THE EFFECT OF CHITOSAN AND ITS DERIVATIVES ON THE DYEABILITY OF SILK

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THE EFFECT OF CHITOSAN AND ITS DERIVATIVES ON THE DYEABILITY OF SILK

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Abstract

Chitosans of different degree of deacetylation (DD) were derived directly from chitin in alkaline solution under different experimental conditions. Chitosans of the same DD with different molecular weights (MW) were prepared using ultrasonic degradation. All chitosans obtained were applied in the study of dye uptake efficiency using various acid dyes on silk under different experimental conditions. The color yield, color difference and colorfastness to washing of the dyed silk fabrics were evaluated using standard techniques. The DD of chitosans was determined using the ^{1}H NMR method. The MW was estimated with a dilute solution viscometry method.

The effect on the DD in deacetylation of chitin due to reaction time, condition, temperature, and the concentration of the alkaline solution is discussed, as is the result of ultrasonic degradation time on the MW and DD. The effect of chitosans of different MW and DD, treatment conditions, and dye structures on the dyeability of silk is also discussed.

O-carboxymethyl (O-CM) chitosans with a low degree of substitution (DS) and a high degree of deacetylation (DD) were prepared by treating chitin with chloroacetic acid in alkaline solution. N/O-(2-hydroxy)propyl-3-trimethyl ammonium chitosan chloride (N/O-HTCC) with different degrees of substitution were prepared by reacting chitosan and glycidyltrimethylammonium chloride (GTMAC) in D.I. water or buffer (pH=10) solution. The obtained chitosan derivatives were characterized using NMR, FTIR, TA, and elemental analysis methods. The dye uptake efficiency of both O-CM chitosans and N/O-HTCC were investigated. Their application for dyeing silk fabrics effectively increased

the dye uptake of acid dyes without lowering color fastness to washing or affecting the fabric hand feel.

Abbreviations

BC	before christ
C-	carbon-
CD	circular dichroism
C.I.	color index
CM	carboxymethyl
DA	degree of acetylation
DD	degree of deacetylation
D.I.	deionic
DP	degree of polymerization
DQ	degrees of quaternization
DS	degree of substitution
DSC	differential scanning calorimeter
EDTA	ethylene diamine tetraacetic acid
FTIR	fourier transfer infra red
GPC	gel permeation chromatography
GTMAC	glycidyltrimethylammonium chloride
IR	infra red
LVN	limiting viscosity number
MW	molecular weight
MWD	molecular weight distribution
N-	nitrogen-
NMR	nuclear magnetic resonance
N/O-HTCC	N/O-(2-Hydroxy)Propyl-3-Trimethyl Ammonium Chitosan Chloride
O-	oxygen-
O-CMCH	O-carboxymethyl chitosan
owf	on the weight of fibre
SINR	Shanghai Institute of Nuclear Research
t	ton
TA	thermal analysis
TGA	thermal gravity analysis
TMCC	N,N,N-trimethyl chitosan ammonium chloride
TMCI	N,N,N-trimethyl chitosan ammonium iodide
UV	ultraviolet

Contents

Chapter 1

Literature Review

1.1 Chitin and Chitosan

Chitosan is a polysaccharide obtained by deacetylating chitin, which is second only to cellulose in the amount produced annually by biosynthesis. Chitin occurs in animals, particularly in crustacea, molluscs and insects where it is an important constituent of the exoskeleton, and in certain fungi where it is the principal fibrillar polymer in the cell wall.

Chitin was first isolated in 1811 by Braconnot, [1] who called it fungine as the alkali-resistant fraction from some of the higher fungi. Braconnot also reported the formation of acetic acid from fungine and concluded that fungine was a new and quite distinct substance differing from the woody material of plants. The name chitin was conferred by Odier [2] in 1823 for what has subsequently been found to be the same compound in insects. In the 19th century, there was a controversy lasting for many years about whether or not chitin was identical to cellulose.

Chitosan was reportedly first discovered by Rouget [3] in 1859 when he boiled chitin in a concentrated potassium hydroxide solution. This resulted in the deacetylation of chitin. Fundamental research on chitosan did not start in earnest until about a century later. In 1934, two patents, one for producing chitosan from chitin and the other for making films and fibers from chitosan, were obtained by Rigby. [4,5] In the same year, the first X-ray pattern of a well-oriented fiber made from chitosan was published by Clark and Smith. [6] R. A. A. Muzzarelli [7] presented the first review of chitin and chitosan in 1977.

Subsequently, international symposiums on chitin and chitosan kept the information up to date. Today more and more academic and industrial scientists join the fundamental research on chitin and chitosan, and try to find new and practical applications for these materials.

1.1.1 Physicochemical Structure

Chitin is chemically defined as poly[β-(1→4)-2-acetamido-2-deoxy-D-glucopyranose], and chitosan as poly[β-(1→4)-2-amino-2-deoxy-D-glucopyranose]. Actually the names 'chitin' and 'chitosan' are widely used in the literature but neither term represents a unique chemical structure. Chitosan is a collective name given to a group of polymers deacetylated from chitin. The difference between chitin and chitosan lies in the degree of deacetylation. Fig.1.1 shows the essential molecular structure of chitin and chitosan, which describes a continuum of copolymers of N-acetyl-D-glucosamine and D-glucosamine residues.

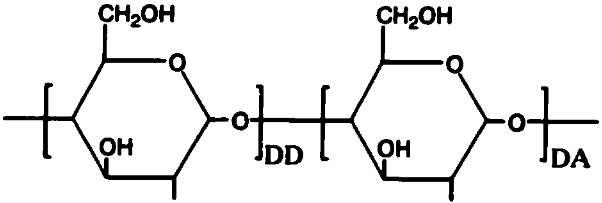


Fig.1.1 The molecular structure of chitin/chitosan (DD is the degree of deacetylation; DA is the degree of acetylation; DD+DA=1)

The terms chitin and chitosan are distinguished by insolubility (chitin) or solubility (chitosan) in dilute aqueous acid solutions. But the properties are frequently dependent on the relative proportions of N-acetyl-D-glucosamine and D-glucosamine residues (DA or

DD). Generally we cannot isolate chitin with DA=100% from its raw material, and the reaction of deacetylating chitin in an alkaline solution cannot reach completion even under several harsh treatments. In general, the term chitosan is used when the DD is more than 70% and chitin when the DD is less than 70%. [8]

The X-ray diffraction studies have revealed that chitin has a highly ordered, crystalline structure. It has been found in three polymorphic forms: α-, β-, and γ-chitin, which differ in the arrangement of the chains within the crystalline regions. [9-11] In α-chitin the chains are anti-parallel, in β-chitin they are parallel, and in γ-chitin two chains are 'up' to each chain 'down' (Fig.1.2). The most abundant form is α-chitin, which also appears to be the most stable since both the β- and γ-chitin may be converted into the α-form by suitable treatments.

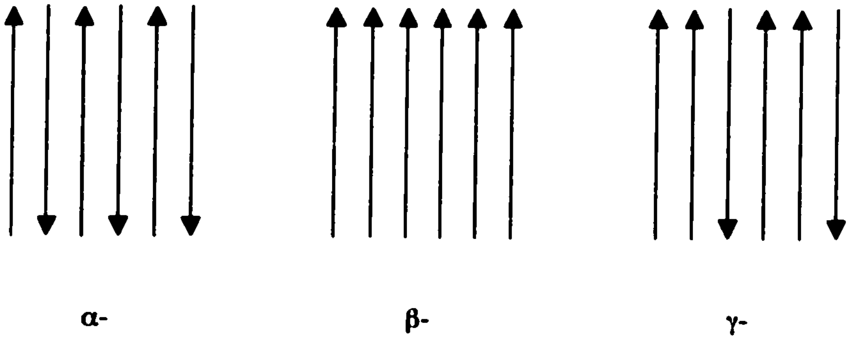


Fig.1.2 Arrangement of the chitin chains in the three forms

Up to now, only a few studies on the molecular conformation of chitosan have been reported, and there is still no one simple model describing chitosan. An analysis of the diffraction spectra of chitin and chitosan revealed a structural resemblance between the two polymers. [12] It has been suggested that the conformation of chitosan is similar to that of α-chitin. [13]

1.1.2 Chitin-Protein Complexes

Chitin from animal sources usually occurs in association with protein, which functions as a lower modulus matrix surrounding the chain. [14] Much of the evidence for the presence of a true proteoglycan structure in native chitins comes from precipitation studies. These studies [15-19] indicated that a covalent bond exists within the chitin-protein complex.

Hackman et al. [15,20-21] detected amino acid in the traces of protein left after exhaustive extraction of native chitins with hot NaOH solution, and identified aspartic acid, histidine, threonine, serine, glutamic acid, glycine, alanine, isoleucine, leucine, valine, methionine, tyrosine, phenylalanine, ornithine and lysine etc. in chitins prepared from puparia of *Lucilia cuprina*, larval cuticles of *Agrianome spinicollis*, carapace of *Scylla serrate*, cuttlefish shell, *Loligo* pen, and *Calliphora* larval cuticle.

A number of possible bonding arrangements between the chitin (or Chitosan) and protein chains have been proposed and these include (Fig.1.3): formation of an amide group between an unacetylated amine group of chitin (or chitosan) and a carboxylic acid group in the protein chain, [15] the latter being either the C-terminal carboxylic acid group or the side group of an acidic amino acid (1.3.1); and bonding through a Schiff's base structure [22] (1.3.2) or through an N-glycosidic structure involving the amide group of asparagine [23] (1.3.3) or an O-glycosidic structure involving serine [23] (1.3.4), or through the carboxylic acid groups of a small number of N-acetylmuramic acid units in the chain and the amine group of a terminal alanyl residue [9,24] (1.3.5).

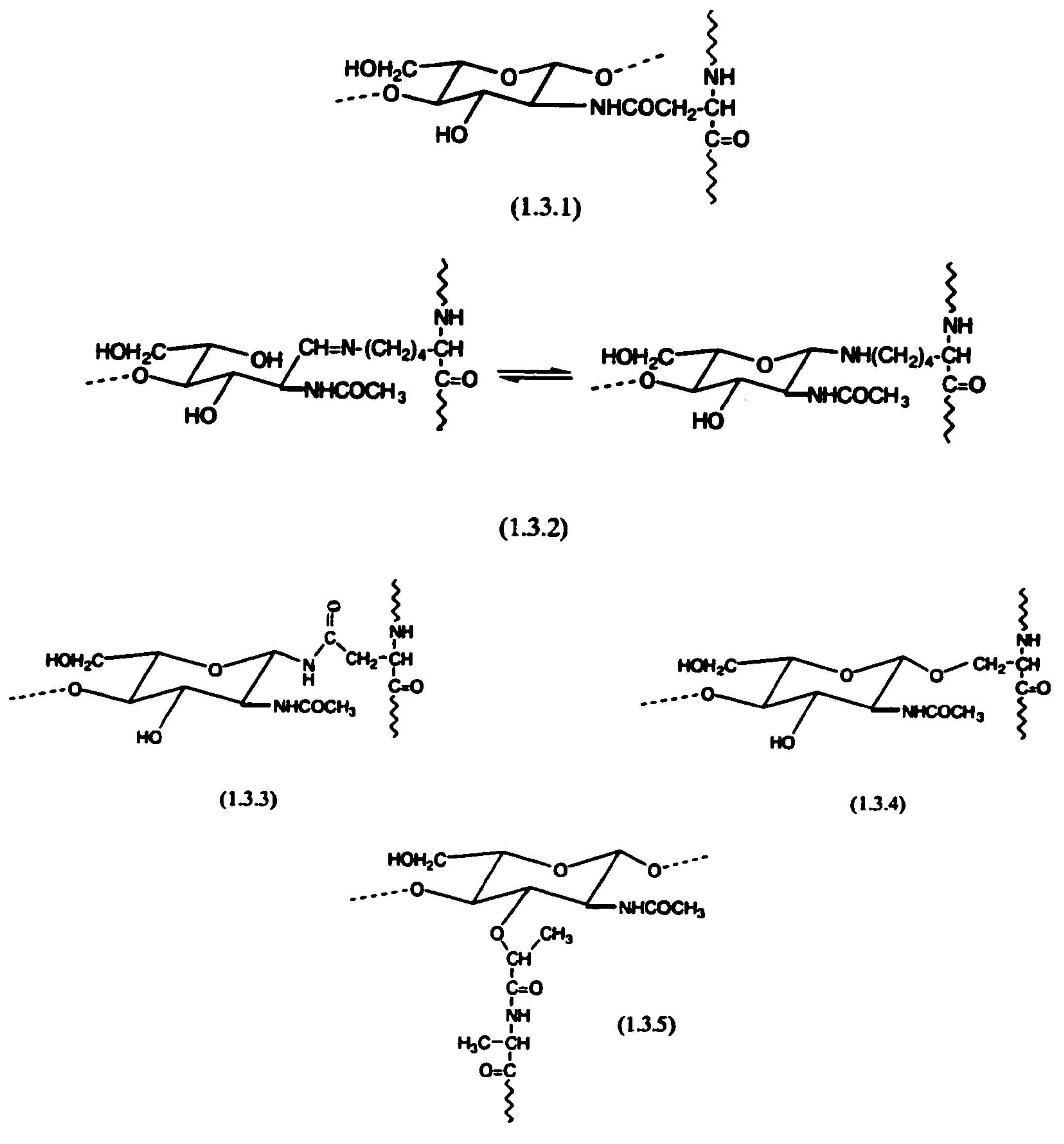


Fig.1.3 Possible bonds involved in the chitin (or chitosan)-protein complexes [9,15,22-24]

Electron microscopy studies [25-27] have shown two morphological types of complexes; one in which cylindrical chitin fibrils are imbedded in a protein matrix in an approximately hexagonal packing arrangement, and the other in which the chain is arranged in layers interspersed with layers of protein. In both morphological types, the absence of intimate mixing of chitin and protein chains is shown by the absence of any staining in the chitin containing regions, indicating that protein chains are only bound to chitin chains at the chitin/protein interface. These proposed morphologies are supported by X-ray diffraction studies. [9,25,28-31]

This indicates the strong affinity of chitin/chitosan to protein, and, at least in theory, makes chitosan/its derivatives an ideal medium to improve the dyeability of silk.

1.1.3 Preparation

In 1977, Allan et al. [32] pointed out that their global estimate of the total annually accessible chitin was 150×10^3t, of which 56×10^3t was from krill, 39×10^3t from shellfish, 32×10^3t from fungi, 22×10^3t from clams and oysters and 1×10^3t from squid. This total is much less than the estimated total of chitin produced annually by biosynthesis—one species alone, the marine copepods, is estimated to produce 10^9t of chitin annually. [33]

Chitin of these origins is closely associated with proteins, inorganic material that is mainly $CaCO_3$, pigments and lipids. Various procedures have been adopted to remove these impurities and no standard process has been developed. Demineralisation is commonly carried out by the treatment with HCl, and deproteinisation is with NaOH. The order of these two steps are carried out has varied with different workers. The choice of processing conditions may be governed to some extent by the purpose for which the chitin is required, since partial deacetylation during deproteinisation is not a disadvantage if the chitin is subsequently to be converted to chitosan, while some hydrolysis of the polymer chain during the demineralisation process can be tolerated if the chain is to be used in the form of particles or converted to microcrystalline chitin. These processing steps are introduced as follows.

