resistant agents.

PCA-Ts:

FTIR-ATR (cm^{-1}): 3437 (vO-H, acid), 2982 (vC-H), 1706 (vC=O ester), 1393 (δC-H), 1183 (v C-O-C ester)

^{1}H-NMR (400MHz, DMSO-d_6), δ (TMS ppm): 0.93 (s, CH_3, T moiety); 2.64-2.88 (m, CH_2, CA moieties), 4.03 (m, CH_2, T moiety)

PCA-Ps:

FTIR-ATR (cm^{-1}): 3453 (vO-H, acid), 2988 (vC-H), 1708 (vC=O, ester), 1397 (δC-O-H), 1176 (v C-O-C ester)

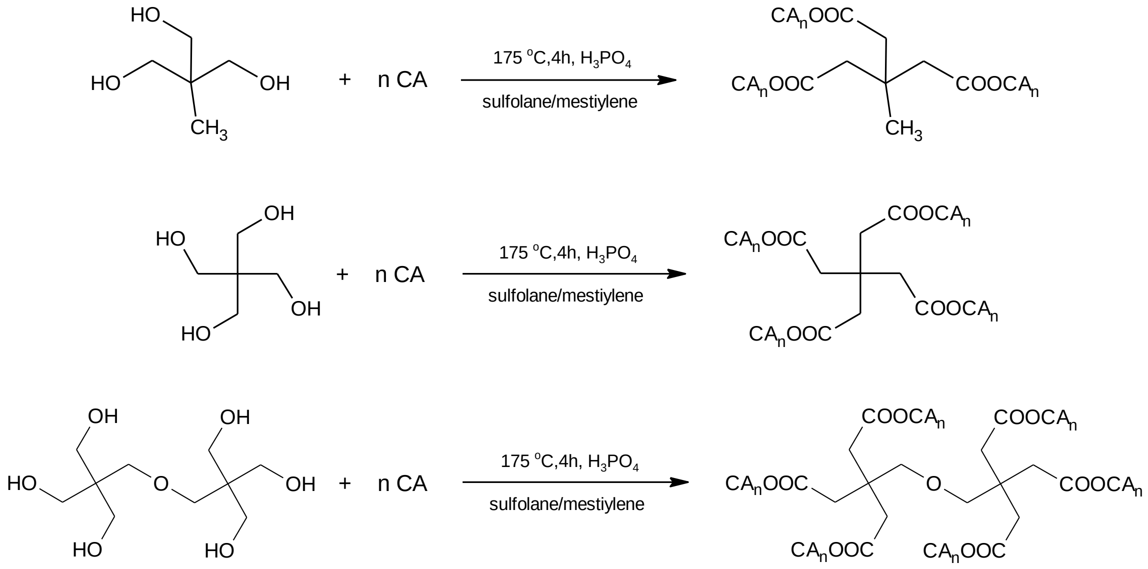
^{1}H-NMR (400MHz, DMSO-d_6), δ (TMS ppm): 2.77-2.94(m, CH_2, MA moieties), 4.08 (m, CH_2, P moiety)

PCA-Ds:

FTIR-ATR (cm^{-1}): 3452 (vO-H, acid), 2969 (vC-H), 1708 (vC=O ester), 1395 (δC-O-H), 1168 (v C-O-C ester)

^{1}H-NMR (400MHz, DMSO-d$_6$), δ (TMS ppm): 2.63-3.01 (m, CH$_2$, CA moieties), 4.09 (m, CH$_2$, D moiety)

Scheme 3-1



3.2.3 Polymer Characterisations

Each FTIR spectrum recorded as an average of 16 scans on a Perkin Elmer Spectrum 100 spectrophotometer equipped with a universal attenuated total internal reflectance (ATR) accessory.

^{1}H NMR spectra were recorded using a Varian Unity Inova 400 NMR spectrometer under ambient temperature. DMSO-d$_6$ was used as the solvent with tetramethylsilane (TMS) as the internal reference for the analysis.

The molecular weights of the polymers were estimated by gel permeation chromatography (GPC) with the use of Waters system. The system equipped with a

Waters 1515 isocratic pump coupled with a series of Styragel® HMW columns (HR1, HR4, and HR6; molecular weight range 10^2-10^7), calibrated with mono-dispersed polystyrene standards (PS) (PolyScience), and a Waters 2414 refractive index detector. THF was used as the eluent at a flow rate of 1.0 ml/min. The column was maintained at 30°C during analysis.

3.2.4 Modification of Cotton Fabric

The newly developed dendritic PCA polymers were mixed with NaH_2PO_2, a typical catalyst for cellulose esterification in the finishing study. The finishing aqueous solutions were comprised of 10w/w% of different PCAs as the cellulose cross-linker, 6w/w% of NaH_2PO_2 as the catalyst and 5w/w% of ethanol as dispersing agent. Acidity of finishing solutions was kept constant at pH of 2. Cotton fabrics were impregnated with the finishing solutions using a Rapid Labortex P-80 horizontal padding machine imposing a constant pressure of 1kg/cm^2 to achieve wet pick-up of 75±5%. Sequentially the fabrics were dried at 100°C for 2min, and then thermally cured at 180°C for 1.5min using a Mathis LTE Labdryer.

3.2.5 Fabric Characterisations & Evaluations

Properties of cotton fabrics modified with the newly developed dendritic polymers were evaluated based on the following standard approaches and procedures. The formation of cross-links of modified cotton fabrics was studied based on FTIR-ATR. Prior to FTIR analysis, modified fabric samples were treated with 0.1M NaOH solution and rinsed with deionised water to differentiate carbonyl (C=O) stretching of carboxyls and esters. All modified fabric samples were conditioned under standard condition at 65±2% relative humidity and 21±1°C prior to evaluations. Spectra of dried fabric samples were recorded using a Perkin Elmer FTIR spectrophotometer 100 equipped with an ATR sampling accessory. Each FTIR spectrum was recorded as an average of 128 scans and normalised against 1317cm^{-1} which is originated from the C-H bending of cellulose molecules [7]–[10].

Wrinkle-resistant performance was evaluated in accordance with the AATCC 66-2008 test method. Specimens (40mm x 15mm) in both warp and weft alignment were folded face-to-face and back-to-back. Folded specimens were compressed with a 500g-weight for 5min. The wrinkle recovery angles (WRA) of specimens were measured by a Daiei Kagakuseiki Seisakusho wrinkle recovery tester after 5min of relaxation and recovery. WRAs were reported as an average of eight measurements of the sum in warp and weft directions with the analytical tolerance limited to 5%. The change in wrinkle recovery angle (ΔWRA) was expressed according to the following equation.

$$\Delta WRA = \frac{WRA_m - WRA_o}{WRA_o} \times 100\%$$

where as WRA_m= WRA of modified fabric
WRA_o = WRA of control fabric

Mechanical properties included tensile strength and tearing strength, were evaluated according to ASTM D5034-2009 and ASTM D1424-2009 test methods respectively. The tearing strength of modified cotton fabrics were evaluated using a James H. Heal digital Elmendorf tearing tester with a standard capacity of 1600g or 3200g chosen to measure the strength. Specimens were cut according to the standard notched template in both warp and weft directions. Individual notched specimen was fixed onto the tester. The pendulum was depressed downwards until tearing of a specimen was completed. Tearing force (Ft) was reported as an average result of eight measurements in both warp and weft directions. When evaluating the tensile strength of modified cotton fabrics, a tensile tester, Instron 4411, was used based on constant rate of extension (CRE) tensile testing method. Specimens (150mm x10mm) in both warp and weft alignment were mounted vertically on the tester for the test. Longitudinal grabbing force was applied along the testing direction until the specimen broke. Tensile strength reported as the averaged breaking force (Fb) of eight measurements in both warp and weft directions with the analytical tolerance limited to 5%. The change in mechanical properties was expressed in terms of change in forces (ΔF) according to the below equations.

$$\Delta Ft = \frac{Ft_m - Ft_o}{Ft_o} \times 100\%$$

$$\Delta Fb = \frac{Fb_m - Fb_o}{Fb_o} \times 100\%$$

where as Ft_m = tearing or tensile force of modified fabric
Ft_o = tearing or tensile force of control fabric
Fb_m = tearing or tensile force of modified fabric
Fb_o = tearing or tensile force of control fabric

Whiteness and yellowness were evaluated using a GretagMacbeth Colour-Eye 7000A reflectance spectrophotometer under the standard illuminant of D_{65} and viewed at 10^o standard observer in accordance with the AATCC 110-2005 and ASTM E313-2010 test methods. The whiteness and yellowness were expressed in terms of whiteness index (WI) and yellowness index (YI) respectively.

3.3 Results and Discussion

3.3.1 Cross-linker Synthesis and Characterisation

Series of dendritic PCA polymers were synthesised based on azeotropic polycondensation with sulfolane-mesitylene solvent system. CA reacted with polyols of various arms and of different mole ratios to form novel PCAs. CA was attempted to condense with various polyols included, glycerol(G), triol(T), tetrol (P) and hexol(D). The resultant dendritic PCAs of different branching architectures were namely, PCA-Gs (CA with glycerol), PCA-Ts (CA with triol), PCA-Ps (CA with tetrol) and PCA-Ds (CA with hexol). The polymerisation results were tabulated in Table 3-1.

Table 3-1 Summary of dendritic PCAs prepared by azeotropic polycondensation [a]

Sample code	ratio [b]	*f* [c]	M_n x10^3 [d]	M_w x10^3 [d]	PDI [e]	Yield%
PCA-G(12)	12	3	0.41	0.81	1.96	Trace
PCA-G(18)	18	3	0.48	0.82	1.72	Trace
PCA-G(24)	24	3	0.45	0.78	1.75	Trace
PCA-G(30)	32	3	0.58	1.1	1.89	trace
PCA-T(9)	9	3	1.6	2.2	1.38	83.99
PCA-T(12)	12	3	2.2	3.1	1.41	87.39
PCA-T(15)	15	3	2	2.2	1.31	78.44
PCA-T(18)	18	3	1.8	2.2	1.28	74.32
PCA-T(30)	30	3	1.6	2.1	1.29	76.84
PCA-P(8)	8	4	1.6	2.2	1.37	72.21
PCA-P(12)	12	4	2.3	3.3	1.43	66.73
PCA-P(16)	16	4	2.9	4.8	1.65	70.49
PCA-P(20)	20	4	2.2	2.8	1.3	67.85
PCA-P(32)	32	4	1.6	2.4	1.5	70.25
PCA-D(12)	12	6	2.3	3	1.3	49.82
PCA-D(18)	18	6	3.3	5.7	1.7	65.04
PCA-D(24)	24	6	4.5	7.4	1.63	42.41
PCA-D(36)	36	6	5.5	8.1	1.49	43.79

[a] Azeotropic polycondensation carried out at 175°C under nitrogen atmosphere for 4hrs in the presence of 5mol% H_3PO_4. [b] ratio refer to molar feed ratio of CA : polyol. [c] *f* = no. of branches. [d] Estimated by GPC in THF on the basis of a PS calibration expressed in Da. [e]PDI = polydispersity (M_w/M_n).

In general, clear yellowish pastes of dendritic PCAs were obtained in the syntheses. The yield obtained by precipitation of crude products was ranging from 42% to 87% by weight. As summarised in Table 3-1, series of low molecular weight polymeric dendritic PCAs were prepared with the polyols adopted in the study in the presence of H_3PO_4 as the catalyst. Upon azeotropic polycondensation reaction at 175°C for 4 hours under nitrogen atmosphere, PCAs with M_n of 1.6 $\times10^{-3}$ Da to 5.5 $\times10^{-3}$ Da and the polydispersity (PDI) ranging from 1.3 to 1.7 were obtained.

Considering the series of syntheses between CA and G, the major products obtained were estimated to be oligomeric PCA-Gs with M_n of approximately 0.4 $\times10^{3}$ Da to 0.6 $\times$ 10^3 Da. These oligomeric products with 2 to 3 CA moieties were postulated bonding to the G core in the synthesis trials of various feed ratios. Differentiated from the other polyols, G comprises of a secondary hydroxyl. This would reduce the reactivity towards esterifaction with carboxyl of CA resulted in the formation of oligomeric products. Yet, G is susceptiable to oxidation. G might undergo internal dehydration or oxidation instead of condensation with CA. When considering other polyols, feed ratios between CA to polyols in the system essentially controlled the resultant molecular weight of resultant polymers. The actual molecular weights estimated by GPC complied with the theoretical values when feed ratios were small (i.e. $\leq$24). When feed ratio was considerably large ($\geq$30), the growth in molecular weights was significantly hindered. Molecular sizes of dendritic PCA were not growing large in the systems. Branched polyols B_f incorporated in a polycondensation system of polyfunctional monomers are regarded as chain stoppers hampering the growth in molecular weights [11]–[13]. This would be an important factor in building low molecular weight polymeric cross-linkers for cellulosic textiles.

Considering the branching behaviour between CA and polyols, the yield of product generally was more favourable for polymerisation when T was served as the core moiety (i.e. branching factor *f* =3). The yield of product was able to achieve up to 70% to 87%. When P or D employed as the core moiety, the yield of product was significantly diminished to less than 70%. *f* and the stereochemistry of the core moieties characterised the degree of steric hindrance for the incoming CA monomer. Steric hindrance was suggested as the major cause influencing the yield of product. Larger value of *f* = 4 or 6 of the core molecules was the attributes for the retarded growth of branches emanating from the core polyols with short hydroxyl arms (Core-CH_2-OH).

Developing PCAs composed of various numbers of branches was attempted with the inclusion of different polyols as the core molecules in this part of the study. In general, the FTIR data (Figure 3-2) revealed the successful esterification between carboxyl of CA with hydroxyls of polyols of T, P and D. Diagnostic absorption bands originated from ester functionalities at 1710cm^{-1} (νC=O) and 1200cm^{-1} (νC-O-C) demonstrated polyesters were formed in the azeotropic polymerisation of CA and polyols with respect to an overview of the polymer spectra.

In this study, anhydrous CA was used. In the polymer spectra, disappearance of diagnostic absorption band originated from C=O stretching of the anhydride moiety of

CA at 1755 cm^{-1} suggested that CA carboxyl was consumed in the polycondensation reaction [14]–[16]. Regarding the reactivity of hydroxyls, CA was assumed to react with primary hydroxyls of polyols prior proceeding to further polymerisation. This assumption was verified based on the evaluation of FTIR spectra of PCAs prepared. The disappearance of the distinguished peak of OH of polyols suggested the condensation between all hydroxyl branches and carboxyls of CA. The absorption band at 1100-1000cm^{-1} of C-OH stretching (νC-OH) and the band at 666cm^{-1} of C-O-H bending of hydroxyl of polyols disappeared after azeotropic polycondensation as depicted in Figure 3-2 [17]–[22]. Sharp absorption bands at 3500cm^{-1} and 3290cm^{-1} originated from O-H stretching of CA hydroxyl was absent in the polymer spectra in the FTIR spectra indicated that mutual polycondensation of CA occurred. CA carboxyls not only reacted with hydroxyl of polyols, but also condensed with CA hydroxyl. The board peaks at 3400-2600cm^{-1} originated from O-H of carboxylic acids of CA retained in all PCA products. Free COOH present in the products could furnish the cross-linking ability PCA products with cotton cellulose in the sequential wrinkle-resistant finishing.

The chemical compositions and architectures of the dendritic PCAs would be elucidated based on the diagnostic peaks present in ^{1}H-NMR spectra (Figure 3-3). In this synthesis, polyols of various *f* were adopted in the attempt to develop dendritic PCA polymeric cross-linkers. Regarding the reactivity of hydroxyls, CA was suggested to condense preferentially with primary hydroxyls of polyols prior proceeding to further polycondensation or undergoing intramolecular dehydration. This assumption was verified with the analysis of ^{1}H-NMR spectra of the products. A distinguishing peak in the NMR spectrum of the each PCA polymers as shown in Figure 3-3 at ~δ4 is attributable to the methylene protons of the polyol. The peak intensity is approximately corresponding to the feed ratio of CA to polyol incorporated in the polymerisation.

Complementary to GPC data, the relative integrals of the NMR resonance of methylene protons of polyols to the methylene protons of CA suggested that polyols were served as the core moieties in the dendritic architectures of PCA products. Hence the integral of resonance originated from methylene protons of CA at ~δ2.8-2.9 indicated the number of CA attached to a polyol core. In such manner, polyols were essentially served as core moieties in the dendritic PCAs as postulated in Scheme 3-1.

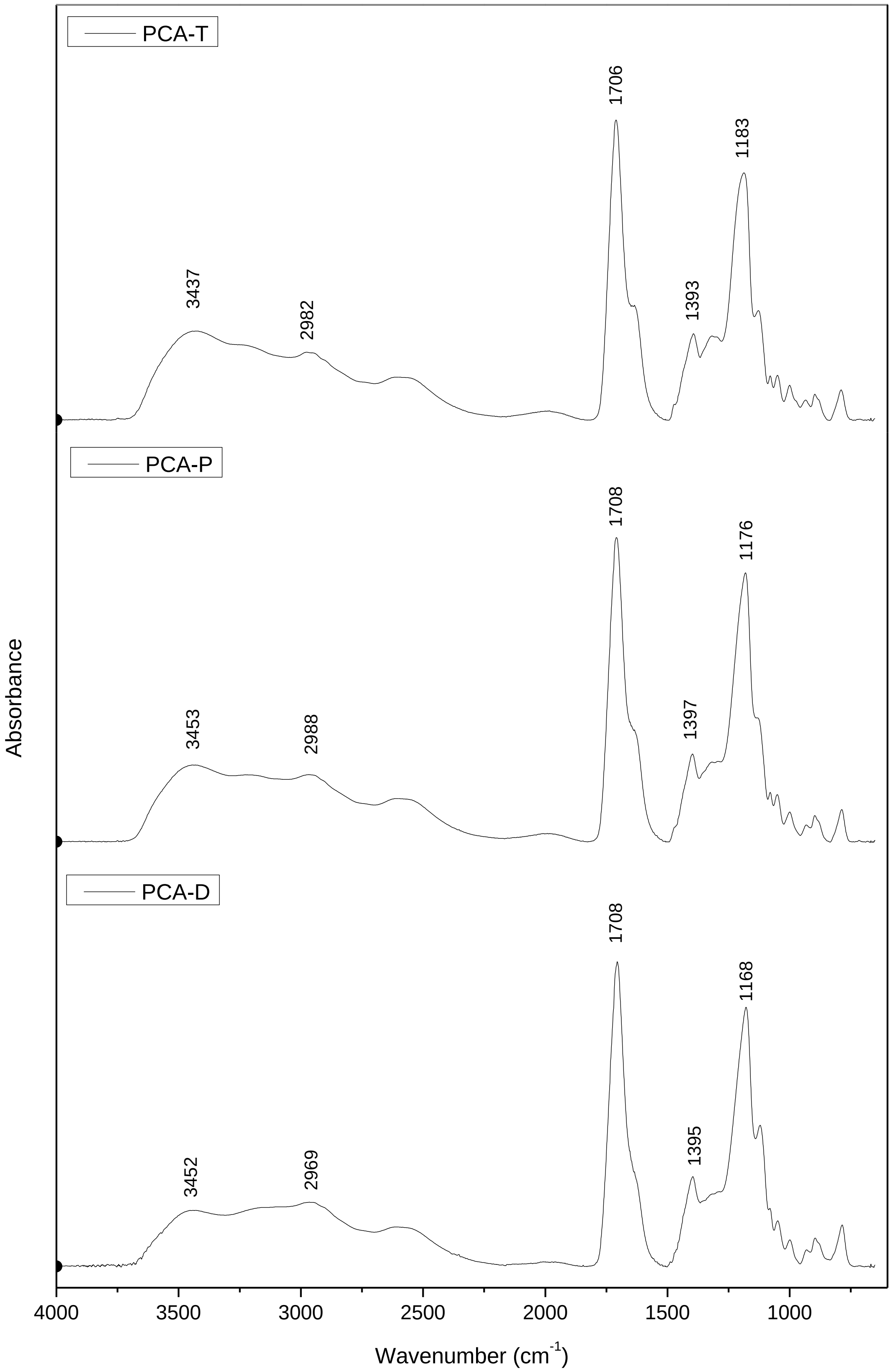


Figure 3-2 FTIR spectra of dendritic PCA polymers with various polyol cores: PCA-T(9) (upper), PCA-P(8) (middle) and PCA-D(12) (bottom)

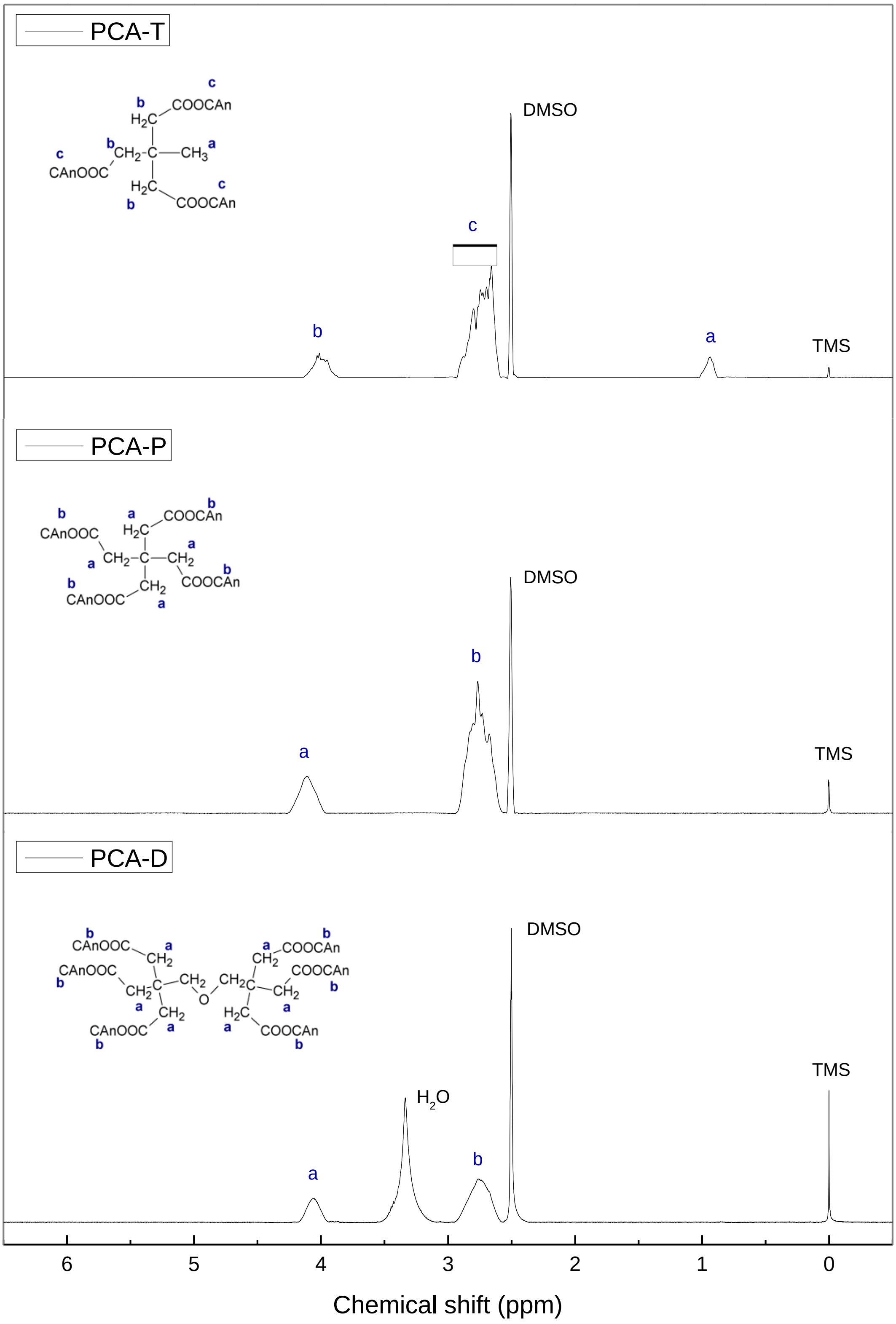


Figure 3-3 ^{1}H-NMR spectra of dendritic PCA polymers with various polyol cores: PCA-T(9) (upper), PCA-P(8) (middle) and PCA-D(12) (bottom)

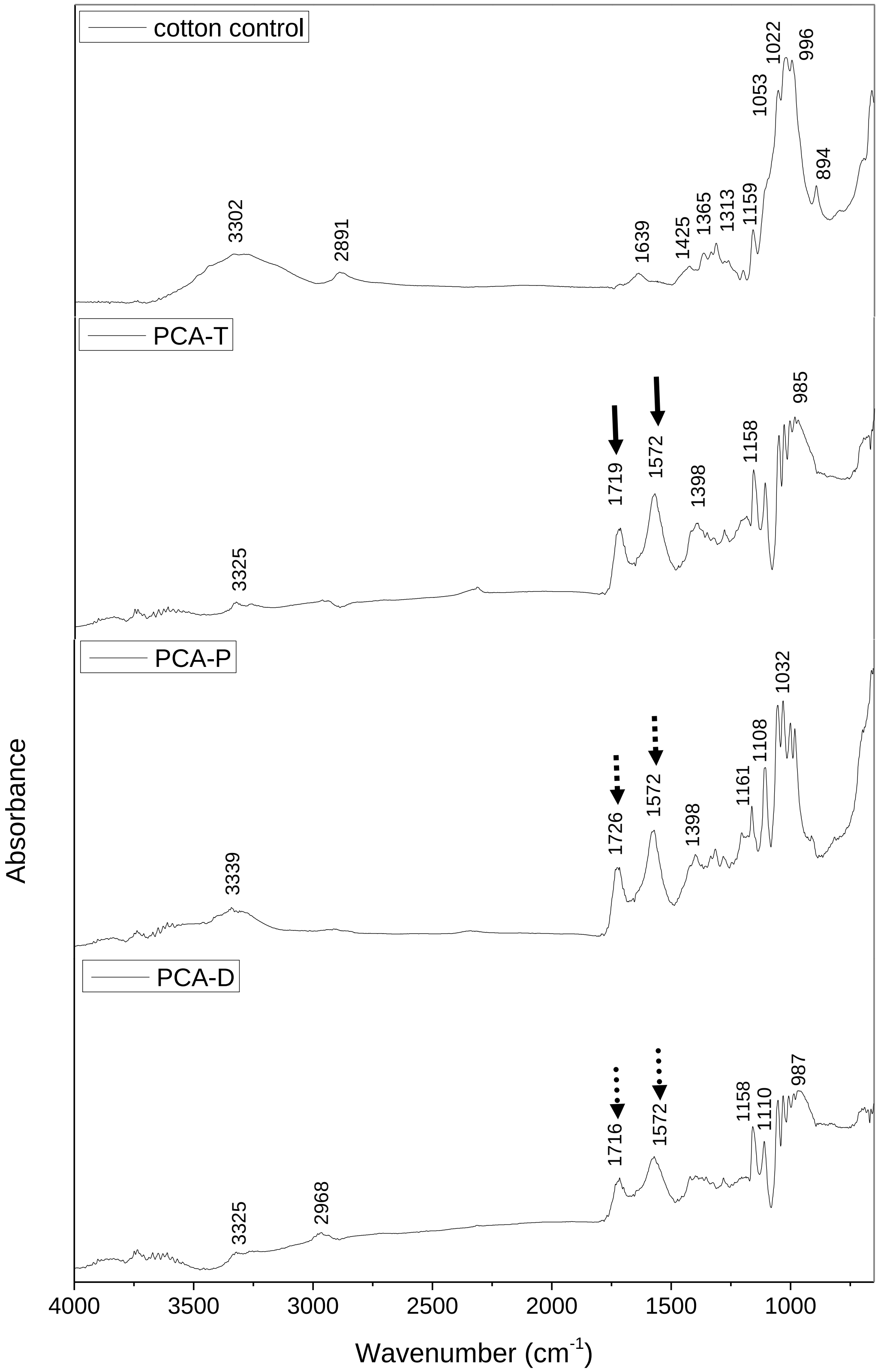
3.3.2 Fabric Performance and Evaluations of Modified Cotton

Dendritic PCA polymers of various branching architectures and molecular weights were used for the wrinkle-resistant finishing study. Dendritic PCA polymers of various f ranging from 3 to 6, and M_n of 1.6 x10^3 Da to 4.5 x10^3 Da were employed as the cross-linkers. Table 3-2 tabulates the summary of fabric performance modified with the selected dendritic PCAs as the cross-linkers. In the finishing study, 10w/w% of the selected PCA coupling with 6w/w% of NaH_2PO_2 was employed for cross-linking cotton fabrics. Cotton fabrics impregnated with PCA polymers were subjected to curing at 180°C for 1.5min. The influence of molecular composition of the dendritic PCA cross-linkers on the wrinkle recovery performance of the cotton fabric was evaluated accordingly.

3.3.2.1 FTIR-ATR Characterisation of Modified Cotton

The formation of cross-links of fabric substrates was verified based on FTIR-ATR. In Figure 3-4, the plain cotton fabric prior to modification was characterised with the presence of a board peak corresponding to O-H stretching (3330cm^{-1}) contributed to the hydrophilicity of natural cellulosic fabrics. The vibration of OH is principally associated with absorbed moisture (1650cm^{-1}) on the fabric. A sharp peak at 2890cm^{-1} denoted C-H stretching of C6 of glucose units of cellulose. Other associated weak deformation of C-H included wagging and bending at 1420cm^{-1}, 1370cm^{-1} and 1310cm^{-1}. In the fingerprint region of the spectrum, C-O-C bridge (1160cm^{-1}), in-plane ring stretching (1050cm^{-1}), C-O stretching (1020cm^{-1} and 990cm^{-1}) and C-O-C β-linkage between glucose moieties of cellulose (890cm^{-1}) were characterised [23]–[26].

The ATR technique offers a quick and non-destructive evaluation for chemical characteristics of fabric substrates in relation to the respective fabric properties [7-9], [23]–[25], [27]. Prior to fabric evaluation by FTIR-ATR, the modified cotton fabrics were treated with 0.1M NaOH solution. Unreacted carboxyls retained on the fabrics would converted into carboxylates (COO^-) which could be differentiated from the ester carbonyls (C=O) by FTIR. Upon modification with dendritic PCAs, additional ester carbonyls (1720cm^{-1}) and carboxylates (1585cm^{-1}) were detected on the modified cotton fabrics. PCA-T, PCA-P and PCA-D were found to be capable of imparting ester cross-links on the cotton fabric. Esterification using poly(carboxylic acid) for cross-linking unavoidably retains certain amount of acid residue on the fabrics. The residue peak of carboxylates explained the phenomenon that acid-catalysed depolymerisation of cellulose fibres was one of the attributes leading to the loss in mechanical strengths.



(Cotton fabrics impregnated with 10w/w% PCA cross-linker coupling with 6w/w% NaH_2PO_2 were subjected to curing at 180°C for 1.5min.)

Figure 3-4 FTIR-ATR spectra of the cotton fabric modified with various dendritic PCA polymers with different polyol cores.

3.3.2.2 Effect of Branching of Core Polyol

The effectiveness of wrinkle-resistant finishing treatment was expressed in terms of ΔWRA of modified fabrics according to the equation defined in section 3.2.5. Generally speaking, all dendritic PCA polymers employed in the study were efficacious in imparting wrinkle-resistance to the cotton fabric. ΔWRA were ranging from 14% to 51% increment. With the use of dendritic PCAs of various molecular architectures and molecular weights, the influence of molecular composition of the carboxyl-based cross-linkers on the wrinkle recovery performance of the cotton fabric was evaluated accordingly.

Cross-linking efficacy of the carboxyl-based cross-linkers not only depends on the number of reactive groups, but also the molecular size of the cross-linker. Though the number of carboxyl groups present in dendritic PCA cross-linkers is proportional to the respective molecular weights, ΔWRA was not increasing down each series of cross-linkers. Conversely, WRA reduced down the series with the increasing *f* and molecular weights of dendritic PCAs. These two properties of the cross-linkers denoted the overall molecular size of the cross-linker controlling the penetration of the cross-linkers into to the cellulose fibre and hence the cross-linking effectiveness [28]–[32]. As illustrated in Table 3-2, M_n of PCA substantially affected the resultant WRA of the modified fabrics. The degree of cross-linking governs the extent of wrinkle recovery performance of the modified fabrics. ΔWRA reduced down the series with the increasing *f* and molecular weights of dendritic PCAs. When M_n of the dendritic cross-linker was above 2 x10^3 Da, the effectiveness of the cross-linker diminished significantly irrespective of *f*. ΔWRA could only achieve 14% to 19% increment. The improvement in WRA was found to be least prominent. This suggested that dendritic cross-linkers with more than 12 CA moieties would be too bulky to penetrate into cellulose fibres for cross-linking. The modified fabric samples became stiff and starchy was another supporting evidence for such postulation.

Table 3-2 Summary of properties of cotton fabrics modified with dendritic PCAs

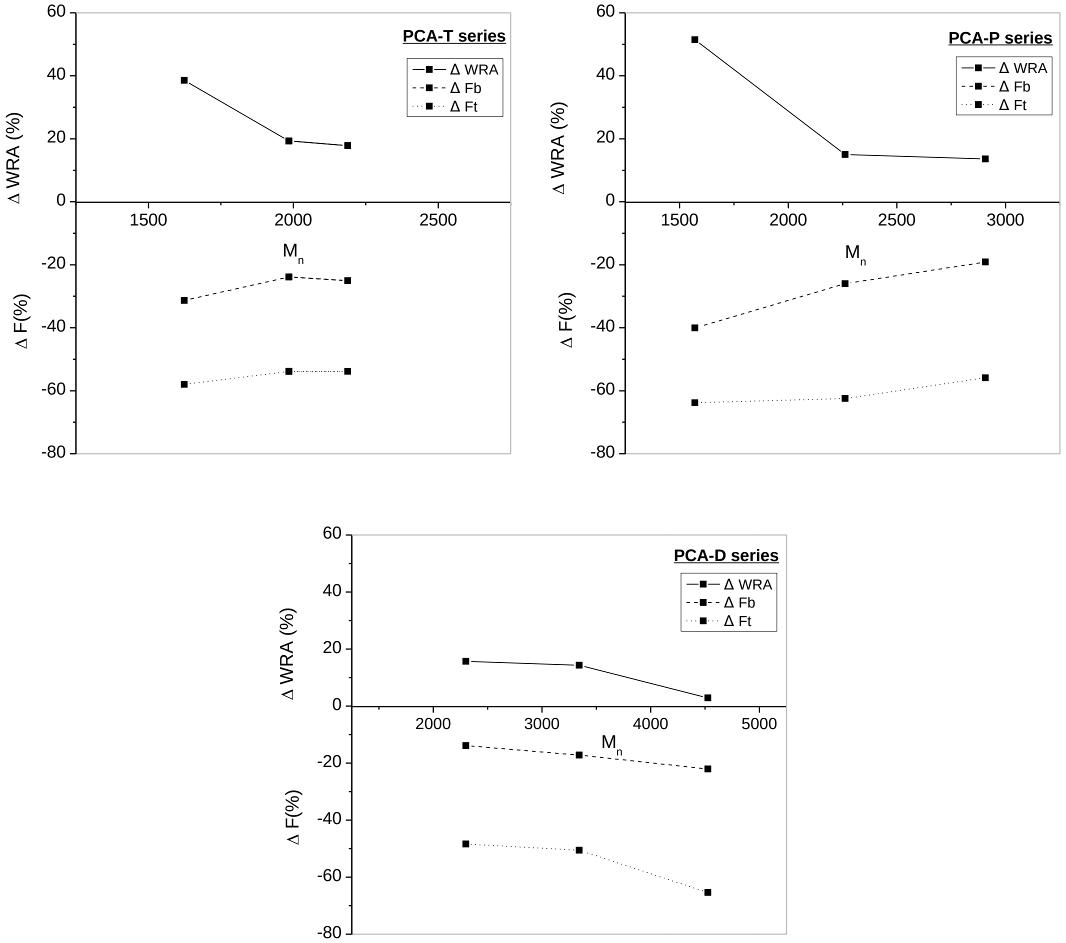
Fabric code	Cross-linker	*f* [a]	M_n x10^3 [b]	WRA (^{o}) [c]	Ft (N) [d]	Fb (N) [e]	WI [f]	YI [g]
control	---	---	---	140	19.65	283.361	75.087	5.407
CA-T1	PCA-T(9)	3	1.6	194	8.26	169.885	70.603	6.627
CA-T2	PCA-T(12)	3	2.2	165	9.22	217.294	68.423	7.252
CA-T3	PCA-T(15)	3	2	167	9.07	215.695	69.015	7.212
CA-P1	PCA-P(8)	4	1.6	212	7.12	194.625	57.119	9.054
CA-P2	PCA-P(12)	4	2.3	161	7.38	209.695	56.687	9.896
CA-P3	PCA-P(16)	4	2.9	159	8.67	229.190	53.618	10.578
CA-D1	PCA-D(12)	6	2.3	162	11.14	273.690	53.343	10.263
CA-D2	PCA-D(18)	6	3.3	160	9.72	234.660	54.878	10.769
CA-D3	PCA-D(24)	6	4.5	144	6.80	220.790	50.239	12.518

[a] *f* = no. of branches of PCA polymer. [b] M_n = no. average molecular weight of PCA estimated by GPC expressed in Da. [c] WRA = averaged sum of wrinkle recovery angles in warp and weft of cotton fabrics in accordance with AATCC 66-2008. [d] Ft = average of tearing force in warp and weft of cotton fabrics in accordance with ASTM D1424-2009. [e] Fb = average of breaking force in warp and weft of cotton fabrics in accordance with ASTM D5034-2009. [f] WI = whiteness index measured in accordance with AATCC 110-2005. [g] YI = yellowness index measured in accordance with ASTM E313-2010 .

When applied the smaller members of PCAs as cross-linkers, ΔWRA could only achieve prominent increment up to 40% to 50%. PCA-T(9) and PCA-P(8) were of similar molecular size (~1.6 x10^{-3} Da) and number of reactive CA moieties. The geometry of the cross-linker also impacted the resultant wrinkle recovery performance of the modified fabric. WRA was promoted to a greater extent when PCA-P(8) was adopted in the wrinkle-resistant finishing. PCA-P(8) was more symmetrical in geometry assisted cross-linking aligned cellulose fibers. ΔWRA could achieve up to 51%. Compared to PCA-T(8), PCA-T(9) with less CA arms emanated from the polyol core facilitate the penetration power of the cross-linker into the cellulose fibres for intermolecular cross-linking. As the result, PCA-T(9) could help mitigate the loss in fabric strengths and fabric yellowing while affording appreciable improvement in WRA up to ~40%. PCA-T(9) was component to assist both strengths and whiteness retention to the largest extent as presented in Table 3-2.