Deproteinisation

Early patents [4,34] claimed the use of a wide range of agents for this step including NaOH, Na_2CO_3, $NaHCO_3$, KOH, K_2CO_3, $Ca(OH)_2$, Na_2SO_3, $NaHSO_3$, $CaHSO_3$, Na_3PO_4 and Na_2S, but NaOH is the preferred agent in the literature. Most treatments [35-44] have typically involved the use of approximately 1.0M NaOH but with a wide variation in temperature and duration of treatment.

The use of enzymes for the removal of protein has been examined by a number of researchers. [41,45] It was concluded that enzymatic treatment of shells did not offer any substantial advantage over the shorter chemical treatments.

Demineralisation

Patents [4,34] reported the demineralisation by a variety of acids including HCl, HNO_3, H_2SO_3, CH_3COOH and HCOOH, but most researchers [35-44] have used HCl for this process. Although the above patents claimed that the demineralisation with acid may be carried out at temperatures from 0 to 100°C, room temperature has been used in all cases, even in the examples specified in the patents, in order to minimize hydrolysis of the polymer chain. However, there is considerable variation in the HCl concentrations and the lengths of time of treatment used by different researchers. Extraction with EDTA at alkaline pH values has been used by Foster and Hackman [46] as a non-degradative demineralisation process.

Decolouration

The exoskeletons of crustacea contain colouring matter, principally carotenoids, the main components being astacene, astaxanthin, canthaxanthin, lutein and β-carotene [47]. They do not appear to be complexed with either the inorganic material or the protein, since treatments that remove these components do not remove the carotenoids. However, they may be removed by extracting the shell with ethanol or acetone after demineralisation by either acid or EDTA treatment. Warm 50% aqueous acetic acid simultaneously demineralises the shell and extracts the carotenoids. [48]

Alternatively, the colouring matters may be destroyed by bleaching and the use of $KMnO_4$, NaOCl, SO_2, $NaHSO_3$, $Na_2S_2O_4$ or H_2O_2 have been claimed in some literature. [4,34]

It has been recognised for some time that chitin, even after demineralisation and deproteinisation treatments, is not a simple chemical entity and that samples vary in chemical and physical properties depending on the source material and the purification process. In view of this, Austin et al. [49] have proposed the term 'chitin isolate' for such materials and consider that these differences arise from variations in the amount and nature of the residual protein, in the extent to which anomerisation of the β-glycosidic bonds has occurred, and in the extent of deacetylation.

One of the main reactions carried out on chitin is deacetylation. Complete deacetylation cannot be achieved. Chitosan with an extent of deacetylation of ~60% or above will be soluble in dilute aqueous acids.

Although amides may in principle be hydrolysed under either acidic or basic conditions, the use of acid hydrolysis is precluded because of the susceptibility of the glycosidic links in chitin to acid hydrolysis. Furthermore, as pointed out by Horton and Lineback, [50] the trans arrangement of the C(2)-C(3) substituents in chitin increases the resistance of the C(2)-acetamido group to alkaline hydrolysis, so that severe treatment conditions are required to bring about deacetylation. At the same time, care must be taken to avoid, or at least minimise, any accompanying degradation of the polymer chain.

Chitosan can be obtained by deacetylating chitin with alkali fusion or aqueous alkali, or with other alternative techniques. The most commonly used method for the deacetylation of chitin is deacetylation with aqueous alkali, but no standard conditions have been established. The most frequently used alkali is NaOH. The extent of deacetylation is governed by the alkali concentration, the temperature, the time of reaction, and the particle size and density. [4,34] Kurita et al. [51] reported that while with 40 wt.% NaOH there is a very rapid initial deacetylation to an acid-soluble product, followed by a slow increase in the extent of deacetylation with time, with solutions having lower concentrations of up to 30 wt.% NaOH there appears to be an upper limit to the extent of deacetylation that may be obtained, and this is insufficient to produce an acid-soluble product (Fig.1.4). This upper limit of deacetylation increases with an increase in the NaOH concentration and also with an increase in the reaction temperature. Furthermore, a multistage treatment interspersed with washing was proved to be effective for increasing the degree of deacetylaton of chitosan. [37,52]

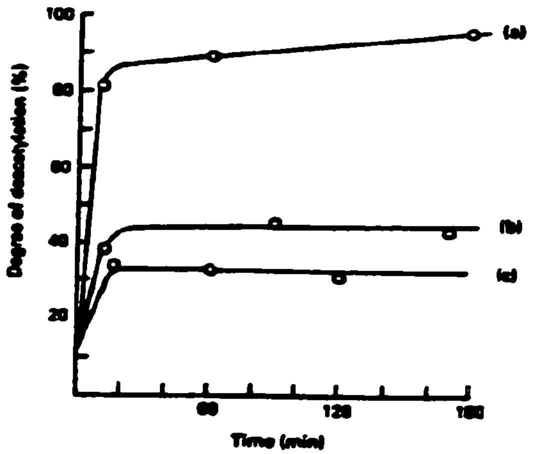


Fig.1.4 Effects of NaOH concentration and temperature on the heterogeneous deacetylation of chitin: (a) 40 wt.% NaOH at 130°C; (b) 30 wt.% NaOH at 112°C; (c) 20wt.% NaOH at 105°C [51]

Kurita et al. [51] also reported that during heterogeneous deacetylation of chitin, the crystallinity as measured by X-ray diffraction decreased slightly up to a degree of deacetylation of 71% and then more rapidly, so that the crystalline peaks had almost disappeared by 81% deacetylation, while by 89% deacetylation the sample was completely amorphous. By 95% deacetylation, the material was again crystalline although the peak positions had moved from $2\theta = 9.2°$ and $19.1°$ to $2\theta = 11.2°$ and $20.4°$. These new peaks were considered to arise from the presence of crystalline chitosan, the small amount (~5%) of N-acetylated D-glucosamine residues being insufficient to prevent the chains taking up the chitosan structure (Fig.1.5). Heterogeneous deacetylation takes place preferentially in the amorphous regions then continues more slowly from surface to centre of the crystalline region, thereby giving rise to block copolymers of poly[β-(1→4)-2-acetamido-2-deoxy-D-glucose] and poly[β-(1→4)-2-amino-2-deoxy-D-glucose] segments. This pattern of deacetylation under heterogeneous conditions, coupled with the fact that there is no evidence of a crystalline chitosan structure in the X-ray diffraction pattern of a sample having 71% deacetylated residues, suggests that the crystalline chitosan diffraction pattern obtained at 95% deacetylation arises from those chain segments originally present in the crystalline region of the chitin and which are only deacetylated in the later stages of the treatment.

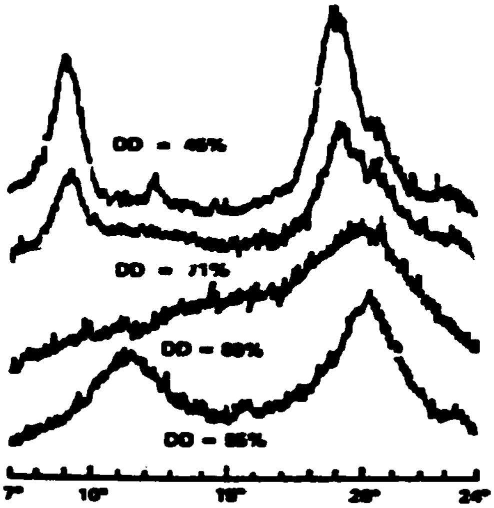


Fig.1.5 X-ray diagram of heterogeneously deacetylated chitin [51]

1.1.4 Analysis

There is no definitive 'standard' material for chitin and chitosan. In many instances, analysis is carried out in order to characterise the material rather than to determine whether or not it conforms to a definite structure. The characteristics most frequently assessed are the degree of deacetylation (or N-acetylation), molecular weight, residual protein, moisture content, ash content, lipid content, heavy metal content and colour; their relative importance depends on the intended use.

1.1.4.1 Degree of Deacetylation

The degree of N-acetylation and the degree of deacetylation (free amine group content) are, of course, inversely related, and the former may be obtained directly by determining the amide group concentration, or indirectly by determining the amine group concentration. Which approach is the more suitable is partly controlled by the relative abundance of the two functional groups and also by any special requirements of the technique, such as a need for sample solubility. In addition, there are a few methods that do not depend on the direct determination of either functional group.

Determination of the N-Acetyl Content

Hydrolytic Techniques

These involve hydrolysis of the N-acetyl groups under either acid or alkaline conditions, followed by determination of the acetic acid produced. Such methods have an advantage in that there is no requirement for the sample to be soluble. The determination of the acetic acid liberated on hydrolysis in HCl has been developed as a technique for the quantitative estimation of the chitin present in a sample, [53-54] although it is necessary in this case to assume that any chitin present is fully N-acetylated and this is not necessarily the case.

IR Spectroscopy

The IR spectrum of α-chitin shows two absorption bands at approximately 1655 and 1625 cm^{-1}, as is characteristic of hydrogen bonded amide groups. Although Darmon and

Rudall noted the disappearance of these bands during deacetylation, [55] their use in determining the degree of N-acetylation was not proposed until some 25 years later. [56]

The use of IR spectroscopy has a number of advantages: it is relatively rapid, makes use of instrumentation found in most laboratories and, provided use is made of an internal reference peak to correct for variation in the amount of material in the beam, the purity of the sample does not need to be determined separately. Furthermore, use of the KBr disc technique means that the method can be used with insoluble samples although the best results are obtained from cast films. In view of these advantages it is not surprising that IR spectroscopy has been used frequently to determine the degree of N-acetylation of chitin and chitosan, and that it is one of the most widely studied techniques for chitin/chitosan analysis. [57]

UV Spectroscopy

Castle, [58] Muzzarelli [59] and Aiba [60] et al. have attempted to use UV spectroscopy quantitatively with chitin and chitosan. Unfortunately, it was concluded that the method was unsuitable for quantitative work.

Circular Dichroism

N-acetyl-D-glucosamine and its oligomers show two CD bands due to the CH_3CONH-group; the first arises from the π-π^* transition and occurs near 190nm and the second, which occurs near 210nm, may be assigned to the n-π^* transition. [61] Domard [62] has shown that this latter transition becomes independent of the DP above, and including, the dimer and that in the solid state it shows a bathochromic shift relative to its position in the CD spectrum of an aqueous solution. The analysis is straightforward with the extent of N-acetylation being calculated from the equation

$$\% \text{ N-acetyl} = 161 \times Hs \times 100/[161 \times Hs + 203(H_{100} - Hs)]$$

Where Hs is the height of the 211nm peak for the sample and H_{100} is the height of this peak for the same concentration, in g dm^{-3}, of a fully N-acetylated sample. In view of the constancy of both the wavelength and the ellipticity per monomer unit, di-N-acetylchitobiose was used to establish H_{100}. The CD method gave results in very good agreement with those produced by the IR method by Miya et al. [63]

NMR Spectroscopy

Determination of the degree of N-acetylation by NMR spectroscopy was first carried out by Hirano and Yamaguchi [64] in their work on N-acetylchitosan gels. Hirai et al. [65] also disclosed a method to determine the degree of deacetylation of chitosan by ^1H NMR spectroscopy. These samples, dissolved in DCOOH or CD_3COOD/D_2O or DCl/D_2O, were analysed from the ratio of N-acetyl methyl protons : (methine and methylene) protons in the ^1H NMR spectrum.

The method is most accurate at high degrees of deacetylation but problems might be expected in the case of α-chitin, which is not soluble in HCOOH and hence, presumably, insoluble in DCOOD. However, the use of hexafluoroacetone, which is a solvent for α-chitin, [66] might enable this technique to be extended to α-chitin, while it has been claimed [67] that the extent of deacetylation of chitin may be readily determined using solid-state ^{13}C CP/MAS NMR spectroscopy.

Determination of the Amine Group Content

Acid-Base Titration

In the method first proposed by Broussignac, [68] chitosan is dissolved in a known excess of acid and the solution is then titrated potentiometrically with NaOH. This gives a titration curve having two inflection points; the difference between the two along the abscissa corresponds to the amount of acid required to protonate the amine groups (Fig.1.6). The amine group concentration is determined using the equation

$$\%\ NH_2 = 16.1(y-x)f/w$$

Where f = molarity of the NaOH solution and w = weight, in grams, of the sample.

This technique has been used by a number of researchers, but its precision has been questioned by Domard and Rinaudo [69] because of the tendency towards precipitation of the chitosan in the neutralisation pH range. They reported an improved technique in which the chitosan is progressively titrated with HCl while the conductivity is monitored to determine the stoichiometry of the interaction.

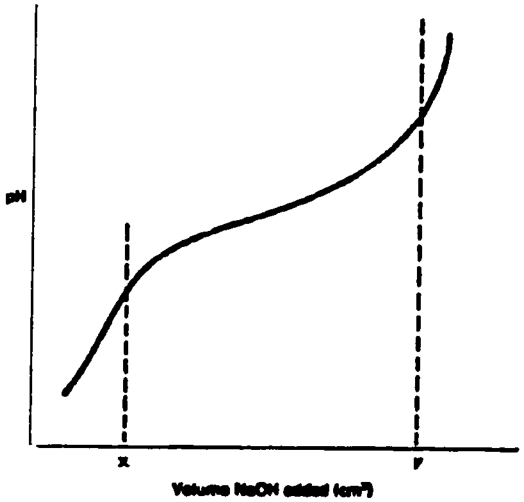


Fig.1.6 Titration curve of chitosan dissolved in excess acetic acid showing the two points used in Broussignac's relationship [68]

Colloid Titration

The colloid titration technique was developed by Terayama [70] as a method for analysing polyelectrolytes in aqueous solutions. It is based on the reaction between cationic and anionic polyelectrolytes where neutralisation of electrical charge proceeds stoichiometrically. Thus, if the concentration of ionic groups in one of the polyelectrolytes is known, the concentration in the other may be calculated from the relative volumes at the end point.

If a cationic polyelectrolyte is titrated with a solution of an anionic polyelectrolyte of known composition, the end point may be detected by the addition of a suitable dye such as Methylene Blue (C.I. Basic Blue 9; C.I. No. 52015) or Toluidine Blue (C.I. Basic Blue 17; C.I. No. 52040), which undergoes a metameric colour change in the presence of free anionic polyelectrolyte.

Metachromatic Titration

Metachromatic titration is similar to colloid titration insofar as it involves polyelectrolyte-induced metachromasy in a suitable dye, but it differs in that there is no second, oppositely charged polyelectrolyte present.

The absorbance at λ_{max} of a dye showing polyelectrolyte-induced metachromasy will decrease with an increase in the concentration of added polyelectrolyte until a minimum value is obtained, after which further additions of polyelectrolyte will have no further effect on the absorbance. The intersection in a plot of Absorbance versus Volume of polyelectrolyte solution added represents the point at which the mixture contains an equivalent number of dye ions and charged groups on the polyelectrolyte.

Periodate Oxidation

$NaIO_4$ can oxidise the α-aminoalcohol group of the deacetylated residues in chitosan while the N-acetylated residues are resistant. Moore and Roberts [71] used the reaction to calculate the extent of deacetylation of chitin and chitosan samples from measurements of the amount of periodate consumed. The values obtained for the amine group content were, in general, greater than those calculated on the basis of the N-acetyl content determined by IR spectroscopy. This was attributed to alkaline degradation of dialdehyde units by the NH_3 liberated during oxidation of the α-aminoalcohol groups, leading to water-soluble fragments that are themselves subject to periodate oxidation so that the periodate consumption is in excess of that required solely for oxidation of the α-aminoalcohol groups.

Residual Salicylaldehyde Analysis

The free amine groups of chitosan react readily with salicylaldehyde to give the yellow Schiff's base N-salicylidenechitosan, the reaction being complete after 16 hours at room temperature using methanol as the reaction medium and a 3:1 mole ratio of salicylaldehyde : amine group. [72] This reaction was used by Domszy and Roberts [73] to determine the amine group content of chitosan, the basis of the technique being the reaction of chitosan with excess salicylaldehyde followed by spectroscopic determination of the salicylaldehyde remaining at the end of the reaction period.

Other methods, e. g. reaction with 2,4-dinitrofluorobenzene, dye adsorption, picric acid adsorption, have been reported and are rarely used to determine the amine group content of chitin and chitosan, because they are inaccurate and unsuitable for the determination.

Determination Based on Overall Composition

Elemental Analysis

Pure chitin (DA = 100%) has a nitrogen content of 6.89% while pure chitosan (DD = 100%) has 8.69% N. Thus, in theory, it is possible to determine the degree of N-acetylation from a knowledge of the nitrogen content of the sample, the relative change between the two extremes being greater for nitrogen than for carbon. However, because of the problems caused by the presence of moisture, which is difficult to eliminate, and the possible presence of some inorganic materials, the use of the N/C ratio is to be preferred. It is also crucial that no residual protein remains on the sample prior to analysis since the average %N and %C in proteins is considerably different from those of either chitin or chitosan.

Gas chromatography and pyrolysis techniques have also been used to measure the degree of deacetylation of chitin and chitosan. These were summarized by Roberts. [74]

1.1.4.2 Molecular Weight

The determination of a molecular weight average for either chitin or chitosan poses a number of problems. Chief among these in the case of chitosan is the possible presence of microgels due to uneven treatment during the deacetylation step, and the tendency of the polymer chains to aggregate on standing in solution, while the limited choice of solvents and the nature of the solutions formed are problems associated with working with chitin. Some of the studies that have been carried out on chitin have made use of water-soluble derivatives but, while such an approach has the benefit of enabling aqueous solutions to be used, it must be remembered that the origin and preparation history of a sample will affect its molecular weight so that attempts to compare molecular weight values obtained by different researchers using different samples, as has on occasion been done, are of little or no worth.

Although a number of techniques have been applied to the determination, only light scattering, GPC, and dilute solution viscosity have been used to any extent. Osmometry, end group analysis, ultracentrifugation and hypoiodate method have also had only limited use for determining the molecular weight of chitin and chitosan.

Light Scattering Spectrophotometry

Light scattering spectrophotometry has been used with chitosan by a number of researchers, [69,75-78] but the measurements are prone to give an overestimate of the molecular weight because of aggregation of the chains on standing.

In carrying out light scattering studies, a very accurate determination of the concentration dependence of the refractive index is most important. The values [69,75-78] obtained for chitosan vary from 0.166 to 0.180 cm^3g^{-1} when measured at 546 nm, and whether this variation is due to differences in solvent or in the structure of the chitosan samples used is not known; no study of the effect of extent of N-acetylation on d*n*/dc has been carried out. However, there is a much greater difference between the two values obtained at approximately 633 nm, one being 25% less than the other. It seems unlikely that so large a difference can be due to the difference in solvent systems in the two cases.

Gel Permeation Chromatography

GPC is a frequently used technique for determining the molecular weights (MW) and molecular weight distributions (MWD) of polymers. In recent years, many researchers [79-82] have employed this technique in studies on chitosan.

The cationic nature of chitosan in acid solution causes difficulties in using GPC for molecular weight determinations of chitosan. For the separation process to operate correctly, it is necessary that there is no interaction between the gel and the polymeric solute. Therefore, in the case of polyelectrolytes any electrostatic effects, whether of repulsion or attraction, must be eliminated.

Dilute Solution Viscometry

Dilute solution viscometry is one of the simplest and fastest methods to determine the molecular weights of polymers, Although it has the disadvantage of not being an absolute method since it requires the determination of constants through correlation of limiting viscosity number (LVN) values with molecular weight (MW) values measured by an absolute method. The most commonly used equation relating LVN values to MW values is the Mark-Houwink equation

$$[\eta] = k\overline{M}_v^{\alpha} \tag{1.1}$$

Where $[\eta]$ is the LVN and k and α are constants that are independent of molecular weight over a considerable range of molecular weights. They are dependent on polymer, solvent, temperature, and in the case of polyelectrolytes, the nature and concentration of the added low-molecular-weight electrolyte. The constants are normally evaluated from a plot of

Log[η] versus Log$\overline{M}_v$ for a series of carefully prepared fractions having very narrow MWD values.

Many researchers [83-86] have proposed several sets of values for k and α for chitosan in their published articles. Wang et al. [87] determined the values of k and α for chitosans with different degrees of deacetylation (DD), in 0.2M CH_3COOH/0.1M CH_3COONa aqueous solution at 30°C by the light scattering method. The relationships for k and α as a function of the DD were obtained as follows:

$$k = 1.64 \times 10^{-30} \times DD^{14.0} \quad (r = 0.996) \tag{1.2}$$

$$\alpha = -1.02 \times 10^{-2} \times DD + 1.82 \quad (r = 0.998) \tag{1.3}$$

The results were explained to be due to a reduction of rigidity of the molecular chain and an increase in the electrostatic repulsion force of the ionic groups along the polyelectrolyte chain in chitosan solution, when the DD of chitosan increases gradually.

1.1.4.3 Other Analyses

Residual protein in chitin/chitosan has been determined with procedures that involve hydrolysis of the residual protein followed by determination of either the loss in weight [88] of the samples or the amino acids [89] produced.

Solid chitin/chitosan samples could be assessed from reflectance measurements on the powdered material, one suitable instrument being the ICS Micro Match, an abridged spectrophotometer that measures the reflectance characteristics at 20nm intervals over the range 400-700nm. The results may be obtained in the form of a Yellowness Index [90] defined as

$$\text{Yellowness Index} = (131.6X - 116.4Z)/Y$$

Where X, Y and Z are the tristimulus values of the sample.

There is no standard procedure for determination of the percentage of insoluble material, but this determination is most simply carried out by dissolving in a suitable solvent, 0.1-0.2M acetic acid for chitosan and DMAc-LiCl or related complex organic solvent for chitin, followed by filtering off, rinsing, and drying any undissolved material which may then be weighed directly.

Chitosan, and to a much lesser extent chitin, readily forms complexes with transition metal ions and other heavy metal ions. Hence, care must be taken in the various preparation steps to avoid contact with such ions, and the use of demineralised water is advisable. Most of the trace metals present in commercial chitosans come from contaminants, equipment, and water, and are not present in the original *in vivo* chitin. At the levels likely to be encountered, the most appropriate method of analysis is atomic absorption spectroscopy following solution of the material in concentrated mineral acid.

The ash, lipids, and nitrogen contents are best determined using the standard procedures (18.025, 18.046 and 18.026 respectively) recommended for the analysis of fish and other marine products by the AOAC. [91] For determination of the moisture content the British Standard for Textiles, [92] which specifies heating at 105±3°C for 4-16h, is appropriate.

1.1.5 Applications

The industrial production and use of chitosan has been steadily increasing since the 1970s. In Japan, for example, the production of chitosan increased 37% each year from 1978 to 1983, the total annual amount reaching 311 tons by 1983 [93] and 1,270 tons by 1986. [94]

At that time, the major applications of chitosan were centered on sludge dewatering, food processing, and metal ion chelation. The present trend, in industrial applications, however, is toward producing high value products, such as cosmetics, drug carriers, feed additives, semipermeable membranes, and pharmaceutics. The difference in value between the products and the low-cost polymers is one of the main driving forces pushing studies on new applications of chitosan. Biotechnology is currently attempting large-scale production of high-value bioproducts like monoclonal antibodies, which were projected at about 1.2 billion U.S. dollars on the world market in 1991. [95] Immobilization techniques have been proven to be an effective way to increase cell density, product concentration, and hence, productivity in a culturing system. Chitosan membranes and gels have great potential for use in immobilized cell culture systems. Li et al. [96] summarized the applications of chitosan in various fields (Table 1.1).

In the textile industry, chitosan is used as print-paste thickener, and is also used to improve the antimicrobial property of textiles. Textile fibres having poor affinity for dyes, e.g., synthetics and glass fibres, can be blended or surface-coated with chitin and chitosan, which makes them more receptive to dyeing with reactive or acid dyes.

It has been found that chitosan could improve the dyeability of textiles. This might be due to the improved electrostatic attraction between the protonated amino group in chitosan and the anionic dye. Cotton and protein fibres are the substrates being explored. Kako et al. [97-106] studied the effect of chitosan treatment on the physico-mechanical and dyeing behaviours of tussah silk fabrics with various dyes, and indicated that the dye exhaustion of acid dyes were increased in proportion to the chitosan add-on. But the relation between dyeing and (1) the DD, (2) the MW of chitosan, however, is rarely investigated. Moreover, limited research was performed on the effect of chemically modified chitosan on dyeing.

Table 1.1 Applications of Chitosan [96]

Applications	Examples
Water treatment	Removal of metal ions Flocculant/Coagulant: Proteins Dyes Amino acids Filtration
Pulp and Paper	Surface treatment Photographic paper Carbonless copy paper
Medical	Bandages, Sponges Artificial blood vessels Blood cholesterol control Tumor inhibition Membranes Dental/Plaque inhibition Skin burns/Artificial skin Eye humor fluid Contact lens Controlled release of drugs Bone disease treatment
Cosmetics	Make up powder Nail polish Moisturizers Fixtures Bath lotion Face, hand and body creams Toothpaste Foam enhancing
Biotechnology	Enzyme immobilization Protein separation Chromatography Cell recovery Cell immobilization Glucose electrode
Agriculture	Seed coating Leaf coating Fruit/Vegetable coating Hydroponic/Fertilizer Controlled agrochemical release
Food	Removal of dyes, solids, acids Preservatives Colour stabilization Animal feed additive
Membranes	Reverse osmosis Permeability control Solvent separation

1.2 Chitosan Derivatives

Chemical modifications of chitosans are increasingly studied as they have the potential to provide new applications for such abundant natural polymers. The reactive nature of chitosan was attributed to the glycosidic oxygen of the main chain, the primary amino group, and the primary and secondary hydroxyl groups of D-glucosamine unit. We herein review three kinds of chitosan derivatives, to which the research relates.

1.2.1 Degraded Chitosans

Both chitin and chitosan, being poly(glycosides), can be hydrolysed in the presence of acids, alkalis, enzymes, ultrasonic wave and so on. The hydrolysed/degraded chitins/chitosans are in evidence the essential derivatives of chitin and chitosan.

1.2.1.1 Acid Hydrolysis

Many researchers [107-112] proposed that the acid hydrolysis of chitosan is slower than that of chitin because under acid conditions the amine group is protonated and the C(2)-NH_3^+ group shields the glycosidic oxygen from protonation, which is the first step in the acid hydrolysis reaction. Rupley [113] indicated that the de-N-acetylation occurs in both the hydrolysis of chitin and chitosan. But the studies [111,114-115] on the hydrolysis of chitin and chitosan by H_2SO_4 show that hydrolysis is accompanied by O- and N-sulphation of chitosan and by O-sulphation of chitin, with no evidence of concurrent de-N-acetylation of chitin.

The acid hydrolysis of chitin/chitosan is frequently used for the preparation of the chitin/chitosan oligomers (monomer, dimer and trimer etc), [111-113,116-119] which are separated by gel filtration chromatography etc. In addition, it is used for the production of microcrystalline chitin and chitosan, [120-123] formation of which involves controlled mineral acid hydrolysis followed by subjection to high shear forces while suspended in water to give gel-like thixotropic dispersions.

1.2.1.2 Alkaline Degradation

Alkaline degradation of chitin is a well-known phenomenon, occurring most noticeably during the deacetylation of chitin to produce chitosan. A number of procedures have been proposed for reducing the deleterious effects of alkali during this process and these include the use of an inert atmosphere such as nitrogen [4,69,80,124-125] or argon, [126] the addition of an oxygen scavenger such as thiophenol, [69,124-125] or the use of a reducing agent such as $NaBH_4$ [124]. However, very little fundamental work have been done and no mechanistic studies appear to have been carried out.

Batista [125] proposed mechanisms for two degradative reactions of both unmodified chitin and unmodified chitosan, the two reactions being random scission of the glycosidic link and end-group peeling, or unzipping, from the reducing terminal unit. On the other hand, oxidation under alkaline conditions could give rise to carbonyl groups at either the C(6) or C(3) positions in chitin and chitosan, and possibly also at C(2) in chitosan. The presence of such groups would make the adjacent glycosidic links very susceptible to alkaline hydrolysis, but the presence of $NaBH_4$ could reduce the extent of degradation either by preventing the formation of these carbonyl groups or by reducing them once formed.

1.2.1.3 Biodegradation

The first specific information about the enzymatic degradation of chitin came from the studies of Karrer et al. [127-128] who obtained N-acetyl-D-glucosamine in high yield from enzymatic hydrolysis of both crustacean and fungal chitin, thereby establishing the chemical similarity of the chitin from both sources. Chitinolytic enzymes have been found in invertebrates, such as snails, [127-132] crustacea and insects [133] and in protozoa, nematods, earthworms, coelenterates and polychaete worms. [134] They have also been found in the digestive tracts of some vertebrate species, such as birds and lizards, that are insectivorous [134-135]. It has also been shown [136-138] that chitinases are separate and distinct from the lysozymes, which also hydrolyse chitin. [139-140]

Chitosan-degrading enzymes were first identified by Monaghan et al. [141] and Ramirez-Leon and Ruiz-Herrera, [142] and they are known to be extremely common in soil from a number of environments: garden, forest, salt marsh and agricultural land. [143] The available evidence to date indicates that chitosanases exhibit maximum activity towards substrates intermediate between chitin and chitosan. Studies [143] with the *P. islandicum* chitosanase indicated that the enzyme shows high specificity towards hydrolysis of the glycosidic link between C(1) of an N-acetyl-D-glucosamine residue and C(4) of a D-glucosamine residue.

Chitosan occurring naturally is produced by enzymatic deacetylation of chitin within the living system [144-146] and the action of chitin deacetylase obtained from *Mucor rouxii* has been studied by Araki and Ito [144-145] using O-hydroxyethyl chitin, colloidal chitin and chitin oligomers as substrates.

Some researchers [147-148] stated that the predominant mode of action for chitin/chitosan biodegradation is 'splitting the second β-N-acetylglucosaminide bond from the non-reducing end'.

1.2.1.4 Ultrasonic Degradation

Wang and Qin [149] found that the rate of degradation of chitosan by ultrasound was very fast in the beginning then slowed down gradually, and the intrinsic viscosity of chitosan decreased 80% after 15 h of ultrasound treatment while the content of NH_2 remained unchanged. Chen et al. [150-152] investigated the effect of ultrasonic conditions on changes in MW and polydispersity of treated chitosan, and the results showed that the treated chitosan was degraded faster in dilute solutions and lower temperature solutions, and degradation increased with prolonged ultrasound time. The polydispersity decreased with ultrasound treatment for all ultrasound conditions studied.

Other researchers [153-156] also pointed out that ultrasound treatment can be applied to degrade molecules and to lower the polydispersity of treated chitosan, and the procedures are fast, simple, and easy to control.

1.2.2 Carboxymethyl Chitosans

1.2.2.1 O-Carboxymethyl Chitosans

The method of preparing O-carboxymethyl chitosan from chitosan has been known for a long time. However, the work [157] involved was lengthy, as it required protection and de-protection of the amino group. This kind of chitosan derivative has the carboxymethyl group substituted exclusively on the oxygen of C_6-carbon of glucosamine unit (Fig.1.7).