Effectiveness in cross-linking of cotton cellulose impinges on the wrinkle recovery performance in conjunction with the resultant mechanical performance and degree of fabric yellowing of modified cotton fabrics. Fabric performance data as tabulated in Table 3-2 indicates the essence of effective cross-linking in relation to strengths and whiteness retention. In each series, cross-linking effectiveness reduced down the group with respect to the increase in molecular weights of the cross-linkers. Simultaneously, the respective fabric strengths and fabric whiteness declined accordingly. Cross-linking of cellulose improves the wrinkle recovery performance of cotton fabrics. Simultaneously, the reaction unavoidably imposes loss in the fabric strengths upon cross-linking reaction. Two major factors influence the mechanical performance of cotton fabrics subjected to wrinkle-resistant finishing. Cross-linking reaction and acid-catalysed cellulose degradation are the attributes leading to the loss in fabric strengths when employing carboxyl-based cross-linkers [25], [27], [33], [34].

Data obtained from fabric characterisation and evaluation indicated that dendritic PCAs with acid groups were efficacious in cellulose cross-linking. Concurrently, they imparted certain degree of cellulose degradation. Besides, experimental results revealed that cross-linking effectiveness utilising carboxyl-based cross-linkers would impinge the degree of loss in strength and fabric whiteness. Figure 3-5 depicts the alteration in the wrinkle recovery performance and fabric strength in relation to M_n of the dendritic PCA cross-linker impregnated. The alteration in wrinkle recovery performance of modified fabrics was expressed in terms of ΔWRA. The changes in tensile and tearing strengths are expressed in terms of ΔFb and ΔFt respectively. M_n denotes the bulkiness of the dendritic PCA cross-linkers and hence the penetrating power into cellulose fibres. The penetrating power of the cross-linkers would affect the possible reactions involved between polycarboxylic acids and cellulose hydroxyls. Esterification may proceed to form intermolecular cross-links, intramolecular cross-links and side grafts [33]. Intermolecular and intramolecular cross-links would limit the mobility of the cellulose macromolecules in equalising external stresses leading to strength tendering. Meanwhile, formation of acidic side grafts would promote acid-catalysed depolymerisation tendering fibre strengths. Such phenomenon was observed when utilising the bulkiest PCA-Ds as cross-linkers, the loss in tearing strength of cotton fabrics was found to be severe.



(Cotton fabrics impregnated with 10w/w% of the selected PCA polymer coupling with 6w/w% of NaH_2PO_2 were subjected to curing at 180°C for 1.5min.)

Figure 3-5 Properties of cotton fabrics modified with dendritic PCA-T, PCA-P and PCA-D in relation to M_n

Take PCA-D series as the example as shown in Figure 3-5. Bulkiness of the PCA-D cross-linkers with M_n of at least 2.3 x10^3 Da and six arms emanating from the hexol core significantly inhibited the penetration into fibres and molecules. Increasing the number of CA moieties down the group, the effect of acid-catalysed depolymerisation became more prominent. As a result, losses in both tearing and tensile strengths were the largest in the group. And hence the colour of modified cotton fabrics was found to the most yellowish. Increasing bulkiness of the cross-linkers would tender the fabric strengths as intramolecular cross-links and side grafts would form preferentially. FTIR spectra as shown in Figure 3-4 reveals additional ester bonds formed. In conjunction with the starchy hand feel of the modified fabrics, acidic side grafts were postulated to form essentially with the impregnation of PCA-D cross-linkers. Acid-catalysed depolymerisation of cotton cellulose was suggested as the prime attribute to the loss in strengths and reduction in whiteness of fabrics when employing bulky carboxyl-based cross-linkers.

Considering the series of PCA-T and PCA-P, smaller candidates such as PCA-T(9) and PCA-P(8) induced to the least strength loss while furnished the most preeminent improvement in wrinkle recovery as depicted in Figure 3-5. Preeminent increment in WRA indicated the effective formation of intermolecular cross-links. These cross-links imparted certain degree of loss in strengths due to restricted intermolecular motion of cross-linked fibres. Intermolecular cross-linking was suggested as the predominant reaction in this case. When going down the groups, improvement in WRA of the respective modified fabrics was abated. Increased in molecular size of cross-linker lowered the penetrating power. Thus, intermolecular cross-linking was attenuated. In contrast to phenomenon observed in PCA-D series, loss in strength was mitigated down the group. Preferential intramolecular cross-linking was proposed to proceed instead of side grafts formation. Carboxyls of larger candidates of PCA-Ts and PCA-Ps would consume to form intramolecular cross-links. As a consequence, loss in strength induced by acid-catalysed depolymerisation could be alleviated as less acidic residue accumulated on the modified fabrics. Besides, fabric yellowing could be meliorated.

3.3.2.3 Comparison between Monomeric and Polymeric Cross-linkers

A series of novel low molecular weight dendritic PCA cross-linkers was successfully prepared by azeotropic polycondensation. The effectiveness of the cross-linking reaction, and the resultant wrinkle-resistant performance and fabric properties were summarised in Table 3-3. The results revealed the explicit difference between monomeric and polymeric cross-linker for cotton cellulose.

Table 3-3 Comparison performance between monomeric CA and polymeric PCA cross-linkers [a]

Fabric code	Cross-linker	M_n x10^3 [b]	WRA (^{o}) [c]	Ft (N) [d]	Fb (N) [e]	WI [f]	YI [g]
control	---	---	140	19.65	283.361	75.087	5.407
CA-10	CA	0.192	190	5.94	163.414	68.487	7.511
CA-T1	PCA-T(9)	1.6	194	8.26	169.885	70.603	6.627

[a] Both fabrics impregnated with finishing bath of pH2, comprised of 10w/w% cross-linker with 7w/w% NaH_2PO_2 and cured at 180^{o}C for 1.5min [b] M_n = no. average molecular weight of PCA estimated by GPC expressed in Da. [c] WRA = averaged sum of wrinkle recovery angles in warp and weft of cotton fabrics in accordance with AATCC 66-2008. [d] Ft = average of tearing force in warp and weft of cotton fabrics in accordance with ASTM D1424-2009. [e] Fb = average of breaking force in warp and weft of cotton fabrics in accordance with ASTM D5034-2009. [f] WI = whiteness index measured in accordance with AATCC 110-2005. [g] YI = yellowness index measured in accordance with ASTM E313-2010 .

Among the dendritic PCA cross-linkers, PCA-T(9) could offer the optimal balance of fabric properties of the cotton fabric in terms of wrinkle-resistant performance, mechanical strength and colour retention. It was selected to compare to its monomeric counterpart, CA. As illustrated in Table 3-3, the low molecular weight polymeric PCA-T(9) was successfully assisted the retention in fabric strength and colour in the study. The fabrics modified with CA or PCA-T(9) could achieve similar improvement in wrinkle-resistant performance. Meanwhile, the polymeric cross-links formed between cotton fibres helps reduced slippage between fibres while afforded flexibility to the fabrics. Hence, the losses in tensile and tearing strengths were alleviated by 12% and 6% respectively. Polymeric reduced slippage between fibres while afforded flexibility to the fabrics. Moreover, fabric modified with CA was found to be more yellowish. Hydroxyl and carboxyls of CA moieties in PCA-T(9) were partially consumed in the polycondensation reaction during synthesis. As the results, CA moieties of PCA-T(9) is less susceptible to thermal transformation into aconitic acid and other unsaturated compounds imparting yellowish colour to the fabric substrate [5], [35-36]. Dendritic polymeric PCA-T was explicitly capable of retaining fabric strengths and colour compared to its monomeric counterpart.

3.4 Conclusions

A series of novel low molecular weight dendritic PCA cross-linkers were successfully prepared by azeotropic polycondensation of CA and branched polyols, except with glycerol. The dendritic molecular architecture of the dendritic polymers was revealed with the utility of advanced analytical techniques. Newly developed dendritic PCAs of various branching architectures with M_n ranging from 1.6×10^3 to 4.5×10^3 Da were adopted in the wrinkle-resistant finishing of cotton fabrics. The effectiveness of the cross-linking reaction, and the resultant wrinkle recovery performance and other fabric properties were evaluated in correlation with the molecular size and architecture of the newly developed dendritic cross-linkers.

In the present study, the efficacy of dendritic PCA as cellulose cross-linker for cotton fabrics was verified. Bulkiness of the cross-linker was found to be a detrimental factor attributed not only to the resultant wrinkle recovery performance, but also the deterioration in fabric strength. In significance, when utilising PCA-T polymers as cellulose cross-linkers for plain woven cotton fabrics was capable of affording relatively superior WRA, while assisting strengths and whiteness retention to the greatest extent.

This attempt in employing dendritic polymeric cross-linkers for cotton cellulose opened up a novel avenue for the continual pursue of non-formaldehyde based finishing for textiles. Low molecular weight dendritic PCA polymers presented a promising platform as wrinkle-resistant finishing agents for cotton textile.

3.5 Bibliography

[1] M. M. Barbooti and D. A. Al-Sammerrai, “Thermal decomposition of citric acid,” *Thermochim. Acta*, vol. 98, pp. 119–126, 1986.

[2] J. W. Fischer, L. H. Merwin, and R. A. Nissan, “NMR investigation of the thermolysis of citric acid,” *Appl. Spectrosc*., vol. 49, no. 1, pp. 120–126, 1995.

[3] D. Wyrzykowski, E. Hebanowska, G. Nowak-Wiczk, M. Makowski, and L. Chmurzyński, “Thermal behaviour of citric acid and isomeric aconitic acids,” *J. Therm. Anal. Calorim*., vol. 104, no. 2, pp. 731–735, 2010.

[4] C. Schramm and B. Rinderer, “Influence of additives on the formation of unsaturated PCAs produced during durable-press curing with citric acid*,” Color. Technol.*, vol. 115, no. 10, pp. 306–311, 1999.

[5] B. A. K. Andrews, E. J. Blanchard, and R. M. Reinhardt, “Fabric whiteness retention in durable press finishing with citric acid,” *Text. Chem. Color*., vol. 25, no. 3, pp. 52–54, 1993.

[6] Y. Lu and C. Q. Yang, “Fabric yellowing caused by citric acid as a crosslinking agent for cotton,” *Text. Res. J.*, vol. 69, no. 9, pp. 685–690, 1999.

[7] C. Q. Yang and X. Wang, “Infrared spectroscopy studies of the cyclic anhydride as the intermediate for the ester crosslinking of cotton cellulose by polycarboxylic acids. III. molecular weight of a crosslinking agent,” J*. Polym. Sci. Part A Polym. Chem*., vol. 35, no. 3, pp. 557–564, 1997.

[8] C. Q. Yang and X. Wang, “Formation of cyclic anhydride intermediates and esterification of cotton cellulose by multifunctional carboxylic acids: an infrared spectroscopy study,” *Text. Res. J.,* vol. 66, no. 9, pp. 595–603, 1996.

[9] C. Q. Yang, “FT-IR spectroscopy study of the ester crosslinking mechanism of cotton cellulose,” *Text. Res. J*., vol. 61, no. 8, pp. 433–440, 1991.

[10] C. Q. Yang, “Effect of pH on nonformaldehyde durable press finishing of cotton fabric: FT-IR Spectroscopy study: part II: formation of the anhydride intermediate,” *Text. Res. J*., vol. 63, no. 12, pp. 706–711, 1993.

[11] R. A. T. M. Van Benthem, “Novel hyperbranched resins for coating applications,” *Prog. Org. Coatings*, vol. 40, no. 1–4, pp. 203–214, 2000.

[12] W. J. Feast and N. M. Stainton, “Synthesis, structure and properties of some hyperbranched polyesters,” *J. Mater. Chem*., vol. 5, no. 3, pp. 405–411, 1995.

[13] E. Malmström and A. Hult, “Hyperbranched polymers: a review,” *J. Macromol. Sci. Part C*, vol. 37, no. 3, pp. 555–579, 1997.

[14] B. Tisserat, R. H. O’kuru, H. Hwang, A. A. Mohamed, and R. Holser, “Glycerol citrate polyesters produced through heating without catalysis,” *J. Appl. Polym. Sci*., vol. 125, no. 5, pp. 3429–3437, 2012.

[15] J. Yang, A. R. Webb, S. J. Pickerill, G. Hageman, and G. A. Ameer, “Synthesis and evaluation of poly(diol citrate) biodegradable elastomers,” *Biomaterials*, vol. 27, no. 9, pp. 1889–1898, 2006.

[16] P. Kucharczyk, I. Poljansek, V. Sedlarik, V. Kasparkova, A. Salakova, J. Drbohlav, U. Cvelbar, and P. Saha, “Functionalization of polylactic acid through direct melt polycondensation in the presence of tricarboxylic acid,” *J. Appl. Polym. Sci*., vol. 122, no. 2, pp. 1275–1285, 2011.

[17] M. Nagata, T. Machida, W. Sakai, and N. Tsutsumi, “Synthesis, characterization , and enzymatic degradation studies on novel network aliphatic polyesters,” *Macromolecules,* vol. 31, pp. 6450–6454, 1998.

[18] B.-H. Kim, J. Jang, and S.-W. Ko, “Durable press finish of cotton fabric using malic acid as a crosslinker,” *Fibers Polym*., vol. 1, no. 2, pp. 116–121, 2000.

[19] R. M. Silverstein, F. X. Webster, and D. Kiemle, *Spectrometric Identification of Organic Compounds*, 7th ed. New York: John Wiley & Sons, Inc., 2005.

[20] M. J. Miri, K. E. Nori, R. M. Andrew, and C. Ge, "Copolyester synthesis using glycerol from biodiesel production," in *Renewable and Sustainable Polymers*, G. F. Payne and P. B. Smith, Eds. American Chemical Society, 2011, pp. 11–35.

[21] H. F. Shurvell, "Spectra-structure correlations in the mid-and far-infrared," in *Handbook of Vibrational Spectroscopy, Volume 3: Sample Characterization and Spectral Data Processing,* J. M. Chalmer and P. R. Griffiths, Eds. New York: John Wiley & Sons, Inc., 2002, pp. 1783–1837.

[22] J. M. Halpern, R. Urbanski, A. K. Weinstock, D. F. Iwig, R. T. Mathers, and H. A. von Recum, "A biodegradable thermoset polymer made by esterification of citric acid and glycerol," *J. Biomed. Mater. Res. Part A*, vol. 102, no. 5, pp. 1467–1477, 2014.

[23] N. Abidi, E. Hequet, C. Turner, and H. Sari-Sarraf, "FTIR analysis of crosslinked cotton fabric using a ZnSe-universal attenuated total reflectance," *J. Appl. Polym. Sci*., vol. 96, no. 2, pp. 392–399, Apr. 2005.

[24] C. Chung, M. Lee, and E. K. Choe, "Characterization of cotton fabric scouring by FT-IR ATR spectroscopy," *Carbohydr. Polym*., vol. 58, no. 4, pp. 417–420, 2004.

[25] C. Q. Yang, "Predicting the performance of durable press finished cotton fabric with infrared spectroscopy," *Text. Res. J.*, vol. 69, no. 2, pp. 145–151, 1999.

[26] C. Sawatari, Y. Sekiguchi, and T. Yagi, "Durable water-repellent cotton fabrics prepared by low-degree substitution of long chain alkyl groups," *Text. Res. J*., vol. 68, no. 7, pp. 508–514, 1998.

[27] I. S. Kang, C. Q. Yang, and G. C. Lickfield, "Mechanical strength of durable press finished cotton fabrics: part I: effects of acid degradation and crosslinking of cellulose by polycarboxylic acids," *Text. Res. J*., vol. 68, no. 11, pp. 865–870, 1998.

[28] Z. Mao and C. Q. Yang, "Polymeric multifunctional carboxylic acids as crosslinking agents for cotton cellulose: poly(itaconic acid) andin situ polymerization of itaconic acid," *J. Appl. Polym. Sci*., vol. 79, no. 2, pp. 319–326, 2001.

[29] C. Q. Yang, C. Hu, and G. C. Lickfield, "Crosslinking cotton with poly(itaconic acid) and in situ polymerization of itaconic acid : fabric mechanical strength retention," *J. Appl. Polym. Sci.*, vol. 87, pp. 2023–2030, 2003.

[30] C. Q. Yang, X. Wang, and I.-S. Kang, "Ester crosslinking of cotton fabric by polymeric carboxylic acids and citric acid," *Text. Res. J*., vol. 67, no. 5, pp. 334–342, 1997.

[31] C. Q. Yang, W. Wei, and G. C. Lickfield, "Mechanical strength of durable press finished cotton fabric: part II: comparison of crosslinking agents with different molecular structures and reactivity," *Text. Res. J.*, vol. 70, no. 2, pp. 143–147, 2000.

[32] K. J. Yoon, J. H. Woo, and Y. S. Seo, “Formaldehyde free cross-linking agents based on maleic anhydride copolymers,” *Fibers Polym*., vol. 4, no. 4, pp. 182–187, 2003.

[33] W. Xu and Y. Li, “Crosslinking analysis of polycarboxylic acid durable press finishing of cotton fabrics and strength retention improvement,” *Text. Res. J.,* vol. 70, no. 7, pp. 588–592, 2000.

[34] E. A. Immergut and B. G. Ranby, “Heterogeneous acid hydrolysis of native cellulose fibers,” *Ind. Eng. Chem*., vol. 48, no. 7, pp. 1183–1189, 1956.

[35] M. M. Barbooti and D. A. Al-Sammerrai, “Thermal decomposition of citric acid,” *Thermochim. Acta,* vol. 98, pp. 119–126, 1986.

[36] D. Wyrzykowski, E. Hebanowska, G. Nowak-Wiczk, M. Makowski, and L. Chmurzyński, “Thermal behaviour of citric acid and isomeric aconitic acids,” *J. Therm. Anal. Calorim*., vol. 104, no. 2, pp. 731–735, 2010.

Chapter Four-

Development and Application of Linear-dendritic Polycitric Acid Cross-linker

4.1 Introduction

In view of the success in preparing dendritic PCA with branched polyols as the core molecules in the previous chapter, yet colour of the products and hence fabric yellowing is still the major deficiency for further improvement. To suppress such deficiency, other polyols and synthesis approach were attempted to build CA based polymeric cross-linkers for cellulosic textile materials. Several polymeric glycols with two active functional primary hydroxyls terminals (B_2) were selected as the linear spacer molecules to build linear-dendritic PCA cross-linkers.

Low molecular weight polyethylene glycols (PEGs) are typical low toxicity hydrophilic modifier in textile finishing assisting strength and whiteness retention of fabrics [1]–[4]. In this chapter, a series of linear-dendritic PCA polymers were prepared via bulk polycondensation with PEGs of various molecular weights. Various PEGs of different chain lengths were adopted to verify the effect of spacer length in the linear-dendritic polymers serving as the wrinkle-resistant finishing agents. Chemical structures of individual reactants are illustrated in Figure 4-1. The newly prepared PCA polymers were sequentially subjected to the wrinkle-resistant finishing study. The wrinkling phenomenon of the modified cotton textiles was then evaluated.

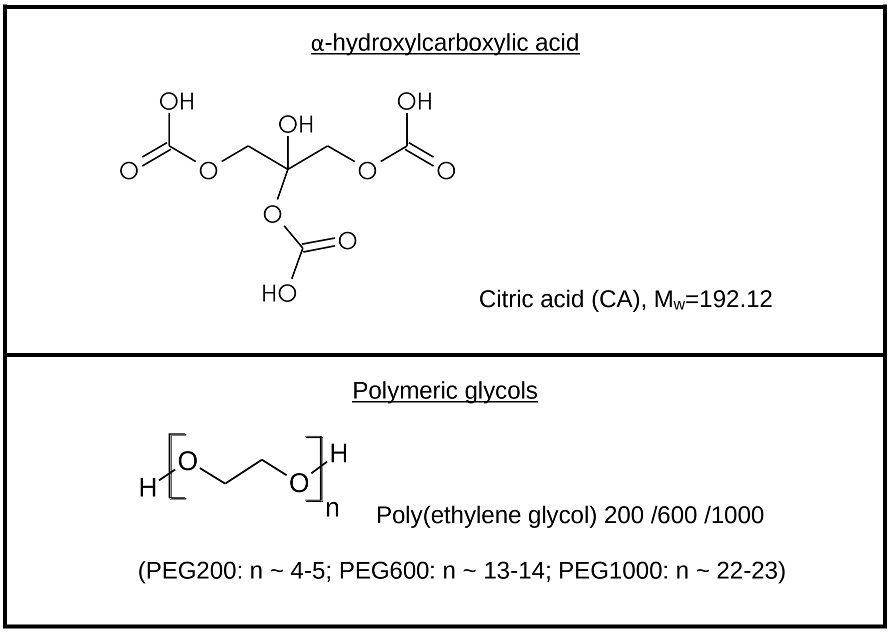


Figure 4-1 CA and PEGs used in the preparation of linear-dendritic PCA cross-linkers

4.2 Experimental

4.2.1 Materials

Anhydrous CA and PEG1000 were purchased from Acros Organics. PEG200 and PEG600 were supplied by AccuChem Co. 1,2,3,4-butanetetracarboxylic acid (BTCA), sodium hypophosphite monohydrate ($NaH_2PO_2 \cdot H_2O$) and sodium hydroxide (NaOH) were supplied by International Laboratory. Absolute ethanol and Silyouwet T168 were supplied by VWR and Dymatic Co. respectively. Tetrahydrofuran (THF) was purchased from Duskan Pure Chemicals. Dimethyl sulfoxide-d_6 (DMSO-d_6) was obtained from Acros Organics. All chemicals were used as received. 100% plain woven semi-bleached cotton fabric (160 x 72, 127g/m^2) was used for the wrinkle-resistant finishing study.

4.2.2 Synthesis of polymeric cross-linker

CA in a combination with various PEGs (i.e., PEG200, PEG600 or PEG1000) were mixed and reacted to form linear-dendritic polymers via bulk polycondensation as shown in Scheme 4-1. General procedures are summarised as below.

In a 100ml round bottom flask, CA (0.26mol) and the designated PEG (0.026mol to 0.065mol) were melted at 160˚C with constant stirring for 1 hour under reduced pressure. The resultant polymers were dissolved in deionised water and dialysed against pure deionised water using dialysis tubing (semi-permeable cellulose ester membrane, MWCO of 500-1000Da, SpectrumLabs) for 18 hours under ambient temperature. Purified products were dried by rotatory evaporation and sequentially dried under vacuum. Purified products were pale yellowish pastes.

PCA-PEG2s:

FTIR-ATR (cm^{-1}): 3420 (νO-H, acid), 2935 (νC-H,), 1712 (νC=O ester), 1396 (δ C-H), 1192 (νC-O-C ester), 1120 (νC-O-C ether)

^{1}H-NMR (400MHz, DMSO-d_6), δ (TMS ppm): 2.62-2.75 (m, CH_2, CA moiety), 3.49-3.56 (-OCH_2CH_2O-, PEG200 moiety); 4.07-4.13 (-CH_2COO-, PEG200 moiety)

PCA-PEG6s:

FTIR-ATR (cm^{-1}): 3424 (ν O-H, acid), 2922 (νC-H,), 1714 (νC=O ester), 1396 (δ C-H), 1196 (νC-O-C ester), 1078 (νC-O-C ether)

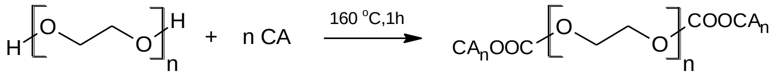
^{1}H-NMR (400MHz, DMSO-d_6), δ (TMS ppm): 2.63-2.74 (m, CH_2, CA moiety), 3.47 (-OCH_2CH_2O-, PEG600 moiety); 4.07-4.12 (-CH_2COO-, PEG600 moiety)

PCA-PEG10s:

FTIR-ATR (cm^{-1}): 3436 (ν O-H, acid), 2916 (ν C-H,), 1714 (ν C=O ester), 1395 (δ C-H), 1186 (ν C-O-C ester), 1077(ν C-O-C ether)

^{1}H-NMR (400MHz, DMSO-d_6), δ (TMS ppm): 2.61-2.75 (m, CH_2, CA moiety), 3.45-3.48 (-OCH_2CH_2O-, PEG1000 moiety), 4.08-4.11 (-CH_2COO-, PEG1000 moiety)

Scheme 4-1



4.2.3 Polymer Characterisations

Each FTIR spectrum recorded as an average of 16 scans on a Perkin Elmer Spectrum 100 spectrophotometer equipped with a universal attenuated total internal reflectance (ATR) accessory.

^{1}H NMR spectra were recorded using a Varian Unity Inova 400 NMR spectrometer under ambient temperature. DMSO-d_6 was used as the solvent with tetramethylsailne (TMS) as the internal reference for the analysis.

The molecular weights of the polymers were estimated by gel permeation chromatography (GPC) with the use of Waters system. The system equipped with a Waters 1515 isocratic pump coupled with a series of Styragel® HMW columns (HR1, HR4, and HR6; molecular weight range 10^2 -10^7), calibrated with mono-dispersed polystyrene standards (PS) (PolyScience), and a Waters 2414 refractive index detector.

THF was used as the eluent at a flow rate of 1.0 ml/min. The column was maintained at 30°C during analysis.

Thermogravimetric analysis (TGA) of the polymers (5mg) was performed by using a Mettler-Toledo thermogravimetric analyser studied under nitrogen atmosphere heating at a rate of 20°C/min.

4.2.4 Modification of Cotton Fabric

The newly developed linear-dendritic PCAs serving as cross-linkers were mixed with NaH_2PO_2, a typical catalyst for cellulose esterification in the finishing study. Cotton fabrics were impregnated with the solutions of different formulations using a Rapid Labortex P-80 horizontal padding machine imposing a constant pressure of 1kg/ cm^2 to achieve wet pick-up of 70±5% and sequentially dried at 100°C for 3min. The fabrics were then thermally cross-linked at 180°C for 1.5min using a Werner Mathis LabDryer curing machine. The several variables of finishing recipes were studied included the concentration of PCA-PEGs (20 w/w% to 30w/w%), acidity of the padding solution (pH 2 or 3), the inclusion of additives, BTCA (2w/w%) and Sliyouwet T618 (4w/w%). All recipes contained 7w/w% of NaH_2PO_2 as the catalyst and 5w/w% ethanol as the dispersing agent.

4.2.5 Fabric Characterisations and Evaluations

Properties of cotton fabrics modified with PCA-PEGs were evaluated based on the following standard approaches and procedures. All modified fabric samples were conditioned under standard condition at 65±2% relative humidity and 21±1°C prior to evaluations. The formation of cross-links of modified cotton fabrics was studied based on FTIR-ATR. Modified fabric samples were treated with 0.1M NaOH solution and rinsed with deionised water to differentiate carbonyl (C=O) stretching of carboxyls and esters [5]–[8]. Spectra of dried fabric samples were recorded using a Perkin Elmer FTIR spectrophotometer 100 equipped with an ATR sampling accessory. Each FTIR spectrum was recorded as an average of 128 scans.

Wrinkle-resistant performance was evaluated in accordance to the AATCC 66-2008 test method. Specimens (40mm x 15mm) in both warp and weft alignment were folded face-to-face and back-to-back. Folded specimens were compressed with a 500g-weight for 5min. The wrinkle recovery angles (WRA) of specimens were measured by a Daiei Kagakuseiki Seisakusho wrinkle recovery tester after 5min of relaxation and recovery. WRAs were reported as an average of eight measurements of the sum in warp and weft directions with the analytical tolerance limited to 5%. The change in wrinkle recovery angle (ΔWRA) was expressed according to the following equation.

$$\Delta WRA = \frac{WRA_m - WRA_o}{WRA_o} \times 100\%$$

where as WRA_m= WRA of modified fabric
WRA_o = WRA of control fabric

Mechanical properties included tensile strength and tearing strength, were evaluated according to ASTM D5034-2009 and ASTM D1424-2009 test methods respectively. The tearing strength of modified cotton fabrics were evaluated using a James H. Heal digital Elmendorf tearing tester with a standard weight of 1600g or 3200g chosen to measure the strength. Specimens were cut according to the standard notched template in both warp and weft directions. Individual notched specimen was fixed onto the tester. The pendulum was depressed downwards until tearing of a specimen was completed. Tearing force (Ft) was reported as an average result of eight measurements in both warp and weft directions. When evaluating the tensile strength of modified cotton fabrics, a tensile tester, Instron 4411, was used based on constant rate of extension (CRE) tensile testing method. Specimens (150mm x10mm) in both warp and weft alignment were mounted vertically on the tester for the test. Longitudinal grabbing force was applied along the testing direction until the specimen broke. Tensile strength reported as the averaged breaking force (Fb) of eight measurements in both warp and weft directions with the analytical tolerance limited to 5%. The change in mechanical properties was expressed in terms of change in forces (ΔF) according to the below equations.

$$\Delta Ft = \frac{Ft_m - Ft_o}{Ft_o} \times 100\%$$

$$\Delta Fb = \frac{Fb_m - Fb_o}{Fb_o} \times 100\%$$

where as Ft_m = tearing or tensile force of modified fabric
Ft_o = tearing or tensile force of control fabric
Fb_m = tearing or tensile force of modified fabric
Fb_o = tearing or tensile force of control fabric

Whiteness and yellowness were evaluated using a GretagMacbeth Colour-Eye 7000A reflectance spectrophotometer under the standard illuminant of D_{65} and viewed at 10^o standard observer in accordance with the AATCC 110-2005 and ASTM E313-2010 test methods. The whiteness and yellowness were expressed in terms of whiteness index (WI) and yellowness index (YI) respectively.

4.3 Results and Discussion

4.3.1 Cross-linker Synthesis and Characterisation

Series of linear-dendritic PCA polymers were synthesised via bulk polycondensation. The resultant polymers of various PEG spacer lengths were named as PCA-PEG2 (CA with PEG200), PCA-PEG6 (CA with PEG600) and PCA-PEG10 (CA with PEG1000). The polymerisation results were tabulated in Table 4-1.

Table 4-1 Summary of linear-dendritic PCAs prepared by bulk-polycondensation [a]

Sample code	ratio [b]	M_n x10^3 [c]	M_w x10^3 [c]	PDI [d]	Yield%
PCA-PEG2(4)	4	0.79	1.1	1.3	46.74
PCA-PEG2(6)	6	1.2	1.4	1.18	45.84
PCA-PEG2(8)	8	1.6	2	1.21	31.90
PCA-PEG2(10)	10	1.1	1.2	1.13	33.06
PCA-PEG6(4)	4	1.2	1.3	1.11	64.24
PCA-PEG6(6)	6	1.6	1.9	1.15	67.58
PCA-PEG6(8)	8	2	2.2	1.13	44.91
PCA-PEG6(10)	10	1.8	2.2	1.25	30.43
PCA-PEG10(4)	4	1.6	1.9	1.17	92.05
PCA-PEG10(6)	6	2.1	2.5	1.2	93.54
PCA-PEG10(8)	8	2.3	2.9	1.28	82.94
PCA-PEG10(10)	10	2.7	3.4	1.3	79.19
PCA-PEG10(12)	12	3.1	3.6	1.16	60.05

[a] Bulk polycondensation carried out at 160°C under reduced pressure for 1hr. [b] ratio refer to molar feed ratio of CA : PEG. [d] Estimated by GPC in THF on the basis of a PS calibration expressed in Da. [d]PDI = polydispersity (M_w/M_n).

In general, all purified PCA-PEGs were clear pastes, in pale yellow to yellow. The yield obtained by dialysis of crude products ranging from 30% to 94% by weight. As summarised in Table 4-1, series of low molecular weight polymeric products of PCA-PEGs were prepared with M_n of 0.79 x10^3 Da to 3.1 x10^3 Da and polydispersity (PDI) ranging from 1.1 to 1.3. The feed ratio between CA to PEG in the system essentially controlled the resultant molecular weight of the resultant polymer. M_n estimated by GPC complied with the feed ratio between CA and the respective PEG upon bulk polycondensation reaction for 1 hour at 160°C under reduced pressure without inclusion of a catalyst.

Polymeric glycols B_2 incorporated in a polycondensation system of polyfunctional monomers are regarded as chain stoppers hampering the growth in molecular weights [9]–[11]. This would be an important attribute of building low molecular weight polymeric cross-linkers for cellulosic textiles. In significance, chain length of PEG was revealed as the modulator in the growth of the dendritic portion of the PCA-PEG polymer. Utilising short chains PEGs limited the growth of molecular weight below 2 $\times 10^3$ Da. PEG200 with n ~4.5 failed to develop linear-dendritic products comprised of over 10 CA moieties. PEG of short chain length hampered continual condensation of CA monomers and hence limited the growth into larger macromolecules. When the chain length of PEG increased to n~22.5 (in the case of PEG1000), 10 to 12 moieties of CA was found in the resultant polymers of PCA-PEG10(10) and PCA-PEG10(12). Increasing chain length of PEG was found to be able to promote the growth of CA moieties in the products. Insertion of PEG as the spacer between dendritic PCA moieties could help alleviate steric hindrance of further condensation of CA monomers to the growing PCA-PEG molecule.

Chain lengths of PEGs not only affect the growth of molecular weights of linear-dendritic PCA-PEG polymers, but also essentially impact the yield of product. Among PEGs used in the present study, PEG1000 of the longest chain length enabled to form products with yields over 80% in the synthesis trials of various feed ratios. Spacer length between the dendritic PCA moieties was the major attributes modulating further condensation of CA monomers to the growing PCA-PEG-PCA molecule. Mutual condensation of forming oligomeric PCAs, such as CA-CA dimer or CA-CA-CA trimer was more favourable when PEG200 or PEG600 incorporated in the system. The yield of product of PCA-PEG2 polymers obtained from dialysis was significantly lower than that of the series of PCA-PEG6 and PCA-PEG10 products. The reaction was suggested to shift towards intramolecular dehydration of CA monomers and CA moieties in the product. Systems of PCA-PEG2 were generally in dark shade of colour, in yellow to bright yellow. This indicated that a certain portion of unsaturated moieties was present acting as the chromospheres.

Diagnostic absorption bands originated from ester functionalities at 1710cm^{-1} (C=O stretching) and 1200cm^{-1} (-C-O-C stretching) demonstrated polyesters were formed in the bulk polymerisation of CA and PEGs as illustrated in Figure 4-2. Esterification between CA and all PEGs was revealed. In this study, anhydrous CA was used. In the polymer spectra, disappearance of diagnostic absorption band originated from C=O stretching of the anhydride moiety of CA at 1755cm^{-1} suggested that CA carboxyls were consumed in the polycondensation reaction [12]–[14]. Sharp absorption bands at 3500cm^{-1} and 3290cm^{-1} originated from O-H stretching of CA hydroxyl was absent in the polymer spectra in the FTIR spectra indicated that mutual polycondensation of CA occurred. CA carboxyls not only reacted with CA hydroxyl, but also condensed with PEG hydroxyls. Distinguished absorption bands originated from the stretching of methylene (-CH_2^-) and ether (-C-O-C-) moieties of PEGs at ~2900cm^{-1} and 1100cm^{-1} were retained in the product spectra [15]–[18]. This indicated that PEG was present in the PCA polymers.

The board peaks at 3400-2600cm^{-1} originated from O-H of carboxylic acid groups of CA retained in all in the PCA-PEGs polymer spectra. Free COOH present in the products could furnish the cross-linking capability PCA products with cotton cellulose in the sequential wrinkle-resistant finishing. 1648cm^{-1} denoted the interaction between carbonyls with absorbed moisture. PCA-PEGs were substantially hydrophilic.

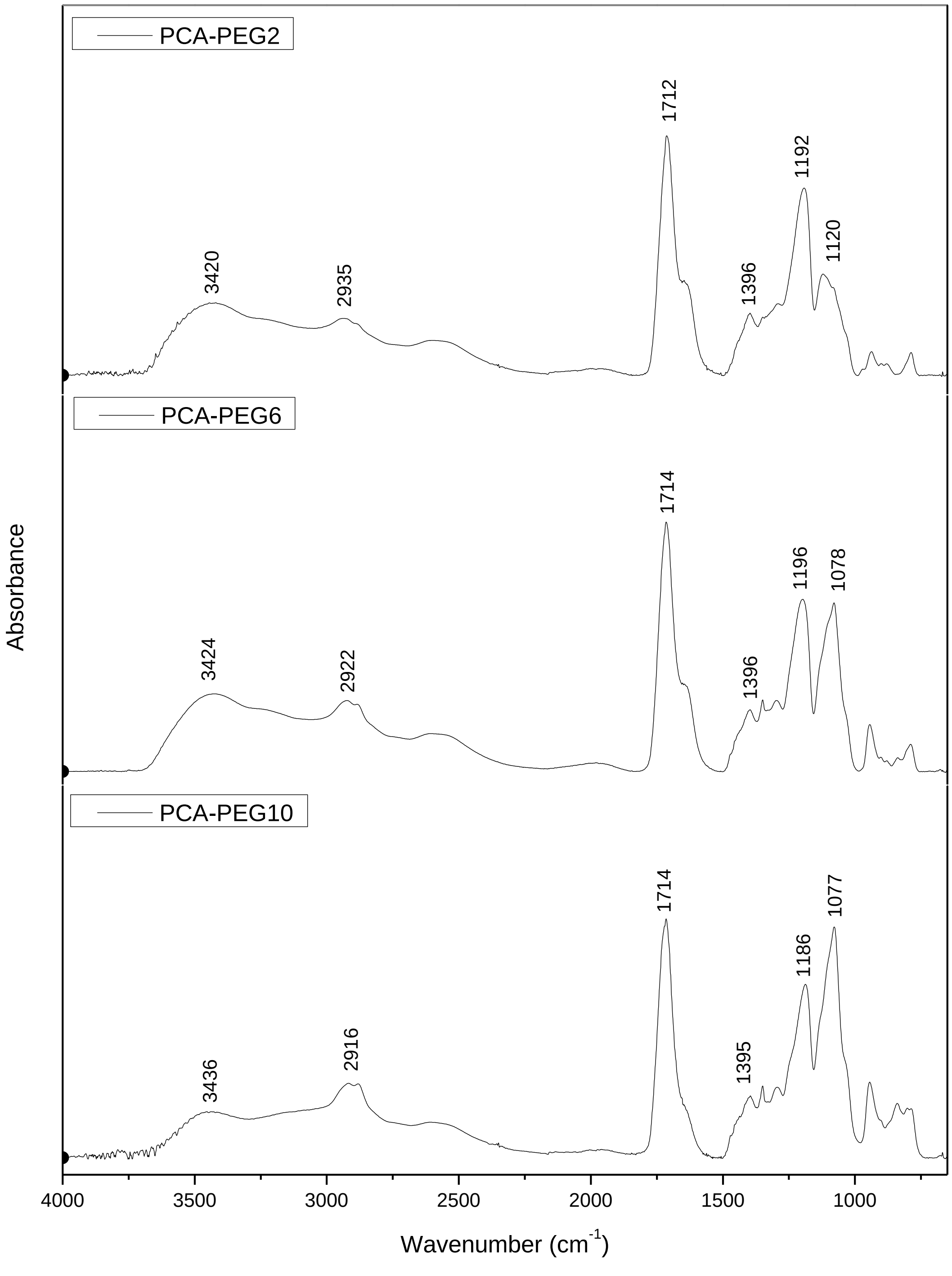


Figure 4-2 FTIR spectra of PCA-PEG polymers with various spacers: PCA-PEG2(8) (upper), PCA-PEG6(8) (middle) and PCA-PEG10(8) (bottom)

The chemical composition and architecture of the linear-dendritic PCA-PEG-PCA were elucidated based on the diagnostic peaks present in ^{1}H-NMR spectra (Figure 4-3). In the syntheses, PEGs of various chain lengths were adopted in the attempt to develop PCA-PEG-PCA linear-dendritic polymeric cross-linkers. Linear PEGs were postulated to serve as the spacers in the newly developed PCA-PEG-PCA polymers between two dendritic CA blocks. Regarding the reactivity of hydroxyls, CA was suggested to condense preferentially with two primary hydroxyls of PEGs prior proceeding to further polycondensation or undergoing intramolecular dehydration. This assumption was verified with the analysis of ^{1}H-NMR spectra of the products. The diagnostic resonance of primary hydroxyl of PEGs at ~δ4.5 was absent in the polymer spectra. Meanwhile, a distinguishing peak in the polymers spectra at ~δ4 is attributable to the methylene protons of PEGs which were adjacent to ester linkages [19], [20].