With the product O-carboxymethyl chitosan, water solubility was not achieved unless the degree of substitution (DS) of carboxymethyl group per glucosamine monomer unit was at least one. [157]

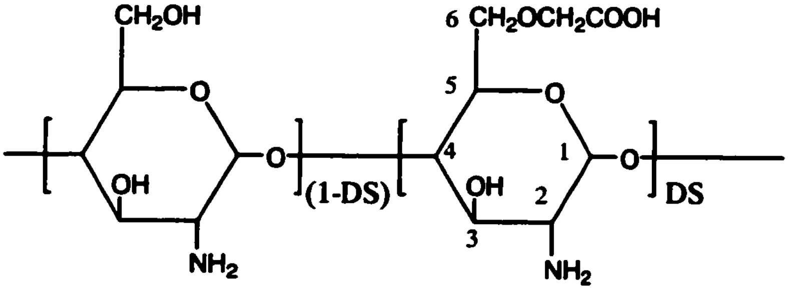


Fig.1.7 Molecular structure of O-carboxymethyl chitosan

Park et al. [158] prepared O-carboxymethyl chitin directly from chitin by treating the suspended chitin in aqueous NaOH solution (42%) with sodium monochloroacetate at 30°C for 5h. After filtering off the unreacted suspension of chitin through glass wool, the pH of the filtrate was adjusted to 7 with aqueous HCl solution; the solution was then dialysed for 3 days against deionized water. In this procedure, no organic solvent was used. The alkali treatment was performed at a higher temperature (30°C) to permit deacetylation of chitin (DD = 33%). There are two disadvantages to this method: the yields of products are low (<50%), and their water solubilities are poor (an observable separate gel phase forms).

1.2.2.2 N-Carboxymethyl Chitosans

N-carboxymethyl chitosan is prepared by treating chitosan with glyoxylic acid and then reducing it. [159] This chitosan derivative has the carboxymethyl group substituted exclusively on the amino group of glucosamine unit (Fig.1.8). The N-carboxymethyl chitosans obtained as white, free-flowing powders were reported to be soluble in water at all pH values, regardless of their DS that ranged from 0.25 to 1.0. [159]

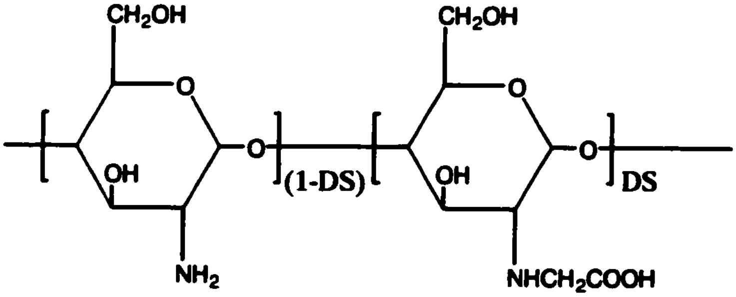


Fig.1.8 Molecular structure of N-carboxymethyl chitosan

1.2.2.3 N,O-Carboxymethyl Chitosans

In 1986, Hayes [160] disclosed a novel carboxymethyl derivative of chitosan having carboxymethyl groups substituted both on the amine group and on the hydroxyl group, with the DS less than 1.0. The NMR spectrum of the product labelled with C-13 confirmed the presence of both $-NH^{13}CH_2COONa$ and $-O^{13}CH_2COONa$ groups with the signal attributed to the latter group being considerably larger than that of the former. Methods for the preparation of the N,O-carboxymethyl chitosan derivative were also reported, including the process of loosening the coiling and interlocking of chitosan polymer chains in the solid phase by swelling the solid polymer. For some of the materials, the degree of water solubility is limited to a point where the material partly forms an observable separate gel phase as well as partly dissolving in water. The degree of water solubility of these derivatives is variable, as it appears to vary with the molecular weight of the material as well as with the DS.

There are some improved methods [161-162] with the "decrystallization" of chitosan in the solid phase while it is dispersed as slurry in a diluent liquid medium. The 'causticized' or 'neutralized' slurry (pH: 7.5 to 14) was then reacted with monochloroacetic acid, which would have caused formation of N,O-carboxymethyl chitosan.

Muzzarelli [163] also reported an alternative route to N,O-carboxymethyl chitosan as follows: Chitosan, suspended in NaOH (42%), is reacted with monochloroacetate (20°C, 24h) and then neutralized with HCl. Glyoxylic acid is added to the solution in the ratio glyoxylate/amine close to 1.6/1.0. The resulting solution (pH 3.5) is treated with sodium borohydride to pH 4.8 over a period of 24h and then dialysed against deionized water, and liophilized to yield N,O-carboxymethyl chitosan sodium salt. This procedure has a number of advantages: It does not require heating, and the synthesis is conducted totally in aqueous media.

Studies [160,164-166] of the substituent distribution on N,O-carboxymethyl chitosan by NMR method etc. indicated that the substitution occurs more readily on the hydroxyl oxygen atom than on the amine nitrogen atom, apparently because the amine centres are involved in internal hydrogen bonding within the structure of the chitosan polymer and are not as accessible as the alcoholic side chain for substitution reaction. It is found generally that the ratio of primary amine to secondary amine units in N,O-carboxymethyl chitosan is about 2:1. Hence, with only a small proportion (typically 20%-25%) of the nitrogen atoms in N,O-carboxymethyl chitosan having carboxymethyl groups and an even smaller proportion (typically 10%-15%) of them having acetyl groups. Over half the amine groups remain free.

1.2.3 Quaternary Ammonium Derivatives of Chitosan

1.2.3.1 N-2-Quaternized Derivatives of Chitosan

In 1986, Domard et al. [167] first reported a new method for the quaternization of chitosan. N,N,N-trimethyl chitosan ammonium iodide (TMCI) was obtained by reaction of a low acetyl content chitosan with methyl iodide and sodium hydroxide under controlled conditions (Fig.1.9). The reaction was performed to obtain derivatives of chitosan of various degrees of quaternization (DQ). For DQ greater than 25%, polymers are soluble in water at all pH values. Dung et al. [168] used NMR spectroscopy to characterize the molecular structure of TMCI. N,N,N-trimethyl chitosan ammonium chloride (TMCC) was prepared by reductive methylation of chitosan by MeI and the counterion I^- was exchanged with Cl^- in an aqueous NaCl solution. [169-170] The molecular structure of TMCC was confirmed by NMR and FT-IR spectroscopies, [169-170] and the TMCC was applied as a potential absorption enhancer for hydrophilic drugs [169] and as antimicrobial finishing agents for textiles. [170]

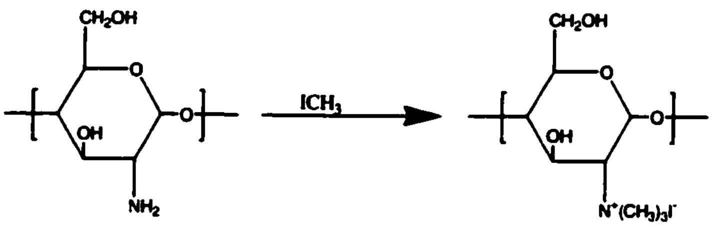


Fig.1.9 Reaction for the obtaining of TMCI

C. H. Kim et al. [171-173] synthesized some novel N-2-quaternized derivatives of chitosan, and explored their antibacterial activity. The amino group of chitosan was first alkylated via Schiff's base intermediate and then treated the alkylated derivative using MeI to give the water-soluble cationic polyelectrolyte (chitosan quaternary ammonium salt). The antibacterial activity studies of these chitosan derivatives showed that the activity increases with an increase in the chain length of the alkyl substituent, and this increased activity could be ascribed to the contribution of the increased hydrophobic properties of the derivatives.

1.2.3.2 N-(2-Hydroxy)Propyl-3-Trimethyl Ammonium Chitosan Chlorides (HTCC)

In 1986, Lang et al. [174] first published the preparation of HTCC from chitosan and glycidyltrimethylammonium chloride (GTMAC), characterization of the resulting derivatives was not reported. In the work of Loubaki et al., [175] modification of chitosan by GTMAC at various stoichiometries in distilled water was studied using elemental analysis and FT-IR spectroscopy. Moreover, the resulting derivative of chitosan was characterised by ^{13}C and ^{1}H NMR spectroscopy. All the results are consistent with N-monoalkylation (Fig.1.10).

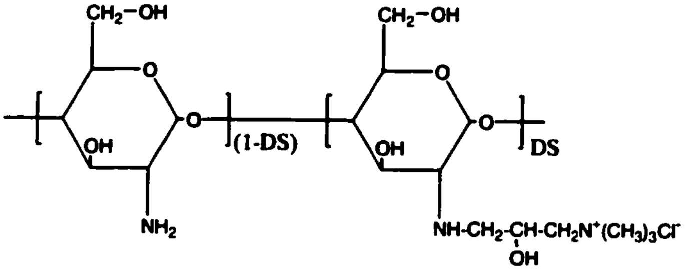


Fig.1.10 Molecular structure of HTCC

To date, HTCC has also been prepared by other workers in distilled water/acidic aqueous solution, and has been applied as wood preservative, [176] antimicrobial agent for cotton finishing [177] and flocculating/sterilizing agent for refinery wastewater. [178]

1.2.3.3 Other Chitosan Derivatives

Asao [179] reported the synthesis of water-soluble cationic chitosan derivatives. A dispersion of 20 g powdered chitosan (DD = 87 mol. %) in isopropanol was treated with an aqueous solution containing 3-chloro-2-hydroxypropyltrimethylammonium chloride and NaOH at 60°C for 5h; after filtration of the mixture, the solid obtained was washed and dried to give 38.3 g cationic chitosan.

Suzuki [180-181] prepared the chitosan derivatives containing quaternary ammonium groups by mixing chitosan with a compound having aldehyde and quaternary ammonium groups, adding reducing agents, and reacting the amino groups at 2-positions of D-glucosamine units by reductive alkylation for selectively introducing the quaternary ammonium groups. For example, 96%-deacetylated chitin was reacted with 4-[3-(trimethylammonium)propoxy]benzaldehyde iodide in the presence of $NaBH_4$ to give a derivative.

1.3 Silk and Its Dyeing

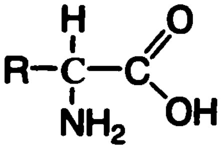
1.3.1 Silk Fibers

Silk is a natural protein fiber, which is produced by the larva of certain insects. According to Chinese legend, silk culture began in 2640 B C when Empress Hsi Ling Shi became interested in silkworms and learned how to reel the silk and make it into fabric. Through her efforts China developed a silk industry that the country monopolized for 3,000 years. Today, major producers of silk are China (54 percent), India (14 percent), and Japan (11 percent), [182] and most silk fibers are converted to apparel fabrics; minor amounts of silk fibers are used in upholstery, draperies, and bed linens.

1.3.1.1 Structure

The silk polymer is a chain of amino acids forming a protein (polypeptide) called fibroin. The fibroin is composed of 15-18 different amino acids, depending on the type of silk fiber. Three amino acids—glycine, alanine, and serine—make up about 86% of the fibroin polymer (Fig.1.11). [183] The relatively small size of these amino acids compared to those in keratin polymers (wool fiber) permits the fibroin polymers to crystallize readily. Silk fiber is estimated to be about 70-75% crystalline and, correspondingly, about 30-25% amorphous. [183] The chains lie close enough together that numerous hydrogen bonds are formed. Ionic bonds are formed also but are not the major force of attraction between fibroin chains.

Further, the fibroin protein occurs only in a pleated beta -sheet configuration (Fig.1.12). [184] The length of the polymer chain is slightly greater in silk fiber than in wool fiber. The differences in the number of types of amino acids, their relative sizes, and the configurations of the polymer chain account for many of the differences in the properties of silk and wool fibers.



Glysine (~44.6%) R = H

Alanine (~29.4%) R = CH_3

Serine (~12.1%) R = HO-CH_2

Fig.1.11 The three amino acids that occur most frequently along the fibroin polypeptide polymer in silk fiber

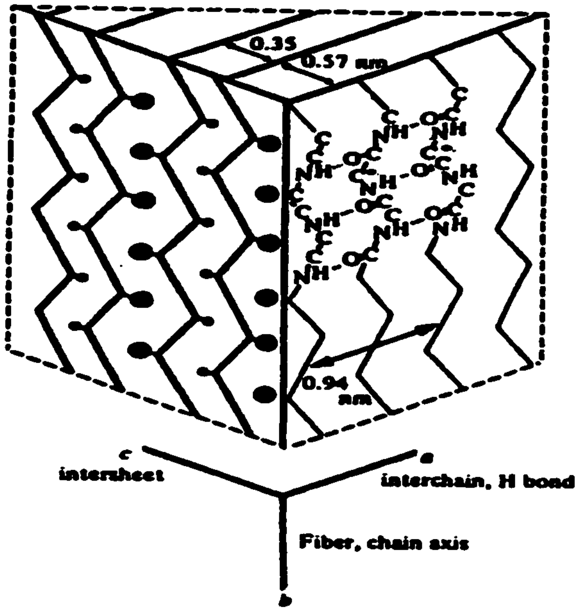


Fig.1.12 The antiparallel beta-pleated sheet configuration of the fibroin protein polymer (The chain axis is parallel to the fiber axis) [184]

Once the sericin (water-soluble gum) is dissolved away, the filaments separate and, when viewed under a scanning electron microscope, appear as shown in Fig.1.13 and 1.14. [185]

Silk filaments are uneven in diameter along their length. Cultivated silk filaments have a triangular cross-sectional shape with rounded corners; wild silk filaments are almost rectangular. Wild silk is more ribbon-like in shape than cultivated silk.