The peak intensities were approximately corresponding to the feed ratios of CA to PEG employed in the polymerisation for all polymeric glycols adopted. The relative integrals of the NMR resonance of methylene protons (-CH_2-COO-) of the glycol to the methylene protons of CA complied with the GPC estimation and theoretical feed ratios. In such a manner, PEG was essentially served as linear block in between two dendritic CA blocks as postulated in Scheme 4-1.

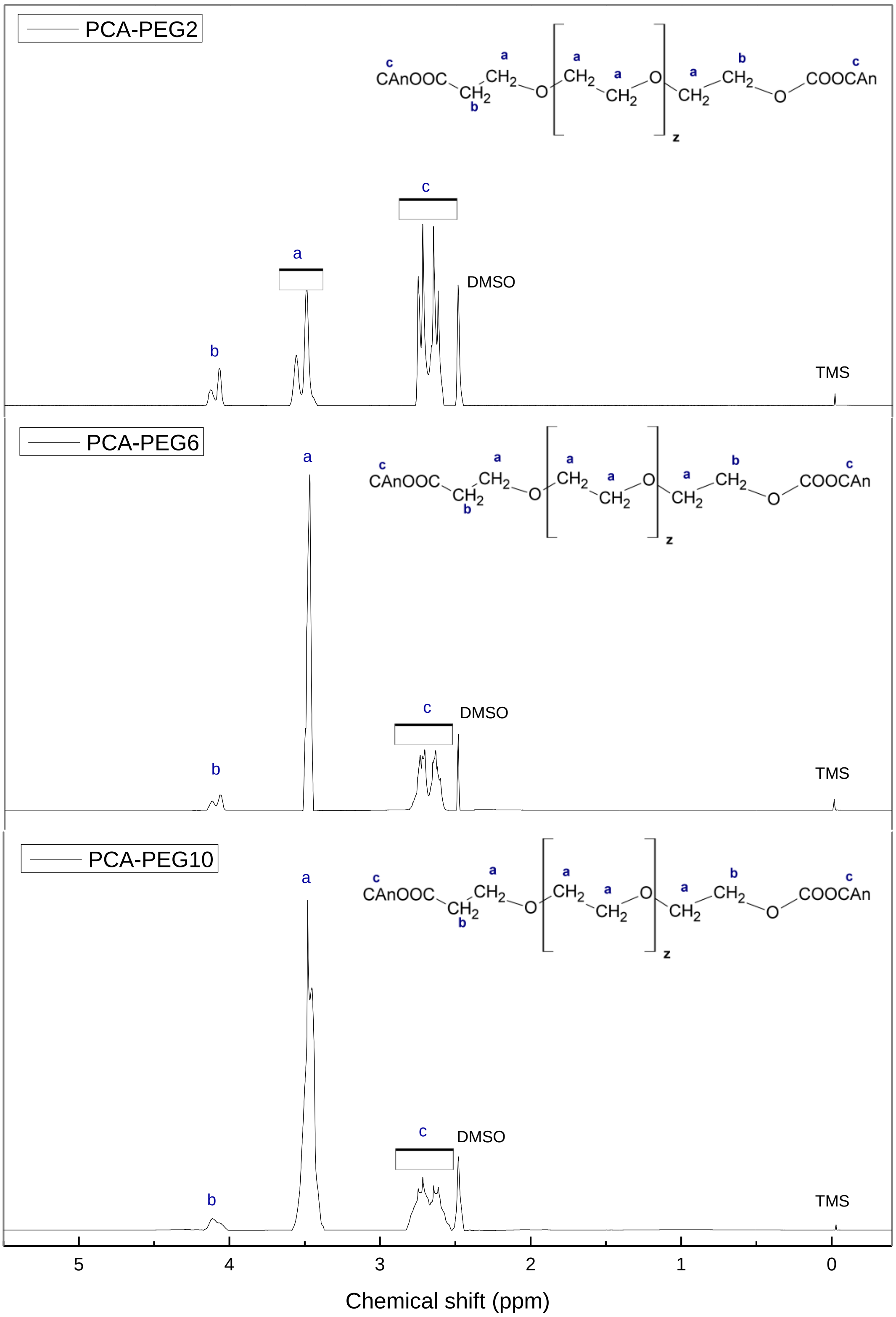
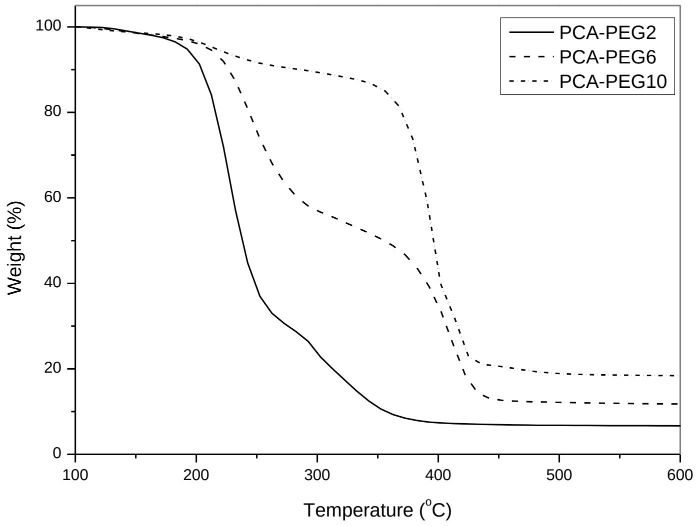


Figure 4-3 ^{1}H-NMR spectra of linear-dendritic PCA-PEG polymers with various spacers: PCA-PEG2(8) (upper), PCA-PEG6(8) (middle) and PCA-PEG10(8) (bottom)

Thermal stability of linear-dendritic PCA was evaluated by TGA. The thermograms are presented in Figure 4-4. In general, the initial 5% percent weight losses were determined to be around 200˚C to 210˚C. Difference in spacer length of the dendritic polymers affected the thermal resistance. As illustrated in the TGA thermograms, the linear-dendritic PCA-PEG with longer spacer length were found to be relatively thermally stable.



(TGA thermograms were measured under nitrogen atmosphere at a heating rate of 20°C/min)

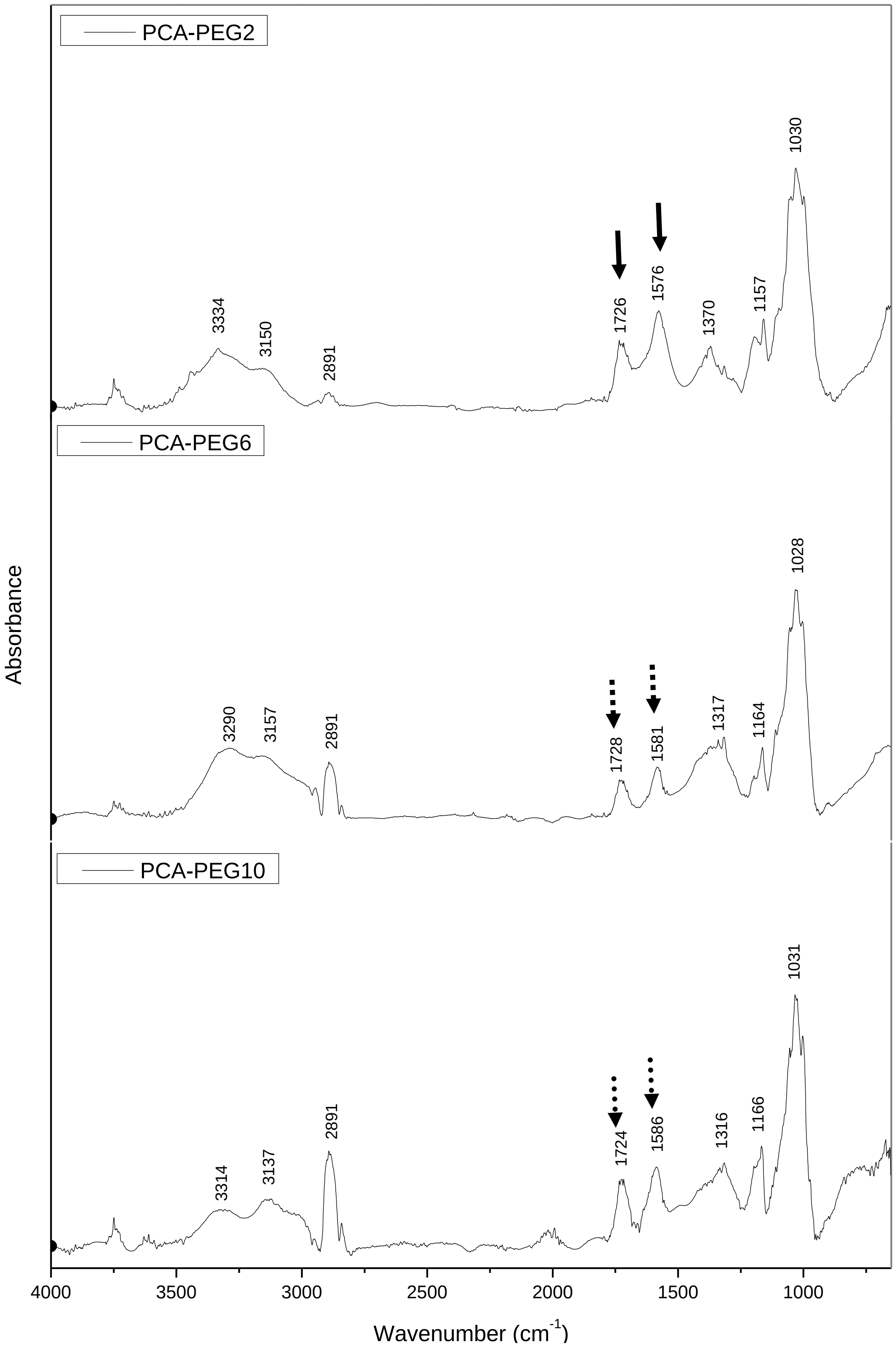
Figure 4-4 TGA thermograms of linear-dendritic PCA composed of various PEG spacers

4.3.2 Fabric Performance and Evaluations of Modified Cotton

To afford easy-care cotton textiles, finishing parameters included the finishing formulation and the treatment condition are crucial factors in attaining the designated functional performance while achieving overall balanced properties of the modified textiles [21], [22]. In this part of the wrinkle-resistant finishing study, several PCA-PEGs were selected to investigate the efficacy this group of linear-dendritic polymers as cellulose cross-linkers. In addition, three major variables of finishing formulation included the concentration of cross-linker (15w/w% to 30w/w%), acidity of the finishing solution (pH 2 to 3) and inclusion of additives (BTCA and Silyouwet T168) were evaluated.

4.3.2.1 FTIR-ATR Characterisation of Modified Cotton

As discussed in 3.3.2 in the previous chapter, the formation of ester cross-links of the cotton impregnated and cured with linear-dendritic PCA-PEG polymers was revealed based on FTIR-ATR with the post-treatment of NaOH solution [5]–[7], [23]–[26]. Upon modification with PCA-PEGs, additional ester carbonyls (1720cm^{-1}) and carboxylates (1585cm^{-1}) were detected on the modified cotton fabrics as shown in Figure 4-5. Meanwhile, absorption band at ~2900cm^{-1} originated from C-H stretching was intensified due to the presence of PEG spacer moiety in the cross-links. This indicated the formation of PCA-PEG-PCA cross-links between cotton cellulose. Esterification using poly(carboxylic acid) for cross-linking unavoidably retains certain amount of acid residue on the fabrics. The residue peak of carboxylates explained the phenomenon that acid-catalysed depolymerisation of cellulose fibres was one of the attributes leading to the loss in mechanical strengths.



(Cotton fabric impregnated with the finishing solution of pH 3, comprised of 15w/w% PCA-PEG cross-linkers coupling with 7w/w% NaH_2PO_2 were subjected to curing at 180°C to 1.5min.)

Figure 4-5 FTIR-ATR spectra of the cotton fabrics modified with PCA-PEG2(8) (upper), PCA-PEG6(8) (middle) and PCA-PEG10(8) (bottom)

4.3.2.2 Effect of Spacer Length of Linear Moiety

Various PEGs were employed to build linear-dendritic PCA-PEG polymers. In particular, PCA-PEG2(8), PCA-PEG6(8) and PCA-PEG10(8) were selected to investigate the efficacy this group of polymers as cellulose cross-linkers. In this part of the finishing study, 15w/w% of the selected PCA-PEG polymer coupling with 7w/w% of NaH_2PO_2 was employed for cross-linking cotton fabrics. Cotton fabrics impregnated with PCA-PEG polymers solution of pH3 were subjected to curing at 180°C for 1.5min. The influence of molecular composition of the carboxyl-based cross-linkers on the wrinkle recovery performance of the cotton fabric was evaluated accordingly. The resultant performance of the modified cotton fabrics is summarised in Table 4-2.

The degree of cross-linking governs the extent of wrinkle recovery performance of the modified fabrics. The alteration of wrinkle recovery performance of modified fabrics was evaluated and compared to the performance of the control cotton fabric. The alteration was expressed in terms of ΔWRA. All PCA-PEGs were comprised of 8 CA moieties for cellulose cross-linking while with different spacer lengths. As illustrated in Table 4-2, ΔWRA exhibited a decreasing trend in relation to the spacer length. Increasing spacer length would diminish the penetration power of the PCA-PEG cross-linker into fibres of cotton cellulose. Thus, cross-linking effectiveness of PCA-PEG reduced.

Table 4-2 Summary of properties of cotton fabrics modified with linear-dendritic PCA-PEGs with various spacer lengths

Fabric code	Cross-linker	Spacer length	M_n x10^3 [a]	WRA(°) [b]	Ft(N) [c]	Fb(N) [d]	WI [e]	YI [f]
control cotton	---	---	---	140	19.65	283.361	75.087	5.407
PEG2	PCA-PEG2(8)	4-5	0.78	248	10.17	200.733	59.274	9.815
PEG6	PCA-PEG6(8)	13-14	1.6	224	12.15	210.736	62.988	8.924
PEG10	PCA-PEG10(8)	22-23	2.6	214	14.84	227.312	66.406	7.825

[a] M_n = no. average molecular weight of PCA estimated by GPC expressed in Da. [b] WRA = averaged sum of wrinkle recovery angles in warp and weft of cotton fabrics in accordance with AATCC 66-2008. [c] Ft = averaged sum of tearing force in warp and weft of cotton fabrics in accordance with ASTM D1424-2009. [d] Fb = averaged sum of braking force in warp and weft of cotton fabrics in accordance with ASTM D5034-2009. [e] WI = whiteness index measured in accordance with AATCC 110-2005. [f] YI = yellowness index measured in accordance with the ASTM E313-2010.

Tearing and tensile strengths were altered after the finishing treatment. The changes in tensile and tearing strengths are expressed in terms of ΔFb and ΔFt respectively. New PCA-PEG-PCA cross-links formed between cellulose restricted intermolecular motion between cross-linked fibres leading to a reduction in tensile strength. Loss in Fb was found to be proportional to the increment in ΔWRA. On the whole, the loss in Fb was about 20% to 30% using the selected PCA-PEG for cotton cross-linking. In particular, the alteration in ΔFt in the present study was found to be intriguing. Increasing spacer length helped alleviate the loss in tearing strength. Aliphatic linear moiety of PEG in between dendritic CA moieties afforded additional strength to compensate loss in tearing strength induced by acid-catalysed depolymerisation of cotton fibres [3], [5], [27]–[30]. PCA-PEG, in particular PCA-PEG10(8) was capable of retaining loss in tearing strength of cotton fabrics by 20% compared to utilising PCA-PEG2(8).

Furthermore, employing PEG as the spacer moiety in the polymeric cross-linker could reduce fabric yellowing. Yellowness index revealed the least extent of fabric yellowing imparted in finishing treatment when utilising cross-linkers with longer spacer length. Utilising PCA-PEG with moderate spacer length on one hand, could furnish appreciable improvement in wrinkle recovery performance. On the other hand, it could facilitate tearing strength retention and whiteness retention.

4.3.2.3 Comparison between Monomeric and Polymeric Cross-linkers

A series of novel low molecular weight linear-dendritic PCA-PEG cross-linkers was successfully prepared by bulk polycondensation. The effectiveness of the cross-linking reaction, and the resultant wrinkle-resistant performance and fabric properties were summarised in Table 4-3. The results revealed the explicit difference between monomeric and polymeric cross-linker for cotton cellulose.

Among the linear-dendritic PCA-PEG cross-linkers, PCA-PEG10(8) could offer the optimal balance of fabric properties of the cotton fabric in terms of mechanical strength and colour retention. It was selected to compare to the monomeric CA counterpart. As illustrated in Table 4-3, the low molecular weight polymeric PCA-PEG-10(8) was brilliantly assisted the retention in fabric strength and colour in the study. Though the improvement in wrinkle-resistant of fabric modified with PCA-PEG10(8) was found to be less prominent, the losses in tensile and tearing strengths were alleviated by 50% and 27% respectively. Polymeric PEG spacer of the PCA-PEG10 afforded flexibility to the fabrics. Linear-dendritic polymeric PCA-PEG10 was explicitly capable of retaining fabric strengths compared with the monomeric CA counterpart.

Table 4-3 Comparison performance between monomeric CA and polymeric PCA-PEG cross-linkers [a]

Fabric code	Cross-linker	M_n x10^3 [b]	WRA (^{o}) [c]	Ft (N) [d]	Fb (N) [e]	WI [f]	YI [g]
control	---	---	140	19.65	283.361	75.087	5.407
CA-10	CA	0.192	190	5.94	163.414	68.487	7.511
PEG10	PCA-PEG10(8)	2.6	191	15.67	240.38	70.442	6.705

[a] Both fabrics impregnated with finishing bath of pH2, comprised of 10w/w% cross-linker with 7w/w% NaH_2PO_2 and cured at 180^{o}C for 1.5min [b] M_n = no. average molecular weight of PCA estimated by GPC expressed in Da. [c] WRA = averaged sum of wrinkle recovery angles in warp and weft of cotton fabrics in accordance with AATCC 66-2008. [d] Ft = average of tearing force in warp and weft of cotton fabrics in accordance with ASTM D1424-2009. [e] Fb = average of breaking force in warp and weft of cotton fabrics in accordance with ASTM D5034-2009. [f] WI = whiteness index measured in accordance with AATCC 110-2005. [g] YI = yellowness index measured in accordance with ASTM E313-2010 .

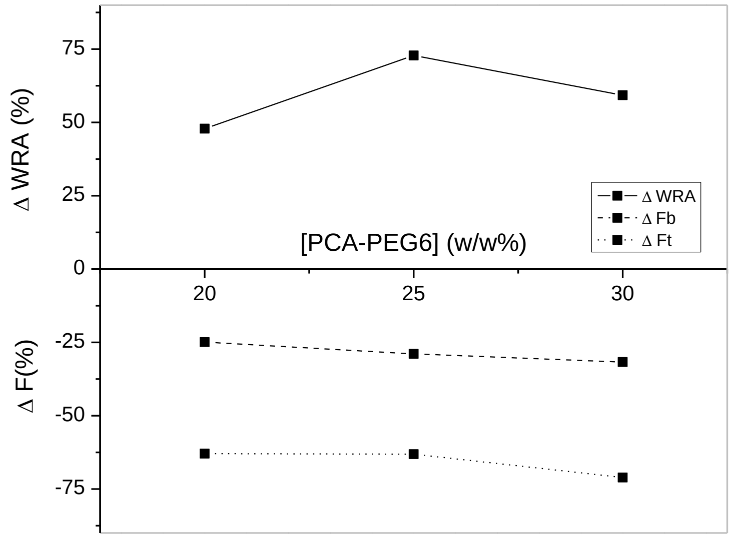
4.3.2.4 Effect of Finishing Variables on Cross-linking

Three major variables of finishing formulation included the concentration of cross-linker, acidity of the finishing solution and inclusion of additives were evaluated. In this part of the finishing study, PCA-PEG6(6) of M_n ~1.6 x10^3 Da was adopted as the cross-linker.

4.3.2.4.1 Effect of Concentration of Cross-linker

Three concentrations of PCA-PEG6(6), included 20w/w%, 25w/w% and 30w/w%, were adopted to study the effect of cross-linker concentration on the properties of the modified cotton fabrics. Figure 4-6 presents the variation in ΔWRA in relation to the cross-linker concentration. ΔWRA reached a maximum increment when the cotton fabric was impregnated with 25w/w% PCA-PEG cross-linker. Wrinkle recovery performance could not be further enhanced with the increase in concentration up to 30w/w%. Saturation of impregnated fabric substrate was suggested as the cause for the phenomenon.

Cross-linking cellulose unavoidably would induce loss in fabric strengths. Loss in strength was found to be proportional to the increase in cross-linker concentration. In particular, when cross-linker concentration increased up to 30w/w%, the loss in strengths due to acid-catalysed depolymerisation became predominant. Loss in both tearing and tensile strengths proceeded to the greatest extent. In the range of concentrations evaluated, 25w/w% of PCA-PEG6 could furnish the cotton substrate with the most brilliant ΔWRA up to over 70% increment.



(Cotton fabrics impregnated with the finishing bath of pH2, comprised of the designated amount of PCA-PEG6(6) coupling with 7w/w% NaH_2PO_2 and 5w/w% ethanol were subjected to curing at 180°C for 1.5min.)

Figure 4-6 Properties of modified cotton fabrics in relation to concentration of PCA-PEG cross-linker

4.3.2.4.2 Effect of Acidity of Finishing Bath

The carboxyl-based cross-linkers impart wrinkle-resistant property to the cellulosic textiles by means of esterification between carboxyls (COOH) of the cross-linker with the hydroxyl (OH) groups of cellulose via the formation of cyclic anhydride intermediate. Acidity of the finishing solution influences the formation of the anhydride intermediate. Proton concentration essentially affects the dissociation of COOH into COO^- in an aqueous medium. In the finishing treatment, cotton fabrics impregnated with the finishing bath of designated acidity, comprised of various amount of PCA-PEG6(6) coupling with 7w/w% NaH_2PO_2 and 5w/w% ethanol were subjected to curing at 180°C for 1.5min. Finishing bath of pH2 and pH3 were subjected to evaluation. Properties of the modified fabric was summarised in Table 4-4.

Table 4-4 Summary of properties of cotton fabrics modified with linear-dendritic PCA-PEGs with different acidity of finishing bath

Fabric code	pH [a]	[PCA-PEG] (w/w%)	WRA (°) [b]	Ft (N) [c]	Fb (N) [d]	WI [e]	YI [f]
control cotton	---	---	140	19.65	283.361	75.087	5.407
PEG_20_2	2	20	207	7.28	213.246	64.018	7.821
PEG_25_2		25	242	7.25	201.828	63.092	8.467
PEG_30_2		30	223	5.68	193.872	59.524	10.474
PEG_20_3	3	20	198	11.15	220.453	65.524	7.994
PEG_25_3		25	240	9.82	218.522	63.141	8.726
PEG_30_3		30	208	8.91	208.748	58.855	10.324

[a] original pH = 2, pH was adjusted to 3 using NaOH. [b] WRA = averaged sum of wrinkle recovery angles in warp and weft of cotton fabrics in accordance with AATCC 66-2008. [c] Ft = averaged sum of tearing force in warp and weft of cotton fabrics in accordance with ASTM D1424-2009. [d] Fb = averaged sum of braking force in warp and weft of cotton fabrics in accordance with ASTM D5034-2009. [e] WI = whiteness index measured in accordance with AATCC 110-2005. [f] YI = yellowness index measured in accordance with the ASTM E313-2010.

High acidity of the finishing bath could assist the retention of COOH for esterification of cotton cellulose. When pH of the finishing bath maintained at 2, the modified fabrics would achieve better enhancement in wrinkle recovery performance. Additional 6% to 10%increment in ΔWRA was determined in the range of pH employed in the study. When finishing bath at pH of 3, the loss in strength was diminished. Varying pH induce little impact on the loss in tensile strength. Lowering the acidity to pH

3 facilitated retention in Fb by 2% to 5%. In contrast, acidity of finishing bath was found to be more influential on the alteration in tearing strength. As presented in Table 4-4, lowering acidity of the bath could help retaining Ft by 13% to 19%.

4.3.2.4.3 Effect of Inclusion of Additives

Additives are usually included in the finishing treatment to modulate and balance the overall properties of modified textiles while attaining the designated functional performance [3], [21], [22]. BTCA could offer synergetic effect to the resultant wrinkle recovery performance of modified cotton textiles [27], [31]. 2w/w% of BTCA was incorporated into the finishing bath comprised of the PCA-PEG cross-linker. Sequentially, 4w/w% Silyouwet T618 softener was also added into the finishing bath to evaluate the resultant fabric performance. Silyouwet is polyether-modified silicone which is a hydrophilic water soluble textile softener for aqueous finishing [22], [32]–[34].

In part of the finishing treatment, cotton fabrics impregnated with the finishing bath of pH 2, comprised of various amount of PCA-PEG6(6) coupling with 7w/w% NaH_2PO_2 and 5w/w% ethanol were subjected to curing at 180^oC for 1.5min. The influence of incorporating of BTCA and Silyouwet into the finishing bath was evaluated. Properties of the modified fabric was summarised in Table 4-5.

With the inclusion of a small amount of BTCA into the finishing bath, ΔWRA exhibited a significant increment of 20% to 25% compared to the performance without

BTCA in the system as presented in Table 4-5. ΔWRA with respect to the control fabrics could boost up to 90% to 100% improvement. Beside, inclusion of BTCA alleviated fabric yellowness. YI was improved by 7% to 19%. Incorporating Silyouwet could further enhance WRA by around 10% while help to alleviate the strength loss. Silicone softener coated on fibre surfaces acts a lubricant to reduce inter-fibre fiction. Hence, loss in strength loss reduced. Notably, the finishing system comprised of 4w/w% of Silyouwet could aid the retention in tearing strength by ~10%. Generally speaking, inclusion of small amount to BTCA and Silyouwet as additives in the wrinkle-resistant finishing system of PCA-PEG6 was capable of affording positive outcome of overall fabric performance.

Table 4-5 Summary of properties of cotton fabrics modified with linear-dendritic PCA-PEGs with the inclusion of additives

Fabric code	additives[a]	[PCA-PEG] (w/w%)	WRA (°) [b]	Ft (N) [c]	Fb (N) [d]	WI [e]	YI [f]
control cotton	---	---	140	19.65	283.361	75.087	5.407
PEG_20_B	2w/w% BTCA	20	242	7.22	175.265	66.671	7.245
PEG_25_B		25	265	6.43	181.535	66.725	7.789
PEG_30_B		30	258	5.35	169.518	63.065	8.467
PEG_20_BS	2w/w% BTCA + 4w/w% Silyouwet T618	20	238	8.95	190.015	68.077	7.223
PEG_25_BS		25	283	7.47	183.985	67.403	7.512
PEG_30_BS		30	267	7.26	175.485	63.178	8.837

[a] BTCA and/or Silyouwet T618 were added into the finishing solutions . [b]WRA = averaged sum of wrinkle recovery angles in warp and weft of cotton fabrics in accordance with AATCC 66-2008. [c] Ft = averaged sum of tearing force in warp and weft of cotton fabrics in accordance with ASTM D1424-2009. [d] Fb = averaged sum of braking force in warp and weft of cotton fabrics in accordance with ASTM D5034-2009. [e] WI = whiteness index measured in accordance with AATCC 110-2005. [f] YI = yellowness index measured in accordance with the ASTM E313-2010.

4.4 Conclusions

A series of novel low molecular weight linear-dendritic PCA-PEGs cross-linkers of M_n ranging from 0.79 $x10^3$ Da to 3.1 $x10^3$ Da were successfully prepared by simple bulk polycondensation of critic acid and polymeric glycols. Polydispersity of the products were relatively low, ranging from 1.1 to 1.3. Linear-dendritic polymeric architecture was revealed with the utility of advanced analytical techniques. Newly developed PCA-PEG-PCA with various PEG spacer lengths were subjected to wrinkle-resistant finishing study.

In the present study, utilising linear-dendritic PCA-PEGs polymers as cellulose cross-linkers for plain woven cotton fabrics was capable of affording appreciable improvement in wrinkle recovery performance of the cotton substrate. In significance, increasing spacer length of the PCA-PEGs cross-linkers could assist retention in fabric strengths and fabric whiteness. Nevertheless, incorporation of additives could further balance the overall fabric performance.

4.5 Bibliography

[1] P. Ghosh and D. Das, “Modification of jute by some low molecular weight glycols and a polyol under thermal treatment,” *Eur. Polym. J.,* vol. 36, pp. 2147–2157, 2000.

[2] N. A. Ibrahim, M. H. Abo-Shosha, E. I. Elnagdy, and M. A. Gaffar, “Eco-friendly durable press finishing of cellulose-containing fabrics,” *J. Appl. Polym. Sci*., vol. 84, no. 12, pp. 2243–2253, 2002.

[3] B. A. K. Andrews and B. J. Collier, “Finishing additives in treatments of cotton fabrics for durable press with polycarboxylic acids,” *Ind. Eng. Chem. Res*., vol. 31, no. 8, pp. 1981–1984, 1992.

[4] W. Yao, B. Wang, T. Ye, and Y. Yang, "Durable press finishing of cotton fabrics with citric acid: enhancement of whiteness and wrinkle recovery by polyol extenders," *Ind. Eng. Chem. Res.*, vol. 52, pp. 16118–16127, 2013.

[5] C. Q. Yang and X. Wang, "Infrared spectroscopy studies of the cyclic anhydride as the intermediate for the ester crosslinking of cotton cellulose by polycarboxylic acids. III. molecular weight of a crosslinking agent," *J. Polym. Sci. Part A Polym. Chem*., vol. 35, no. 3, pp. 557–564, 1997.

[6] C. Q. Yang and X. Wang, "Formation of cyclic anhydride intermediates and esterification of cotton cellulose by multifunctional carboxylic acids: an infrared spectroscopy study," *Text. Res. J.*, vol. 66, no. 9, pp. 595–603, 1996.

[7] C. Q. Yang, "FT-IR spectroscopy study of the ester crosslinking mechanism of cotton cellulose," *Text. Res. J*., vol. 61, no. 8, pp. 433–440, 1991.

[8] C. Q. Yang, "Effect of pH on nonformaldehyde durable press finishing of cotton fabric: FT-IR Spectroscopy study: part II: formation of the anhydride intermediate," *Text. Res. J.*, vol. 63, no. 12, pp. 706–711, 1993.

[9] R. A. T. M. Van Benthem, "Novel hyperbranched resins for coating applications," *Prog. Org. Coatings*, vol. 40, no. 1–4, pp. 203–214, 2000.

[10] W. J. Feast and N. M. Stainton, "Synthesis, structure and properties of some hyperbranched polyesters," *J. Mater. Chem*., vol. 5, no. 3, pp. 405–411, 1995.

[11] E. Malmström and A. Hult, "Hyperbranched polymers: a review," *J. Macromol. Sci. Part C*, vol. 37, no. 3, pp. 555–579, 1997.

[12] B. Tisserat, R. H. O'kuru, H. Hwang, A. A. Mohamed, and R. Holser, "Glycerol citrate polyesters produced through heating without catalysis," *J. Appl. Polym. Sci.*, vol. 125, no. 5, pp. 3429–3437, 2012.

[13] J. Yang, A. R. Webb, S. J. Pickerill, G. Hageman, and G. A. Ameer, "Synthesis and evaluation of poly(diol citrate) biodegradable elastomers," *Biomaterials*, vol. 27, no. 9, pp. 1889–1898, 2006.

[14] P. Kucharczyk, I. Poljansek, V. Sedlarik, V. Kasparkova, A. Salakova, J. Drbohlav, U. Cvelbar, and P. Saha, "Functionalization of polylactic acid through direct melt polycondensation in the presence of tricarboxylic acid," *J. Appl. Polym. Sci.,* vol. 122, no. 2, pp. 1275–1285, 2011.

[15] S. Karaman, A. Karaipekli, A. Sar, and A. Biçer, "Polyethylene glycol (PEG)/diatomite composite as a novel form-stable phase change material for thermal energy storage," *Sol. Energy Mater. Sol. Cells*, vol. 95, no. 7, pp. 1647–1653, 2011.

[16] W. Wang, X. Yang, Y. Fang, and J. Ding, “Preparation and performance of form-stable polyethylene glycol/silicon dioxide composites as solid-liquid phase change materials,” *Appl. Energy*, vol. 86, no. 2, pp. 170–174, 2009.

[17] N. A. Alcantar, E. S. Aydil, and J. N. Israelachvili, “Polyethylene glycol-coated biocompatible surfaces,” *J. Biomed. Mater. Res*., vol. 51, no. 3, pp. 343–351, 2000.

[18] J. Billingham, C. Breen, and J. Yarwood, “Adsorption of polyamine, polyacrylic acid and polyethylene glycol on montmorillonite: An in situ study using ATR-FTIR,” *Vib. Spectrosc*., pp. 19–34, 1997.

[19] H. Namazi and M. Adeli, “Novel linear-globular thermoreversible hydrogel ABA type copolymers from dendritic citric acid as the A blocks and poly(ethyleneglycol) as the B block,” *Eur. Polym. J.,* vol. 39, no. 7, pp. 1491–1500, 2003.

[20] A. T. Naeini, M. Adeli, and M. Vossoughi, “Poly(citric acid)-block-poly(ethylene glycol) copolymers-new biocompatible hybrid materials for nanomedicine,” *Nanomedicine Nanotechnology, Biol. Med.,* vol. 6, no. 4, pp. 556–562, 2010.

[21] P. Bajaj, “Finishing of textile materials,” *J. Appl. Polym. Sci*., vol. 83, no. 3, pp. 631–659, 2002.

[22] W. D. Schindler and P. J. Hauser, “Easy-care and durable press finishes of cellulosics,” in *Chemical Finishing of Textiles*, Woodhead Publishing, 2004, pp. 51–72.

[23] I. S. Kang, C. Q. Yang, and G. C. Lickfield, “Mechanical strength of durable press finished cotton fabrics: part I: effects of acid degradation and crosslinking of cellulose by polycarboxylic acids,” *Text. Res. J.,* vol. 68, no. 11, pp. 865–870, 1998.

[24] N. Abidi, E. Hequet, C. Turner, and H. Sari-Sarraf, “FTIR analysis of crosslinked cotton fabric using a ZnSe-universal attenuated total reflectance,” *J. Appl. Polym. Sci*., vol. 96, no. 2, pp. 392–399, Apr. 2005.

[25] C. Chung, M. Lee, and E. K. Choe, “Characterization of cotton fabric scouring by FT-IR ATR spectroscopy,” *Carbohydr. Polym*., vol. 58, no. 4, pp. 417–420, 2004.

[26] C. Q. Yang, “Predicting the performance of durable press finished cotton fabric with infrared spectroscopy,” *Text. Res. J*., vol. 69, no. 2, pp. 145–151, 1999.

[27] C. M. Welch, “Improved strength and flex abrasion resistance in durable press finishing with BTCA,” *Text. Chem. Color*., vol. 29, no. 2, pp. 21–24, 1997.

[28] H. Choi, “Nonformaldehyde polymerization-crosslinking treatment of cotton fabrics for improved strength retention,” *Text. Res. J.*, vol. 62, no. 10, pp. 614–618, 1992.

[29] M. J. Lees, “Formaldehyde-free durable press finishing based on polymaleic acid chemistry,” *J. Text. Inst.,* vol. 90, no. 3, pp. 42–49, 1999.

[30] K. J. Yoon, J. H. Woo, and Y. S. Seo, “Formaldehyde free cross-linking agents based on maleic anhydride copolymers,” *Fibers Polym*., vol. 4, no. 4, pp. 182–187, 2003.

[31] C. M. Welch and G. J. Peters, “Mixed polycarboxylic acids and mixed catalyst in formaldehyde-free durable press finishing,” *Text. Chem. Color*., vol. 29, no. 3, pp. 22–27, 1997.

[32] B. G. Simpson, “The effect of silicone softeners on resin treated cottons,” *Text. Res. J*., vol. 28, no. 2, pp. 170–179, 1958.

[33] F. Fortess, “Silicone resins in textiles,” *Ind. Eng. Chem*., vol. 46, no. 11, pp. 2325–2331, 1954.

[34] H.-M. Choi and Y. M. Kim, “Performance improvement of nonformaldehyde wrinkle resistant finished cotton fabrics treated with dialdehydes,” *Fibers Polym*., vol. 2, no. 4, pp. 190–195, 2001.

Chapter Five-

Development and Application of Dendritic Polymalic Acid Cross-linker

5.1 Introduction

Analogous to CA, the potential of MA is very distinguishing. MA is an A_2B building block, capable of self-polymerising to develop as higher-order cross-linkers. However, MA would not develop as a branched homopolymer. Instead, synthetic poly(malic acid)s is essentially a linear polymer, similar as natural poly(ß -L-malic acid) (ß-PLMA), a microbial polyester isolated from certain species of procaryotic microorganisms, for example, *Physarum polycephalum, Penicillium cyclopium* and *Aureobasidium sp.* [1]–[5]. Synthetic mimics of natural ß-PLMA could be developed by ring-opening polymerisation of benzyl ß-malolactonate starting from aspartic acid [6]–[8]. Another simpler route to produce synthetic PMA is via bulk polymerisation of MA. The linear PMA obtained is comprised of alternative eater linkages of α-type and ß-type moieties as illustrated in Figure 5-1 [4], [5], [8]–[11].

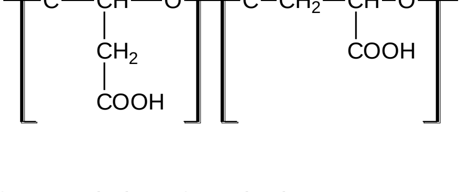


Figure 5-1 Possible types of MA moieties of synthetic PMA prepared by bulk polymerisation [11]

In order to develop dendritic polymers of MA, incorporating polyols B_f as the branching units is one of the feasible strategies [12]–[16]. In this chapter, a series of dendritic PMA polymers were prepared by coupling with various polyols in the system. Chemical structures of individual reactants are illustrated in Figure 5-2. Sequentially, the newly prepared PMA polymers were applied to wrinkle-resistant finishing study. Evaluations of the wrinkling phenomenon and other properties of the modified cotton textiles were studied.

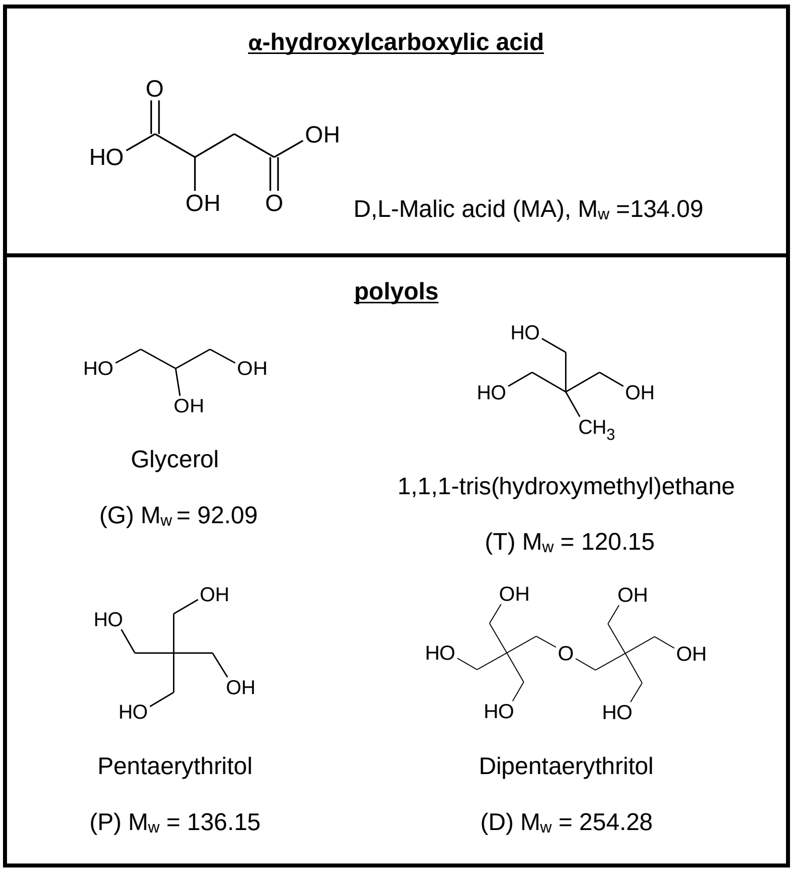


Figure 5-2 MA and polyols used in the development of dendritic PMA cross-linkers

5.2 Experimental

5.2.1 Materials

D,L-MA was purchased from Acros Organics. Glycerol (G) was obtained from Fisher Scientific. 1,1,1-tris(hydroxymethyl)ethane (T) and pentaerythritol (P) obtained were from Sigma-Aldrich. Dipentaerythritol (D) was supplied by AccuChem while sodium hypophosphite monohydrate ($NaH_2PO_2 \cdot H_2O$) and sodium hydroxide were supplied by International Laboratory. Tetrahydrofuran (THF) and diethyl ether were purchased from Duskan Pure Chemicals. Absolute ethanol was supplied by VWR. Dimethyl sulfoxide-d_6 (DMSO-d_6) was obtained from Acros Organics. All chemicals were used as received. 100% plain woven semi-bleached cotton fabric (133 x 77, 115g/m^2) was used for the wrinkle-resistant finishing study.

5.2.2 Synthesis of Polymeric Cross-linker

α-hydroxylcarboxylic acid, MA in a combination with various polyols was mixed and reacted to prepare dendritic polymer via bulk polycondensation. The general scheme for the conversions is illustrated in Scheme 5-1. General procedures are summarised as below.

In a 250ml round bottom flask, MA (0.75mol), and the designated polyol in various molar ratios (G of 0.025mol to 0.083mol; T of 0.025mol to 0.083mol; P of 0.019mol to 0.063mol; D of 0.008mol to 0.042mol) were melted at 125˚C with constant stirring for 4 hours under reduced pressure. Water generated in the reaction was continuously removed from the system by a vacuum pump. Crude products were firstly dissolved in minimum amount of THF and sequentially precipitated in excess diethyl ether. The purified products were dried under reduced pressure. The precipitates were white solids. The yield obtained by precipitation of crude products ranging from 20% to 83% by weight.

Several purified PMAs were subjected to finishing trials to evaluate the feasibility of dendritic PMAs serving as the wrinkle-resistant finishing agents for cotton textiles.

PMA-Gs:

FTIR-ATR (cm^{-1}): 3410 (ν O-H, acid), 2945 (ν C-H), 1710 (ν C=O ester), 1410 (δ C-H), 1165 (ν C-O-C ester).

^{1}H-NMR (500MHz, DMSO-d_6), δ (TMS ppm): 2.66-2.73, 2.88 (m, CH_2, MA moieties), 3.99 (m, CH_2, G moiety), 4.91 (s, CH, G moiety), 5.18 (s, CH, ß-MA moieties), 5.40 (s, CH, α-MA moieties).

^{13}C-NMR (125MHz, DMSO-d_6), δ (TMS ppm): 36.21 (CH_2 MA moieties), 62.72, (CH, G moiety), 65.80, 66.74, 67.73, 67.57, 67.63, 69.62 (CH_2, G moiety; CH, MA moieties), 170.15, 170.60, 171.11, 172.12, 172.29, 171.28 (α-COO, MA moieties), 172.97, 173.25, 173.46, 174.92 (ß-COO, MA moieties)

PMA-Ts:

FTIR-ATR (cm^{-1}): 3426 (ν O-H, acid), 2948 (ν C-H,), 1709 (ν C=O ester), 1398 (δ C-H), 1167 (ν C-O-C ester).

^{1}H-NMR (500MHz, DMSO-d$_6$), δ (TMS ppm): 0.92 (s, CH$_3$, T moiety); 2.07-2.84, 2.94-2.97 (m, CH$_2$, MA moieties), 3.89-3.96 (m, CH$_2$, T moiety), 5.24 (s, CH, ß-MA moieties), 5.38 (s, CH, α-MA moieties).

^{13}C-NMR (125MHz, DMSO-d$_6$), δ (TMS ppm): 16.88 (CH$_3$, T moiety) 36.20 (CH$_2$, MA moieties), 39.11 (C, T moiety), 66.04, 67.21, 67.45, 69.35 (CH$_2$, T moiety; CH, MA moieties), 170.61, 171.10, 172.08, 172.30 (α-COO, MA moieties), 172.84, 173.28, 174.97 (ß-COO, MA moieties)

PMA-Ps:

FTIR-ATR (cm^{-1}): 3428 (ν O-H, acid), 2940 (ν C-H,), 1715 (ν C=O ester), 1399 (δ C-O-H), 1167 (ν C-O-C ester).

^{1}H-NMR (500MHz, DMSO-d$_6$), δ (TMS ppm): 2.77-2.83, 2.94(m, CH$_2$, MA moieties), 4.08 (m, CH$_2$, P moiety), 5.27 (s, CH, ß-MA moieties), 5.41 (s, CH, α-MA moieties).

^{13}C-NMR (125MHz, DMSO-d$_6$), δ (TMS ppm): 36.19 (CH$_2$ MA moieties), 42.65 (C, P moiety), 62.86, 67.18, 69.32 (CH$_2$, P moiety; CH, MA moiety), 170.14, 170.48, 171.25, 172.35 (α-COO, MA moieties), 173.14, 174.97 (ß –COO, MA moieties)

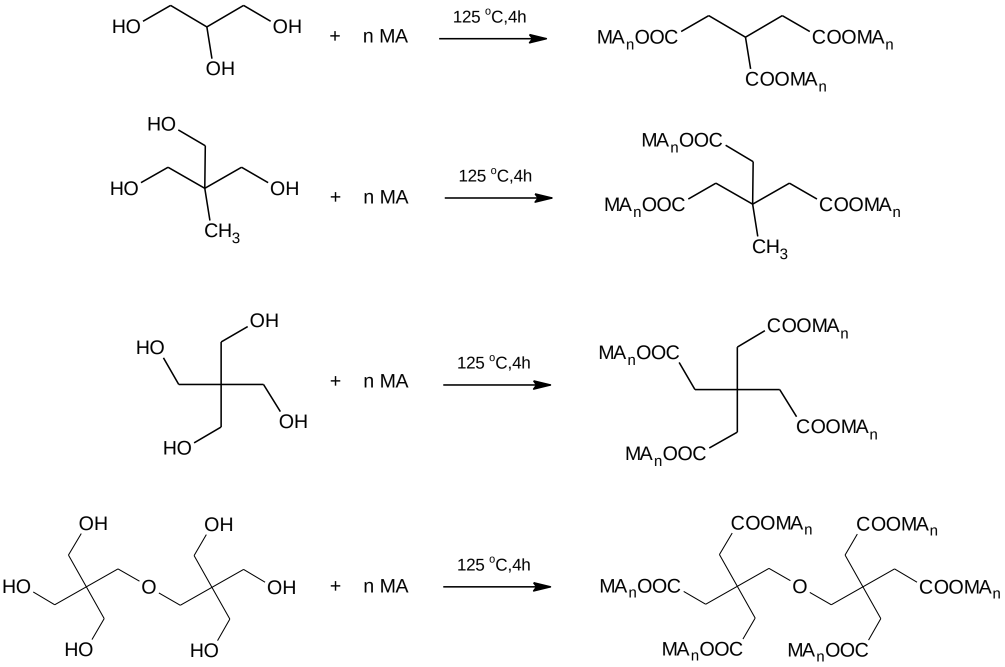
PMA-Ds:

FTIR-ATR (cm^{-1}): 3433 (ν O-H, acid), 2943 (ν C-H,), 1714 (ν C=O ester), 1398 (δ C-O-H), 1165 (ν C-O-C ester).

^{1}H-NMR (500MHz, DMSO-d$_6$), δ (TMS ppm): 2.70-2.77, 2.90 (m, CH$_2$, MA moieties), 4.09 (m, CH$_2$, D moiety), 5.21 (s, CH, ß-MA moieties), 5.41 (s, CH, α-MA moieties).

^{13}C-NMR (125MHz, DMSO-d$_6$), δ (TMS ppm): 36.21 (CH$_2$ MA moieties), 43.42, 44.53 (C, D moiety), 52014, 67.32, 67.42, 69.36 (CH$_2$, D moiety; CH, MA moiety), 170.13, 170.54, 171.15, 172.37(α-COO, MA moieties), 173.20, 174.83, 175.01 (ß-COO, MA moieties)

Scheme 5-1



5.2.3 Polymer Characterisations

Each FTIR spectrum of the polymers recorded as an average of 16 scans on a Perkin Elmer Spectrum 100 spectrophotometer equipped with a universal attenuated total internal reflectance (ATR) accessory.

^{1}H and ^{13}C NMR spectra of the polymers were recorded using a Varian Unity Inova 500 NMR spectrometer under ambient temperature. DMSO-d_6 was used as the solvent with tetramethylsailne (TMS) as the internal reference for the analysis.

The molecular weights of the polymer were estimated by gel permeation chromatography (GPC) with the use of Waters system. The system equipped with a Waters 1515 isocratic pump coupled with a series of Styragel® HMW columns (HR1, HR4, and HR6; molecular weight range 10^2 -10^7), calibrated with mono-dispersed polystyrene standards (PS) (PolyScience), and a Waters 2414 refractive index detector. THF was used as the eluent at a flow rate of 1.0 ml/min. The column was maintained at 30°C during analysis.

Thermogravimetric analysis (TGA) of the polymers (5mg) was performed by using a Mettler-Toledo thermogravimetric analyser studied under nitrogen atmosphere at a heating rate of 20°C/min.

5.2.4 Modification of Cotton Fabric

The newly developed dendritic PMAs were mixed with NaH_2PO_2, a typical catalyst for cellulose esterification in the finishing study. The finishing aqueous solutions were comprised of 20 w/w% of different PMAs as the cellulose cross-linker, 6w/w% of NaH_2PO_2 as the catalyst and 2w/w % of ethanol as dispersing agent. Acidity of finishing solutions was kept constant at pH of 2. Cotton fabrics were impregnated with the solutions comprised of different PMAs using a Rapid Labortex P-80 horizontal padding machine imposing a constant pressure of 1kg/cm^2 to achieve wet pick-up of 75±5%. Sequentially the fabrics were dried at 100°C for 2min, and then thermally cured at 180°C for 1.5min using a Mathis LTE Labdryer.

5.2.5 Fabric Characterisations and Evaluations

Properties of cotton fabrics modified with the newly developed dendritic polymers were evaluated based on the following standard approaches and procedures. The formation of cross-links of modified cotton fabrics was studied based on FTIR-ATR. Prior to FTIR analysis, modified fabric samples were treated with 0.1M NaOH solution and rinsed with deionised water to differentiate carbonyl (C=O) stretching of carboxyls and esters. All modified fabric samples were conditioned under standard condition at 65±2% relative humidity and 21±1°C prior to evaluations. Spectra of dried fabric samples were recorded using a Perkin Elmer FTIR spectrophotometer 100 equipped with an ATR sampling accessory. Each FTIR spectrum was recorded as an average of 128 scans and normalised against 1317cm^{-1} which is originated from the C-H bending of cellulose molecules [17]–[20].

Wrinkle-resistant performance was evaluated in accordance with the AATCC 66-2008 test method. Specimens (40mm x 15mm) in both warp and weft alignment were folded face-to-face and back-to-back. Folded specimens were compressed with a 500g-weight for 5min. The wrinkle recovery angles (WRA) of specimens were measured by a Daiei Kagakuseiki Seisakusho wrinkle recovery tester after 5 min of relaxation and recovery. WRAs were reported as an average of eight measurements of the sum in warp and weft directions with the analytical tolerance limited to 5%. The change in wrinkle recovery angle (∆WRA) was expressed according to the following equation.

$$\Delta WRA = \frac{WRA_m - WRA_o}{WRA_o} \times 100\%$$

where as WRA_m= WRA of modified fabric
WRA_o = WRA of control fabric

Mechanical properties included tensile strength and tearing strength, were evaluated according to ASTM D5034-2009 and ASTM D1424-2009 test methods respectively. The tearing strength of modified cotton fabrics were evaluated using a James H. Heal digital Elmendorf tearing tester with a standard capacity of 1600g or 3200g chosen to measure the strength. Specimens were cut according to the standard notched template in both warp and weft directions. Individual notched specimen was fixed onto the tester. The pendulum was depressed downwards until tearing of a specimen was completed. Tearing force (Ft) was reported as an average result of eight measurements in both warp and weft directions. When evaluating the tensile strength of modified cotton fabrics, a tensile tester, Instron 4411, was used based on constant rate of extension (CRE) tensile testing method. Specimens (150mm x10mm) in both warp and weft alignment were mounted vertically on the tester for the test. Longitudinal grabbing force was applied along the testing direction until the specimen broke. Tensile strength reported as the averaged breaking force (Fb) of eight measurements in both warp and weft directions with the analytical tolerance limited to 5%. The change in mechanical properties was expressed in terms of change in forces (ΔF) according to the below equations.

$$\Delta Ft = \frac{Ft_m - Ft_o}{Ft_o} \times 100\%$$

$$\Delta Fb = \frac{Fb_m - Fb_o}{Fb_o} \times 100\%$$

where as Ft_m = tearing or tensile force of modified fabric
Ft_o = tearing or tensile force of control fabric
Fb_m = tearing or tensile force of modified fabric
Fb_o = tearing or tensile force of control fabric

Whiteness and yellowness were evaluated using a GretagMacbeth Colour-Eye 7000A reflectance spectrophotometer under the standard illuminant of D_{65} and viewed at 10^o standard observer in accordance with the AATCC 110-2005 and ASTM E313-2010 test methods. The whiteness and yellowness were expressed in terms of whiteness index (WI) and yellowness index (YI) respectively.

5.3 Results and Discussion

5.3.1 Cross-linker Synthesis and Characterisation

Various methodologies have been adopted to build PMA [4]–[11]. Typical approaches to develop synthetic PMAs are linear polyesters. In order to build dendritic carboxyl-based cross-linkers based on MA as the major monomer coupled with a polyol as the branching unit was utilised in the polymerisation. MA was attempted to condense with various polyols included, glycerol(G), triol(T), tetrol (P) and hexol(D). The chemical structures of MA and core polyols are shown in Figure 5-2.

The dendritic PMA of different branching architectures were named as PMA-Gs (MA with glycerol), PMA-Ts (MA with triol), PMA-Ps (MA with tetrol) and PMA-Ds (MA with (hexol). White precipitates of dendritic PMAs were obtained in the syntheses. The polymerisation results were tabulated in Table 5-1. In practice, MA could develop as low molecular weight dendritic polymers with the four polyols adopted in the investigation without the presence of catalyst. Upon bulk polycondensation reaction at 125^{o}C for 4 hours under reduced pressure, molecular weights obtained were ranging from 0.9 x10^{3} Da to 3.1 x10^{3} Da in terms of M_n with polydispersity PDI below 1.6. The length of individual branch could be essentially postulated as of similar length [21]. This would be an important factor in building low molecular weight polymeric cross-linkers for cellulosic textiles.

The yield obtained by precipitation of crude products was found to be dependent on the nature of the core polyol and the feed ratio of MA to polyol. Considering the branching behaviour between MA and polyols, the yield of product generally was more favourable for polymerisation when triol (G and T) was served as the core moiety. The yield of product was over 70% up to 83%. When a tetrol (P) or hexol (D) employed as the core moiety, the yield of product was significantly diminished to less than 56%. Increasing the *f* imparting more steric hindrance was suggested to be the major cause to the relative lower yield of product. In addition, larger *f* value of 4 and 6 is suggested as the attribute for the retarded growth of branches emanating from the core polyols with short hydroxyl arms (Core-CH_2-OH).

Developing PMAs composed of various numbers of branches (*f*) was attempted with the inclusion of different polyols as the core moieties. Series of PMAs were prepared with four polyols in this part of the study. In general, the FTIR data (Figure 5-3) revealed the esterification between carboxyl of MA with hydroxyl of polyols. The absence of distinguished O-H stretching at 1100-1000cm^{-1}and C-O-H bending at 666cm^{-1}, originated from the polyol moieties in all PMA polymers as depicted in Figures 5-3, gives an overview of the interaction between MA and polyols [22]–[26]. Comparing the FTIR spectra of MA monomer with the respective polymeric products, the disappearance of absorption band originated from O-H stretching and bending of the hydroxyl at 3440cm^{-1} and 660cm^{-1} indicated the mutual polycondensation of MA in the system [5], [27], [28]. The board peaks at 3400-2600cm^{-1} originated from O-H of carboxylic acids of MA retained in all PMA products. Free COOH present in the products could furnish the cross-linking ability PMA products with cotton cellulose in the sequential wrinkle-resistant finishing.

Table 5-1 Summary of dendritic PMAs prepared by bulk-polycondensation [a]

Sample code	ratio [b]	f [c]	M_n x10^3 [d]	M_w x10^3 [d]	PDI [e]	Yield%
PMA-G(9)	9	3	1.1	1.3	1.31	82.8
PMA-G(12)	12	3	1.4	1.8	1.33	80.9
PMA-G(15)	15	3	1.7	2	1.19	80.1
PMA-G(18)	18	3	2.1	2.5	1.22	69.3
PMA-G(30)	30	3	1	1.2	1.14	62.4
PMA-T(9)	9	3	1.1	1.6	1.42	82.3
PMA-T(12)	12	3	1.5	2.5	1.6	79.2
PMA-T(15)	15	3	2	2.4	1.24	71.5
PMA-T(18)	18	3	2.1	2.7	1.27	61.5
PMA-T(30)	30	3	0.93	1.2	1.25	48.9
PMA-P(12)	12	4	1.6	2.5	1.16	55.7
PMA-P(16)	16	4	2	3.1	1.57	79.5
PMA-P(20)	20	4	2.2	2.7	1.23	52.3
PMA-P(24)	24	4	2.5	3.5	1.42	39.1
PMA-P(40)	40	4	1.5	2.1	1.37	30.8
PMA-D(18)	18	6	2.3	2.9	1.25	48.1
PMA-D(24)	24	6	3.1	4.8	1.52	56.5
PMA-D(30)	30	6	2.4	3.7	1.51	32.5
PMA-D(36)	36	6	2.8	3.1	1.09	19.8
PMA-D(60)	60	6	2.3	2.7	1.19	21.2

[a] bulk polycondensation carried out at 125℃ under reduced pressure for 4hrs. [b] ratio refer to molar feed ratio of MA : polyol. [c] *f* = no. of branches. [d] Estimated by GPC in THF on the basis of a PS calibration expressed in Da. [e] PDI = polydispersity (M_w/M_n).

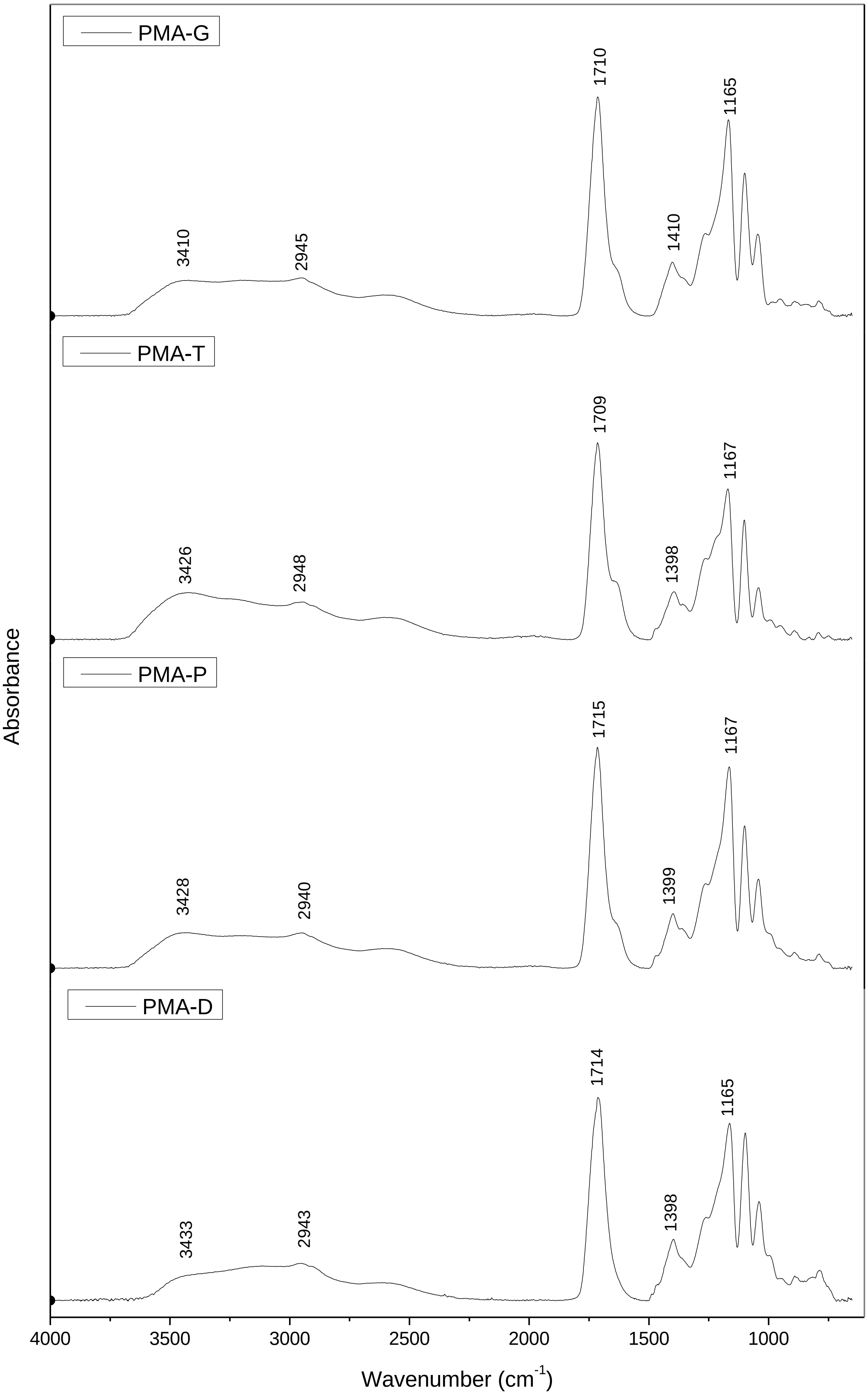


Figure 5-3 FTIR spectra of dendritic PMA polymers with various polyol cores: PMA-G(9), PMA-T(9), PMA-P(12) and PCA-D(18)

The chemical composition of the dendritic PMA would be elucidated based on the diagnostic peaks present in ^{1}H-NMR spectra (Figure 5-4). Regarding the reactivity of hydroxyls, MA was assumed to react with all primary hydroxyls of polyols prior proceeding to further polymerisation. This assumption was verified with the analysis of ^{1}H-NMR spectra of PMA prepared. A distinguishing peak in the PMA polymers NMR spectra as shown in Figure 5-4 at ~δ4 is attributable to the methylene protons of the polyols. The peak intensity is corresponding to the feed ratio of MA to polyol incorporated in the polymerisation. Complementary to GPC data, the relative integral s of the NMR resonance of methylene protons of the polyols to the methine protons of MA suggested that the polyols were served as the core moieties in the dendritic architecture of PMA products. Hence the integral of resonance originated from methine protons of MA at ~δ5 indicated the number MA attached to a polyol core. In such manner, polyols were essentially served as core moieties in the dendritic PMAs as postulated in Scheme 5-1.

In the NMR spectra, the disappearance of chemical shift at ~δ4.3-4.5 originated from hydroxyl protons of the polyols and the emergence of new resonance of methine protons of MA at ~δ5 confirmed co-esterification of MA with polyols and mutual esterification of MA. In the spectrum of PMA-G, the absence of resonance originated from the three hydroxyl protons at δ4.38 and δ4.45 suggested that all hydroxyl of glycerol were esterifed in the system [24], [29]–[31]. The methine proton of glycerol was suggested to shift up-field at δ4.91 in the PMA-G polyesters while the methylene protons resonance was found to be at δ3.99 [31]. In the spectrum of PMA-T, the absence of resonance originated from the three hydroxyl protons at δ4.20-4.23 suggested that all primary hydroxyl of triol were esterifed in the system. Upon esterification, methylene protons were shifted toward up-field at δ3.97. The methyl protons were retained in the PMA-T polyester with the resonance at δ0.91 [31], [30], [33]–[35]. Meanwhile, the absence of resonance originated from the hydroxyl protons at δ4.2 in the spectra of PMA-P and PMA-D, suggested that all primary hydroxyls of tetrol and hexol were esterifed in the systems. Upon esterification, methylene protons were shifted toward up-field at ~δ4.1 [30], [34], [36]–[39]. The branching architecture of the core polyol does not imparted substantial effect on the esterification between MA and the branched polyols. All hydroxyl arms were esterified for small polyols, G and T and also for bulky polyols, P and D.

More information about the linkages between MA-MA moieties could be determined based on NMR data. Ohtani and Kajiyama gave detailed evaluation of MA-MA interaction for synthetic PMA. PMA developed from bulk polymerisation is essentially a linear polymer of α, ß-PMA. Integrals of α-type and ß-type MA moieties are of equal ratio by quantitative analysis of NMR [9]–[11], [40]. The incorporation of polyols in the system was not imposing substantial alteration in the sequence of MA-MA linkage. The relative intensity of integral originated from α-type MA moieties at δ5.4 and the integral originated from ß-type MA moieties at δ5.2 essentially conformed to the literature.

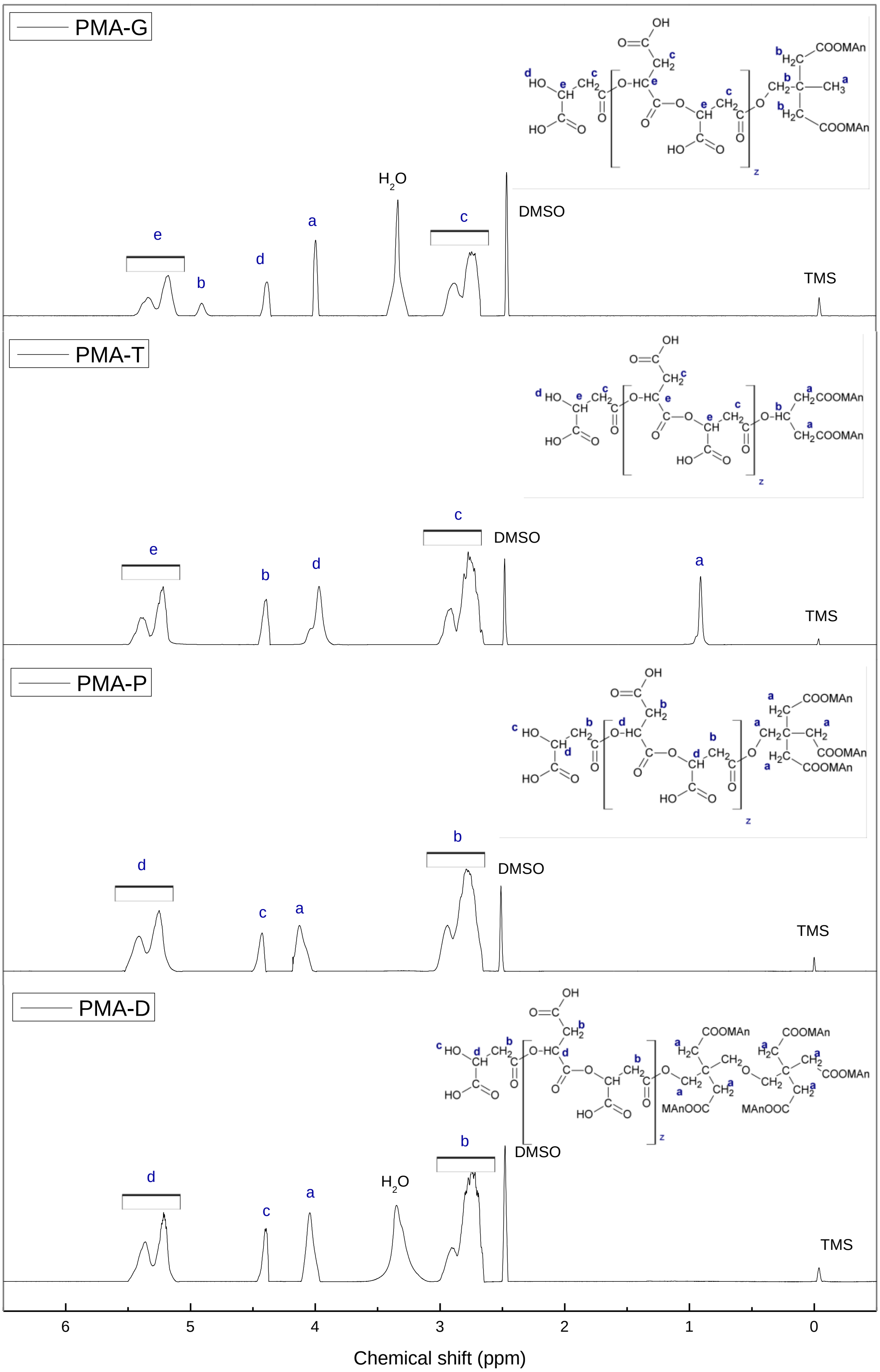


Figure 5-4 ^{1}H-NMR spectra of dendritic PMA polymers with various polyol cores: PMA-G(9), PMA-T(9), PMA-P(20) and PCA-D(24)

Malmström proposed that the temperature dependent phase separation in the reaction system leading to the discrepancy in polymerisation behaviour of AB_2 monomer with different core polyols [14]. Polyols used in the study are essentially of higher melting points (over 190°C, except G) than that of MA (~132°C) as shown in Table 5-2. The dominant reaction path would be considered as polyol melt of the core polyol solubilised in pre-polymer of MA. On one hand, MA undergoes homo-polycondensation to form linear α,ß-oligomers. On the other hand, MA preferentially reacted with primary hydroxyls of the polyols. Overall, dendritic PMAs comprise of a polyol as the core moiety with the linear α,ß-PMA branches emanated from the core.

Table 5-2 Melting points of MA and polyols

	Melting point (°C)
D,L-MA	131-133
G	20
T	193-195
P	253-258
D	215-218

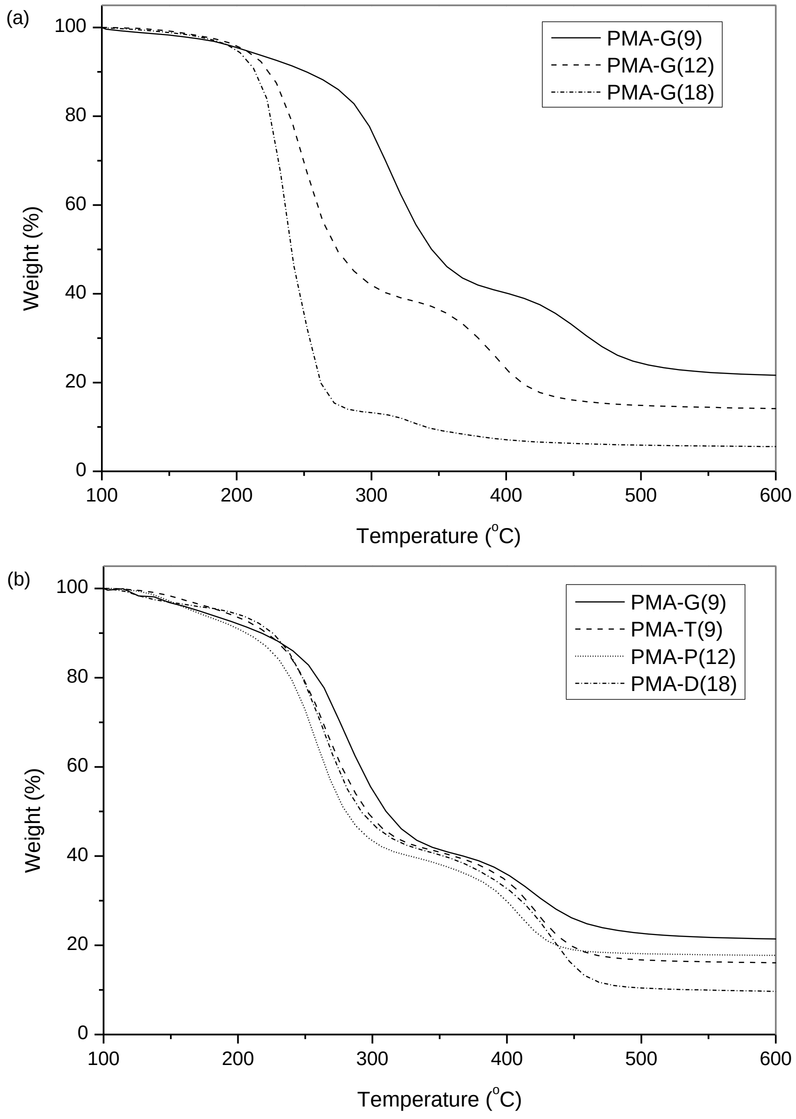
In the present study, when the various feed ratios were employed in the synthesis to evaluate the influence of the ratio to the growth of molecular weights of the dendritic PMA as summarised in Table 5-1. The feed ratios were selected to build the designated number of MA in each arm in the dendritic PMA. The ratio is based on the following expression.

$$Theoretical\ no.of\ MA\ per\ arm = \frac{feed\ ratio}{f}$$

For G and T with $f = 3$ and P with $f = 4$, the growth in the molecular weight of PMA-T(30) and PMA-P(40) significantly hampered when the feed ratio of 30 and 40 respectively. For D with $f = 6$, the hampered growth observed at feed ratio above 30. The number of MA in each arm could not grow up to 10 units as proposed using such ratios. Homo-polycondensation was suggested as the predominant reaction occurred in the systems with large feed ratios [14]. This illustrated that the presence of branched polyols B_f would be an important factor in building low molecular weight polymeric cross-linkers for cellulosic textiles. Branched polyols B_f incorporated in a polycondensation system of polyfunctional monomers are regarded as chain stoppers hampering the growth in molecular weights [12], [13], [42].

Thermal stability of dendritic PMA was evaluated by TGA. The thermograms are presented in Figure 5-5. In general, the initial 5% percent weight losses were determined to be around 180˚C to 200˚C. Difference in length of MA arms and branching architectures of the dendritic polymers affect the thermal resistance. Dendritic PMA with longer arms would be less stable. Take PMA-G series as the example as shown in Figure 5-5a. The length of MA arms is controlled by the feed ratio between MA and the nature of core polyol. Increasing feed ratio imposed a negative shift of thermal resistant power of the polymers. The extent in hydrogen bonding (H-bonding) was suggested as the attribute to the shift. H-bonding interaction in PMA polymers were originated between carboxyls and hydroxyls of MA arms. Hydroxyl was proposed as the end group in each MA arm as demonstrated in the NMR characterisation. H-bonding present in smaller PMA was relatively more extensive compared to that in larger PMA.

As a result, the smaller PMA were relatively thermally stable. The same phenomenon observed for all series of dendritic PMA with different polyols as the core molecule. When considering the variation in branching architectures, thermal stability of dendritic PMA with different polyols are the core molecule did not impose significant impact on the thermal stability as presented in the figure.