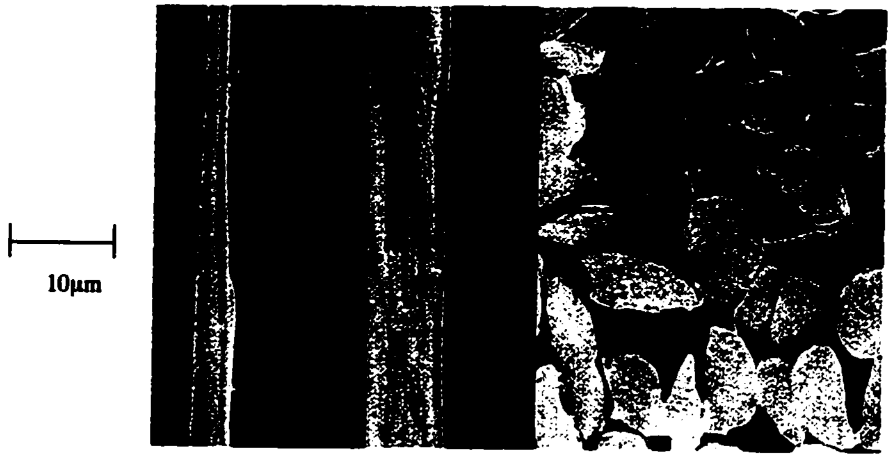


Fig.1.13 Photomicrographs of the longitudinal and cross-sectional views of cultivated, degummed silk [185]

Fig.1.14 Photomicrographs of the longitudinal and cross-sectional views of wild (Tussah) silk [185]

Cultivated silk fiber has no identifiable submicroscopic structure. It is a fine, coagulated stream of protein polymer solution. Wild silk or Tussah silk has an internal fibrillar structure (Fig.1.15). [186]

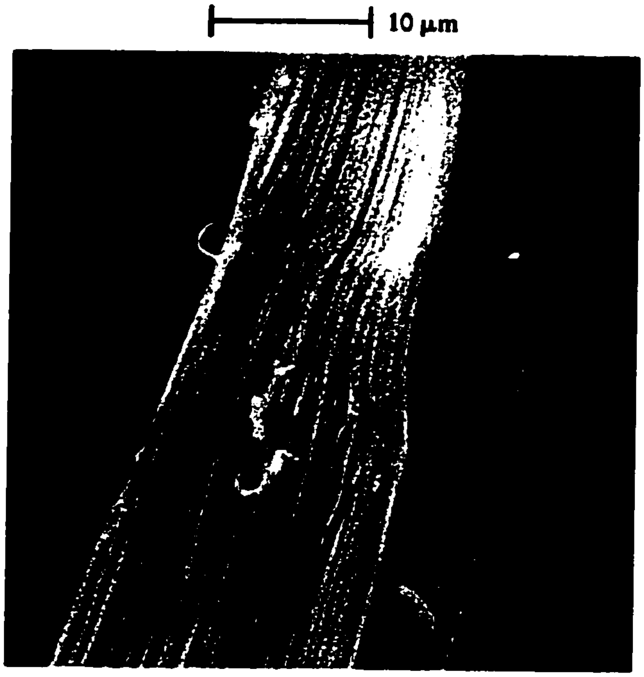


Fig.1.15 Longitudinally split filament of Tussah (wild) silk [186]

1.3.1.2 Applications

Silk has always been associated with expense and luxury, in particular with *haute couture*, which is now a dramatically declining sector of the fashion industry. In recent years, pure silk and silk-blend clothing have found their way into the high street retail shops at affordable prices. This has been largely due to the introduction of ease-of-care and sand-washed (abraded fabric surface) silk garments for both women and men. In addition, the trend for natural products and ecologically sound processing and production methods has added impetus to the rising demand. The opening up of China and the easing of government restrictions and controls have led to an expansion of ready-made Chinese silk goods into western markets. It is anticipated that silk production will continue to meet the demands of an expanding market for such silk goods as woven and knitted outer clothing, drapery and upholstery fabric, underwear, sleep wear, embroidery, and ribbons and edgings.

1.3.2 Dyeing of Silk with Acid Dyes

Under certain conditions, the hydrogen ion attached to the carboxylic acid is transferred to the amino group so that the ends of the fibroin macromolecule acquire opposite charges:

$$H_2N\text{-}Fb\text{-}COOH \longrightarrow H_3{}^{+}N\text{-}Fb\text{-}COO^{-}$$

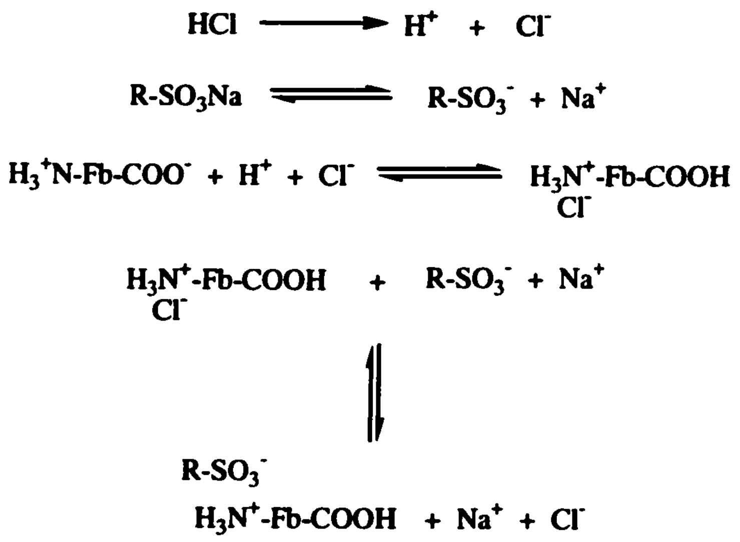
When silk containing such molecules with electrically charged ends is entered into a solution of an acid, say hydrochloric acid, some of the negatively charged carboxylate groups ($-COO^{-}$) take up hydrogen ions released from hydrochloric acid in the solution and become electrically neutral carboxylic acid groups ($-COOH$). The chloride anions, also released from the hydrochloric acid, are absorbed and retained by the positively charged amino ends of the fibroin macromolecule (below).

$$HCl \longrightarrow H^{+} + Cl^{-}$$

$$H_3{}^{+}N\text{-}Fb\text{-}COO^{-} + H^{+} + Cl^{-} \rightleftharpoons \underset{Cl^{-}}{H_3N^{+}}\text{-}Fb\text{-}COOH$$

Thus, when the silk is in an acidic solution, the concentration of the acid in the solution is decreased.

The amount of the acid absorbed by the fibre increases with time until it reaches its maximum, after which it remains constant. This constant value is known as the equilibrium absorption of acid by silk. The value increases as the starting concentration of the acid in the solution increases. From this it follows that when silk is kept in contact with more and more concentrated solutions of the acid for a sufficiently long time to attain equilibrium, more and more positive sites ($-NH_3^+$) are produced in the silk. These sites play an important role in the dyeing of silk with acid dyes. In a solution of acid (HCl), the acid dye interacts with silk by the following mechanism.



$$HCl \longrightarrow H^+ + Cl^-$$

$$R\text{-}SO_3Na \rightleftharpoons R\text{-}SO_3^- + Na^+$$

$$H_3^+N\text{-}Fb\text{-}COO^- + H^+ + Cl^- \rightleftharpoons \underset{Cl^-}{H_3N^+\text{-}Fb\text{-}COOH}$$

$$\underset{Cl^-}{H_3N^+\text{-}Fb\text{-}COOH} + R\text{-}SO_3^- + Na^+ \;\rightleftharpoons\; \overset{R\text{-}SO_3^-}{H_3N^+\text{-}Fb\text{-}COOH} + Na^+ + Cl^-$$

In the initial stages the positive site ($-NH_3^+$) of the silk fibre attracts the comparatively small chloride anions from the dyebath. Subsequently, some of the chloride ions are replaced by the much bigger dye anions, which are held at the positive sites of the fibre by electrostatic forces. In addition, the R groups present in the dye are bound to the fibre by hydrogen bonds etc. Thus, the dye anion is held more strongly on the fibre than the chloride anion. So the chloride anions held at the positive sites in the fibre are continuously replaced by the dye anions.

Though silk has an affinity for acid dyes, the dyed shades tend to be slower than on wool. However, silk exerts its affinity for acid dyes at lower temperatures than wool: The dyeing is usually started at 40°C and the temperature allowed to rise to about 90°C. It is rarely necessary to exceed 90°C and boiling is to be avoided, if possible. Boiling exerts deleterious effects on the tensile strength and luster of silk. Silk may be protected during dyeing by adding up to 100 litres of boiling off liquor (degumming bath) per 1,000 litres of water. If the dyeing requires acid, the liquor is broken with sulphuric acid and in the case of neutral dyeing acid dyes, acetic acid is suggested. Some neutral dyeing acid dyes may be dyed from soap liquor containing 5-20% (on the weight of fibre) Glauber's salt.

Chapter 2

Introduction

2.1 Aim

We aim to study the dyeability (depth, fastness) of silk fabrics with chitosan and its derivatives, and we hope, based on the results of this study, a chitosan or its derivative with better dyeability can be found.

2.2 Research Background

Chitosan and its derivatives could improve the dyeability of textiles. This might be due to the enhanced electrostatic attraction between the protonated amino group in chitosan/its derivatives and the anionic dye. An on-line search on the literature of chitosan and its derivatives in silk from 1967 to now has been performed, and showed that only limited research has been carried out in this area. As mentioned in section 1.1.6, Kako and Katayama[97-106] investigated the effect of chitosan on the dyeing properties of silk fabric. They found that the chitosan treated fabric took up more acid dyes than the untreated fabric, and it was not effective for reactive dyes. They explained the result by the ion exchange mechanism. Davidson and Xue [187] improved the dyeability of wool (also be protein fibre), by treatment of chitosan. However, no previous work was performed to develop the relation between dyeability and chitosan of different degree of deacetylation or molecular weights.

Water-soluble chitosan derivatives are particularly important for our proposed work because water is the most important medium for textile wet processing. Some of these may affect the dyeability and other properties of silk but there was no previous work reported.

2.3 Significance

First, chitosan and its derivatives are prepared from chitin, which is extracted mostly from the shell of sea animals, and is the by-product of the seafood industry. The application of chitosan and its derivatives in textile industry is a way of recycling waste into useful materials.

Second, chitosan and its derivatives are modified natural polymers, which possess many excellent characteristics, e.g. good biocompatibility and biodegradability.

Third, the application of chitosan and its derivatives on silk can greatly improve the colour depth. Since the amount of chitin in nature is so abundant, and the price of chitosan is much cheaper than dyestuffs, the use of chitosan in dyeing will greatly reduce the cost of the dyeing process and the water effluent treatment.

Finally, the fundamental studies of chitosan and its modified derivatives on dyeing of silk fabric can lead to a more in depth understanding of their interrelation, which is rarely explored.

2.4 Methodology

Preparation and characterization of chitosan and its derivatives

Chitin was purchased from commercial sources. Chitosans of different degree of deacetylation and molecular weight were prepared in our laboratory. These chitosans were then characterized mainly by: (a) spectroscopic studies, (b) elemental analysis, (c) dilute solution viscometry study, and (d) thermal analysis.

Two chitosan derivatives of different degrees of substitution: O-carboxymethyl (O-CM) chitosan and N/O-(2-hydroxy)propyl-3-trimethyl ammonium chitosan chloride (N/O-HTCC) were prepared and studied in the same manner.

Applying chitosan and its derivatives on silk fabric

Chitosan and its derivatives were applied on silk fabric by exhaustion and padding methods under various conditions. Different conditions of curing were employed, thus the optimal condition can be determined.

Dyeing of the treated fabric

Dyes of different molecular structures, especially those containing different numbers of hydrophilic/hydrophobic groups, were employed. The exhaustion method was used for study.

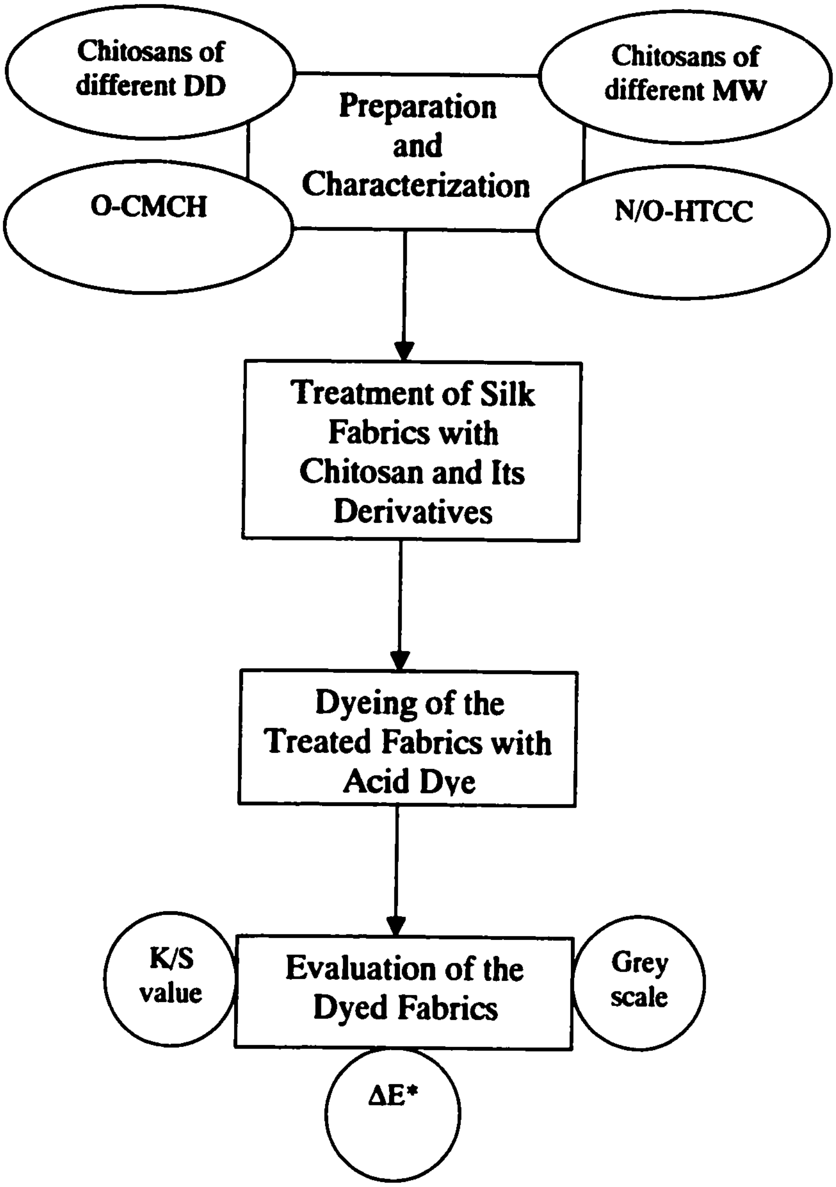
Evaluation of the dyed fabric

The colour depth, colour difference and fastness of the dyed fabric were assessed to determine the effectiveness of chitosan and its derivatives treatments.

Chapter 3

Experimental

These experiments were conducted according to the following flow chart:



3.1 Materials and Chemicals

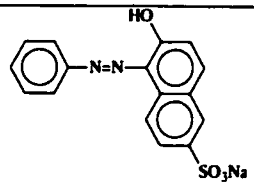
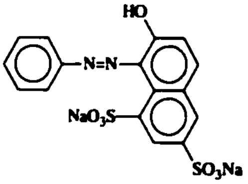
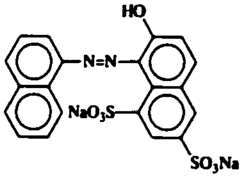
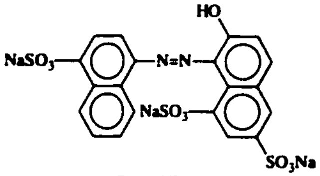
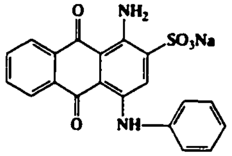
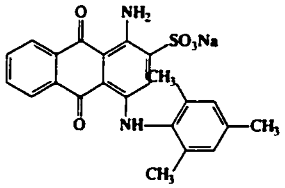
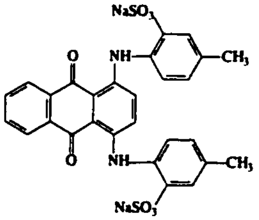
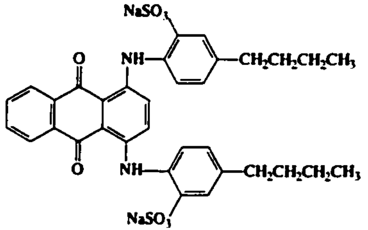
The materials and chemicals used in this research work are listed in Table 3.1.

Table 3.1 The materials and chemicals used

No	Item	Supplier	Specification
1	Chitin Powder	Sigma	Practical grade
2	Sodium Hydroxide	BDH	A.R.
3	Hydrochloric Acid	Riedel-de Haën	G.R.
4	Ethanol	Riedel-de Haën	A.R.
5	Chloroacetic Acid	Aldrich	A.C.S.
6	Glycidyltrimethyl-ammonium chloride (GTMAC)	Fluka	Purity = 63%, d = 1.13
7	Acetic Acid	Aldrich	A.C.S.
8	Sodium Acetate	Aldrich	A.C.S.
9	Sodium Carbonate	Aldrich	A.C.S.
10	Sodium Hydrogencarbonate	Aldrich	A.C.S.
11	Citric Acid	Aldrich	A.C.S.
12	Sodium Citrate Dihydrate	Aldrich	A.C.S.
13	Formic-*d* Acid-*d*	Aldrich	99+ atom % D
14	Deuterium Oxide	Aldrich	100.0 atom % D
15	Silk Fabric	Rong Hua Silk Co. Ltd. (China)	First class, bleached, pure cultivated, warp: 64/cm, weft: 42/cm with the weight of 54.8 g/m^2
16	Silk Fabric	Rong Hua Silk Co. Ltd. (China)	First class, bleached, pure cultivated, warp: 45/cm, weft: 35/cm with the weight of 76.5 g/m^2
17	Albegal B (Leveling Agent)	Ciba	Practical grade
18	Sodium Sulphate Crystals (Glauber Salt)	Harris Hart	Practical grade

Moreover, Aldrich supplied eight acid dyes used in dyeing; their molecular structure is shown in Table 3.2.

Table 3.2 Molecular structures of acid dyes used

Name	Color Index Number	Molecular Structure
AO 12	C.I. 15970	
AO 10	C.I. 16230	
AR 44	C.I. 16250	
AR 18	C.I. 16255	
AB 25	C.I. 62055	
AB 129	C.I. 62058	
AG 25	C.I. 61570	
AG 27	C.I. 61580	

3.2 Preparation and Characterization of Chitosan and Its Derivatives

3.2.1 Chitosans of Different DD

Chitosans of different DD were prepared by heating chitin in alkali solution under different experimental conditions. Table 3.3 summaries the reaction conditions of these chitosans.

Table 3.3 The reaction conditions of chitosans of different DD (liquor ratio = 10:1)

Sample	Raw Material	Concentration of aqueous NaOH Solution (wt.%)	Temperature ± Av. Dev. (°C)	Reaction Time (h)	DD ± Av. Dev. (%)
CH01	Chitin	48	100±2	1	57±1
CH02	CH01	10	100±2	1	72±2
CH03*	Chitin	48	100±2	5x1	95±2
CH04	CH01	40	100±2	1	88±2
CH05	CH01	48	100±2	1	89±2

*Chitosan CH03 (DD=95±2%) was made after consecutive deacetylations of chitin by heating in 48 wt.% of aqueous NaOH solution (liquor ratio = 10:1) at 100±2°C. Chitin was first deacetylated after heating for 1h and the product was separated for second heating, and then the derivative yielded from the second heating was isolated for third heating, and so on was repeated for five times to give CH03.

The DD of these chitosans (Table 3.3) was determined based on ^{1}H NMR data, which were recorded with a Bruker (DPX400) NMR spectrometer. Spectra were run at 80°C in D_2O (Deuterium oxide) in the presence of small amount of DCOOD (Formic acid-d).

3.2.2 Degraded Chitosans of Same DD but Different MW

200mL, 1.0 wt.% of chitosan CH04 (DD=88±2 mol.%) solutions (in 2.0 wt.% of aqueous acetic acid solution) were placed in an ultrasonic bath (28KHz, 420W) and ultrasonically degraded at 70±2°C for different lengths of time. The degraded chitosan solutions were then neutralised with concentrated NaOH solution and separated by centrifuging. The solid obtained was washed with D.I. water twice, and then with methanol. Finally the product was dried in an oven at 60°C, then under vacuum at 60°C over night. The DD of degraded chitosans was determined by ^{1}H NMR method.

The intrinsic viscosity $[\eta]$ of CHO4 and degraded derivatives were measured with an Ubbelohde viscometer (Schote Gerate) in aqueous 0.2M CH_3COOH/0.1M CH_3COONa solution at 30.0±0.1°C. Their MWs were determined by the dilute solution viscometry method using Mark-Houwink equation ($[\eta] = k \cdot M^{\alpha}$), and their coefficient values (k and α) were determined according to Wang's expressions (see Viscometry in Section 1.1.4.2).

3.2.3 O-Carboxymethyl Chitosans (O-CMCH)

3.2.3.1 Pretreatment of Commercial Chitin Powder

The commercial chitin powder was purified according to the reported method (see Section 1.1.4.1), as described below.

Deproteinisation: At 65°C, 100g of commercial chitin powder was soaked in 1000mL of aqueous NaOH solution (1.0M) and stirred for 5h, and then the solution was filtered. The deproteinised chitin was washed with D.I. water. The solid was dried overnight in an oven at 60°C.

Demineralisation: About 85g of deproteinised chitin powder was added in small portions to 1500mL of HCl solution (1.5M) with stirring at 25°C. The mixture was then filtered after being stirred at 25°C for 5h. The solid chitin powder obtained was washed with D.I. water, and was dried overnight in an oven at 60°C.

Decoloration: To about 70g of chitin powder, 1700mL of ethanol was added, and the resulting slurry was stirred at 50°C for 1h. The slurry was then filtered and the solid was washed with D.I. water and dried overnight in a vacuum oven at 60°C.

3.2.3.2 Preparation and Characterization of O-CMCH

To 10 mL of freshly prepared aqueous NaOH solution (40 wt.%), 1g of purified chitin powder and 0.5g of isopropanol were added, and the resulting slurry was stirred under N_2 at 90°C. To the stirring slurry, finely powdered chloroacetic acid was added in small portions. The contents were stirred for a further 24h after the addition was completed. The pH of the mixture was then adjusted to 7.0 with concentrated HCl solution in an ice bath. The mixture was then dialysed in running water for three days. The water of the dialysed mixture was evaporated at 50°C under reduced pressure. The solid collected was dried overnight in a vacuum oven at 60°C. Similar reactions were carried out by treating chitin powder with different amounts of chloroacetic acid (Table 3.4).

Table 3.4 Mole ratio of reactants and the yield of O-carboxymethyl chitosans

Sample	Molar ratio of chloroacetic acid to chitin monomer unit	Appearance	Yield ± Av. Dev. (g)
Chitosan	0.0	Pale brown	0.811±0.001
OCMCH1	0.1	Pale brown	0.815±0.001
OCMCH2	0.3	Pale brown	0.820±0.001
OCMCH3	0.5	Pale brown	0.831±0.001
OCMCH4	2.0	Pale brown	0.827±0.001

Solutions of OCMCH3 (50mg) in 5mL of D.I. water or 0.10M aqueous HCl or NaOH solution were cast on a plastic plate and were allowed to dryness. The film was dislodged and was then dried in a vacuum oven at 60°C overnight. The FTIR spectra of these sample films were obtained with a Nicolet Magna (750) FTIR spectrophotometer. The ^1H NMR spectra of these samples were obtained at 80°C using $DCO_2D + D_2O$ (1 wt.%) as solvent with a Bruker (DPX400) NMR spectrometer. The ^{13}C NMR spectrum of these samples were obtained at 80°C using D_2O as a solvent with an Inova Varian (AS500) NMR instrument. The C% and N% of these samples were measured with an Elementar

(Vario EL) instrument. Their DSC and TGA curves were recorded with Mettler TA instruments.

3.2.4 N/O-(2-Hydroxy)Propyl-3-Trimethyl Ammonium Chitosan Chlorides (N/O-HTCC)

At 80°C, 2g of Chitosan CH05 (DD=89±2%) was soaked in 40mL of D.I. water or carbonate buffer solution (pH=10) with stirring. To the stirring suspension, glycidyltrimethylammonium chloride (GTMAC) was added in small portions. The mixture was stirred for a further 24h after the addition was completed; the chitosan particles were then completely dissolved in water. The solution was ultrafiltrated through membrane (PES-100, SINR, MW cutoff at 10,000); the residue was dissolved in 300 mL of D.I. water and ultrafiltrated again. This operation was repeated five times. Then the residue was dried at 50°C under reduced pressure. The solid collected was dried overnight in a vacuum oven at 60°C. Similar reactions were carried out between CH05 and different amounts of GTMAC in different media (Table 3.5).

Table 3.5 Reaction medium, mole ratio of reactants and the yield of N/O-HTCC

Sample Name	Reaction Medium	Molar ratio of GTMAC to chitosan monomer unit	Appearance	Yield ± Av. Dev. (g)
NQC1	D.I. water	2	Pale brown	3.320±0.001
NQC2	D.I. water	4	Pale brown	4.181±0.001
NQC3	D.I. water	6	Pale brown	4.823±0.001
NQC4	D.I. water	8	Pale brown	5.141±0.001
NOQC1	Carbonate buffer	2	Pale brown	3.812±0.001
NOQC2	Carbonate buffer	4	Pale brown	4.489±0.001
NOQC3	Carbonate buffer	6	Pale brown	5.218±0.001
NOQC4	Carbonate buffer	8	Pale brown	5.283±0.001

Solutions of all samples (50mg) in 5mL of D.I. water were cast on a plastic plate and were allowed to dry. The film was dislodged and was then dried in a vacuum oven at

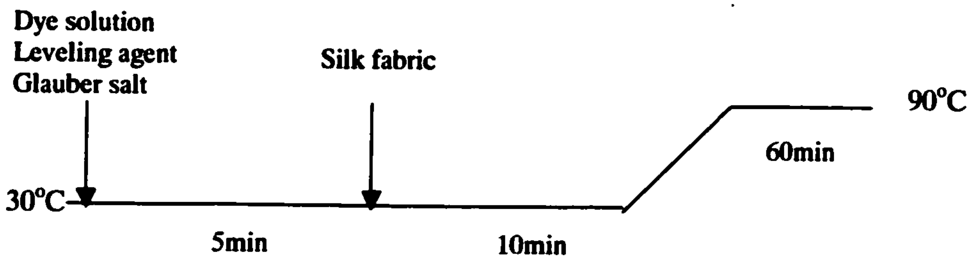
60°C overnight. The FTIR spectra of these sample films were obtained with a Nicolet Magna (750) FTIR spectrophotometer. The ^1H NMR spectra of these samples were obtained at 80°C using D_2O as solvent with a Bruker (DPX400) NMR spectrometer. The C%, N% and Cl% of these samples were measured with an Elementar (Carlo Erba 1106) instrument. Their DSC and TGA curves were recorded with Mettler TA instruments.

3.3 Treatment of Silk Fabrics with Chitosan and Its Derivatives

Chitosans of different DD and MW (No.15, Table 3.1), O-CMCH, and N/O-HTCC (No.16, Table 3.1) were applied on silk fabrics separately by exhaustion process at 90°C for 0.5h (0.5/1.0 wt.% of Chitosan/its derivatives in 1.0 wt.% of aqueous acetic acid solution, liquor ratio = 25:1) and padding (padder: Labortex Co. Ltd., wet: 100%) methods. The final padded fabrics were then dried at around 70°C.

3.4 Dyeing of the Treated Fabrics

Acid dyes (Table 3.2) with different molecular structure and containing different numbers of hydrophilic/hydrophobic groups were employed. The treated silk fabrics were dyed (2, 4, 6% owf) according to the following procedure:



After dyeing, silk fabrics were rinsed with hot D.I. water (60°C, 100 mL, 15 minutes) and cold D.I. water (100 mL, 15 minutes), and were then blown dry. The Leveling agent (1% owf) and Glauber salt (5% owf) were applied in the dyeing process. The liquor ratio was 50:1, and the pH of the solution was adjusted to 4 with citrate buffer.

3.5 Evaluation of the Dyed Fabrics

All dyed fabrics were conditioned in a standard conditioning room (20°C, 65% R.H.) for one day before measurement. The fabric was folded into four layers and then measured with a datacolor (Elrepho 2000) instrument using a 27mm aperture. The minimum reflectance value was used to calculate the color yield (K/S value) using the Kubelka and Munk equation

$$K/S = (1-R)^2 / 2R$$

Where K is the absorption coefficient and S is the scattering coefficient. R is the minimum reflection value of the dyed fabric.

The colour difference ΔE* (D65/10) was calculated according to the CIELAB colour difference formula

$$\Delta E^* = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2}$$

Where

ΔL* = Difference in lightness between the standard and the sample

Δa* = Difference in redness / greenness between the standard and the sample

Δb* = Difference in yellowness / blueness between the standard and the sample

The colorfastness to washing of the dyed silk fabrics was determined according to the international standard, ISO 105-C06: 1994(E), Test A1S. ("Textiles - tests for color fastness - Part C06: Color fastness to domestic and commercial laundering")

Chapter 4

Results and Discussion

4.1 Preparation of Chitosans of Different DD and Their Effect on the Dyeing Behaviours of Silk Fabrics

4.1.1 The Effect of Reaction Time and the Concentration of Aqueous NaOH Solution on the DD in the Deacetylation of Chitin

Chitosans of different DD ranging from 47±1% to 95±2% were prepared through heating the chitin, and then reheating the product obtained, in aqueous NaOH solution of different concentrations and at various lengths of time. The DD of all samples was evaluated based on ^1H NMR data. It is the simplest and most effective method for determining the DD value of chitosan. Differing from Hirai et al.'s method [65], the integral intensity of $-CH_3$ protons, I_{CH3} ($\delta = 2.75$ ppm), of the amide group and C2-H, I_{H2} ($\delta = 3.6$ ppm) were used in this study.

$$DD\% = [1 - (I_{CH3}/3I_{H2})] \times 100$$

Chitosan samples 1 to 5 (S1-S5) were obtained through heating the chitin in 48 wt.% of aqueous NaOH solution (liquor ratio = 10:1) at 93°C for 1-5h respectively. Fig.4.1 shows the DD of these chitosans and the reaction time of deacetyation.

Chitosan samples 6 to 11 (S6-S11) were obtained through reheating samples S1 to S5 respectively using 48 wt.% of aqueous NaOH solution (liquor ratio = 10:1) at 97°C. Fig.4.2 shows the DD of these chitosans and the total reaction time required.