(TGA thermograms were measured under nitrogen atmosphere at a heating rate of 20°C/min)

Figure 5-5 TGA thermograms of dendritic PMAs of (a) various feed ratios and (b) different core polyols

5.3.2 Fabric Performance and Evaluations of Modified Cotton

Dendritic PMA polymers of various branching architectures and molecular weights were used for the wrinkle-resistant finishing study. Dendritic PMA of branching factor (*f*) ranging from 3 to 6, and M_n of 1 x 10^3 Da to 3.2 x 10^3 Da were employed as the cross-linkers. Table 5-3 tabulates the summary of properties of cotton fabrics modified with the selected dendritic PMA cross-linkers. In the finishing study, 20w/w% of the selected PMA polymer coupling with 6w/w% of NaH_2PO_2 was employed for cross-linking cotton fabrics. Cotton fabrics impregnated with PMA polymers were subjected to curing at 180^oC for 1.5min. The influence of molecular composition of the carboxyl-based cross-linkers on the wrinkle recovery performance of the cotton fabric was evaluated accordingly.

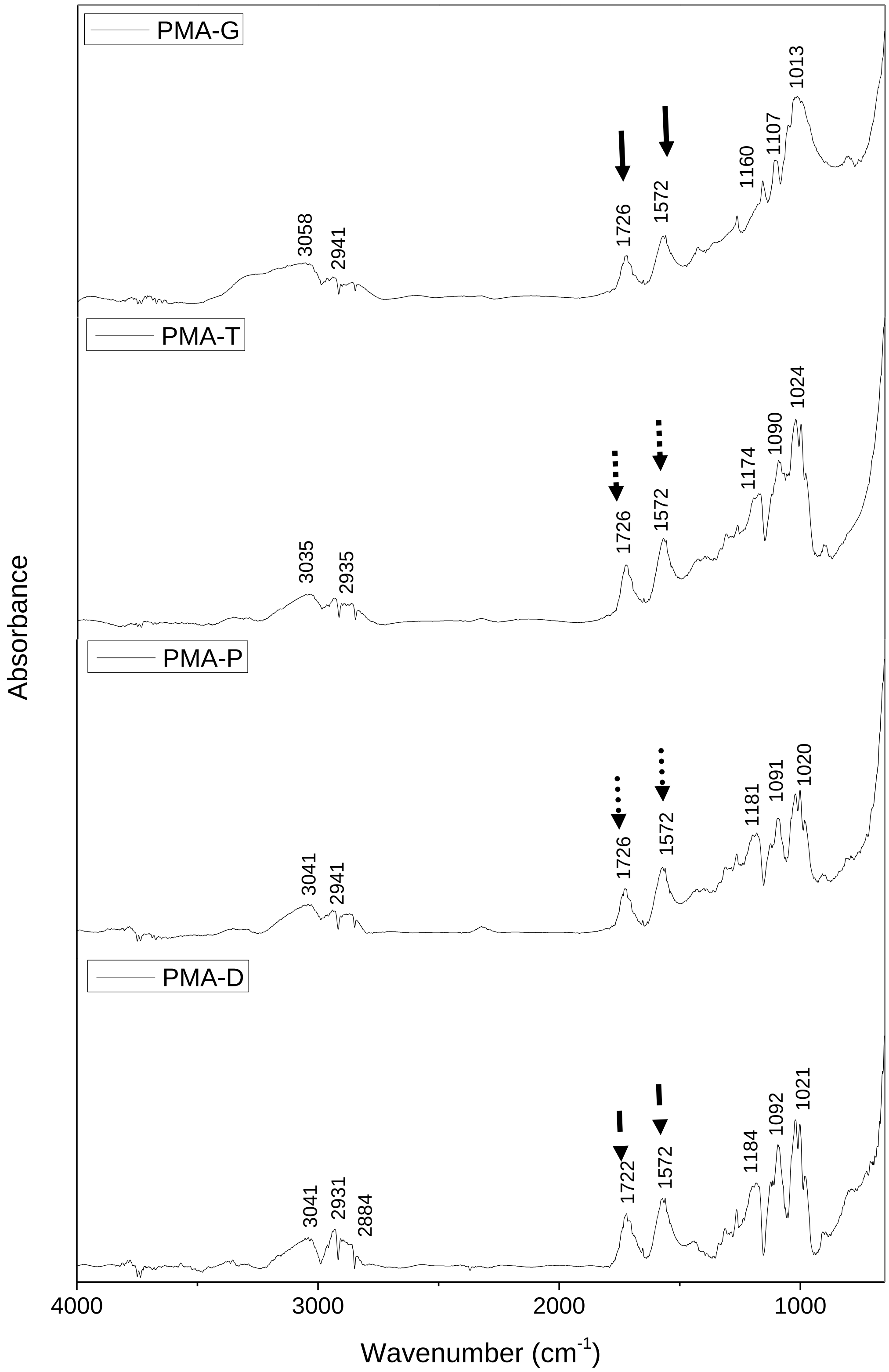
Table 5-3 Summary of properties of cotton fabrics modified with dendritic PMAs

Fabric code	Cross-linker	*f* [a]	M_n x10^3 [b]	WRA (^{o}) [c]	Ft (N) [d]	Fb (N) [e]	WI [f]	YI [g]
control	---	---	---	137	6.22	275.075	66.333	5.686
MA-G1	PMA-G(9)	3	1.1	234	2.76	142.535	62.601	6.991
MA-G2	PMA-G(12)	3	1.4	214	2.59	154.695	61.994	7.315
MA-G3	PMA-G(18)	3	2.1	196	1.67	166.640	60.174	7.834
MA-T1	PMA-T(9)	3	1.1	231	2.85	147.909	62.870	7.078
MA-T2	PMA-T(12)	3	1.5	209	2.34	155.155	60.788	8.266
MA-T3	PMA-T(18)	3	2.1	185	1.71	161.350	59.408	8.740
MA-P1	PMA-P(12)	4	1.6	202	2.59	152.850	62.52	7.097
MA-P2	PMA-P(16)	4	2	189	2.00	157.415	59.643	9.412
MA-P3	PMA-P(24)	4	2.5	173	1.86	165.945	58.172	8.107
MA-D1	PMA-D(18)	6	2.3	186	1.71	152.995	58.865	7.704
MA-D2	PMA-D(24)	6	3.1	160	1.35	163.290	57.378	8.091
MA-D3	PMA-D(36)	6	2.8	164	1.38	157.095	57.499	8.016

[a] *f* = no. of branches of PMA polymer. [b] M_n = no. average molecular weight of PMA estimated by GPC expressed in Da. [c] WRA = averaged sum of wrinkle recovery angles in warp and weft of cotton fabrics in accordance with AATCC 66-2008. [d] Ft = average of tearing force in warp and weft of cotton fabrics in accordance with ASTM D1424-2009. [e] Fb = average of breaking force in warp and weft of cotton fabrics in accordance with ASTM D5034-2009. [f] WI = whiteness index measured in accordance with AATCC 110-2005. [g] YI = yellowness index measured in accordance with ASTM E313-2010 .

5.3.2.1 FTIR-ATR characterisation of modified cotton

As discussed in 3.3.2 in previous chapter, the formation of ester cross-links of the cotton impregnated and cured with dendritic PMAs polymer was revealed based on FTIR-ATR with the post-treatment of NaOH solution [17]–[19], [42], [43]–[45]. Upon modification with PMAs, additional ester carbonyls (1720cm^{-1}) and carboxylates (1585cm^{-1}) were detected on the modified cotton fabrics as shown in Figure 5-6. No other new functionalities were determined from the FTIR spectra of the modified fabric samples. Esterification using poly(carboxylic acid) for cross-linking unavoidably retains certain amount of acid residue on the fabrics. The residue peak of carboxylates explained the phenomenon that acid-catalysed depolymerisation of cellulose fibres was one of the attributes leading to the loss in mechanical strengths.



(Cotton fabrics impregnated with 20w/w% dendritic PMA polymer coupling with 6w/w% of NaH_2PO_2 was subjected to curing at 180°C for 1.5min.)

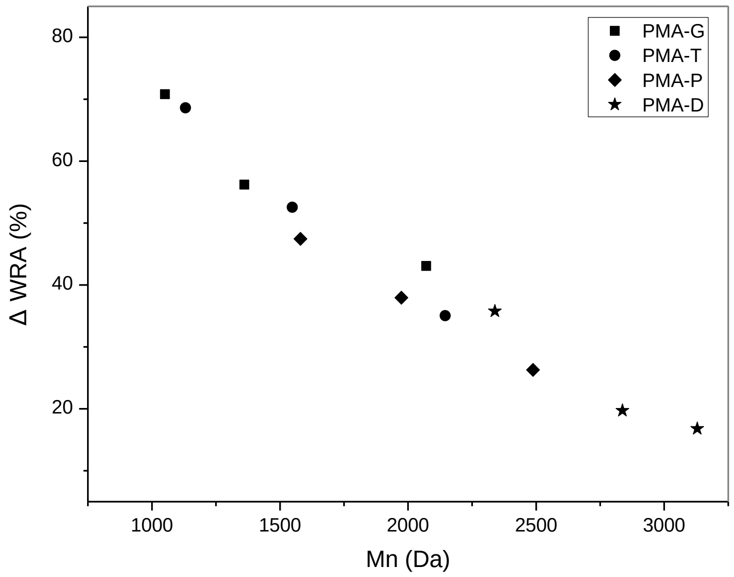
Figure 5-6 Characteristic FTIR-ATR spectra of the cotton fabric modified with various dendritic PMA polymers with different polyol cores.

5.3.2.2 Effect of Branching of Core Polyol

The effectiveness of wrinkle recovery performance of modified fabrics was expressed in terms of ΔWRA. Generally speaking, all dendritic PMA polymers employed in the study were capable of imparting wrinkle-resistance to the cotton fabric. ΔWRA were ranging from 17% up to 76% increment. With the use of dendritic PMA of various molecular architectures and molecular weights, the influence of molecular composition of the carboxyl-based cross-linkers on the wrinkle recovery performance of the cotton fabric was evaluated accordingly. Effectiveness of the carboxyl-based cross-linkers depends not only on the number of reactive groups, but also the molecular size of the cross-linker. The number of carboxyl groups present in dendritic PMA cross-linkers is proportional to the respective molecular weights.

The degree of cross-linking governs the extent of wrinkle recovery performance of the modified fabrics. ΔWRA reduced with the increasing branching factor (*f*) and molecular weights of dendritic PMA. As illustrated in Figure 5-7, ΔWRA exhibited a decreasing trend in relation to M_n. Comparing *f* in each series, larger *f* would retard the increment in WRA. Wrinkle recovery performance to cotton fabrics could be promoted to the greatest extent when employing PMA-G or PMA-T as the cross-linkers ($f = 3$). ΔWRA for cotton fabrics modified the dendritic PMA of $f = 3$ were capable to attain over 40% up to 80% improvements for the selected PMA. When using cross-linkers with $f = 4$ or 6, the improvement in WRA was found to be less prominent. The ΔWRA were found to be below 40%. When the molecular weight of the dendritic cross-linker was above

2 x10^3 Da, the effectiveness of the cross-linker diminished. These two properties of the cross-linkers denoted the overall molecular size of the cross-linker controlling the penetration of the cross-linkers into to the cellulose fibre and hence the cross-linking effectiveness [88], [91], [96], [109], [156].



(Cotton fabrics impregnated with 20w/w% of the selected PMA polymer coupling with 6w/w% of NaH_2PO_2 were subjected to curing at 180°C for 1.5min.)

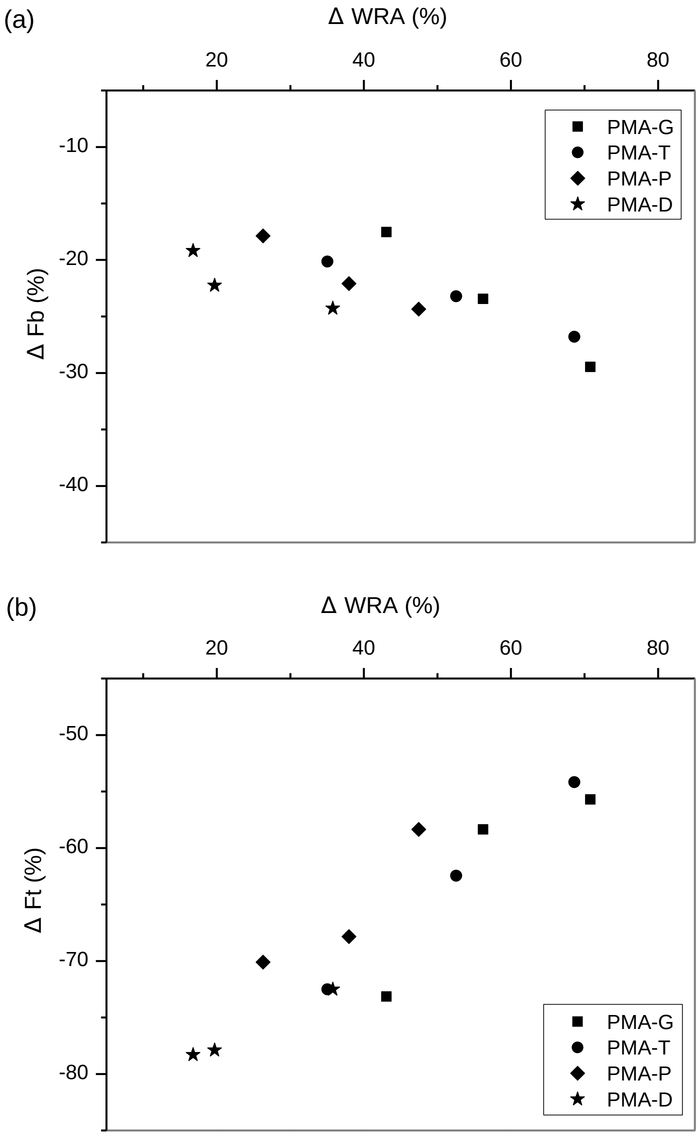
Figure 5-7 Wrinkle recovery performance of cotton fabrics modified with dendritic PMA of various branching architectures and molecular weights

Cross-linking of cellulose improves the wrinkle-resistant performance of cotton fabrics. Simultaneously, the reaction imposes loss in the fabric strengths upon cross-linking reaction. Two major factors influence the mechanical performance of cotton fabrics subjected to wrinkle-resistant finishing. Cross-linking reaction and acid-catalysed cellulose degradation are the attributes leading to the loss in fabric strengths [42], [45],

[51], [52]. Data obtained from fabric characterisation and evaluation indicated that dendritic PMA with acid groups afforded the capability of cellulose cross-linking. Concurrently, they imparted certain degree of cellulose degradation.

Effectiveness in cross-linking of cotton cellulose not only affects the wrinkle recovery performance, but also influences the resultant mechanical performance of the modified cotton fabrics. Figure 5-8 depicts the relationship between the wrinkle recovery performance and the alteration in fabric strengths. The change in tensile and tearing strengths is expressed in terms of ΔFb and ΔFt respectively. ΔFb exhibits a decreasing trend with respect to ΔWRA as illustrated in Figure 5-8a. Increasing cross-links formed between cellulose did not impose large impact on the tensile strength of the modified cotton fabrics. Meanwhile, ΔFt exhibits an increasing trend with respect to ΔWRA as presented in Figure 5-8b. The loss in tensile strength is essentially caused by the formation of intermolecular cross-links. The restricted intermolecular motion between cross-linked fibre lead to reduction in tensile strength.

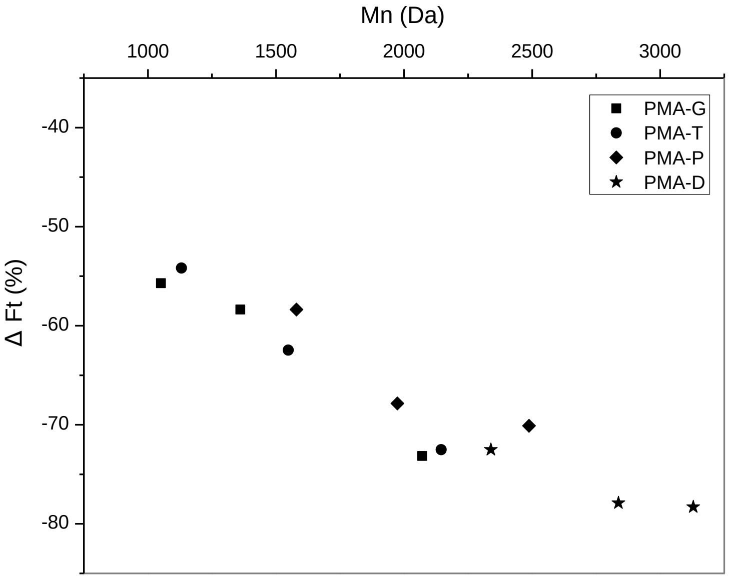
On the whole, the variation in ΔFb was about ±10% using the selected PMA for cotton cross-linking. In significance, the alteration in ΔFt in the present study was found to be intriguing. Effective cross-linking imposed a positive effect in diminishing the loss in tearing strength. For example, when employing PMA-G polymers as cellulose cross-linkers, improvement in WRA for ~30% would reduce loss in Ft by ~20%. Experimental results indicated that effective cross-linking using dendritic PMA as cross-linkers were capable of retaining loss in tearing strength of cotton fabrics. In the course of effective cross-linking, carboxylic acids would be consumed in the esterification of cellulose hydroxyls instead of inducing cellulose degradation. Hence, the loss in strength was reduced. Polymeric structures of cross-linkers is suggested as another compensate for strength loss caused by acid-catalysed cellulose degradation [17], [50], [53]–[55].



(Cotton fabrics impregnated with 20w/w% of the selected PMA polymer coupling with 6w/w% of NaH_2PO_2 were subjected to curing at 180°C for 1.5min.)

Figure 5-8 (a) Tensile strength and (b) tearing strength of cotton fabrics modified with dendritic PMA polymers in relation to wrinkle resistant performance

M_n of cross-linkers not only contributes the cross-linking power of the cross-linkers, but also impinges the fabric strengths of the modified substrate. Figures 5-9 and 5-10 depicts the variation in tearing and tensile strengths expressed in terms of ΔFt and ΔFb in relation to M_n of the cross-linkers respectively. The penetrating power of the cross-linkers would affect the possible reactions involved between polycarboxylic acids and cellulose hydroxyls. Esterification may proceed to form intermolecular cross-links, intramolecular cross-links and side grafts [51].



(Cotton fabrics impregnated with 20w/w% of the selected PMA polymer coupling with 6w/w% of NaH_2PO_2 were subjected to curing at 180^oC for 1.5min.)

Figure 5-9 Tearing property of cotton fabrics modified with dendritic PMA of various branching architectures and molecular weights

ΔFt exhibits a decreasing trend with respect to the increase in M_n as shown in Figure 5-9. Among the series of dendritic PMA, increasing *f* would impart negative impact on the loss in tearing strength. Increasing bulkiness of the cross-linkers would tender the fabric strengths as intramolecular cross-links and side grafts would form preferentially. Intramolecular cross-links would limit the mobility of the cellulose macromolecules in equalising external stresses leading to strength tendering. Meanwhile, the formation of side grafts would promote cellulose degradation. Semi-quantitative evaluation of FTIR data offers an explanation to the phenomenon as tabulated in Table 5-4 [17]–[19], [42], [44], [45]. The absorbance originated from ester carbonyls (C=O) at 1720cm^{-1} and carboxylates (COO^-) at 1585cm^{-1} offers useful information about the degree of cross-linking and the alteration in mechanical strengths. FTIR data revealed that cross-linkers of higher order of M_n with reduced penetrating power into yarns and fibre would shift to form side grafts. The relatively absorbance of originated from carboxylate was found to be larger than that from the ester carbonyls when M_n increased. Hence more acid residue formed on the modified fabrics leading to larger reduction in strength. Such phenomenon was observed when utilising the bulkiest PMA-D polymers as cross-linkers, the loss in tearing strength of cotton fabrics was found to be severe as shown in Figure 5-9.

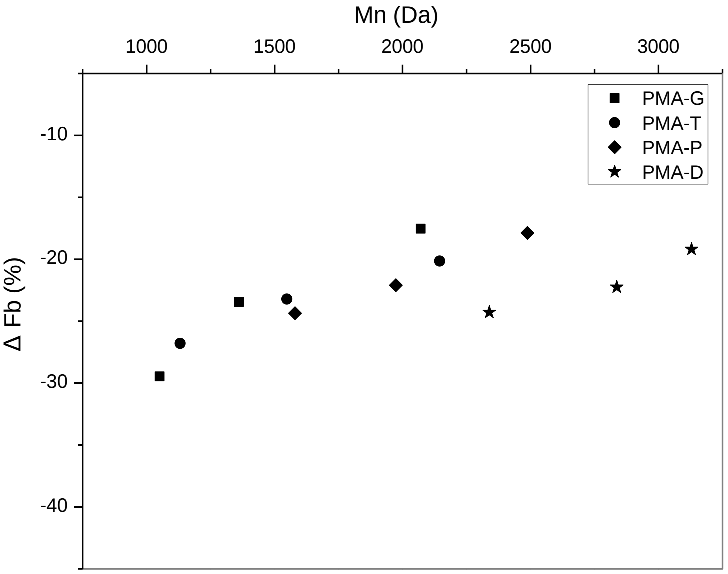
The loss in tensile strength is essentially caused by the formation of intermolecular cross-links. The restricted intermolecular motion between cross-linked fibre lead to reduction in tensile strength. The FTIR of cotton fabrics modified with PMA-G, PMA-T and PMA-P series exhibit similar variation. The ratio between absorbance ester carbonyl to carboxylate (A_{1720}/A_{1585}) was found to be reducing with down the groups as summarised in Table 5-4. The deviation was observed for the PMA-D series. The absorbance of ester carbonyl and carboxylate is relatively higher compared to other series of PMA. And the ratios were found to be ~1. Intramolecular cross-links were suggested as the dominant reaction between PMA-D polymers and cotton cellulose. Cotton fabrics modified with PMA-D became stiff and starchy feel implied that poor penetration of PMA-D leading to surface cross-linking. Intramolecular cross-linking was found to be effective. PMA-D polymers with M_n of at least 2.3 x10^3 Da and six arms emanating from the hexol core significantly inhibited the penetration into fibres and molecules. As a result, the bulkiness of PMA-D diminished the intermolecular cross-links formation into cellulose for cross-linking. The loss in Ft was found to be least significant among the dendritic PMA employed in the wrinkle-resistant finishing study as demonstrated in Figure 5-10.

Employing dendritic PMA as cross-linkers for cotton fabrics would impose acid-catalysed depolymerisation of cotton cellulose. Yet, the finishing did not impose substantial yellowing to the cotton substrate. Whiteness index of the modified fabrics were essentially retained within 10% when employing series of PMA-G and PMA-T as shown in Table 5-3. Increasing bulkiness of cross-linker would impose obvious fabric yellowing. Retarded penetration of the acidic cross-linkers would render more degradation of fibre surface.

Table 5-4 Summary of FTIR data of cotton fabrics modified with various dendritic PMAs

fabric code	Cross-linker	A_{1720}	A_{1585}	A_{1720}/A_{1585}
MA-G1	PMA-G(9)	0.0083	0.0085	0.976
MA-G2	PMA-G(12)	0.0082	0.0089	0.921
MA-G3	PMA-G(18)	0.0084	0.0100	0.838
MA-T1	PMA-T(9)	0.0062	0.0067	0.936
MA-T2	PMA-T(12)	0.0063	0.0068	0.921
MA-T3	PMA-T(18)	0.0065	0.0080	0.818
MA-P1	PMA-P(12)	0.0110	0.0127	0.870
MA-P2	PMA-P(16)	0.0097	0.0013	0.845
MA-P3	PMA-P(24)	0.0096	0.0012	0.776
MA-D1	PMA-D(18)	0.0134	0.0141	0.948
MA-D2	PMA-D(24)	0.0156	0.0151	1.036
MA-D3	PMA-D(36)	0.0085	0.0086	0.984

(A_{1720} and A_{1585} = averaged sum of absorbance at 1720cm^{-1} and 1585cm^{-1} normalised against 1317cm^{-1} obtained in 128 scan of FTIR-ATR spectra of modified cotton fabrics)



(Cotton fabrics impregnated with 20w/w% of the selected PMA polymer coupling with 6w/w% of NaH_2PO_2 were subjected to curing at 180°C for 1.5min.)

Figure 5-10 Tensile property of cotton fabrics modified with dendritic PMA of various branching architectures and molecular weights

5.3.2.3 Comparison between Monomeric and Polymeric Cross-linkers

Series of novel dendritic PCA, linear-dendritic PCA-PEG, and dendritic PMA polymers were successfully prepared by polycondensation reactions. The effectiveness of the cross-linking reaction, and the resultant wrinkle-resistant performance and fabric properties moidified with different polymeric cross-linkers and the respective monomeric counterparts were summarised in Table 5-5.

Table 5-5 Comparison performance between monomeric and polymeric cross-linkers [a]

Fabric code	Cross-linker	M_n x10^3 [b]	WRA (^{o}) [c]	Ft (N) [d]	Fb (N) [e]	WI [f]	YI [g]
control	---	---	140	19.65	283.361	75.087	5.407
CA-10	CA	0.192	190	5.94	163.414	68.487	7.511
CA-T1	PCA-T(9)	1.6	194	8.26	169.885	70.603	6.627
PEG10	PCA-PEG10(8)	2.6	191	15.67	240.38	70.442	6.705
MA-10	MA	0.134	181	10.05	174.92	72.346	6.471
MA-G4	PMA-G(9)	1.1	191	13.19	208.805	71.103	6.526

[a] All fabrics impregnated with finishing bath of pH2, comprised of 10w/w% cross-linker with 7w/w% NaH_2PO_2 and cured at 180^{o}C for 1.5min [b] M_n = no. average molecular weight of PCA estimated by GPC expressed in Da. [c] WRA = averaged sum of wrinkle recovery angles in warp and weft of cotton fabrics in accordance with AATCC 66-2008. [d] Ft = average of tearing force in warp and weft of cotton fabrics in accordance with ASTM D1424-2009. [e] Fb = average of breaking force in warp and weft of cotton fabrics in accordance with ASTM D5034-2009. [f] WI = whiteness index measured in accordance with AATCC 110-2005. [g] YI = yellowness index measured in accordance with ASTM E313-2010 .

The effectiveness of cross-linking by PMA-G(9) was comparable to that by monomeric CA, PCA-T(9) or PCA-PEG10(8). ΔWRA of fabric modified with dendritic PCA-G(9) could be improved by +36% which was similar as those modified with counterparts. Though MA only comprises of 2 carboxyls, monomeric MA could still impart wrinkle-resistance to the cotton fabric as MA would undergo *in-situ* polymerisation during the thermal curing step in the finishing treatment. In particular, fabric substrate modified by MA-based cross-linkers (both monomeric and polymeric) helped retain fabric strength and fabric whiteness compared to CA-based cross-linkers. MA is less susceptible to thermal transformation into unsaturated chromophores. As illustrated in Table 5-5, the deviation in WI and YI were less significant when utilising MA or PMA-G(9) as the cross-linkers. Dendritic PMA-G is of attractive potential to ameliorate fabric discoloration.

In the comparison, PMA-PEG10(8) performed the best in retaining fabric strength. PMA-G performance this aspect was also found to be comparable to PMA-PEG while relatively more effective than PCA-T. MA was less bulky than CA. Though PMA-G and PCA-T are of similar degree of polymerisation, the respective M_n is quite different. PMA-G was smaller in molecular size could penetrate into cellulose fibres more effectively for cross-linking reaction.

5.4 Conclusions

A series of novel low molecular weight dendritic PMA polymers were successfully prepared by bulk polycondensation of malic acid with four branched polyols incorporated in the system. The dendritic molecular architecture of the dendritic polymers was revealed with the utility of advanced analytical techniques. The dendritic PMAs of various branching architectures with M_n ranging 1 x10^3 Da to 3 x10^3 Da were adopted in the wrinkle-resistant finishing of cotton fabrics. The effectiveness of the cross-linking reaction, and the resultant wrinkle-resistant performance and fabric properties were evaluated in correlation with the molecular size and architecture of the newly developed dendritic cross-linkers.

In the present study, utilising dendritic polymers in the series of PMA-G and PMA-T for cross-linking cotton cellulose is capable of affording the better WRA improvement while imparting the lesser loss in overall strengths compared to bulkier series of PMA-P and PMA-D. In particular, PMA-G(9) was found to be the most effective cellulose cross-linker. PMA-G(9) was component to assist strength retention to the largest extent while affording the best wrinkle recovery performance of the modified cotton textiles. Meanwhile, cotton textile modified with this dendritic PMA could attain minimum fabric yellowing.

With respect to the continual pursue of non-formaldehyde based chemical finishing, this series of syntheses and application of dendritic PMAs presents a promising group of novel wrinkle-resistant finishing agents for cotton textiles.

5.5 Bibliography

[1] N. Nagata, T. Nakahara, T. Tabuchi, R. Morita, J. R. Brewer, and S. Fujishige, “Characterization of poly(ß-L-malic acid) produced by Aureobasidium sp.A-91,” *Polym. J.,* vol. 25, no. 6, pp. 585–592, 1993.

[2] N. Nagata, T. Nakahara, and T. Tabuchi, “Fermentative production of poly(ß,L-malic acid), a polyelectrolytic biopolyester, by Aureobasidium ap.,” *Biosci. Biotechnol. Biochem. Biochem*., vol. 57, no. 4, pp. 638–642, 1993.

[3] S. Cammas, P. Guerin, J. P. Girault, E. Holler, Y. Gache, and M. Vert, “Natural poly(malic acid): NMR shows a poly(3-hydroxy acid)-type structure,” Macromolecules, vol. 26, pp. 4681–4684, 1993.

[4] S. Liu and A. Steinbüchel, “Investigation of poly(ß-L-malic acid) production by strains of Aureobasidium pullulans,” *Appl. Microbiol. Biotechnol*., vol. 46, pp. 273–278, 1996.

[5] H. Zhang, J. Cai, J. Dong, D. Zhang, L. Huang, Z. Xu, and P. Cen, “High-level production of poly(ß-L-malic acid) with a new isolated Aureobasidium pullulans strain,” *Appl. Microbiol. Biotechnol*., vol. 92, no. 2, pp. 295–303, 2011.

[6] O. Coulembier, P. Degée, J. L. Hedrick, and P. Dubois, “From controlled ring-opening polymerization to biodegradable aliphatic polyester: especially poly(ß-malic acid) derivatives,” Prog. Polym. Sci., vol. 31, no. 8, pp. 723–747, 2006.

[7] M. Vert, “Chemical routes to poly(ß-malic acid) and potential applications of this water-soluble bioresorbable poly(ß-hydroxy alkanoate),” *Polym. Degrad. Stab*., vol. 59, no. 1–3, pp. 169–175, 1998.

[8] S. Cammas, I. Renard, V. V. Langlois, P. Guérin, and P. Guerin, “Poly (ß-malic acid): obtaining high molecular weights by improvement of the synthesis route,” *Polymer (Guildf)*., vol. 37, no. 18, pp. 4215–4220, 1996.

[9] T. Kajiyama, H. Kobayashi, T. Taguchi, and K. Kataoka, “Improved synthesis with high yield and increased molecular weight of poly(α,ß-malic acid) by direct polycondensation,” *Biomacromolecules,* vol. 5, pp. 169–174, 2004.

[10] T. Kajiyama, T. Taguchi, H. Kobayashi, K. Kataoka, and J. Tanaka, “Synthesis of high molecular weight poly(α,ß-malic acid) for biomedical use by direct polycondensation,” *Polym. Degrad. Stab*., vol. 81, no. 3, pp. 525–530, 2003.

[11] N. Ohtani, Y. Kimura, and T. Kitao, “Preparation of poly(malic acid) and its ester derivatives by direct polycondensation of malic acid and ß-ethyl malate,” *Kobunshi Ronbunshu*, vol. 44, no. 9, pp. 701–709, 1987.

[12] W. J. Feast and N. M. Stainton, “Synthesis, structure and properties of some hyperbranched polyesters,” *J. Mater. Chem.*, vol. 5, no. 3, pp. 405–411, 1995.

[13] E. Malmström and A. Hult, “Hyperbranched polymers: a review,” *J. Macromol. Sci. Part C*, vol. 37, no. 3, pp. 555–579, 1997.

[14] E. Malmström and A. Hult, “Kinetics of formation of hyperbranched polyesters based on 2,2-bis(methylol)propionic acid,” *Macromolecules*, vol. 29, pp. 1222–1228, 1996.

[15] S. H. Kim, Y.-K. Han, K.-D. Ahn, Y. H. Kim, and T. Chang, “Preparation of star-shaped polylactide with pentaerythritol and stannous octoate,” *Macromol. Chem. Phys.*, vol. 194, pp. 3229–3236, 1993.

[16] M. Johansson, E. Malmström, and A. Hult, “Synthesis, Characterization, and curing of hyperbranched allyl ether-maleate functional ester resins,” *J. Polym. Sci. Part A Polym. Chem.*, vol. 31, pp. 619–624, 1993.

[17] C. Q. Yang and X. Wang, “Infrared spectroscopy studies of the cyclic anhydride as the intermediate for the ester crosslinking of cotton cellulose by polycarboxylic acids. III. molecular weight of a crosslinking agent,” *J. Polym. Sci. Part A Polym. Chem.*, vol. 35, no. 3, pp. 557–564, 1997.

[18] C. Q. Yang and X. Wang, “Formation of cyclic anhydride intermediates and esterification of cotton cellulose by multifunctional carboxylic acids: an infrared spectroscopy study,” *Text. Res. J.*, vol. 66, no. 9, pp. 595–603, 1996.

[19] C. Q. Yang, “FT-IR spectroscopy study of the ester crosslinking mechanism of cotton cellulose,” *Text. Res. J.*, vol. 61, no. 8, pp. 433–440, 1991.

[20] C. Q. Yang, “Effect of pH on nonformaldehyde durable press finishing of cotton fabric: FT-IR Spectroscopy study: part II: formation of the anhydride intermediate,” *Text. Res. J.*, vol. 63, no. 12, pp. 706–711, 1993.

[21] Y. Phuphuak and S. Chirachanchai, “Simple preparation of multi-branched poly(L-lactic acid) and its role as nucleating agent for poly(lactic acid),” *Polymer (Guildf).*, vol. 54, no. 2, pp. 572–582, 2013.

[22] B.-H. Kim, J. Jang, and S.-W. Ko, “Durable press finish of cotton fabric using malic acid as a crosslinker,” *Fibers Polym.*, vol. 1, no. 2, pp. 116–121, 2000.

[23] R. M. Silverstein, F. X. Webster, and D. Kiemle, *Spectrometric Identification of Organic Compounds*, 7th ed. New York: John Wiley & Sons, Inc., 2005.

[24] M. J. Miri, K. E. Nori, R. M. Andrew, and C. Ge, “Copolyester synthesis using glycerol from biodiesel production,” in *Renewable and Sustainable Polymers*, G. F. Payne and P. B. Smith, Eds. American Chemical Society, 2011, pp. 11–35.

[25] H. F. Shurvell, “Spectra-structure correlations in the mid-and far-infrared,” in *Handbook of Vibrational Spectroscopy, Volume 3: Sample Characterization and Spectral Data Processing*, J. M. Chalmer and P. R. Griffiths, Eds. New York: John Wiley & Sons, Inc., 2002, pp. 1783–1837.

[26] J. M. Halpern, R. Urbanski, A. K. Weinstock, D. F. Iwig, R. T. Mathers, and H. A. von Recum, “A biodegradable thermoset polymer made by esterification of citric acid and glycerol,” *J. Biomed. Mater. Res. Part A*, vol. 102, no. 5, pp. 1467–1477, 2014.

[27] Y. Fan, Y. Fan, Y. Wang, and J. Ma, “Unexpected fluorescence emission of poly(α,ß-L-malic acid) in aqueous medium,” *J. Appl. Polym. Sci.*, vol. 106, pp. 1640–1647, 2007.

[28] J.-J. Max and C. Chapados, “Infrared spectroscopy of aqueous carboxylic acids: malic acid,” J*. Phys. Chem. A*, vol. 106, no. 27, pp. 6452–6461, 2002.

[29] I. Arvanitoyannis, A. Nakayama, N. Kawasaki, and N. Yamamoto, “Novel star-shaped polylactide with glycerol using stannous octoate or tetraphenyl tin as catalyst: 1. synthesis, characterization and study of their biodegradability*,” Polymer (Guildf).*, vol. 36, no. 15, pp. 2947–2956, 1995.

[30] S. J. Lee, B. R. Han, S. Y. Park, D. K. Han, and S. C. Kim, “Sol-gel transition behavior of biodegradable three-arm and four-arm star-shaped PLGA-PEG block copolymer aqueous solution,” *J. Polym. Sci. Part A Polym. Chem.*, vol. 44, pp. 888–899, 2006.

[31] C. L. E. Nijst, J. P. Bruggeman, J. M. Karp, L. Ferreira, A. Zumbuehl, C. J. Bettinger, and R. Langer, “Synthesis and characterization of photocurable elastomers from poly(glycerol-co-sebacate),” *Biomacromolecules*, vol. 8, pp. 3067–3073, 2007.

[32] M. Nagata, T. Machida, W. Sakai, and N. Tsutsumi, “Synthesis, characterization, and enzymatic degradation studies on novel network aliphatic polyesters,” *Macromolecules*, vol. 31, pp. 6450–6454, 1998.

[33] L. Beaufort, L. Delaude, and A. F. Noels, “A new tripodal ligand system based on the iminophosphorane functional group. Part 1: Synthesis and characterization,” *Tetrahedron*, vol. 63, pp. 7003–7008, 2007.

[34] J. Bernard, A. Favier, L. Zhang, A. Nilasaroya, T. P. Davis, C. Barner-Kowollik, and M. H. Stenzel, “Poly(vinyl ester) star polymers via xanthate-mediated living radical polymerization : from poly(vinyl alcohol) to glycopolymer stars,” *Macromolecules*, vol. 38, pp. 5475–5484, 2005.

[35] J. Diot, M. I. García-Moreno, S. G. Gouin, C. O. Mellet, K. Haupt, and J. Kovensky, “Multivalent iminosugars to modulate affinity and selectivity for glycosidases,” *Org. Biomol. Chem.*, vol. 7, pp. 357–363, 2009.

[36] A. M. Aberle, F. Tablin, J. Zhu, N. J. Walker, D. C. Gruenert, and M. H. Nantz, “A novel tetraester construct that reduces cationic lipid-associated cytotoxicity. Implications for the onset of cytotoxicity,” *Biochemistry*, vol. 37, pp. 6533–6540, 1998.