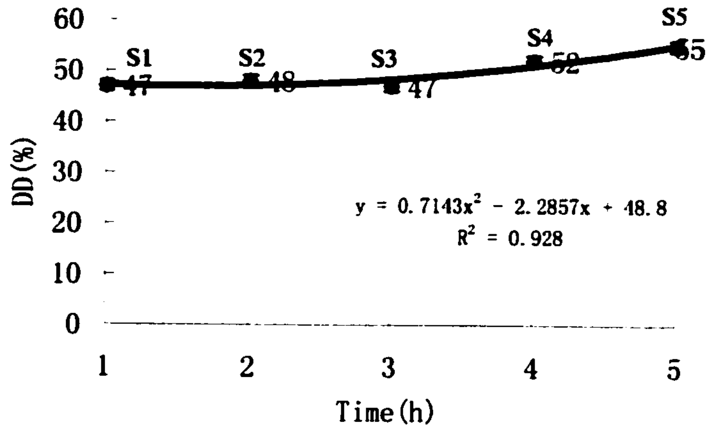


Fig.4.1 DD of chitosan samples (S1 to S5) against treatment time (48 wt.% of aqueous NaOH solution, 93°C, liquor ratio = 10:1)

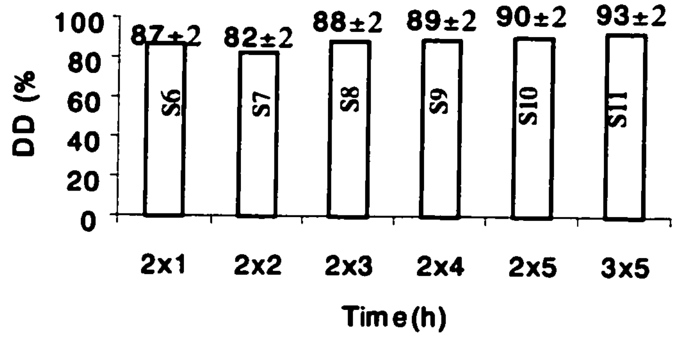


Fig.4.2 DD of chitosan samples (S6 to S11) against total treatment time (48 wt.% of aqueous NaOH solution, 97°C, liquor ratio = 10:1)

In our study, the results obtained showed that the DD increased fast from ~12% to 47±1% in the first hour of alkali treatment of chitin and then increased slowly as time increased. This fast rate of deacetylation in the first hour also was observed in the further hydrolysis of the product obtained. The results match previous report [51] very much. This can be explained by the process of heterogeneous deacetylation: The heterogeneous deacetylation firstly occurs in the amorphous region of chitin/chitosan particle, and then occurs at the surface of crystal region, finally occurs in the inner of the crystal region. The DD increases rapidly at the beginning when the heterogeneous deacetylation occurs in the amorphous region of the chitin/chitosan particle, and then increases slowly when the heterogeneous deacetylation occurs at the surface or in the inner of crystal region. With the heterogeneous deacetylation, we were unable to obtain a sample with DD = 100% even by treating the deacetylated sample again with NaOH solution at about 100°C.

Sample CH01 (DD = 57±1%) was used for the study of chitosan deacetylation under different concentrations of NaOH solutions. Samples were heated in aqueous NaOH solutions (liquor ratio = 10:1) of different concentrations, and the results were shown in Fig.4.3.

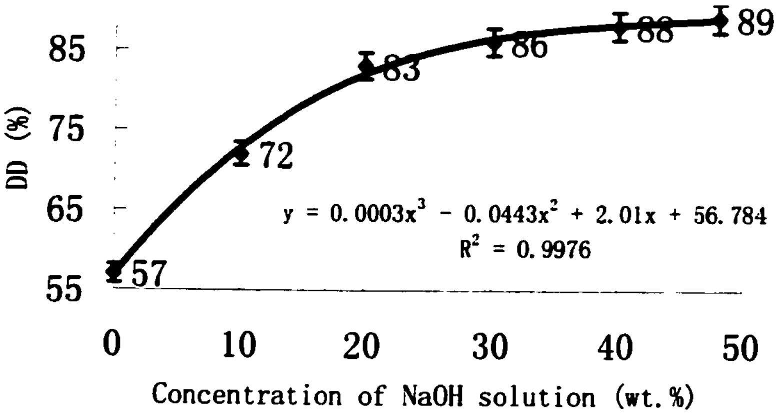


Fig.4.3 DD against concentration of aqueous NaOH solutions (liquor ratio = 10:1, 100±2°C, 1h)

It was obvious that the DD increased significantly as the concentration of aqueous NaOH solution increased from 0 wt.% to 20 wt.%, but with only little increase when the concentration was above 20 wt.%. Therefore, 30 wt.% of aqueous NaOH solution was considered appropriate for chitosan deacetylation.

4.1.2 Exhaustion Time of Chitosan Treatment of Silk Fabrics

Chitosan (DD = 93±2%) was applied to silk fabrics by the exhaustion (1 wt.% of chitosan in 1 wt.% aqueous acetic acid solution, liquor ratio = 50:1, 90±1°C), padding (wet = 100±2%) and curing (150±2°C, 3 minutes) methods under various conditions. The treated silk fabrics then were dyed (4%owf, pH = 4 adjusted by HCl solution) and their color yields (K/S values) were measured with a Datacolor (Elrepho 2000) instrument after conditioning (20°C, 65% R.H., 1 day). The results (Table 4.1) indicated that a 30 minute period is the best length of time for the exhaustion process, and curing is not necessary for the chitosan treatment of silk fabric. The 30 minute period is long enough to coat the silk with chitosan. A longer period at a high temperature may cause acid degradation of chitosan, and increase the water solubility of chitosan, which will then reduce the effect of chitosan on the dye uptake of silk. Curing may affect the affinity between chitosan and silk, and the degree of crystallization of chitosan acetate. Their effects on the dyeability of silk are complicated and may be offset.

Table 4.1 K/S values of dyed silk fabrics treated with chitosan (DD=93±2%)

Exhaustion time (Min.)	Curing	Dyestuff (C.I.)*	Wave length (nm) at minimum reflectance	K/S Value ± Av. Dev.
0	yes	AO 12	480	8.83±0.09
30	yes	AO 12	480	9.01±0.09
60	yes	AO 12	480	8.99±0.09
90	yes	AO 12	480	8.37±0.08
90	no	AO 12	480	8.44±0.08
0	yes	AO 10	500	5.04±0.05
30	yes	AO 10	500	8.06±0.08
60	yes	AO 10	500	7.89±0.08
90	yes	AO 10	500	7.61±0.08
90	no	AO 10	500	7.38±0.07
0	yes	AR 44	520	8.10±0.08
30	yes	AR 44	520	10.1±0.1
60	yes	AR 44	520	9.85±0.09
90	yes	AR 44	520	9.11±0.09
90	no	AR 44	520	9.46±0.09

*For the molecular structures of dyes, see Table 3.2.

4.1.3 pH Adjustment of Dyeing Bath before Dyeing

The pH of dyeing baths was adjusted with either HCl or citrate buffer. The results of pH change on the dyeing of silk fabrics in terms of color yield and color fastness to washing of the dyed silk were recorded in Table 4.2. The dye used was AR 18 (Table 3.2), and the chitosan used was S11 (DD = 93%).

Table 4.2 Effect of pH adjustment method on the dyeing properties of silk fabric

Silk fabric	pH adjustment method	pH value			K/S value ± Av. Dev.	Grey Scale
		Before dyeing	After dyeing	Gain (%)		
Blank	By HCl solution	4.00	5.48	37.0	1.43±0.01	2–3
Blank	By citrate buffer	4.00	4.12	3.00	3.07±0.03	2
Chitosan treated	By HCl solution	4.00	4.40	10.0	3.74±0.04	2
Chitosan treated	By citrate buffer	4.00	4.05	1.25	3.90±0.04	2

The results indicated a greater increase in pH value in the blank adjusted with HCl than in that with citrate buffer after dyeing process. The color yield (K/S value) of the former is much lower than the latter. However, in the chitosan treatment process the color yield of the citrate adjusted dyeing is only a little higher than that adjusted with HCl. The efficiency of color uptake in the citrate buffer solution probably was reduced due to the uptake of anionic groups of the buffer to the chitosan. Thus, the lead of using citrate in dyeing is abated.

4.1.4 Effect of Chitosans of Different DD on the Dyeability of Silk Fabrics

The color yields (K/S values), color fastness to washing (grey scale), CIE L*a*b* values and color difference (ΔE*) of silk fabrics treated with chitosans CH01, CH02, CH03 and dyed with acid dyes are summarized in Table 4.3a to 4.3d.

Table 4.3a Effect of chitosans on the dyeability of silk fabrics

Chitosan Conc. (wt.%)	Dyestuff (C.I.)*	Depth (%owf)	K/S value ± Av. Dev.			Gain of K/S value (%)			Grey Scale		
			CH01	CH02	CH03	CH01	CH02	CH03	CH01	CH02	CH03
0.0	AO 12	2	4.70±0.05	4.70±0.05	4.70±0.05	0.00	0.00	0.00	1–2	1–2	1–2
0.5	AO 12	2	5.00±0.05	9.10±0.09	9.20±0.09	6.00	92.0	95.0	1–2	1–2	1–2
1.0	AO 12	2	6.70±0.07	10.5±0.1	10.9±0.1	42.0	122	130	1–2	1–2	1–2
0.0	AO 12	4	9.90±0.09	9.90±0.09	9.90±0.09	0.00	0.00	0.00	1–2	1–2	1–2
0.5	AO 12	4	9.90±0.09	11.8±0.1	11.9±0.1	0.00	19.0	20.0	1–2	1–2	1–2
1.0	AO 12	4	12.6±0.1	12.9±0.1	15.1±0.2	27.0	30.0	53.0	1–2	1–2	1–2
0.0	AO 12	6	11.1±0.1	11.1±0.1	11.1±0.1	0.00	0.00	0.00	1–2	1–2	1–2
0.5	AO 12	6	15.8±0.2	16.8±0.2	18.1±0.2	42.0	51.0	63.0	1–2	1–2	1–2
1.0	AO 12	6	16.9±0.2	16.9±0.2	18.8±0.2	52.0	52.0	69.0	1–2	1–2	1–2
0.0	AO 10	2	0.80±0.01	0.80±0.01	0.80±0.01	0.00	0.00	0.00	1	1	1
0.5	AO 10	2	1.20±0.01	2.40±0.02	2.40±0.02	56.0	207	209	1	1	1
1.0	AO 10	2	2.60±0.03	4.20±0.04	4.20±0.04	240	440	444	1	1	1
0.0	AO 10	4	2.80±0.03	2.80±0.03	2.80±0.03	0.00	0.00	0.00	1	1	1
0.5	AO 10	4	2.90±0.03	3.70±0.04	3.70±0.04	3.00	30.0	31.0	1	1	1
1.0	AO 10	4	3.30±0.03	7.50±0.07	7.90±0.08	16.0	167	181	1	1	1
0.0	AO 10	6	3.90±0.04	3.90±0.04	3.90±0.04	0.00	0.00	0.00	1	1	1
0.5	AO 10	6	4.20±0.04	6.40±0.06	6.80±0.06	10.0	65.0	76.0	1	1	1
1.0	AO 10	6	4.60±0.04	8.10±0.08	8.90±0.09	18.0	110	130	1	1	1
0.0	AR 44	2	3.80±0.04	3.80±0.04	3.80±0.04	0.00	0.00	0.00	1–2	1–2	1–2
0.5	AR 44	2	4.50±0.04	9.20±0.09	10.7±0.1	21.0	145	185	1–2	1–2	1–2
1.0	AR 44	2	5.40±0.05	10.9±0.1	11.0±0.1	43.0	191	194	1–2	1–2	1–2
0.0	AR 44	4	6.20±0.06	6.20±0.06	6.20±0.06	0.00	0.00	0.00	1–2	1–2	1–2
0.5	AR 44	4	9.00±0.09	12.4±0.1	14.5±0.1	45.0	99.0	134	1–2	1–2	1–2
1.0	AR 44	4	10.2±0.1	13.0±0.1	16.4±0.2	64.0	110	164	1–2	1–2	1–2
0.0	AR 44	6	6.60±0.06	6.60±0.06	6.60±0.06	0.00	0.00	0.00	1–2	1–2	1–2
0.5	AR 44	6	10.4±0.1	12.5±0.1	15.0±0.1	58.0	88.0	127	1–2	1–2	1–2
1.0	AR 44	6	11.6±0.1	13.2±0.1	17.1±0.2	74.0	99.0	159	1–2	1–2	1–2
0.0	AR 18	2	1.20±0.01	1.20±0.01	1.20±0.01	0.00	0.00	0.00	1	1	1
0.5	AR 18	2	4.90±0.05	5.00±0.05	5.00±0.05	304	309	316	1	1	1
1.0	AR 18	2	7.50±0.07	7.80±0.08	7.90±0.08	521	545	555	1	1	1
0.0	AR 18	4	2.70±0.03	2.70±0.03	2.70±0.03	0.00	0.00	0.00	1	1	1
0.5	AR 18	4	5.10±0.05	7.80±0.08	7.90±0.08	90.0	193	196	1	1	1
1.0	AR 18	4	8.50±0.08	10.7±0.1	10.8±0.1	220	303	307	1	1	1
0.0	AR 18	6	3.20±0.03	3.20±0.03	3.20±0.03	0.00	0.00	0.00	1	1	1
0.5	AR 18	6	8.00±0.08	9.60±0.09	10.1±0.1	151	199	215	1	1	1
1.0	AR 18	6	10.7±0.1	11.0±0.1	11.2±0.1	233	244	248	1	1	1

*For the molecular structures of dyes, see Table 3.2.

Table 4.3b Effect of chitosans on the dyeability of silk fabrics

Chitosan Conc. (wt.%)	Dyestuff (C.I.)*	Depth (%owf)	K/S value ± Av. Dev.			Gain of K/S value (%)			Grey Scale		
			CH01	CH02	CH03	CH01	CH02	CH03	CH01	CH02	CH03
0.0	AB 25	2	5.40±0.05	5.40±0.05	5.40±0.05	0.00	0.00	0.00	2	2	2
0.5	AB 25	2	5.60±0.05	5.70±0.06	5.70±0.06	4.00	5.00	5.00	2	2	2
1.0	AB 25	2	5.60±0.05	5.80±0.06	5.80±0.06	5.00	7.00	7.00	2	2	2
0.0	AB 25	4	9.60±0.09	9.60±0.09	9.60±0.09	0.00	0.00	0.00	1–2	1–2	1–2
0.5	AB 25	4	9.90±0.10	10.3±0.1	10.3±0.1	3.00	6.00	7.00	1–2	1–2	1–2
1.0	AB 25	4	10.6±0.1	11.2±0.1	11.5±0.1	10.0	16.0	19.0	1–2	1–2	1–2
0.0	AB 25	6	10.9±0.1	10.9±0.1	10.9±0.1	0.00	0.00	0.00	1–2	1–2	1–2
0.5	AB 25	6	12.4±0.1	12.5±0.1	12.6±0.1	14.0	15.0	15.0	1–2	1–2	1–2
1.0	AB 25	6	14.1±0.1	15.7±0.2	16.1±0.2	29.0	44.0	47.0	1–2	1–2	1–2
0.0	AB 129	2	4.10±0.04	4.10±0.04	4.10±0.04	0.00	0.00	0.00	3	3	3
0.5	AB 129	2	4.60±0.04	4.60±0.04	4.60±0.04	12.0	13.0	14.0	3	3	3
1.0	AB 129	2	4.60±0.04	5.50±0.05	6.90±0.06	14.0	36.0	71.0	3	3	3
0.0	AB 129	4	7.30±0.07	7.30±0.07	7.30±0.07	0.00	0.00	0.00	3	3	3
0.5	AB 129	4	8.20±0.08	8.90±0.09	9.00±0.09	12.0	22.0	23.0	3	3	3
1.0	AB 129	4	9.10±0.09	9.40±0.09	9.90±0.09	25.0	29.0	35.0	3	3	3
0.0	AB 129	6	8.80±0.09	8.80±0.09	8.80±0.09	0.00	0.00	0.00	3	3	3
0.5	AB 129	6	11.2±0.1	11.3±0.1	11.3±0.1	26.0	27.0	28.0	3	3	3
1.0	AB 129	6	11.9±0.1	12.7±0.1	13.2±0.1	35.0	44.0	49.0	3	3	3
0.0	AG 25	2	5.10±0.05	5.10±0.05	5.10±0.05	0.00	0.00	0.00	3	3	3
0.5	AG 25	2	5.80±0.05	7.70±0.08	9.40±0.09	13.0	50.0	84.0	3	3	3
1.0	AG 25	2	6.30±0.06	9.40±0.09	10.1±0.1	24.0	83.0	97.0	3	3	3
0.0	AG 25	4	9.70±0.09	9.70±0.09	9.70±0.09	0.00	0.00	0.00	2–3	2–3	2–3
0.5	AG 25	4	11.4±0.1	13.4±0.1	14.3±0.1	18.0	38.0	47.0	2–3	2–3	2–3
1.0	AG 25	4	14.2±0.1	15.7±0.1	16.3±0.2	46.0	62.0	68.0	2–3	2–3	2–3
0.0	AG 25	6	11.3±0.1	11.3±0.1	11.3±0.1	0.00	0.00	0.00	2–3	2–3	2–3
0.5	AG 25	6	15.4±0.1	15.4±0.1	16.1±0.2	36.0	37.0	43.0	2–3	2–3	2–3
1.0	AG 25	6	18.0±0.2	18.2±0.2	18.2±0.2	60.0	61.0	62.0	2–3	2–3	2–3
0.0	AG 27	2	5.50±0.05	5.50±0.05	5.50±0.05	0.00	0.00	0.00	4	4	4
0.5	AG 27	2	6.70±0.07	8.10±0.08	9.20±0.09	22.0	47.0	68.0	4	4	4
1.0	AG 27	2	7.50±0.07	8.80±0.08	10.6±0.1	37.0	61.0	94.0	4	4	4
0.0	AG 27	4	11.0±0.1	11.0±0.1	11.0±0.1	0.00	0.00	0.00	3–4	3–4	3–4
0.5	AG 27	4	13.3±0.1	13.4±0.1	13.5±0.1	21.0	22.0	22.0	3–4	3–4	3–4
1.0	AG 27	4	14.1±0.1	16.0±0.2	16.1±0.2	28.0	45.0	46.0	3–4	3–4	3–4
0.0	AG 27	6	14.3±0.1	14.3±0.1	14.3±0.1	0.00	0.00	0.00	3–4	3–4	3–4
0.5	AG 27	6	18.5±0.2	18.6±0.2	19.2±0.2	29.0	30.0	34.0	3–4	3–4	3–4
1.0	AG 27	6	19.0±0.2	19.7±0.2	19.8±0.2	33.0	38.0	39.0	3–4	3–4	3–4

*For the molecular structures of dyes, see Table 3.2.