[37] Z. G. Xie, C. H. Lu, X. S. Chen, L. Chen, Y. Wang, X. L. Hu, Q. Shi, and X. Bin Jing, “Synthesis and characterization of novel poly(ester carbonate)s based on pentaerythritol,” *J. Polym. Sci. Part A Polym. Chem.*, vol. 45, pp. 1737–1745, 2007.

[38] H. Kricheldorf, H. Hachmann-Thiessen, and G. Schwarz, “Di-, tri- and tetrafunctional poly(ε-caprolactone)s by bi(OAc)3 -catalyzed ring-opening polymerizations of ε-caprolactone,” *Macromolecules*, vol. 37, pp. 6340–6345, 2004.

[39] C. Cai, L. Wang, and C.-M. Dong, “Synthesis, characterization, effect of architecture on crystallization, and spherulitic growth of poly(L-lactide)-b-poly(ethylene oxide) copolymers with different branch arms,” *J. Polym. Sci. Part A Polym. Chem*., vol. 44, pp. 2034–2044, 2006.

[40] T. Kajiyama, H. Kobayashi, T. Taguchi, Y. Komatsu, K. Kataoka, and J. Tanaka, “Study on the hydrolytic degradation of poly(α,ß-malic acid) by direct polycondensation,” *Mater. Sci. Eng. C*, vol. 24, no. 6–8, pp. 821–825, 2004.

[41] R. A. T. M. Van Benthem, “Novel hyperbranched resins for coating applications,” *Prog. Org. Coatings*, vol. 40, no. 1–4, pp. 203–214, 2000.

[42] I. S. Kang, C. Q. Yang, and G. C. Lickfield, “Mechanical strength of durable press finished cotton fabrics: part I: effects of acid degradation and crosslinking of cellulose by polycarboxylic acids,” *Text. Res. J.*, vol. 68, no. 11, pp. 865–870, 1998.

[43] N. Abidi, E. Hequet, C. Turner, and H. Sari-Sarraf, “FTIR analysis of crosslinked cotton fabric using a ZnSe-universal attenuated total reflectance,” *J. Appl. Polym. Sci*., vol. 96, no. 2, pp. 392–399, Apr. 2005.

[44] C. Chung, M. Lee, and E. K. Choe, “Characterization of cotton fabric scouring by FT-IR ATR spectroscopy,” *Carbohydr. Polym*., vol. 58, no. 4, pp. 417–420, 2004.

[45] C. Q. Yang, “Predicting the performance of durable press finished cotton fabric with infrared spectroscopy,” *Text. Res. J*., vol. 69, no. 2, pp. 145–151, 1999.

[46] C. Q. Yang, X. Wang, and I.-S. Kang, “Ester crosslinking of cotton fabric by polymeric carboxylic acids and citric acid,” *Text. Res. J*., vol. 67, no. 5, pp. 334–342, 1997.

[47] C. Q. Yang, C. Hu, and G. C. Lickfield, “Crosslinking cotton with poly(itaconic acid) and in situ polymerization of itaconic acid : fabric mechanical strength retention,” *J. Appl. Polym. Sci*., vol. 87, pp. 2023–2030, 2003.

[48] C. Q. Yang, W. Wei, and G. C. Lickfield, “Mechanical strength of durable press finished cotton fabric: part II: comparison of crosslinking agents with different molecular structures and reactivity,” *Text. Res. J.*, vol. 70, no. 2, pp. 143–147, 2000.

[49] Z. Mao and C. Q. Yang, “Polymeric multifunctional carboxylic acids as crosslinking agents for cotton cellulose: poly(itaconic acid) andin situ polymerization of itaconic acid,” *J. Appl. Polym. Sci*., vol. 79, no. 2, pp. 319–326, 2001.

[50] K. J. Yoon, J. H. Woo, and Y. S. Seo, “Formaldehyde free cross-linking agents based on maleic anhydride copolymers,” *Fibers Polym*., vol. 4, no. 4, pp. 182–187, 2003.

[51] W. Xu and Y. Li, “Crosslinking analysis of polycarboxylic acid durable press finishing of cotton fabrics and strength retention improvement,” *Text. Res. J.*, vol. 70, no. 7, pp. 588–592, 2000.

[52] E. A. Immergut and B. G. Ranby, “Heterogeneous acid hydrolysis of native cellulose fibers,” *Ind. Eng. Chem*., vol. 48, no. 7, pp. 1183–1189, 1956.

[53] M. J. Lees, “Formaldehyde-free durable press finishing based on polymaleic acid chemistry,” *J. Text. Inst.*, vol. 90, no. 3, pp. 42–49, 1999.

[54] H. Choi, “Nonformaldehyde polymerization-crosslinking treatment of cotton fabrics for improved strength retention,” *Text. Res. J*., vol. 62, no. 10, pp. 614–618, 1992.

[55] C. M. Welch, “Improved strength and flex abrasion resistance in durable press finishing with BTCA,” *Text. Chem. Color.*, vol. 29, no. 2, pp. 21–24, 1997.

Chapter Six –

Development and Application of Vinyl-Functionalised Polymalic Acid Cross-linker

6.1 Introduction

Much more work has contributed to the study of the use of polymeric cross-linkers to modify cellulosic materials for the purpose of retaining mechanical strength and whiteness of substrates. In particular, unsaturated dicarboxylic acids and hydroxylcarboxylic acids are potential compounds to serve as cross-linkers for cellulosic materials. These carboxylic acids could also serve as cellulose cross-linkers upon *in-situ* self-polymerisation or free radical polymerisation during modification to form multi-functional polymeric compounds and sequentially participated in cellulose cross-linking with the presence of phosphorus based catalysts and initiators in aqueous medium [1]–[15].

Most of the prior technologies developed to date still suffering from various key deficiencies included severe strength loss, release of toxic substances and of exceedingly high cost for commercialisation [3], [13], [16]–[26]. Investigating platforms for wrinkle-resistant finishing based on naturally available reagents for the industry inevitably remains in surge. With the advance in biotechnology, the production of biomass various carboxylic acids included MA and IA becomes feasible. Microbial fermentation furnishes the sustainable supply of natural acids to develop cellulose cross-linkers [1], [27]–[35].

In the previous chapter, MA-based dendritic polymers were successfully developed and the efficacy in serving as cellulose cross-linkers has been verified. In view of the promising performance of PMAs, PMA with additional functionality was investigated in this chapter. In this chapter, a novel polymeric cross-linker was developed using MA and IA. The potential utility of a phosphorous based catalyst, NaH_2PO_2 was demonstrated. A simple synthesis system was then developed for preparing polymeric carboxyl-based cross-linker with additional functionality. In this case, vinyl functionality was incorporated. Chemical structures of individual reactants are illustrated in Figure 6-1. Sequentially, the newly prepared PMA-IA polymer was applied to wrinkle-resistant finishing study. The effectiveness of utilising such cross-linker with dual functionalities for imparting wrinkle resistance to cotton textiles was evaluated.

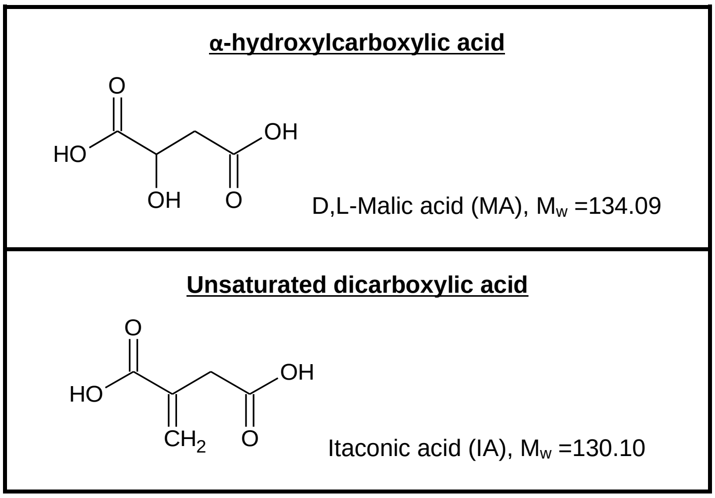


Figure 6-1 MA and IA used in the development of vinyl-functionalised polymeric cross-linker

6.2 Experimental

6.2.1 Materials

D,L-MA and IA were purchased from Acros Organics and Sigma-Aldrich Co respectively. Sodium hypophosphite monohydrate ($NaH_2PO_2 \cdot H_2O$) and sodium hydroxide (NaOH) were supplied by International Lab. Triton X-100 was supplied by BDH Chemicals. Potassium persulfate ($K_2S_2O_8$) was purchased from Acros Organics. Tetrahydrofuran (THF) and diethyl ether were obtained from Duskan Pure Chemicals. Dimethyl sulfoxide-d_6 (DMSO-d_6) was obtained from Acros Organics. All chemicals were used as received. 100% plain woven semi-bleached cotton fabric (90 x 72, 110g/m^2) was used for the wrinkle-resistant finishing study.

6.2.2 Synthesis of Polymeric Cross-linker

α-hydroxylcarboxylic acid, MA in a combination with an unsaturated dicarboxylic acid, IA was mixed and reacted to prepare vinyl-functionalised PMA polymer via bulk polycondensation with additional vinyl functionality. The general scheme for the conversions is illustrated in Scheme 6-1. Selected purified PMA-IA was subjected to finishing trials to evaluate the feasibility of vinyl-functionalised PMAs serving as the wrinkle-resistant finishing agents for cotton textiles. General procedures are summarised as below.

In a 100ml round bottom flask, MA (0.37mol), IA (0.0.125mol to 0.093mol) and NaH_2PO_2 (0mol to 0.037mol) were melted and reacted at the designated temperature (110°C to 140°C) with stirring for 4 hours under reduced pressure. Water generated in the reaction was continuously removed from the system by a vacuum pump. Crude products were firstly dissolved in minimum amount of water. The filtrates were dried and sequentially re-dissolved in THF and precipitated in excessive amount of diethyl ether. The purified products were dried under reduced pressure. The precipitates were a pale yellowish solid.

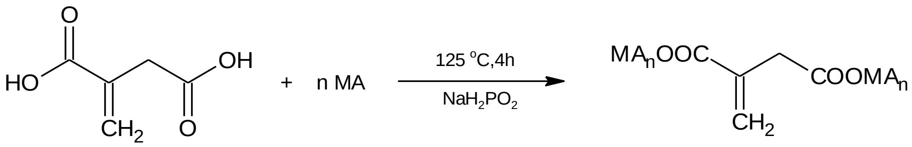
PMA-IA(10):

FTIR-ATR (cm^{-1}): 3111(ν OH acid), 2932 (ν C-H), 1723 (ν C=O ester), 1404 (δ C-O-H), 1171 (ν C-O stretching).

^{1}H-NMR (500MHz, DMSO-d_6, δ ppm): 2.76-2.93 (CH_2, MA moieties), 3.19-3.20 (s, CH_2, IA moieties), 5.23 (s, CH, α-MA moieties), 5.40 (s, CH, β-MA moieties), 5.77 (s, =CH_2, IA moieties), 6.16 (s, =CH_2, IA moieties)

^{13}C-NMR (125MHz, DMSO-d_6), δ (TMS ppm): 35.58 (CH_2, IA moieties), 36.28 (CH_2, MA moieties), 67.20, 67.48, 69.63 (CH, MA moieties), 128.07, 134.41, (C=C, IA moiety), 166.19 (α-COO, IA moiety) 169.12, 169.64, 170.14, 170.48, 170.73, 171.08, 171.21, 171.25, 172.16 (β-COO, IA moiety, α-COO, MA moieties), 172.91, 173.07, 174.28, 174.58 (ß-COO, MA moieties)

Scheme 6-1



6.2.3 Polymer Characterisations

Each FTIR spectrum of the polymers recorded as an average of 16 scans on a Perkin Elmer Spectrum 100 spectrophotometer equipped with a universal attenuated total internal reflectance (ATR) accessory.

^{1}H and ^{13}C NMR spectra of the polymers were recorded using a Varian Unity Inova 500 NMR spectrometer under ambient temperature. DMSO-d_6 was used as the solvent with tetramethylsailne (TMS) as the internal reference for the analysis.

The molecular weights of the polymer were estimated by gel permeation chromatography (GPC) with the use of Waters system. The system equipped with a Waters 1515 isocratic pump coupled with a series of Styragel® HMW columns (HR1, HR4, and HR6; molecular weight range 10^2 -10^7), calibrated with mono-dispersed polystyrene standards (PS)(PolyScience), and a Waters 2414 refractive index detector. THF was used as the eluent at a flow rate of 1.0 ml/min. The column was maintained at 30°C during analysis.

Thermogravimetric analysis (TGA) of the polymers (5mg) was performed by using a Mettler-Toledo thermogravimetric analyser studied under nitrogen atmosphere at a heating rate of 20°C/min.

6.2.4 Modification of Cotton Fabric

The newly developed vinyl functionalised-PMA-IA(10) was mixed with NaH_2PO_2 as the catalyst to form aqueous finishing solutions. Cotton fabrics were impregnated with the solutions of different recipes using a Rapid Labortex P-80 horizontal padding machine imposing a constant pressure of 1kg/ cm^2 to achieve wet pick-up of 85±5% and sequentially dried at 80°C for 3min. The fabrics were thermally cross-linked under the selected curing temperature and time using a Mathis LTE Labdryer. The finishing recipes and condition were studied with respect to the parameters included the concentration of PMA-IA(10) (5w/w% to 20w/w%), acidity of the padding solution (pH 2 to 3.5), the concentration of catalyst (2.5w/w% to 10w/w%), the concentration of additives (0 w/w% to 2w/w%), curing temperature (130°C to 170°C) and curing time (1.5min to 4.5 min). All solutions contained 1w/w% Triton X-100 as the non-ionic surfactant.

6.2.5 Fabric Characterisations and Evaluations

Properties of cotton fabrics modified with the newly developed polymers were evaluated based on the following standard approaches and procedures. The formation of cross-links of modified cotton fabrics was studied based on FTIR-ATR. Prior to FTIR analysis, modified fabric samples were treated with 0.1M NaOH solution and rinsed with deionised water to differentiate carbonyl (C=O) stretching of carboxyls and esters. All modified fabric samples were conditioned under standard condition at 65±2% relative humidity and 21±1°C prior to evaluations. Spectra of dried fabric samples were recorded using a Perkin Elmer FTIR spectrophotometer 100 equipped with an ATR sampling accessory. Each FTIR spectrum was recorded as an average of 128 scans and normalised against 1317cm^{-1} which is originated from the C-H bending of cellulose molecules [36]–[39].

Wrinkle-resistant performance was evaluated in accordance with the AATCC 66-2008 test method. Specimens (40mm x 15mm) in both warp and weft alignment were folded face-to-face and back-to-back. Folded specimens were compressed with a 500g-weight for 5min. The wrinkle recovery angles (WRA) of specimens were measured by a Daiei Kagakuseiki Seisakusho wrinkle recovery tester after 5min of relaxation and recovery. WRAs were reported as an average of eight measurements of the sum in warp and weft directions with the analytical tolerance limited to 5%. The change in wrinkle recovery angle (∆WRA) was expressed according to the following equation.

$$\Delta WRA = \frac{WRA_m - WRA_o}{WRA_o} \times 100\%$$

where as WRA_m= WRA of modified fabric
WRA_o = WRA of control fabric

Mechanical properties included tensile strength and tearing strength, were evaluated according to ASTM D5034-2009 and ASTM D1424-2009 test methods respectively. The tearing strength of modified cotton fabrics were evaluated using a James H. Heal digital Elmendorf tearing tester with a standard capacity of 1600g or 3200g chosen to measure the strength. Specimens were cut according to the standard notched template in both warp and weft directions. Individual notched specimen was fixed onto the tester. The pendulum was depressed downwards until tearing of a specimen was completed. Tearing force (Ft) was reported as an average result of eight measurements in both warp and weft directions. When evaluating the tensile strength of modified cotton fabrics, a tensile tester, Instron 4411, was used based on constant rate of extension (CRE) tensile testing method. Specimens (150mm x10mm) in both warp and weft alignment were mounted vertically on the tester for the test. Longitudinal grabbing force was applied along the testing direction until the specimen broke. Tensile strength reported as the averaged breaking force (Fb) of eight measurements in both warp and weft directions with the analytical tolerance limited to 5%. The change in mechanical properties was expressed in terms of change in forces (ΔF) according to the below equations.

$$\Delta Ft = \frac{Ft_m - Ft_o}{Ft_o} \times 100\%$$

$$\Delta Fb = \frac{Fb_m - Fb_o}{Fb_o} \times 100\%$$

where as Ft_m = tearing or tensile force of modified fabric

Ft_o = tearing or tensile force of control fabric

Fb_m = tearing or tensile force of modified fabric

Fb_o = tearing or tensile force of control fabric

6.3 Results and Discussion

6.3.1 Cross-linker Synthesis and Characterisations

A series of low molecular weight vinyl-functionalised polymers, PMA-IAs, were prepared by bulk polycondensation of MA with IA in the presence of NaH_2PO_2. The polymerisation results were tabulated in Table 6-1. Polymerisation behaviour illustrated the essence of inclusion of NaH_2PO_2 in this system. Inclusion of NaH_2PO_2 was found to be influential in terms of the resultant molecular weight and yield of product. The concentration of NaH_2PO_2 varying from 0mol% to 10 mol% exhibited a non-linear behaviour with respect to molecular weight and yield of PMA-IA. Upon bulk polycondensation reaction at 125^{o}C for 4 hours under reduced pressure, molecular weights obtained were ranging from 0.54 x10^3 Da to 1.3 x10^3 Da in terms of M_n with polydispersity (PDI) below 1.4 with the incorporation of various concentration of catalyst. Yield of product was determined to be 70% or above.

Without the addition of NaH_2PO_2 in the system, an oligomeric compound (PMA-IA-C0) (M_w = 0.76 x10^3 Da; M_n = 0.54 x10^3 Da) was formed with an estimated yield of ~70%. Inclusion of NaH_2PO_2 into the system promoted the degree of polymerisation and yield of product. NaH_2PO_2 is an effective catalyst for esterification of hydroxyl functionalities with polycarboxylic acids [23], [25], [37], [38], [40]–[42]. MA is an α-hydroxyl dicarboxylic acid. NaH_2PO_2 was postulated to assist the esterification between IA and MA and mutual polymerisation of MA via the formation of cyclic intermediate. As shown in Table 6-1, molecular weight and yield of product were increasing with the concentration of NaH_2PO_2 present in the system. Yet, adding 10mol% of NaH_2PO_2 could not further increase the molecular weight and yield of PMA-IA. Molecular weight and yield of product reduced accordingly. Inclusion of excess amount of NaH_2PO_2 was suggested to shift the reaction equilibrium to depolymerisation. When 5mol% (0.019 mol) of NaH_2PO_2 was added into the system, PMA-IA-C5 achieved the largest molecular weight (M_w = 1.6x10^3 Da; M_n = 1.3 x10^3 Da) and yield of product (~90%) in this work. PDI was determined to be 1.26 estimated by GPC. The actual molecular weight estimated by GPC complied with the theoretical value in the presence of 5mol% NaH_2PO_2.

Reaction temperature affected the catalysis of NaH_2PO_2 in the polycondensation reaction. In the range of reaction temperature attempted, 125^{o}C was found to be more appropriate for the polycondensation of MA coupled with IA in the presence of 5mol% NaH_2PO_2. Catalytic performance of NaH_2PO_2 is higher at elevated temperatures [40], [43]. Moreover, at a lower temperature of 110^{o}C, MA and IA were not melted completely in the reaction mixture retarded the growth of marcomolecules. Elevated temperature up to 140^{o}C would to shift the reaction equilibrium to depolymerisation or intramolecular dehydration leading to reduction in molecular weight. Colour of the product obtained at 140^{o}C was relatively more yellowish compared to that prepared at 110^{o}C or 125^{o}C. The yellowish colour implied that the product may compose to unsaturated moieties under elevated polymerisation temperature.

IA incorporated in a system is regarded as chain stoppers hampering the growth in molecular weights [44]–[46]. In the present study, various feed ratios of MA to IA were employed in the synthesis to evaluate the influence of the ratio to the growth of the polymer as summarised in Table 6-1. The actual molecular weight estimated by GPC complied with the feed ratios when the ratio ≤ 10. When the feed ratio exceeded 10, the growth of molecular weights of PMA-IA was significantly dropped to ~0.8 x10^3 Da. PMA-IA(10) was sequentially employed for the modification of cotton fabrics.

Table 6-1 Summary of PMA-IAs prepared by bulk-polycondensation

Sample code	ratio [d]	NaH_2PO_2 [mol%]	M_n x10^3 [e]	M_w x10^3 [e]	PDI [f]	Est. Yield% [e]
PMA-IA-C0 [a]	10	0	0.54	0.67	1.24	69.60
PMA-IA-C2.5 [a]	10	2.5	0.65	0.92	1.41	77.80
PMA-IA-C5 [a]	10	5	1.3	1.6	1.26	90.87
PMA-IA-C10 [a]	10	10	0.78	1	1.33	65.12
PMA-IA(T110) [b]	10	5	0.7	0.67	1.51	69.60
PMA-IA(T125) [b]	10	5	1.2	1.6	1.25	92.23
PMA-IA(T140) [b]	10	5	1	1.4	1.38	90.87
PMA-IA(2) [c]	2	5	0.54	0.77	1.41	73.07
PMA-IA(4) [c]	4	5	0.65	0.93	1.43	79.68
PMA-IA(6) [c]	8	5	0.78	1.1	1.45	78.93
PMA-IA(10) [c]	10	5	1.3	1.6	1.24	89.17
PMA-IA(30) [c]	30	5	0.8	1.1	1.34	84.92
PMA-IA(40) [c]	40	5	0.75	1.1	1.5	85.41

[a] Bulk polycondensation carried out at 125°C under reduced pressure for 4hrs. [b] polycondensation carried out with feed ratios of 10 in the presence of 5mol% $NaH_2PO_2 \cdot H_2O$ under reduced pressure for 4hrs. [c] polycondensation carried out in the presence of 5mol% $NaH_2PO_2 \cdot H_2O$ at 125°C under reduced pressure for 4hrs. [d] ratio refer to molar feed ratio of MA : IA. [e] Estimated by GPC in THF on the basis of a PS calibration expressed in Da. [f] PDI = polydispersity (M_w/M_n).

Esterification reaction was revealed In general, the FTIR data (Figure 6-2) revealed the interaction between hydroxyl of MA with carboxyl of IA and mutual polycondensation of MA. On one hand, distinct O-H stretching and out-of-plane bending (~3400cm^{-1} , 1104cm^{-1} and 660cm^{-1}) of MA hydroxyl and O-H vibrations (1437cm^{-1}, 1216cm^{-1} and 913cm^{-1}) of IA carboxyl disappeared in the FTIR spectrum of PMA-IA as shown in Figure 6-2 [1], [7], [47]–[49]. On the other hand, the carbonyl C=O shifted from 1732cm^{-1} to 1720cm^{-1} and C-O-C stretching of ester (1170cm^{-1}) intensified. The alteration indicated that additional esters linkages were found in PMA-IA. Comparing the FTIR spectra of MA monomer with the respective polymeric products, the disappearance of absorption band originated from O-H stretching and bending of the hydroxyl at 3440 cm^{-1} and 660 cm^{-1} indicated the mutual polycondensation of MA in the system [47], [48], [50]. The board peaks at 3400-2600cm^{-1} originated from O-H of carboxylic acids of MA retained in all PMA products. Free COOH present in the products could furnish the cross-linking capability to PMA products with cotton cellulose in the sequential wrinkle-resistant finishing. The vinyl functionality of IA could not be determined by FTIR. C=C (1627cm^{-1}) of IA was buried in absorbance band of absorbed moisture present in the polymer [47].

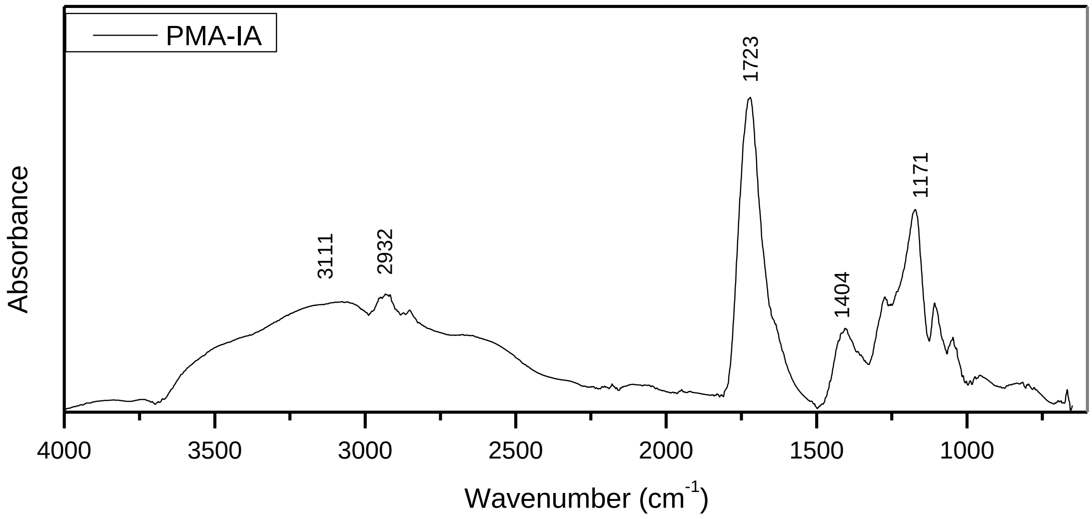


Figure 6-2 FTIR-spectrum of PMA-IA(10) polymeric vinyl cross-linker

The chemical composition of the vinyl-functionalised PMA would be elucidated based on the diagnostic peaks present in ^{1}H-NMR spectra (Figure 6-3a) and ^{13}C-NMR spectra (Figure 6-3b). In Figure 6-3a, the resonance originated from methylene protons of IA shifted towards up-field at ~δ3.22 revealed the esterification of ß-carboxyl of IA with MA. In Figure 6-3b, the resonance of α-carboxyl carbon of IA shifted towards down-field from δ168 to δ166 upon esterification [49], [51]–[53]. The above results confirmed the formation of IA diester with MA. The distinct resonance at δ5.77 and δ6.16 originated from allyl protons indicated that the vinyl group of IA remained intact in the polycondensation reaction [51], [52], [54].

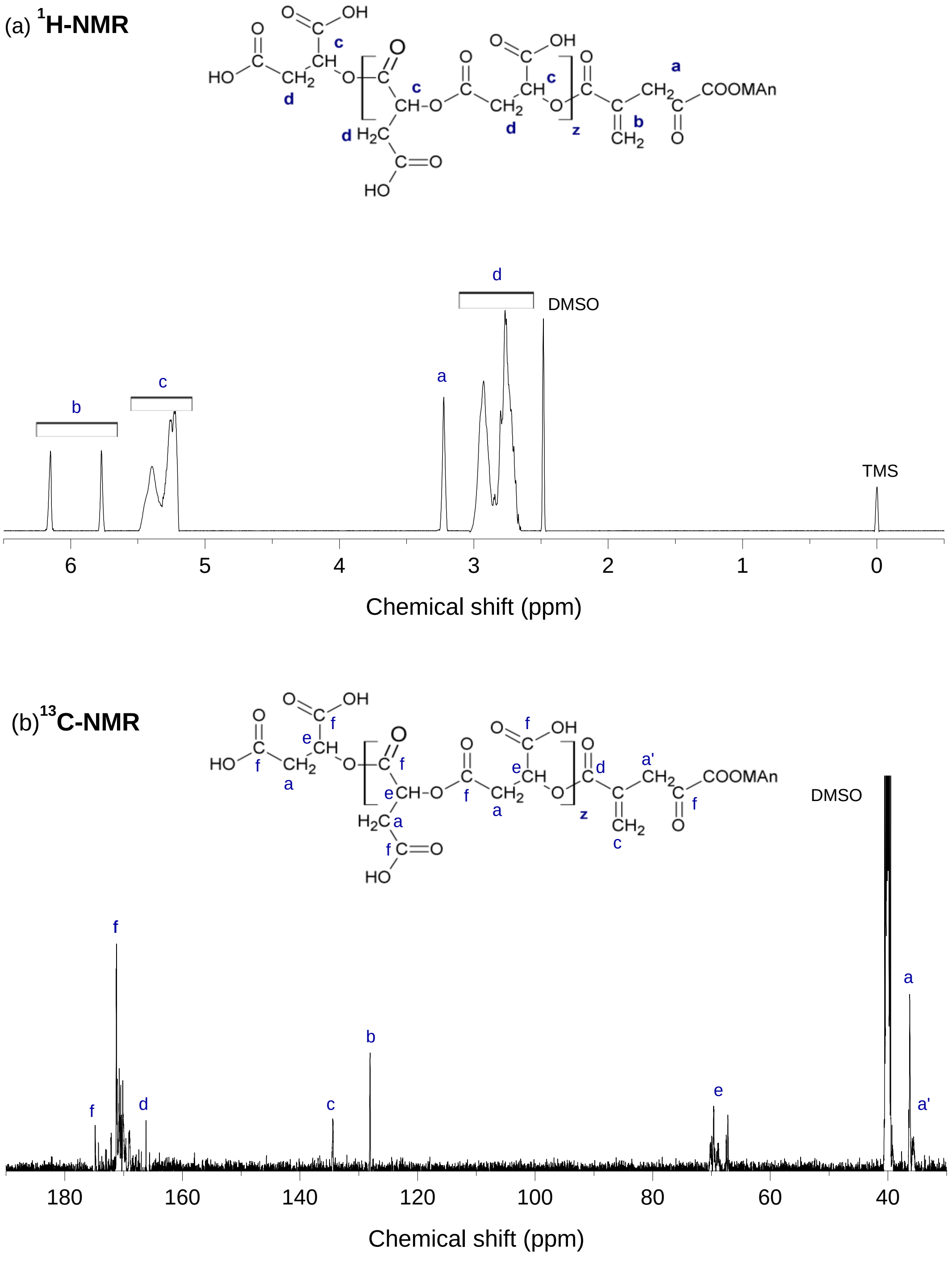
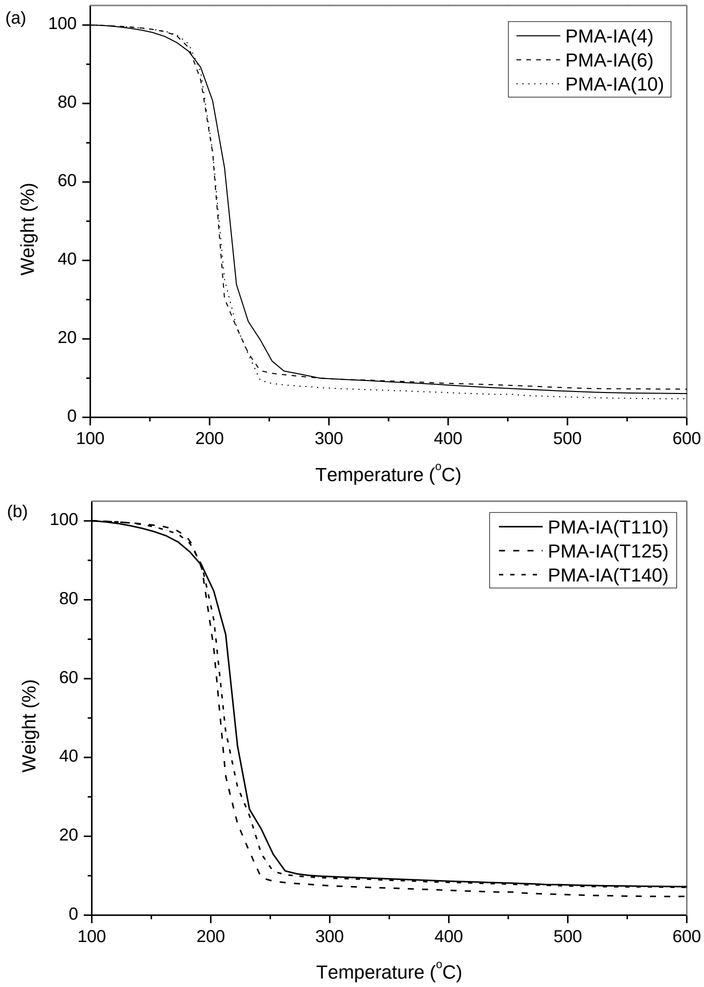


Figure 6-3 NMR-spectra of PMA-IA(10) polymer: (a) ^{1}H-NMR; (b) ^{13}C-NMR

The emergence of new resonance originated from methine protons of MA at ~δ5 confirmed co-esterification of MA with IA and mutual esterification of MA. No terminal hydroxyl was determined in the polymer revealed that the MA arms were composed of carboxyl groups essentially. More information about the linkages between MA-MA moieties could be determined based on ^{1}H-NMR spectra as shown in Figure 6-3. The incorporation of IA in the system was not imposing substantial alteration in the sequence of MA-MA linkage. The relative intensity of integral originated from α-type MA moieties at δ5.4 and the integral originated from ß-type MA moieties at δ5.2 essentially conformed to the literature [55]–[58].

Melting temperature of IA (~162°C) used in the study is essentially higher than that of MA (~132°C). The dominant reaction path would be considered as a melt of IA solubilised in the pre-polymer of MA [59]. On one hand, MA undergoes homo-polycondensation to form linear α,ß-oligomers. On the other hand, hydroxyl of MA could react with carboxyls of IA. Overall, PMA-IA(10) comprised of vinyl moiety with the linear α,ß-PMA branches growing from the two ends of IA.

Thermal stability of vinyl PMA-IA was evaluated by TGA. The thermograms are presented in Figure 6-4. In general, the initial 5% percent weight losses were determined to be around 168˚C to 183˚C. Varying feed ratios (Figure 6-4a) or reaction temperatures (Figure 6-5b) did not impose a substantial change of thermal resistant power of the polymers. IA originally possesses low thermal stability. Generally speaking, polycondensation introduced additional COOH and OH groups slightly reduced the thermal resistant power of the polymer [60].



(TGA thermograms were measured under nitrogen atmosphere at a heating rate of 20°C/min)

Figure 6-4 TGA thermograms of PMA-IA composed of (a) various feed ratios and (b) polymerised at various temperatures.

6.3.2 Fabric Performance and Characterisation

PMA-IA(10) was selected and employed to investigate the efficacy this group of vinyl-functionalised PMA-IA polymers as cellulose cross-linkers. To afford easy-care cotton textiles, finishing parameters included the finishing formulation and the treatment condition are crucial factors in obtaining overall balanced properties of the modified textiles while attaining the designated functional performance [61], [62]. In this wrinkle-resistant finishing study, the concentration of cross-linker, acidity of the finishing solution, the concentration of catalyst, the concentration of additives, curing temperature and curing time were evaluated. Table 6-2 summarised the properties of cotton fabric modified with the newly developed vinyl-functionalised PMA-IA polymer.

Table 6-2 Summary of properties of cotton fabrics modified with vinyl-functionalised PMA-IA(10) under different finishing conditions

Fabric code	Variable	WRA (^{o}) [h]	Ft (N) [i]	Fb (N) [j]	WI [k]	YI [l]
control	---	161	5.23	234.51	62.235	5.783
Fabric code	[PMA-IA][a]	WRA (^{o}) [h]	Ft (N) [i]	Fb (N) [j]	WI [k]	YI [l]
IA-C1	5	197	4.51	165.57	61.654	6.140
IA-C2	10	222	4.90	170.40	61.805	6.180
IA-C3	15	236	4.60	150.20	60.194	6.386
IA-C4	20	242	3.82	151.81	56.716	6.913
Fabric code	pH[b]	WRA (^{o}) [h]	Ft (N) [i]	Fb (N) [j]	WI [k]	YI [l]
IA-A1	2	222	4.90	150.20	61.805	6.180
IA-A2	2.5	216	5.40	175.29	61.283	6.203
IA-A3	3	211	5.92	183.86	58.742	6.947
IA-A4	3.5	203	6.78	192.15	59.457	6.725

Fabric code	$[NaH_2PO_2]$[c]	WRA (^{o})[h]	Ft (N)[i]	Fb (N)[j]	WI[k]	YI[l]
IA-S1	0	213	4.37	128.59	53.158	8.697
IA-S2	2.5	227	4.75	162.01	60.053	6.630
IA-S3	5	232	5.06	177.16	61.277	6.171
IA-S4	10	223	4.90	150.20	61.805	6.180

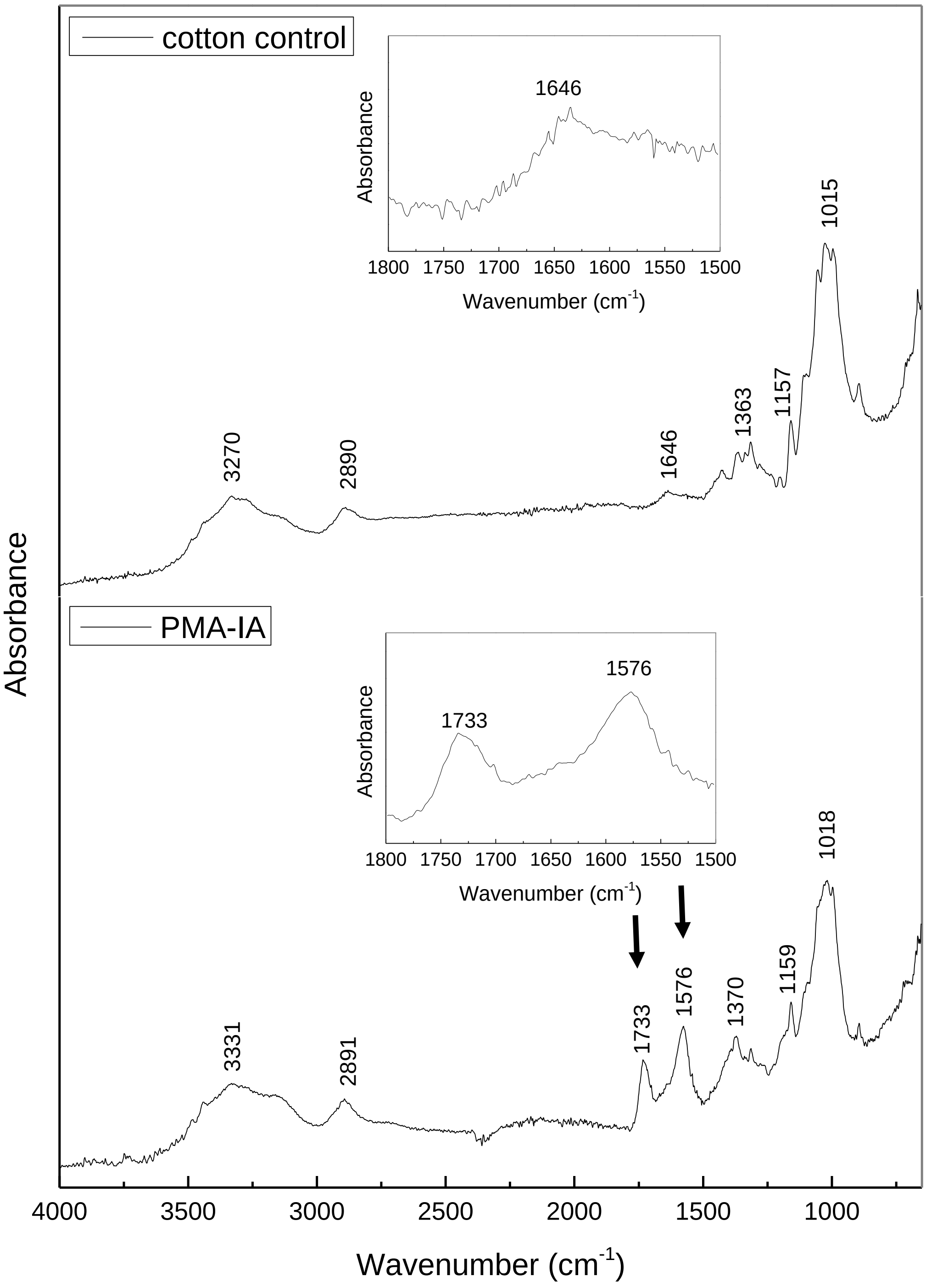
Fabric code	$[K_2S_2O_8]$[d]	WRA (^{o})[h]	Ft (N)[i]	Fb (N)[j]	WI[k]	YI[l]
IA-K1	0	232	5.06	177.16	61.277	6.171
IA-K2	1	244	4.12	150.22	61.805	6.182
IA-K3	2	238	2.61	160.48	55.308	8.001

Fabric code	Time (min)	WRA (^{o})[h]	Ft (N)[i]	Fb (N)[j]	WI[k]	YI[l]
IA-T1[e]	1.5	179	6.21	209.20	64.120	5.522
IA-T2[e]	3	194	6.63	192.63	62.936	5.826
IA-T3[e]	4.5	186	6.54	181.46	61.586	6.136
IA-T4[f]	1.5	188	6.51	172.61	63.166	5.794
IA-T5[f]	3	201	6.28	181.24	61.698	6.139
IA-T6[f]	4.5	210	5.66	170.44	61.857	6.160
IA-T7[g]	1.5	214	6.51	164.64	62.090	6.066
IA-T8[g]	3	232	6.28	177.16	61.568	6.321
IA-T9[g]	4.5	238	5.66	150.50	59.921	6.626

[a] fabrics impregnated with finishing bath of pH2, comprised of designated amount of PMA-IA(10) coupling with 10w/w% NaH_2PO_2 and cured at 170^{o}C for 3min; [b] fabrics impregnated with finishing bath designated acidity, comprised of 10 w/w% PMA-IA(10) coupling with 10w/w% NaH_2PO_2 cured at 170^{o}C for 3min [c] fabrics impregnated with finishing bath of pH2, comprised of designated amount of NaH_2PO_2 coupling with 10 w/w% PMA-IA(10) cured at 170^{o}C for 3min [d] fabrics impregnated with the finishing bath of pH2, comprised of designated amount of $K_2S_2O_8$ coupling with 10 w/w% PMA-IA(10), 5w/w% NaH_2PO_2 cured at 170^{o}C for 3min [e] fabrics impregnated with finishing bath of pH2, comprised of w/w% PMA-IA(10), 5w/w% NaH_2PO_2 at designated time at 130 ^{o}C , [f] 150 ^{o}C and [g] 170 ^{o}C [h] WRA = averaged sum of wrinkle recovery angles in warp and weft of cotton fabrics in accordance with AATCC 66-2008. [i] Ft = average of tearing force in warp and weft of cotton fabrics in accordance with ASTM D1424-2009. [j] Fb = average of breaking force in warp and weft of cotton fabrics in accordance with ASTM D5034-2009. [k] WI = whiteness index measured in accordance with AATCC 110-2005. [l] YI = yellowness index measured in accordance with ASTM E313-2010.

6.3.2.1 FTIR-ATR Characterisation of Modified Cotton

The formation of ester cross-links of the cotton impregnated and cured with PMA-IA polymer was revealed based on FTIR-ATR with the post-treatment of NaOH solution [36], [38], [39], [63]–[66]. Upon wrinkle-resistant finishing treatment with PMA-IA, additional ester carbonyls (1723cm^{-1}) and carboxylates (1575cm^{-1}) were detected on the modified cotton fabrics as shown in Figure 6-5. No other new functionalities were determined from the FTIR spectra of the modified fabric samples. Esterification using poly(carboxylic acid) for cross-linking unavoidably retains certain amount of carboxyls on the fabrics. The residue peak of carboxylates explained the phenomenon that the loss in mechanical strengths of the cotton fabrics was mainly induced by acid-catalysed depolymerisation of cellulose fibres. FTIR-ATR characterisation in relation to fabric properties and performance will be discussed with respect to the finishing parameters in the next section.



(Cotton fabric impregnated with the finishing solution of pH2, comprised of 10w/w% PMA-IA(10) coupling with 5w/w% NaH_2PO_2 and 1w/w% Triton X-100 was subjected to curing at 170^{o}C to 3min.)

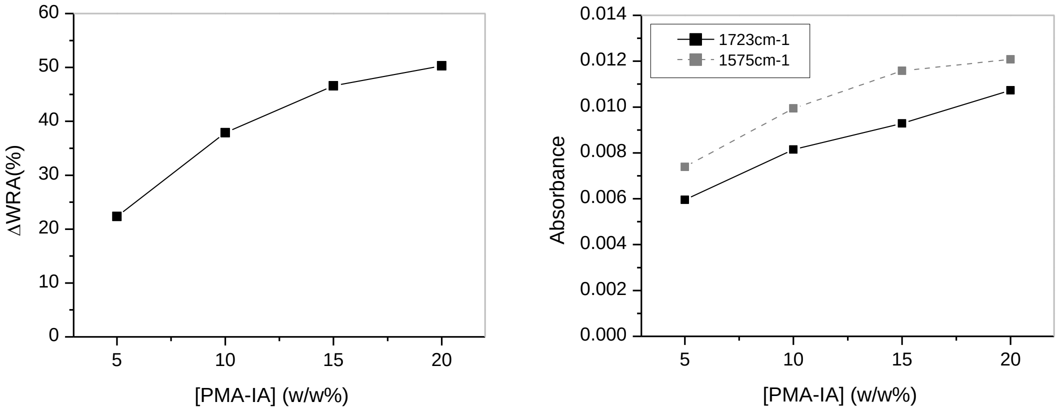
Figure 6-5 Characteristic FTIR-ATR spectra of the control cotton fabric (top) and the fabric modified with PMA-IA(10) (bottom)

6.3.2.2 Effect of Variables on Cross-linking

The degree of cross-linking governs the extent of wrinkle recovery performance of the modified fabrics. The effectiveness of wrinkle recovery performance of modified fabrics was evaluated and compared to the performance of plain cotton fabric. The effectiveness was expressed in terms of ∆WRA in relation to the finishing parameters included the concentration of cross-linker (5w/w% to 20w/w%), acidity of the finishing solution (pH 2 to 3.5), the concentration of catalyst (2.5w/w% to 10w/w%), the concentration of additive (0w/w% to 2w/w%), curing temperature (130°C to 170°C) and curing time (1.5min to 4.5min) were evaluated.

6.3.2.2.1 Effect of Concentration of Cross-linker

Increasing percent of cross-linker available in the finishing bath would enhance the probability of cross-linking reaction between COOH of PMA-IA with OH of cellulose molecules. FTIR analysis also reflected the degree of cross-linking via esterification [67]. As presented in Figure 6-6, increasing PMA-IA concentration in finishing solutions promoted wrinkle recovery performance of the cotton fabrics. The increment in ∆WRA was promoted from 22% to 50% approaching a linear relationship with respect to the increase in concentration of PMA-IA from 5w/w% to 20w/w%. The growth of ester carbonyls at 1723cm^{-1} mirrored the upward trend of ∆WRA with the concentration of PMA-IA in parallel as illustrated in the figure.



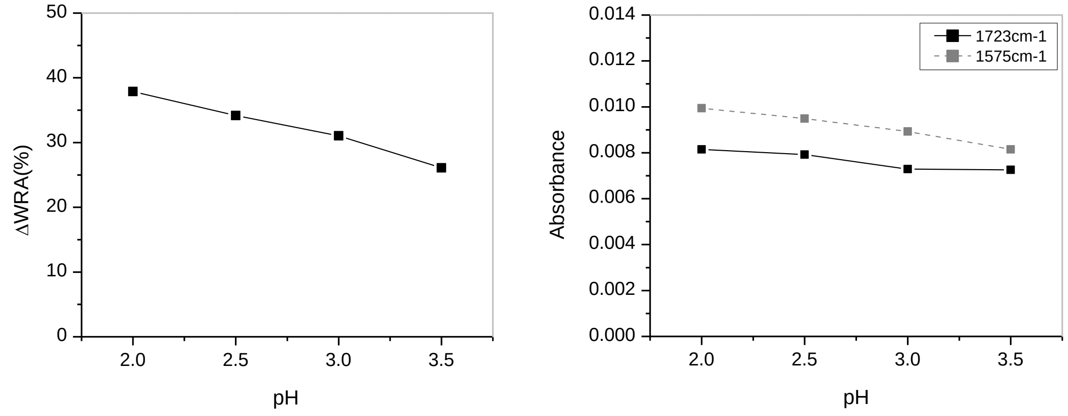
(Cotton fabrics impregnated with the finishing bath of pH2, comprised of the designated amount of PMA-IA(10) coupling with 10w/w% NaH_2PO_2 and 1w/w% Triton X-100 were subjected to curing at 170°C for 3min.)

Figure 6-6 Effect of concentration of PMA-IA on cellulose cross-linking

6.3.2.2.2 Effect of Acidity of Finishing Bath

The polycarboxylic acid based cross-linkers impart wrinkle-resistant property to the cellulosic textiles by means of esterification between carboxyls (COOH) of the cross-linker with the hydroxyl (OH) groups of cellulose via the formation of cyclic anhydride intermediate. Acidity of the finishing solution influences the formation of the anhydride intermediate [37]. Proton concentration essentially affects the dissociation of COOH into COO^- in aqueous medium. In the part of the evaluation, pH of finishing bath comprised of 10w/w% PMA-IA with 5w/w% NaH_2PO_2 was 2. NaOH was use to adjust the pH of the finishing bath to 2.5 to 3.5 to evaluate the effect of acidity of the bath in relation to the resultant wrinkle-resistant performance of the fabric substrate.

Low pH could assist the retention of concentration of COOH during esterification of cotton cellulose. When solution pH was as low as 2, ΔWRA afforded a considerable improvement of approximately 40%. Adjusting pH to above 2 would reduce the cross-linking efficacy as illustrated in Figure 6-7. Certain portion of COOH was converted as COO^- during pH adjustment losing the ability for cross-linking cellulose. Hence, the ΔWRA dropped about 14% constantly with respect to reducing acidity in the finishing bath as illustrated in the figure. The amount of ester carbonyl (1723cm^{-1}) on the modified cotton fabrics determined by FTIR analysis complied with the trend of ΔWRA with respect to variation in pH.



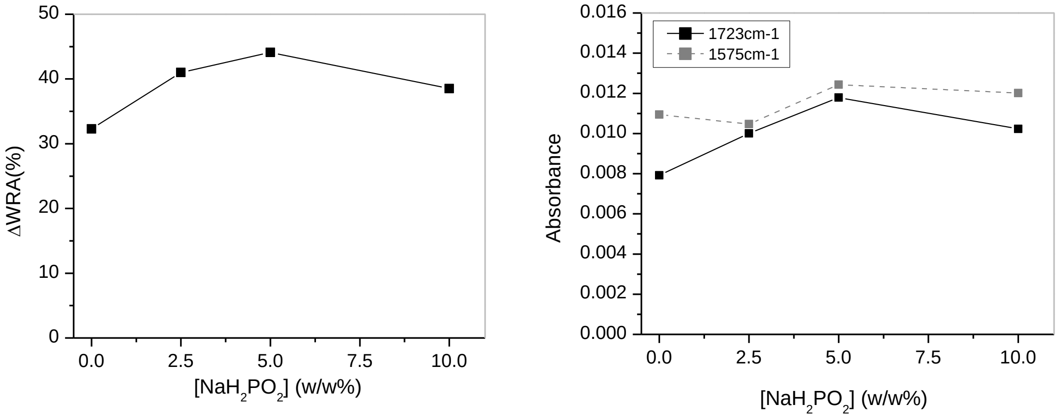
(Cotton fabrics impregnated with the finishing bath of designated acidity, comprised of 10 w/w% PMA-IA(10) coupling with 10w/w% NaH_2PO_2 and 1w/w% Triton X-100 were subjected to curing at 170^{o}C for 3min.)

Figure 6-7 Effect of acidity of finishing bath on cellulose cross-linking

6.3.2.2.3 Effect of Concentration of Catalyst

NaH_2PO_2 is one of the attributes determining the cross-linking efficiency coupling poly(carboxylic acid) based cross-linkers in the wrinkle-resistant finishing for cellulosic textiles. NaH_2PO_2 is suggested to be the most promising catalyst in the cross-linking reaction of cellulose with polycarboxylic acids via the formation of cyclic anhydride intermediates [37], [40], [41], [68]. The dose of NaH_2PO_2 in relation to wrinkle recovery performance of the cotton fabrics modified with PMA-IA cross-linker was illustrated in Figure 6-8. Without the inclusion of NaH_2PO_2, certain degree of esterification was found to be feasible under the finishing condition adopted at a curing temperature of 170°C for 3 min. ΔWRA achieved 32%. The esterification was postulated to proceed solely via dehydration [40]. When the finishing bath comprised of 5w/w% of NaH_2PO_2, ΔWRA achieved a local maximum of 44% of improvement.

Further increase in NaH_2PO_2 concentration could not afford additional improvement in terms of wrinkle-resistant performance. The ΔWRA diminished to 39% when 10w/w% of NaH_2PO_2 included in the finishing bath. Meanwhile, a high concentration of NaH_2PO_2 deteriorated the mechanical strength. Recent research revealed the complexity of poly(carboxylic acid)– NaH_2PO_2 system. NaH_2PO_2 may not solely catalyse the anhydride formation. NaH_2PO_2 may possibly react with anhydride intermediate to form acylphosphinates in thermal treatment with polycarboxylic acid cross-linkers. The catalytic efficiency may be diminished [22]. The FTIR data determined a slight reduction in both carboxyls and carboxylates detected on the modified cotton fabrics by FTIR as illustrated in Figure 6-8. The cross-linking reaction could not be further promoted with the increasing NaH_2PO_2. Up to the present stage, small amount of NaH_2PO_2 added into the system was found to be sufficient to help improving wrinkle-resistant performance.



(Cotton fabrics impregnated with the finishing bath of pH2, comprised of the designated amount of NaH_2PO_2 coupling with 10 w/w% PMA-IA(10) and 1w/w% Triton X-100 were subjected to curing at 170^oC for 3min.)

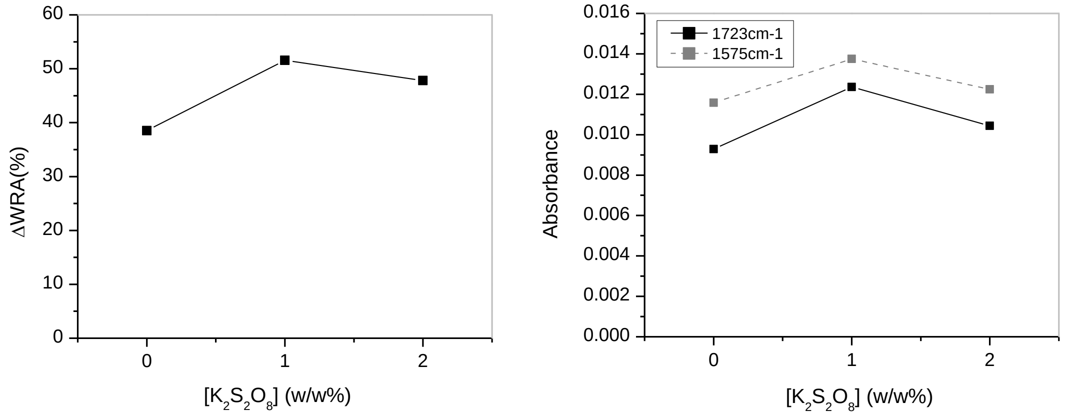
Figure 6-8 Effect of the concentration of catalyst on cellulose cross-linking

6.3.2.2.4 Effect of Inclusion of Additives

Yang's group [4], [10], [13] suggested polymerisation of vinyl moieties could afford poly-functional cross-linkers for modifying cellulosic fabrics. A combination of NaH_2PO_2 and $K_2S_2O_8$ was suggested to be effective to impart wrinkle recovery property to cotton fabrics using unsaturated dicarboxylic acids as cellulosic cross-linkers. IA with vinyl moiety was capable of polymerising in the presence of NaH_2PO_2 and $K_2S_2O_8$ in aqueous medium. $K_2S_2O_8$ serves as the free radical initiator. PMA-IA cross-linker possessed a vinyl moiety was adopted in this finishing study. In this study, 1w/w% and 2w/w% of $K_2S_2O_8$ were used to evaluate the effect of the presence of vinyl moiety in the PMA-IA cross-linker. When 1w/w% of $K_2S_2O_8$ was added into the finishing system, ΔWRA was further promoted up to approximately 50% as shown in Figure 6-9. Meanwhile, no C=C residue of IA at $1645cm^{-1}$ was detected on modified fabrics by FTIR-

ATR analysis (Figure 6-5). This indicated that PMA-IA with the vinyl moieties were reacted and could impart additional wrinkle recovery property on the modified cotton fabrics [8], [10], [69].

$K_2S_2O_8$ is not only an effective radical initiator for unsaturated dicarboxylic acids, but also is competent to generate cellulose radicals via oxidative hydrogen abstraction. Common oxidative pathways would act on hydroxyls of cellulose. Via this pathway, vinyl moiety of PMA-IA was suggested to react with the cellulose macroradicals to impart wrinkle-resistance to the cotton fabrics lead to the significant increase in ΔWRA [8], [70]. However, the improvement in WRA did not proportionally promoted with the amount of $K_2S_2O_8$ added into the finishing bath. $K_2S_2O_8$ may also attack C-C linkages between C2 and C3 or C3 and C4 of the glucopyranose leading to oxidative hydrolysis of cellulose chains into shorter fragments [71], [72]. Such type of interaction between $K_2S_2O_8$ with cotton cellulose would impart negative impact on the wrinkle recovery performance. Oxidative depolymerisation would provoke severe loss in fibre tenacity. Crease recovery work significantly diminished would reduce the recovery ability of the fibres upon external stress or bending [73], [74]. Hence, a small dose of $K_2S_2O_8$ in the finishing bath was found to be more appropriate for the finishing system with PMA-IA in the present study to achieve further improvement in WRA.



(Cotton fabrics impregnated with the finishing bath of pH2, comprised of the designated amount of $K_2S_2O_8$ coupling with 10 w/w% PMA-IA(10), 5w/w% NaH_2PO_2 and 1w/w% Triton X-100 were subjected to curing at 170^{o}C for 3min.)

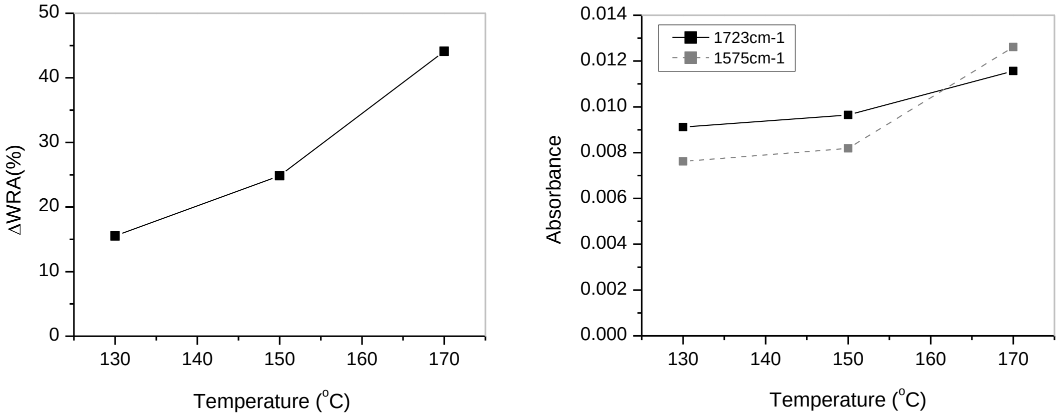
Figure 6-9 Effect of inclusion of additive on cellulose cross-linking

6.3.2.2.5 Effect of Curing Temperature and Time

When furnishing cotton substrate with wrinkle-resistant properties, curing temperature and time are the two major operation parameters to control in the finishing treatment. These two parameters control the rate of esterification between PMA-IA and cellulose chains in the presence of catalyst, and hence determine the degree of cross-linking. As illustrated in Figure 6-10 and 6-11, increasing curing temperature and time promoted wrinkle-resistant performance of the modified cotton fabrics. Wrinkle recovery performance of modified cotton fabrics was temperature dependent. In the range of temperature employed, all of them were capable of imparting wrinkle-resistant property to the cotton substrate. Curing temperature plays a vital role in the catalytic esterification with NaH_2PO_2. Literature reported that the catalytic reaction is favourable at temperature over 160˚C in general [12], [22], [40]. Elevating curing temperature assists to activate the esterification of cellulose with NaH_2PO_2 via the formation of cyclic anhydride.

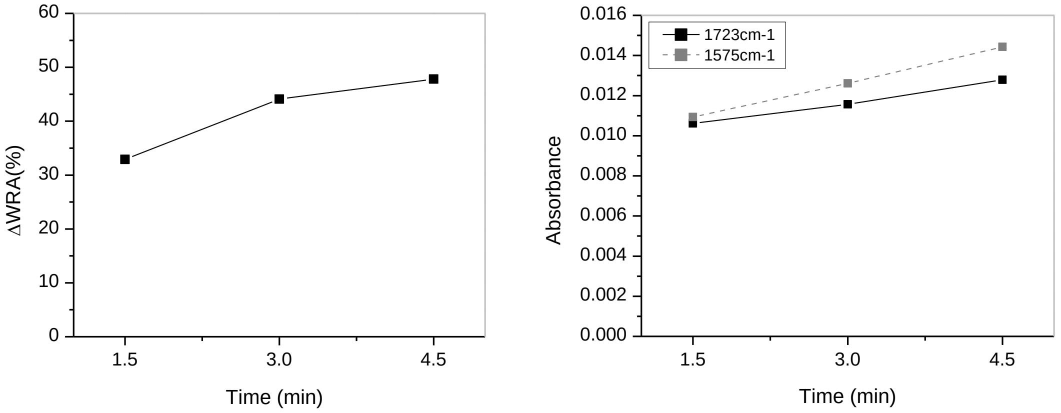
The effect of curing temperature on cellulose cross-linking was presented in Figure 6-10 taking at the typical curing time of 3min as an example. Ester carbonyls detected on modified fabrics by FTIR-ATR was the highest among the curing temperature studied. The intensity of ester carbonyl increased significantly in relation to curing temperature complied with the literatures. The temperature exhibited a crucial role in the catalytic esterification with NaH_2PO_2 at 170˚C. When curing temperature was reduced to below 170˚C, the formation of cross-links was comparatively less effective. Particularly at 130˚C, ∆WRA slightly improved by approximately 16% in the range of curing times studied. Under such condition, PMA-IA was postulated to impart wrinkle-resistant property to the fabric via dehydration. Absorbance of ester carbonyls detected on modified fabrics by FTIR was the lowest among the curing temperature studied. In all curing temperatures studied, the physicochemical properties of cotton fabrics exhibited similar trend in relation to curing time.

The effect of curing time on cellulose cross-linking was presented in Figure 6-11 at 170˚C as an example. When the curing temperature at 170˚C, ∆WRA improvement of the modified fabrics was more prominent, ranging from 37% to 48% in the curing time, 1.5min to 4.5min studied as shown in Figure 6-11. Wrinkle recovery performance of modified cotton fabrics was time dependent. Lengthened curing time would allow more time for interaction between reactive carboxyls of PMA-IA cross-linker and hydroxyls of cotton cellulose. In all curing time evaluated in the present study, modifying the cotton substrates for 1.5min was capable of rendering certain degree of improvement in ΔWRA. In significant, the increment in WRA was capable of exceeding 35% at 170°C within 1.5min curing time. As presented in Figure 6-11, the absorbance of ester carbonyls at 1723cm^{-1} was growing with increasing curing time from 1.5min to 4.5min. Prolonged curing time for 4.5min always imparted the most brilliant wrinkle recovery property as shown in Figure 6-11. Additional increment in ΔWRA usually could be rendered under elevated curing temperature and prolonged curing time at the expenses of deteriorated mechanical strength.



(Cotton fabrics impregnated with the finishing bath of pH2, comprised of w/w% PMA-IA(10), 5w/w% NaH_2PO_2 and 1w/w% Triton X-100 were subjected to curing at designated temperature for 3min.)

Figure 6-10 Effect of curing temperature on cellulose cross-linking



(Cotton fabrics impregnated with the finishing bath of pH2, comprised of w/w% PMA-IA(10), 5w/w% NaH_2PO_2 and 1w/w% Triton X-100 were subjected to curing at 170^{o}C for the designated treatment time.)

Figure 6-11 Effect of curing time on cellulose cross-linking

6.3.2.3 Effect of Variables on Mechanical Strength of Modified Cotton

The alteration in mechanical properties of modified cotton fabrics was evaluated and compared to the performance of plain cotton fabrics. The alteration was expressed in terms of change in tearing force and breaking force (ΔFt and ΔFb) in relation to the finishing parameters included the concentration of cross-linker, acidity of the finishing solution, the concentration of catalyst, the concentration of additives, curing temperature and curing time as presented in Figure 6-12. Wrinkle-resistant finishing imparts physicochemical alteration to the cellulosic materials. Incorporation of additional cross-links between fibres and substrate degradation resulted in deterioration in mechanical properties of the substrate [65], [66]. Cross-links formed in between fibres reduce flexibility and hindered movement of fibres upon external stress. Thus, increased interaction between fibres reduces the tearing force and breaking force of the fabric. Cellulose inherently is susceptible to acid-catalysed hydrolysis. Depolymerisation of cellulose reduces fibre tenacity resulted in reduction in mechanical strength of the fibres and fabrics.

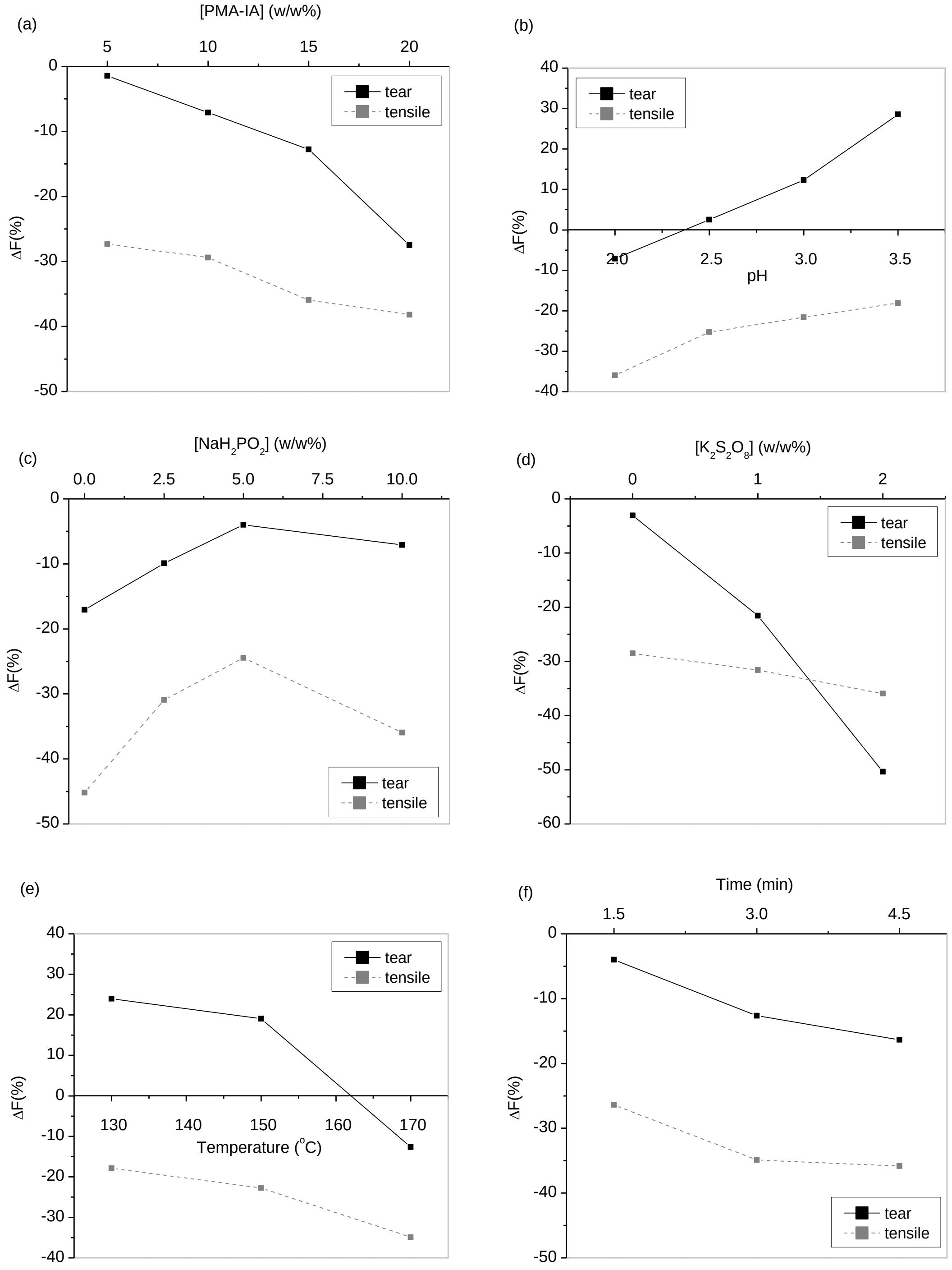


Figure 6-12 Effect of finishing variables on mechanical strength of the modified cotton (variables included a) concentration of cross-linker, b) acidity of finishing bath, c) concentration of catalyst, d) inclusion of additives, e) curing temperature and f) curing time).

6.3.2.3.1 Effect of Concentration of Cross-linker

To impart wrinkle-resistant property to cellulosic fabrics, a novel poly(carboxylic acid) PMA-IA was designed and prepared for the finishing study. Various concentration of PMA-IA was adopted to study the interaction between the cross-linker and the cellulosic substrate. FTIR-ATR provided spectroscopic information concerning the alteration of mechanical properties of the fabrics as illustrated in Figure 6-6. The absorbance at 1723cm^{-1} originated from ester carbonyls was proportionally increased with PMA-IA concentration in the finishing bath. The degree of cross-linking processed progressively. Hence, frictional force between cross-linked fibres increased. Simultaneously, more residue carboxylate (1575cm^{-1}) detected on the substrates with respect to the increasing concentration of PMA-IA. PMA-IA catalysed the degradation of fabric substrate was promoted with the inclusion of the acidic cross-linker. Combing the effect of the two factors, ΔFt and ΔFb were reduced by 7% to 26% and 27% to 38% respectively according to Figure 6-12a. On the whole, both properties exhibited decreasing trends with respect to the range of PMA-IA concentration employed. In particular, when the finishing solution contained 10w/w% PMA-IA, the overall mechanical strength loss achieved a local minimum which was suggested as an equilibrium point of cross-linking and depolymerisation of cotton cellulose.

6.3.2.3.2 Effect of Acidity of Finishing Bath

When utilising poly(carboxylic acid) as a cross-linker in wrinkle-resistant finishing, mechanical properties of cellulosic fabrics are unavoidably deteriorated. Acidity is the prime attribute to the cellulose hydrolysis. ß-1,4-glycosidic linkages between glucoses of cellulose would be cleaved upon hydrolysis [66], [75]–[78]. Thus, mechanical properties of the fabric substrate deteriorated upon reduced degree of polymerisation and crystallinity of cellulose. As shown in Figure 6-7, a comparatively high concentration of carboxylates detected at 1575cm^{-1} on the cotton fabric impregnated with the finishing bath of pH 2. This implied that more carboxyls retained on the cross-linked surface when the fabric was modified under relatively acidic condition. Thus, mechanical strength loss was comparatively significant, ΔFt of -7% and ΔFb of -36% respectively as illustrated Figure 6-12b. Further raising pH to 2.5 to 3.5, the loss in mechanical strength was inhibited substantially. In particular, ΔFb was restrained to less than -18%. When the pH was larger than 2.5, cross-linking was less effective. Ester carbonyls determined on the modified fabrics were of lower intensity of 0.79A to 0.73A. Meanwhile, the carboxylate intensity at 1575cm^{-1} formed on the modified fabrics constantly decreased with the degree of cross-linking. Tuning the acidity of the finishing bath not only manipulates the cross-linking effectiveness of the substrate, but also governs the mechanical properties of the material [66].

6.3.2.3.3 Effect of Concentration of Catalyst

NaH_2PO_2 is determined to be the most promising catalyst in the cross-linking reaction of cellulose with polycarboxylic acids. In the finishing system, NaH_2PO_2 was adopted as the catalyst for the cross-linking cotton fabrics accordingly. As illustrated in Figure 6-8, without the inclusion of NaH_2PO_2, esterification was found to be feasible at 170°C curing temperature for 3min. ΔWRA achieved +32%. However, the fabric strength loss was determined to be the greatest without the inclusion of NaH_2PO_2. The absorbance at 1575cm^{-1} originated from carboxylates detected was significantly larger than that at 1723cm^{-1} from ester carbonyls the modified fabric as shown in Figure 6-8. NaH_2PO_2 facilitated carboxyls to form of cyclic anhydride intermediate reducing propensity of acid-catalysed depolymerisation of cotton cellulose [24], [42]. The experimental results indicated the essence of inclusion of NaH_2PO_2 in the system in retaining mechanical strength.

With respect to the range of NaH_2PO_2 concentration studied, the resulted wrinkle recovery performance and mechanical properties of the modified cotton fabrics exhibited a non-linear trend. When 5w/w% NaH_2PO_2 was added into the finishing bath, ΔWRA achieved a local maximum and mechanical strength retained comparatively superior as shown in Figure 6-12c. FTIR data indicated the degree of cross-links (1730 cm^{-1}) formed reached a maximum absorbance of 1.24A. Further increase NaH_2PO_2 concentration could not afford additional improvement in terms of wrinkle-resistant performance while imposed negative effect on the mechanical properties of the modified fabric. Meanwhile, a high dose of NaH_2PO_2 deteriorated the mechanical strength. When 10w/w% NaH_2PO_2 included in the finishing bath, ∆Fb was dropped significantly by 36%.

6.3.2.3.4 Effect of Inclusion of Additive

As presented and discussed in previous section, inclusion of small amount of $K_2S_2O_8$ could further enhance wrinkle recovery performance of the modified cotton fabrics. As shown in Figure 6-9, ∆WRA was further promoted up to approximately 50% when 1w/w% of $K_2S_2O_8$ was added into the finishing system. Meanwhile, the loss in mechanical strength was able to retain within 30% as illustrated in Figure 6-12d. However, excessive amount $K_2S_2O_8$ should not be added into the system. $K_2S_2O_8$ would be the additional attribute to the deterioration in mechanical strength upon the finishing treatment using PMA-IA. $K_2S_2O_8$ may also attack C-C linkages between C2 and C3 or C3 and C4 of the glucopyranose leading to oxidative hydrolysis of cellulose chains into shorter fragments via oxidative hydrolysis. $K_2S_2O_8$ would imposing detrimental effect on mechanical properties [8], [11], [71], [72]. Notably as shown in Figure 6-12d, ∆Ft was dramatically fallen to -50% when 2w/w% of $K_2S_2O_8$ was added. Appropriate control of the dose of $K_2S_2O_8$ employed in the finishing system is essential to furnish cotton fabric with better wrinkle recovery performance, at the same time, retaining a low level of strength loss.

6.3.2.3.5 Effect of Curing Temperature and Time

After impregnated the cotton fabrics with cross-linkers, curing step is the key to impart wrinkle-resistant to cellulosic fabrics in the finishing treatment. Curing temperature and time are the prime parameters in the finishing. As discussed in previous section, these two parameters control the degree of cross-linking and disrupt the mechanical properties of the fabric materials. The deterioration in mechanical properties was closely related to the curing temperature. An example was taken at 3min as presented in Figure 6-12e.

At the elevated curing temperature at 170˚C, cellulose cross-linking and depolymersation proceeded to the greatest extent among the curing temperature evaluated in this part of the study. Absorbance originated from both ester carbonyl and carboxylate reached the highest intensity as shown in the Figure 5-11. Consequently, ∆Ft and ∆Fb reduced to the most prominent extent at 170˚C as indicated in Figure 6-12e. When the temperature was set at 130˚C or 150˚C, mechanical strength of the modified fabrics was always capable of rendering certain degree of retention. Relative to ester carbonyls, a lower concentration of carboxylates was detected confirmed the minimum loss of mechanical strength of the substrate as discussed in Figure 5-11. Meanwhile, absorbance of carbonyls determined at 130˚C and 150˚C was unexpectedly higher than the absorbance originated from carboxylates.

The interaction between the reactive carboxyls of PMA-IA and hydroxyls of cellulose was time dependent. Among all curing temperatures adopted in this study, the effect with respect to curing time exhibited similar tendency on the mechanical properties of cotton fabrics, for example, at 170°C as shown in Figure 6-12f. Prolonged curing time facilitated the improvement in terms of WRA of the modified fabrics as present in Figure 6-11. On the contrary, lengthening the time imposed adverse effect on mechanical properties of the fabrics as illustrated in Figure 6-12f. The absorbance of ester carbonyl increased with curing time, yet the increment was only significant at 170˚C. In all curing time studied, from 1.5min to 4.5min, ∆Ft and ∆Fb of the modified fabrics reduced the most prominently at the elevated curing temperature at 170˚C. This indicated that curing time was a critical parameter for NaH_2PO_2 catalysed cross-linking reaction compared to cross-linking via dehydration. At 130˚C and 150˚C, the cross-linking reaction was suggested via dehydration [12], [22], [40].

Prolonged curing time up to 4.5min always imparted the most brilliant ∆WRA at all temperatures. However, lengthening the interaction between acidic PMA-IA cross-linker and cellulose molecules would boost irreversible depolymerisation of cellulose chains via hydrolysis leading to deteriorated fabric strength and serviceability [66], [75]–[78]. Curing time was suggested to confine as shortest as possible.

6.3.2.4 Comparison between Monomeric and Polymeric Cross-linkers

The novel low molecular weight vinyl-functionalised PMA-IA polymer was successfully prepared by bulk polycondensation in the presence of NaH_2PO_2. The effectiveness of the cross-linking reaction, and the resultant wrinkle-resistant performance and fabric properties of modified with monomeric MA and polymeric MA-based cross-linkers were summarised in Table 6-3.

Table 6-3 Comparison performance between monomeric MA and polymeric PMA cross-linkers [a]

Fabric code	Cross-linker	M_n x10^3 [b]	WRA (^{o}) [c]	Ft (N) [d]	Fb (N) [e]	WI [f]	YI [g]
control	---	---	161	5.27	234.51	62.335	5.783
MA-10	MA	0.134	224	4.57	162.11	62.404	5.863
MA-G5	PMA-G(9)	1.1	225	3.19	208.81	71.103	6.526
IA-T8	PMA-IA(10)	1.3	232	6.28	177.16	61.568	6.321
IA-K2	PMA-IA(10)	1.3	244	4.12	150.22	61.805	6.182

[a] All fabrics impregnated with finishing bath of pH2, comprised of 10w/w% cross-linker with 7w/w% NaH_2PO_2 and cured at 170^{o}C for 1.5min [b] M_n = no. average molecular weight of PCA estimated by GPC expressed in Da. [c] WRA = averaged sum of wrinkle recovery angles in warp and weft of cotton fabrics in accordance with AATCC 66-2008. [d] Ft = average of tearing force in warp and weft of cotton fabrics in accordance with ASTM D1424-2009. [e] Fb = average of breaking force in warp and weft of cotton fabrics in accordance with ASTM D5034-2009. [f] WI = whiteness index measured in accordance with AATCC 110-2005. [g] YI = yellowness index measured in accordance with ASTM E313-2010 .

Compared to monomeric MA and dendritic PMA-G, vinyl-functionalised PMA-IA was capable of imparting more brilliant improvement in wrinkle-recovery performance and retaining fabric strengths. Comparing the wrinkle-resistant performance of fabrics

IA-T8 and MA-G5, fabric cross-linked by PMA-IA exhibited a larger increment in ΔWRA by 4% and with better strength retention. PMA-IA is of comparatively linear in branching architecture compared to dendritic PMA-G. Similar as the case between dendritic PCA-T and PCA-PEG as presented in previous chapters, the cross-linker comprised of linear segments would facilitate the retention of fabric strengths.

The efficacy in incorporated vinyl moiety into the cross-linker was verified. Comparing the fabrics IA-T8 and IA-K2, the increment of ΔWRA could be further promoted by 8%. A small dose of $K_2S_2O_8$ added into the PMA-IA finishing system allowed further cross-links formed between the vinyl moieties of PMA-IA. However, PMA-IA would lead to relatively significant fabric yellowing compared to the control fabric. This is the major disadvantage for further improvement of the present system.

6.4 Conclusions

A novel PMA cross-linker with vinyl functionality was successfully prepared by one-step bulk polycondensation of MA and IA with the presence of NaH_2PO_2 under optimal condition. The vinyl moiety was detected in the PMA polymer with the utility of advanced analytical techniques. PMA-IA(10) with M_w of ~1.2 $\times10^3$ Da was adopted for sequential wrinkle-resistant finishing of cotton fabrics.

The interaction between the newly developed PMA-IA and cotton cellulose in relation to the finishing parameters has been extensively evaluated in this section of wrinkle-resistant finishing study. Inclusion of a small dose of $K_2S_2O_8$ was capable of promoting wrinkle recovery performance of the fabric substrate by further polymerisation at the vinyl group of the PMA-IA cross-linker. PMA-IA-NaH_2PO_2 would be a prospective system with the improved balance of wrinkle-resistant performance and mechanical properties of the cellulosic substrate.

6.5 Bibliography

[1] L. Wei, J. Wang, H. Zhou, W. Jin, Z. Hu, and J. Ni, “Directional breeding of high itaconic acid yielding strain of Aspergillus terreus with a new plate technique,” *Adv. Microbiol.*, vol. 3, pp. 376–381, 2013.

[2] K. J. Yoon, J. H. Woo, and Y. S. Seo, “Formaldehyde free cross-linking agents based on maleic anhydride copolymers,” *Fibers Polym.*, vol. 4, no. 4, pp. 182–187, 2003.

[3] C. Q. Yang and Y. Lu, “In-situ polymerization of maleic acid and itaconic acid on cotton: MALDI/TOF mass spectroscopy and light-scattering study,” *Text. Res. J.*, vol. 70, no. 4, pp. 359–362, 2000.

[4] C. Q. Yang and Y. Lu, “In-situ polymerization of maleic acid and itaconic acid and crosslinking of cotton fabric,” *Text. Res. J.*, vol. 69, no. 10, pp. 782–789, 1999.

[5] H. Peng, C. Q. Yang, X. Wang, and S. Wang, “The combination of itaconic acid and sodium hypophosphite as a new cross-linking system for cotton,” *Ind. Eng. Chem. Res.*, vol. 51, no. 35, pp. 11301–11311, 2012.

[6] H. Peng, C. Q. Yang, and S. Wang, “Nonformaldehyde durable press finishing of cotton fabrics using the combination of maleic acid and sodium hypophosphite,” *Carbohydr. Polym.*, vol. 87, no. 1, pp. 491–499, 2012.

[7] Z. Mao and C. Q. Yang, “Polymeric multifunctional carboxylic acids as crosslinking agents for cotton cellulose: poly(itaconic acid) andin situ polymerization of itaconic acid,” J. *Appl. Polym. Sci.,* vol. 79, no. 2, pp. 319–326, 2001.

[8] D. Chen, C. Q. Yang, and X. Qiu, “Aqueous polymerization of maleic acid and cross-linking of cotton cellulose by poly(maleic acid),” *Ind. Eng. Chem. Res.*, vol. 44, pp. 7921–7927, 2005.

[9] H. Choi, “Nonformaldehyde polymerization-crosslinking treatment of cotton fabrics for improved strength retention,” *Text. Res. J.*, vol. 62, no. 10, pp. 614–618, 1992.

[10] C. Q. Yang and X. Gu, “Polymerization of maleic acid and itaconic acid studied by FT-Raman spectroscopy,” *J. Appl. Polym. Sci.*, vol. 81, pp. 223–228, 2001.

[11] C. Q. Yang, C. Hu, and G. C. Lickfield, “Crosslinking cotton with poly(itaconic acid) and in situ polymerization of itaconic acid : fabric mechanical strength retention,” *J. Appl. Polym. Sci.*, vol. 87, pp. 2023–2030, 2003.

[12] C. Q. Yang, Q. He, and B. Voncina, “Cross-linking cotton cellulose by the combination of maleic acid and sodium hypophosphite. 2. fabric fire performance,” *Ind. Eng. Chem. Res.*, vol. 50, no. 10, pp. 5889–5897, 2011.

[13] C. Q. Yang, X. Wang, and Y. Lu, “Infrared spectroscopy studies of cyclic anhydrides as intermediates for ester crosslinking of cotton cellulose by polycarboxylic acids. IV. In situ free radical copolymerization of maleic acid and itaconic acid on cotton,” *J. Appl. Polym. Sci.*, vol. 75, no. 2, pp. 327–336, Jan. 2000.

[14] P. Ghosh and D. Das, “Modification of cotton by acrylic acid (AA) in the presence of NaH_2O_4 and $K_2S_2O_8$ as catalysts under thermal treatment,” *Eur. Polym. J.*, vol. 36, pp. 2505–2511, 2000.

[15] B.-H. Kim, J. Jang, and S.-W. Ko, “Durable press finish of cotton fabric using malic acid as a crosslinker,” *Fibers Polym.*, vol. 1, no. 2, pp. 116–121, 2000.

[16] B. A. K. Andrews, “Wrinkle-resistant cotton and formaldehyde release,” *Colourage,* vol. 41, no. 10, pp. 87–93, 1995.

[17] T. F. Cooke and H. D. Weigmann, “The chemistry of formaldehyde release from durable press fabrics,” *Text. Chem. Color*., vol. 14, no. 5, pp. 100/25–106/31, 1982.

[18] T. F. Cooke and H. D. Weigmann, “The chemistry of formaldehyde release from durable press fabrics-part 2,” *Text. Chem. Color*., vol. 14, no. 6, pp. 136/33–144/41, 1982.

[19] A. C. De Groot and H. I. Maibach, “Does allergic contact dermatitis from formaldehyde in clothes treated with durable-press chemical finishes exist in the USA?,” *Contact Dermatitis*, vol. 62, pp. 127–136, 2010.

[20] S. Varadarajan and N. Bhattacharyya, “Eco-textiles regulations, labels, processing, and testing,” 1996.

[21] B. A. K. Andrews and B. J. Collier, “Finishing additives in treatments of cotton fabrics for durable press with polycarboxylic acids,” Ind. Eng. Chem. Res., vol. 31, no. 8, pp. 1981–1984, 1992.

[22] C. E. Morris, N. M. Morris, and B. J. Trask-morrell, “Interaction of meso-1,2,3,4-butanetetracarboxylic acid with phosphorus-containing catalysts for esterification cross-linking of cellulose,” *Ind. Eng. Chem. Res*., vol. 35, no. 3, pp. 950–953, 1996.

[23] C. M. Welch, “Tetracarboxylic acids as formaldehyde-free durable press finishing agents,” *Text. Res. J.,* vol. 58, no. 8, pp. 480–486, 1988.

[24] C. M. Welch and B. A. K. Andrews, “Ester crosslinks: a route to high performance non-formaldehyde finishing of cotton,” *Text. Chem. Color*., vol. 21, no. 2, pp. 13–17, 1989.

[25] C. M. Welch and G. J. Peters, “Mixed polycarboxylic acids and mixed catalyst in formaldehyde-free durable press finishing,” *Text. Chem. Color.*, vol. 29, no. 3, pp. 22–27, 1997.

[26] C. Q. Yang, X. Wang, and I.-S. Kang, “Ester crosslinking of cotton fabric by polymeric carboxylic acids and citric acid,” *Text. Res. J.*, vol. 67, no. 5, pp. 334–342, 1997.

[27] H. Song and S. Y. Lee, “Production of succinic acid by bacterial fermentation*,” Enzyme Microb. Technol.*, vol. 39, pp. 352–361, 2006.

[28] S. J. Lee, D.-Y. Lee, T. Y. Kim, and B. H. Kim, “Metabolic engineering of Escherichia coli for enhanced production of succinic acid, based on genome comparison and in silico gene knockout simulation,” *Appl. Environ. Microbiol.*, vol. 71, no. 12, pp. 7880–7887, 2005.

[29] S. Okino, R. Noburyu, M. Suda, T. Jojima, M. Inui, and H. Yukawa, “An efficient succinic acid production process in a metabolically engineered Corynebacterium glutamicum strain,” *Appl. Microbiol. Biotechnol.*, vol. 81, pp. 459–464, 2008.

[30] X. Wang, C. S. Gong, and G. T. Tsao, “L-Malic acid production from fumaric acid by a laboratory Saccharomyces cerevisiae strain SHY2,” *Biotechnol. Lett.,* vol. 18, no. 12, pp. 1441–1446, 1996.

[31] T. P. West, “Malic acid production from thin stillage by Aspergillus species,” *Biotechnol. Lett.,* vol. 33, no. 12, pp. 2463–2467, 2011.

[32] S. Y. Moon, S. H. Hong, T. Y. Kim, and S. Y. Lee, “Metabolic engineering of Escherichia coli for the production of malic acid,” *Biochem. Eng. J.,* vol. 40, pp. 312–320, 2008.

[33] T. Willke and K.-D. Vorlop, “Biotechnological production of itaconic acid,” *Appl. Microbiol. Biotechnol.*, vol. 56, no. 3–4, pp. 289–295, 2001.

[34] K. Yao and C. Tang, “Controlled polymerization of next-generation renewable monomers and beyond,” *Macromolecules,* vol. 46, no. 5, pp. 1689–1712, 2013.

[35] G. T. Tsao, N. J. Cao, J. Du, and C. S. Gong, “Production of multifunctional organic acids from renewable resources,” in *Advances in Biochemical Engineering and Biotechnology Volume 65: Recent Progress in Bioconversion of Lignocellulosics*, G. T. Tsao, Ed. Berlin: Springer Berlin Heidelberg, 1999, pp. 243–280.

[36] C. Q. Yang, “FT-IR spectroscopy study of the ester crosslinking mechanism of cotton cellulose,” *Text. Res. J.*, vol. 61, no. 8, pp. 433–440, 1991.

[37] C. Q. Yang, “Effect of pH on nonformaldehyde durable press finishing of cotton fabric: FT-IR Spectroscopy study: part II: formation of the anhydride intermediate,” *Text. Res. J.,* vol. 63, no. 12, pp. 706–711, 1993.

[38] C. Q. Yang and X. Wang, “Formation of cyclic anhydride intermediates and esterification of cotton cellulose by multifunctional carboxylic acids: an infrared spectroscopy study,” *Text. Res. J.*, vol. 66, no. 9, pp. 595–603, 1996.

[39] C. Q. Yang and X. Wang, “Infrared spectroscopy studies of the cyclic anhydride as the intermediate for the ester crosslinking of cotton cellulose by polycarboxylic acids. III. molecular weight of a crosslinking agent,” *J. Polym. Sci. Part A Polym. Chem.,* vol. 35, no. 3, pp. 557–564, 1997.

[40] E. L. Gillingham, D. M. Lewis, and B. Voncina, “An FTIR study of anhydride formation on heating butane tetracarboxylic acid in the presence of various catalysts,” *Text. Res. J.*, vol. 69, no. 12, pp. 949–955, 1999.

[41] X. Gu and C. Q. Yang, “FT-IR and FT-Raman spectroscopy study of the cyclic anhydride intermediates for esterification of cellulose: I. formation of anhydrides without a catalyst,” *Res. Chem. Intermed.*, vol. 24, no. 9, pp. 979–996, 1998.

[42] C. M. Welch and G. J. Peters, “Malic acid as a nonformaldehyde DP finishing agent activated by BTCA and polymer additives,” *Text. Chem. Color.,* vol. 29, no. 10, pp. 33–37, 1997.

[43] C. Q. Yang, “FTIR spectroscopy study of the formation of cyclic anhydride intermediates of polycarboxylic acids catalyzed by sodium hypophosphite,” *Text. Res. J.,* vol. 70, no. 1, pp. 64–70, 2000.

[44] R. A. T. M. Van Benthem, “Novel hyperbranched resins for coating applications,” *Prog. Org. Coatings,* vol. 40, no. 1–4, pp. 203–214, 2000.

[45] E. Malmström and A. Hult, “Hyperbranched polymers: a review,” *J. Macromol. Sci. Part C*, vol. 37, no. 3, pp. 555–579, 1997.

[46] W. J. Feast and N. M. Stainton, “Synthesis, structure and properties of some hyperbranched polyesters,” J*. Mater. Chem*., vol. 5, no. 3, pp. 405–411, 1995.

[47] J.-J. Max and C. Chapados, “Infrared spectroscopy of aqueous carboxylic acids: malic acid,” *J. Phys. Chem. A,* vol. 106, no. 27, pp. 6452–6461, 2002.

[48] H. Zhang, J. Cai, J. Dong, D. Zhang, L. Huang, Z. Xu, and P. Cen, “High-level production of poly(ß-L-malic acid) with a new isolated Aureobasidium pullulans strain,” *Appl. Microbiol. Biotechnol.,* vol. 92, no. 2, pp. 295–303, 2011.

[49] M. Nazi, R. M. A. Malek, and R. Kotek, “Modification of ß-cyclodextrin with itaconic acid and application of the new derivative to cotton fabrics,” *Carbohydr. Polym.,* vol. 88, no. 3, pp. 950–958, 2012.

[50] Y. Fan, Y. Fan, Y. Wang, and J. Ma, “Unexpected fluorescence emission of poly(α,ß-L-malic acid) in aqueous medium,” *J. Appl. Polym. Sci.,* vol. 106, pp. 1640–1647, 2007.

[51] L. Michlovská, L. Vojtová, L. Mravcová, and J. Jancár, “Thermogelling water solutions of multifunctional macromonomers based on PLGA-PEG-PLGA triblock copolymers,” *Challenges Mod. Technol*., vol. 2, no. 1, pp. 12–15, 2011.

[52] L. Michlovská, L. Vojtová, L. Mravcová, S. Hermanová, J. Kuerík, and J. Jancár, “Functionalization conditions of PLGA-PEG-PLGA copolymer with itaconic anhydride,” *Macromol. Symp.*, vol. 295, no. 1, pp. 119–124, 2010.

[53] J. W. Fischer, L. H. Merwin, and R. A. Nissan, “NMR investigation of the thermolysis of citric acid,” *Appl. Spectrosc.,* vol. 49, no. 1, pp. 120–126, 1995.

[54] T. Okuda, K. Ishimoto, H. Ohara, and S. Kobayashi, “Renewable biobased polymeric materials: facile synthesis of itaconic anhydride-based copolymers with poly(L-lactic acid) grafts,” *Macromolecules,* vol. 45, no. 10, pp. 4166–4174, 2012.

[55] T. Kajiyama, H. Kobayashi, T. Taguchi, Y. Komatsu, K. Kataoka, and J. Tanaka, “Study on the hydrolytic degradation of poly(α,ß-malic acid) by direct polycondensation,” *Mater. Sci. Eng. C,* vol. 24, no. 6–8, pp. 821–825, 2004.

[56] T. Kajiyama, H. Kobayashi, T. Taguchi, and K. Kataoka, “Improved synthesis with high yield and increased molecular weight of poly(α,ß-malic acid) by direct polycondensation,” *Biomacromolecules*, vol. 5, pp. 169–174, 2004.

[57] T. Kajiyama, T. Taguchi, H. Kobayashi, K. Kataoka, and J. Tanaka, “Synthesis of high molecular weight poly(α,ß-malic acid) for biomedical use by direct polycondensation,” *Polym. Degrad. Stab*., vol. 81, no. 3, pp. 525–530, 2003.

[58] N. Ohtani, Y. Kimura, and T. Kitao, “Preparation of poly(malic acid) and its ester derivatives by direct polycondensation of malic acid and ß-ethyl malate,” *Kobunshi Ronbunshu*, vol. 44, no. 9, pp. 701–709, 1987.

[59] E. Malmström and A. Hult, “Kinetics of formation of hyperbranched polyesters based on 2,2-bis(methylol)propionic acid,” *Macromolecules*, vol. 29, pp. 1222–1228, 1996.

[60] F. Wang, T. K. Bronich, A. V. Kabanov, R. D. Rauh, and J. Roovers, “Synthesis and evaluation of a star amphiphilic block copolymer from poly(epsilon-caprolactone) and poly(ethylene glycol) as a potential drug delivery carrier,” *Bioconjug. Chem.*, vol. 16, no. 2, pp. 397–405, 2005.

[61] P. Bajaj, “Finishing of textile materials,” *J. Appl. Polym. Sci.*, vol. 83, no. 3, pp. 631–659, 2002.

[62] W. D. Schindler and P. J. Hauser, “Easy-care and durable press finishes of cellulosics,” in *Chemical Finishing of Textiles*, Woodhead Publishing, 2004, pp. 51–72.

[63] N. Abidi, E. Hequet, C. Turner, and H. Sari-Sarraf, “FTIR analysis of crosslinked cotton fabric using a ZnSe-universal attenuated total reflectance,” *J. Appl. Polym. Sci.*, vol. 96, no. 2, pp. 392–399, Apr. 2005.

[64] C. Chung, M. Lee, and E. K. Choe, “Characterization of cotton fabric scouring by FT-IR ATR spectroscopy,” *Carbohydr. Polym.*, vol. 58, no. 4, pp. 417–420, 2004.

[65] C. Q. Yang, “Predicting the performance of durable press finished cotton fabric with infrared spectroscopy,” *Text. Res. J.*, vol. 69, no. 2, pp. 145–151, 1999.

[66] I. S. Kang, C. Q. Yang, and G. C. Lickfield, “Mechanical strength of durable press finished cotton fabrics: part I: effects of acid degradation and crosslinking of cellulose by polycarboxylic acids,” *Text. Res. J.*, vol. 68, no. 11, pp. 865–870, 1998.

[67] D. M. Lewis and B. Voncina, “Durable press finishing of cotton with polycarboxylic acids. II. ester crosslinking of cotton with dithiosuccinic acid derivative of S-triazine,” J. *Appl. Polym. Sci.*, vol. 66, pp. 171–177, 1997.

[68] C. Q. Yang and G. D. Bakshi, “Quantitative analysis of the nonformaldehyde durable press finish on cotton fabric: acid-base titration and infrared spectroscopy,” *Text. Res. J.*, vol. 66, no. 6, pp. 377–384, 1996.

[69] C. Q. Yang, W. Zhou, G. C. Lickfield, and K. Parachura, “Cellulase treatment of durable press finished cotton fabric: effects on fabric strength, abrasion resistance, and handle,” *Text. Res. J.*, vol. 73, no. 12, pp. 1057–1062, 2003.

[70] M. W. Sabaa and S. M. Mokhtar, “Chemically induced graft copolymerization of itaconic acid onto cellulose fibers,” Polym. Test., vol. 21, no. 3, pp. 337–343, 2002.

[71] B. Tosh and C. R. Routray, “Grafting of cellulose based materials : a review,” *Chem. Sci. Rev. Lett.*, vol. 3, no. 10, pp. 74–92, 2014.

[72] S. Liu and G. Sun, “Radical graft functional modification of cellulose with allyl monomers: Chemistry and structure characterization,” *Carbohydr. Polym.,* vol. 71, no. 4, pp. 614–625, 2008.

[73] G. S. Buck and F. A. McCord, “Crease-resistance and cotton,” *Text. Res. J.*, vol. 19, no. 4, pp. 216–247, 1949.

[74] F. Shi and Y. Wang, “Modelling crease recovery behaviour of woven fabrics,” *J. Text. Inst*., vol. 100, no. 3, pp. 218–222, 2009.

[75] R. D. Fagan, H. E. Grethlein, A. O. Converse, and A. Porteous, “Kinetics of the acid hydrolysis of cellulose found in paper refuse,” *Environ. Sci. Technol.*, vol. 5, no. 6, pp. 545–547, Jun. 1971.

[76] E. A. Immergut and B. G. Ranby, “Heterogeneous acid hydrolysis of native cellulose fibers,” *Ind. Eng. Chem.*, vol. 48, no. 7, pp. 1183–1189, 1956.

[77] N. S. Mosier, A. Sarikaya, C. M. Ladisch, and M. R. Ladisch, “Characterization of dicarboxylic acids for cellulose hydrolysis,” *Biotechnol. Prog.*, vol. 17, no. 3, pp. 474–480, 2001.

[78] J. F. Saeman, “Kinestics of wood saccharification: hydrolysis of cellulose and decomposition of sugars in dilute acid at high temperature,” *Ind. Eng. Chem. Res*., vol. 37, no. 1, pp. 43–52, 1945.

Chapter Seven – Conclusion and Recommendation

7.1 General Conclusion

In this project, two naturally available hydroxylcarboxylic acids, citric acid (CA) and malic acid (MA) were utilised as the basic building blocks in the development and study wrinkle-resistant finishing agents for cotton textiles based on polymer chemistry. Various structures of polymeric cross-linkers were developed. In the synthesis various branched polyols, included glycerol (G), 1,1,1-tris(hydroxymethyl)ethane (T), pentaerythritol (P) and dipentaerythritol (D) have been incorporated in the systems to develop dendritic cross-linkers. In particular, poly(ethylene glycol)s (PEGs) of various chain lengths included PEG200, PEG600 and PEG1000, were empolyed in developing linear-dendritic cross-linkers. Itaconic acid (IA) was adopted in developing polymeric cross-linkers with additional functionality. The molecular compositions and architectures of the polymers were revealed with the utility of advanced analytical techniques.

Newly developed low molecular weight dendritic polymers of polycitric acid (PCAs) and polymalic acid (PMAs) of various branching architectures were selected as the cross-linker in the wrinkle-resistant finishing of cotton fabrics. The effectiveness of the cross-linking reaction, and the resultant wrinkle-resistant performance and fabric properties were evaluated in correlation with the molecular size and architecture of the cross-linkers. On the whole, dendritic carboxyl-functionalised polymers of M_n less than

$2x10^3$Da were found to be effective cellulose cross-linkers. In the wrinkle-resistant finishing study, various variable parameters were also evaluated accordingly.

Both groups of dendritic polymers were efficacious in furnishing the cotton substrate with wrinkle-resistant properties. In particular, linear-dendritic PCAs presented the potential perspective of incorporating flexible polymeric moiety in the cross-linker catering to the strength retention purpose. Meanwhile, dendritic PMAs were component in whiteness retention in conjunction with appreciable enhancement in wrinkle-resistance of the fabric substrate. Carboxyl-functionalised polymers could further be modified with additional functionalities by inclusion of co-monomers in the synthesis system or incorporation of additives in the finishing bath. For the moment, vinyl moiety of IA present in the PMA cross-linker was confirmed to be efficacious for further polymerisation assisting retention in fabric strengths the presence of potassium persulfate as the radical initiator.

The present study would encourage further research and development of polymeric cross-linkers for cellulosic textile materials on the basis of naturally available monomers as an alternative of the conventional wrinkle-resistant finishing based on petrochemical-based poly(carboxylic acid)s.

7.1.1 Development and Study of Dendritic Polycitric Acid Cross-linkers

Three series of low molecular weight dendritic PCAs were successfully prepared by azeotropic polycondensation of CA and various branched polyols included T, P and D. The dendritic molecular compositions and architectures were revealed with the utility of advanced analytical techniques. Newly developed dendritic PCAs of various branching architectures with M_n ranging 1.6 x10 ^{3}Da to 4.5 x10^3 Da were adopted in the wrinkle-resistant finishing of cotton fabrics.

In the present study, the efficacy of dendritic PCA as cellulose cross-linker for cotton fabrics was verified. Bulkiness of the cross-linker was found to be a detrimental attribute not only to the resultant wrinkle recovery performance, but also the deterioration in fabric strength and imparting yellowness. In significance, utilising dendritic PCA-T with M_n less than 2 x10^3 Da was efficacious in imparting relatively superior wrinkle-resistant to cotton substrate, while assisted strengths and whiteness retention to the greatest extent.

7.1.2 Development and Study of Linear-dendritic Polycitric Acid Cross-linkers

A series of novel low molecular weight linear-dendritic PCA-PEGs cross-linkers of M_n ranging from 7.9 x10^2 Da to 2.7 x10^3 Da was successfully prepared by simple bulk polycondensation of CA and polymeric glycols. Polydispersity of the products were relatively low, ranging from 1.2 to 1.3. Linear-dendritic polymeric architecture was revealed with the utility of advanced analytical techniques. Newly developed PCA-PEG-PCA with various PEG spacer lengths were subjected to wrinkle-resistant finishing study.

In the present study, utilising linear-dendritic PCA-PEGs polymers as cellulose cross-linkers for plain woven cotton fabrics was capable of affording appreciable improvement in wrinkle recovery performance of the cotton substrate. In significance, increasing spacer length of the PCA-PEGs cross-linkers could assist retention in fabric strengths and fabric whiteness. Nevertheless, incorporation of additives such as BTCA and silicone softener could further balance the overall fabric performance.

7.1.3 Development and Study of Dendritic Polymalic Acid Cross-linkers

Four series of novel low molecular weight dendritic PMAs were successfully prepared by bulk polycondensation of MA with four branched polyols included G, T, P and D incorporated in the system. The dendritic molecular compositions and architectures were revealed with the utility of advanced analytical techniques. The dendritic PMAs of various branching architectures with M_n ranging 1 $x10^3$ Da to 3x 10^3 Da were adopted in the wrinkle-resistant finishing of cotton fabrics.

In the present study, utilising dendritic polymers in the series of PMA-G and PMA-T for cross-linking cotton cellulose were capable of affording the better WRA improvement while mitigating loss in overall strengths compared to bulkier series of PMA-P and PMA-D counter parts. In particular, PMA-G(9) was found to be the most effective cellulose cross-linker. PMA-G(9) was component to ameliorate strength retention to the largest extent while bestowing the most superior wrinkle recovery performance of the modified cotton textiles. Meanwhile, cotton textile modified with this dendritic PMA could attain minimum fabric yellowing.

7.1.4 Development and Study of Vinyl-functionalised Polymalic Acid Cross-linkers

A novel PMA cross-linker with vinyl functionality was successfully prepared by one-opt bulk polycondensation of MA and IA with the use of NaH_2PO_2 as the catalyst. The presence of additional vinyl moiety originated from IA was revealed with the utility of advanced analytical techniques PMA-IA(10) with M_w of ~1.2 $x10^3$Da was adopted for sequential wrinkle-resistant finishing of cotton fabrics.

The interaction between the newly developed PMA-IA and cotton cellulose in relation to the finishing parameters has been extensively evaluated in the present wrinkle-resistant finishing study. The utility of the vinyl group of PMA-IA with the inclusion of small dose of $K_2S_2O_8$ was capable of imparting positive effect on wrinkle recovery performance of the substrate. PMA-IA-NaH_2PO_2 would be a prospective system with the improved balance of wrinkle-resistant performance and mechanical properties of the cellulosic substrate. This part of the study impetus further modification of dendritic carboxyl-functionalised polymers catering to multi-purpose finishing.

7.2 Recommendation for Future Work

7.2.1 Development of Dendritic Cross-linkers

Scientific efforts towards the utilisation of renewable and sustainable resource have expanded tremendously in the last two decade, utility of sustainable cellulose cross-linkers are of the quest of customers and the industry [1-10]. The present work lays down the platform for the development of dendritic cross-linkers utilising naturally available hydroxylcarboxylic acids. Yet, the reactants were obtained from synthetic sources in the present study. Formaldehyde free, cost-effective and sustainable wrinkle-resistant finishing is still the goal to be achieved. In the future, acid monomers and polyols could be obtained or prepared from biomass fermentation. The whole development would be more sustainable.

For the moment, star shaped polyols were utilised in the development of dendritic cross-linkers. Polyols of other architectures could furnish and expand the scope of dendritic architectures of macromolecules. Sugar alcohols such as xylitol, sorbitol or mannitol could be used as the branching units in the future. The interaction between carboxyl-functionalised dendritic cross-linker and the textile substrates could further exploit.

Exploitation of incorporating additional functionalities to the dendritic cross-linkers is nurturing. Additional functionalities could expand the scope and capability for sequential applications. In present work, IA functionalised with vinyl and carboxyl has been explored in incorporating appended property to the cross-linker. For the moment, vinyl moiety of IA present in the PMA cross-linker was confirmed to be efficacious for further polymerisation assisting retention in fabric strengths. Other co-reactant(s) may be incorporated into the system to prepare dendritic polymer for the designated purposes in the future. Multi-functional finishing is burgeoning in textile industry [11-19]. Polyfunctional finishing agents are receiving attention.

Conventional thermal finishing treatment is commonly adopted approach in textile industry. Nevertheless, this kind of treatment would degradation of fabric substrates. Unavoidably, loss in strengths and yellowing of the fabrics would aggravate under elevated treatment temperatures. Incorporation of photoreactive functionalities could facilitate the development of photo-crosslinking of cotton textiles. Photo-crosslinking could abate deterioration in fabric performance after wrinkle-resistant finishing.

7.2.2 Application as Wrinkle-resistant Finishing Agent

In the present study, multi-functionalised cross-linker, the vinyl-functionalised PMA-IA was utilised in the wrinkle-resistant finishing treatment of cotton fabrics. In this case, radical initiator, $K_2S_2O_8$ was added into the treatment imparting additional cross-linking reactions between cellulose and the cross-linker. Imperfectly, $K_2S_2O_8$ would impart oxidative degradation of cellulosic substrate. Other radical initiator could be explored in the reaction of vinyl moieties.

Sodium hypophosphite which is a phosphorous based catalyst is commonly employed in this wrinkle-resistant finishing study. In the present study, this catalyst was found to be effective in catalysing the cross-linking reaction of PCA and PMA based dendritic polymers with cotton cellulose. Though this group of catalyst has been confirmed their efficacy in coupling poly(carboxylic acid) for cellulose cross-linking, the negative impact on the ecology is arousing attention in the industry. Exploration of utilising non-phosphorous catalysts would help alleviating environmental concern concerned with eutrophication in rivers, lakes and coastal areas aggravated by the phosphorus containing textile effluent [20-22].

7.3 Bibliography

[1] S. Mecking, “Nature or petrochemistry? - Biologically degradable materials,” *Angew. Chemie - Int. Ed.*, vol. 43, no. 9, pp. 1078–1085, 2004.

[2] A. Corma, S. Iborra, and A. Velty, “Chemical routes for the transformation of biomass into chemicals,” *Chem. Rev.*, vol. 107, pp. 2411–2502, 2007.

[3] A. Behr, J. Eilting, K. Irawadi, J. Leschinski, and F. Lindner, “Improved utilisation of renewable resources: new important derivatives of glycerol,” *Green Chem.,* vol. 10, no. 1, pp. 13–30, 2008.

[4] H. Song and S. Y. Lee, “Production of succinic acid by bacterial fermentation,” *Enzyme Microb. Technol.*, vol. 39, pp. 352–361, 2006.

[5] G. T. Tsao, N. J. Cao, J. Du, and C. S. Gong, “Production of multifunctional organic acids from renewable resources,” in *Advances in Biochemical Engineering and Biotechnology Volume 65: Recent Progress in Bioconversion of Lignocellulosics*, G. T. Tsao, Ed. Berlin: Springer Berlin Heidelberg, 1999, pp. 243–280.

[6] X. Wang, C. S. Gong, and G. T. Tsao, “L-Malic acid production from fumaric acid by a laboratory Saccharomyces cerevisiae strain SHY2,” *Biotechnol. Lett.*, vol. 18, no. 12, pp. 1441–1446, 1996.

[7] T. P. West, “Malic acid production from thin stillage by Aspergillus species,” *Biotechnol. Lett.*, vol. 33, no. 12, pp. 2463–2467, 2011.

[8] C. Williams and M. Hillmyer, “Polymers from renewable resources: a perspective for a special issue of polymer reviews,” *Polym. Rev.*, vol. 48, no. 1, pp. 1–10, 2008.

[9] K. Yao and C. Tang, “Controlled polymerization of next-generation renewable monomers and beyond,” *Macromolecules,* vol. 46, no. 5, pp. 1689–1712, 2013.

[10] L. Mialon, R. Vanderhenst, A. G. Pemba, and S. A. Miller, “Polyalkylenehydroxybenzoates (PAHBs): biorenewable aromatic/aliphatic polyesters from lignin,” *Macromol. Rapid Commun.*, vol. 32, no. 17, pp. 1386–1392, 2011.

[11] L. Karimi, M. Mirjalili, M. E. Yazdanshenas, and A. Nazari, “Effect of nano TiO2 on self-cleaning property of cross-linking cotton fabric with succinic acid under UV irradiation,” *Photochem. Photobiol.*, vol. 86, no. 5, pp. 1030–1037, 2010.

[12] A. Nazari, M. Montazer, A. Rashidi, M. Yazdanshenas, and M. B. Moghadam, “Optimization of cotton crosslinking with polycarboxylic acids and nano TiO2 using central composite design,” *J. Polym. Sci. Part A Polym. Chem.,*, vol. 117, pp. 2740–2748, 2010.

[13] Y.-S. Chung, K.-K. Lee, and J.-W. Kim, “Durable press and antimicrobial finishing of cotton fabrics with a citric acid and chitosan treatment,” *Text. Res. J.*, vol. 68, no. 10, pp. 772–775, 1998.

[14] A. Hebeish, F. A. Abdel-Mohdy, M. M. G. Fouda, Z. Elsaid, S. Essam, G. H. Tammam, and E. A. Drees, “Green synthesis of easy care and antimicrobial cotton fabrics,” *Carbohydr. Polym.*, vol. 86, no. 4, pp. 1684–1691, 2011.

[15] M. Nazi, R. M. A. Malek, and R. Kotek, “Modification of ß-cyclodextrin with itaconic acid and application of the new derivative to cotton fabrics,” *Carbohydr. Polym.*, vol. 88, no. 3, pp. 950–958, 2012.

[16] J. Szejtli, “Cyclodextrins in the textile industry,” *Starch,* vol. 55, no. 5, pp. 191–196, 2003.

[17] C. Q. Yang, Q. He, and B. Voncina, “Cross-linking cotton cellulose by the combination of maleic acid and sodium hypophosphite. 2. fabric fire performance,” *Ind. Eng. Chem. Res*., vol. 50, no. 10, pp. 5889–5897, 2011.

[18] V. Ameri Dehabadi, H.-J. Buschmann, and J. S. Gutmann, “Durable press finishing of cotton fabrics: an overview,” *Text. Res. J.*, vol. 83, no. 18, pp. 1974–1995, 2013.

[19] Y.-L. Lam, C.-W. Kan, and C.-W. M. Yuen, “Developments in functional finishing of cotton fibres- wrinkle-resistant, flame-retardant and antimicrobial treatments,” *Text. Prog.*, vol. 44, no. 3–4, pp. 175–249, 2012.

[20] D. J. Conley, H. W. Paerl, R. W. Howarth, D. F. Boesch, S. P. Seitzinger, K. E. Havens, C. Lancelot, and G. E. Likens, “Controlling eutrophication: nitrogen and phosphorus,” *Science* (80-.)., vol. 323, no. 5917, pp. 1014–1015, 2009.

[21] G. Billen, J. Garnier, C. Deligne, and C. Billen, “Estimates of early-industrial inputs of nutrients to river systems: Implication for coastal eutrophication,” *Sci. Total Environ.*, vol. 243–244, pp. 43–52, 1999.

[22] S. Rana, S. Pichandi, S. Parveen, and R. Fangueiro, “Regenerated cellulosic fibers and their implications on sustainability,” in *Roadmap to Sustainable Textiles and Clothing*, Singapore: Springer, 2014, pp. 239–276.