Table 4.3c Effect of chitosans on the dyeability of silk fabrics

Chitosan Conc. (wt.%)	Dyestuff (C.I.)*	Depth (%owf)	CIE L*a*b* (D65/10)									ΔE* ± Av. Dev.		
			CH01			CH02			CH03			CH01	CH02	CH03
			L*	a*	b*	L*	a*	b*	L*	a*	b*			
0.0	AO 12	2	70.5	39.8	54.6	70.5	39.8	54.6	70.5	39.8	54.6	0.00±0.00	0.00±0.00	0.00±0.00
0.5	AO 12	2	69.5	40.2	55.3	66.2	43.5	59.7	64.8	43.5	63.2	1.30±0.01	7.60±0.07	11.0±0.1
1.0	AO 12	2	68.2	42.9	60.3	66.0	44.9	62.9	63.5	44.6	63.3	6.90±0.07	10.7±0.1	12.2±0.1
0.0	AO 12	4	65.2	46.5	64.4	65.2	46.5	64.4	65.2	46.5	64.4	0.00±0.00	0.00±0.00	0.00±0.00
0.5	AO 12	4	64.8	46.7	63.1	61.7	47.8	65.0	61.4	50.6	66.4	1.40±0.01	3.80±0.04	5.90±0.06
1.0	AO 12	4	63.4	49.0	67.3	59.9	49.6	66.6	60.1	51.8	65.8	4.20±0.04	6.50±0.06	7.50±0.07
0.0	AO 12	6	62.7	49.2	65.8	62.7	49.2	65.8	62.7	49.2	65.8	0.00±0.00	0.00±0.00	0.00±0.00
0.5	AO 12	6	59.0	50.7	66.7	59.3	52.2	67.4	58.2	53.1	67.8	4.10±0.04	4.80±0.05	6.30±0.06
1.0	AO 12	6	58.6	53.3	67.5	56.8	52.1	65.7	56.7	54.5	66.3	6.00±0.06	6.60±0.07	8.00±0.08
0.0	AO 10	2	81.9	17.4	27.8	81.9	17.4	27.8	81.9	17.4	27.8	0.00±0.00	0.00±0.00	0.00±0.00
0.5	AO 10	2	80.8	20.8	34.7	75.0	29.1	45.9	75.0	26.4	48.1	7.80±0.08	22.6±0.2	23.3±0.2
1.0	AO 10	2	77.3	26.8	46.6	75.7	28.7	49.8	73.0	29.6	52.9	21.5±0.2	25.5±0.2	29.3±0.3
0.0	AO 10	4	77.1	27.2	47.9	77.1	27.2	47.9	77.1	27.2	47.9	0.00±0.00	0.00±0.00	0.00±0.00
0.5	AO 10	4	76.6	27.9	48.8	74.6	30.9	48.4	72.0	30.7	56.4	1.20±0.01	4.50±0.04	10.5±0.1
1.0	AO 10	4	77.0	28.0	49.9	70.6	32.9	59.6	70.5	37.9	64.2	2.20±0.02	14.5±0.1	20.6±0.2
0.0	AO 10	6	75.8	29.4	53.1	75.8	29.4	53.1	75.8	29.4	53.1	0.00±0.00	0.00±0.00	0.00±0.00
0.5	AO 10	6	74.6	30.9	54.6	71.1	37.9	60.6	70.7	34.9	63.1	2.40±0.02	12.3±0.1	52.1±0.5
1.0	AO 10	6	74.7	30.9	55.7	70.1	38.1	63.4	69.6	32.6	60.1	3.20±0.03	14.6±0.1	53.4±0.5
0.0	AR 44	2	57.9	45.0	11.5	57.9	45.0	11.5	57.9	45.0	11.5	0.00±0.00	0.00±0.00	0.00±0.00
0.5	AR 44	2	55.3	45.3	12.1	48.5	50.2	16.7	45.1	52.0	16.9	2.70±0.03	11.9±0.1	15.6±0.2
1.0	AR 44	2	54.6	48.6	13.6	47.2	51.1	17.7	43.2	48.8	15.6	5.30±0.05	13.8±0.1	15.7±0.2
0.0	AR 44	4	50.9	46.9	13.5	50.9	46.9	13.5	50.9	46.9	13.5	0.00±0.00	0.00±0.00	0.00±0.00
0.5	AR 44	4	47.4	50.0	16.4	44.6	50.1	18.6	40.0	49.8	18.3	5.50±0.06	8.70±0.08	12.3±0.1
1.0	AR 44	4	45.9	50.2	17.3	41.7	51.1	19.9	39.9	51.2	21.5	7.10±0.07	12.0±0.1	14.3±0.1
0.0	AR 44	6	49.3	48.8	15.4	49.3	48.8	15.4	49.3	48.8	15.4	0.00±0.00	0.00±0.00	0.00±0.00
0.5	AR 44	6	45.9	48.8	16.1	41.3	49.1	19.3	41.1	49.4	19.5	3.50±0.03	8.90±0.09	9.20±0.09
1.0	AR 44	6	41.9	48.3	17.2	40.9	49.3	18.9	39.5	48.1	18.0	7.60±0.08	9.10±0.09	10.2±0.1
0.0	AR 18	2	69.8	36.6	8.60	69.8	36.6	8.60	69.8	36.6	8.60	0.00±0.00	0.00±0.00	0.00±0.00
0.5	AR 18	2	55.9	49.7	16.4	56.3	51.1	17.4	54.5	51.6	17.3	20.6±0.2	21.7±0.2	23.1±0.2
1.0	AR 18	2	55.6	48.4	15.6	50.5	51.2	20.0	51.0	54.2	21.3	19.7±0.2	26.8±0.3	28.7±0.3
0.0	AR 18	4	63.2	45.5	12.3	63.2	45.5	12.3	63.2	45.5	12.3	0.00±0.00	0.00±0.00	0.00±0.00
0.5	AR 18	4	55.5	51.0	17.4	52.0	54.1	20.7	51.3	53.8	21.0	10.7±0.1	16.4±0.2	16.9±0.2
1.0	AR 18	4	50.4	51.4	18.4	48.1	55.5	23.3	47.8	55.2	23.9	15.4±0.2	21.2±0.2	21.6±0.2
0.0	AR 18	6	61.7	47.7	14.3	61.7	47.7	14.3	61.7	47.7	14.3	0.00±0.00	0.00±0.00	0.00±0.00
0.5	AR 18	6	51.0	55.1	22.1	49.5	55.9	23.2	49.6	56.5	23.5	15.2±0.2	17.2±0.2	17.6±0.2
1.0	AR 18	6	48.8	54.4	22.0	48.0	54.7	22.9	45.6	54.1	23.6	16.4±0.2	17.6±0.2	19.7±0.2

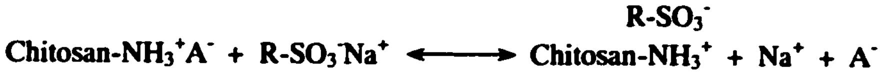
*For the molecular structures of dyes, see Table 3.2.

Table 4.3d Effect of chitosans on the dyeability of silk fabrics

Chitosan Conc. (wt.%)	Dyestuff (C.I.)*	Depth (%owf)	CIE L*a*b* (D65/10)									ΔE* (± 1%)		
			CH01			CH02			CH03			CH01	CH02	CH03
			L*	a*	b*	L*	a*	b*	L*	a*	b*			
0.0	AB 25	2	48.9	-6.70	-35.4	48.9	-6.70	-35.4	48.9	-6.70	-35.4	0.00	0.00	0.00
0.5	AB 25	2	47.7	-6.70	-35.4	47.8	-7.10	-36.3	47.3	-6.50	-35.8	1.20	1.50	1.70
1.0	AB 25	2	46.8	-6.80	-35.9	46.7	-6.40	-36.3	45.5	-5.90	-36.5	2.20	2.40	3.70
0.0	AB 25	4	40.6	-3.80	-37.8	40.6	-3.80	-37.8	40.6	-3.80	-37.8	0.00	0.00	0.00
0.5	AB 25	4	39.6	-3.20	-37.7	38.1	-3.40	-37.9	37.0	-2.80	-38.0	1.20	2.50	3.70
1.0	AB 25	4	38.9	-3.30	-37.8	37.1	-2.30	-37.8	37.1	-2.00	-38.0	1.80	3.80	3.90
0.0	AB 25	6	35.9	-1.80	-37.3	35.9	-1.80	-37.3	35.9	-1.80	-37.3	0.00	0.00	0.00
0.5	AB 25	6	34.7	-0.80	-37.5	34.2	-0.40	-38.2	33.2	-0.30	-37.3	1.60	2.40	3.10
1.0	AB 25	6	35.6	-2.00	-35.7	33.4	-1.40	-35.5	31.8	0.90	-37.4	1.60	3.10	4.90
0.0	AB 129	2	49.5	-3.50	-35.3	49.5	-3.50	-35.3	49.5	-3.50	-35.3	0.00	0.00	0.00
0.5	AB 129	2	48.7	-3.40	-35.8	48.9	-4.70	-31.7	44.6	-3.70	-32.5	0.90	3.80	5.60
1.0	AB 129	2	45.2	-3.00	-33.8	46.1	-4.70	-30.8	43.1	-3.00	-33.2	4.60	5.80	6.80
0.0	AB 129	4	41.2	0.00	-38.0	41.2	0.00	-38.0	41.2	0.00	-38.0	0.00	0.00	0.00
0.5	AB 129	4	40.1	-2.00	-33.1	39.9	-2.20	-33.0	36.8	-0.90	-33.9	5.40	5.60	6.10
1.0	AB 129	4	38.9	-2.40	-32.7	37.3	-1.50	-32.7	37.2	-1.80	-31.7	6.30	6.70	7.70
0.0	AB 129	6	38.1	2.20	-39.3	38.1	2.20	-39.3	38.1	2.20	-39.3	0.00	0.00	0.00
0.5	AB 129	6	35.4	0.70	-34.0	32.8	1.20	-34.6	34.0	0.00	-32.5	6.10	7.20	8.20
1.0	AB 129	6	34.8	-0.70	-31.8	33.8	-0.60	-31.8	32.2	0.30	-31.4	8.70	9.10	10.0
0.0	AG 25	2	48.6	-25.4	-11.6	48.6	-25.4	-11.6	48.6	-25.4	-11.6	0.00	0.00	0.00
0.5	AG 25	2	47.7	-26.3	-11.6	43.7	-25.2	-11.0	42.7	-26.0	-10.7	1.30	4.90	6.00
1.0	AG 25	2	46.4	-25.9	-11.4	40.2	-26.4	-10.4	38.0	-25.6	-9.30	2.30	8.50	10.8
0.0	AG 25	4	39.2	-25.4	-11.3	39.2	-25.4	-11.3	39.2	-25.4	-11.3	0.00	0.00	0.00
0.5	AG 25	4	37.6	-25.8	-10.5	33.7	-24.7	-9.60	33.2	-24.4	-9.00	1.80	5.80	6.50
1.0	AG 25	4	35.0	-26.2	-9.90	32.3	-23.3	-8.90	31.4	-24.4	-9.00	4.50	7.60	8.20
0.0	AG 25	6	37.2	-24.1	-10.8	37.2	-24.1	-10.8	37.2	-24.1	-10.8	0.00	0.00	0.00
0.5	AG 25	6	33.5	-24.7	-9.40	32.9	-24.2	-9.60	32.4	-23.4	-9.20	4.00	4.50	5.10
1.0	AG 25	6	31.3	-22.4	-8.70	31.1	-23.2	-8.80	27.4	-20.6	-7.20	6.50	6.50	11.0
0.0	AG 27	2	48.2	-29.5	-11.1	48.2	-29.5	-11.1	48.2	-29.5	-11.1	0.00	0.00	0.00
0.5	AG 27	2	46.6	-28.0	-10.9	43.6	-28.1	-9.90	43.3	-28.2	-10.4	2.20	5.00	5.10
1.0	AG 27	2	47.4	-26.9	-10.8	42.7	-28.8	-10.6	42.8	-28.1	-10.1	2.70	5.60	5.70
0.0	AG 27	4	38.0	-25.9	-10.0	38.0	-25.9	-10.0	38.0	-25.9	-10.0	0.00	0.00	0.00
0.5	AG 27	4	37.1	-26.6	-9.20	35.2	-26.5	-9.40	35.3	-27.4	-9.30	1.40	2.90	3.20
1.0	AG 27	4	35.8	-27.3	-9.20	33.7	-26.6	-8.80	32.9	-25.2	-8.40	2.70	4.50	5.40
0.0	AG 27	6	34.5	-23.6	-8.70	34.5	-23.6	-8.70	34.5	-23.6	-8.70	0.00	0.00	0.00
0.5	AG 27	6	33.4	-24.8	-8.40	31.4	-24.1	-8.00	30.8	-24.3	-8.20	1.70	3.20	3.80
1.0	AG 27	6	28.9	-23.4	-7.70	28.8	-22.5	-7.50	27.5	-20.5	-6.90	5.70	5.90	7.90

*For the molecular structures of dyes, see Table 3.2.

The data in Table 4.3a to 4.3d showed that chitosan significantly improved the dye exhaustion of silk fabric dyed with acid dye without lowering the color fastness to washing when compared with the untreated silk fabrics. This quite agrees with the reported result. [97-106] The color yield (K/S value) and color difference (ΔE*) increased as the concentration of chitosan increased from 0.5% to 1.0% and the DD from 57% to 95% due to the electrostatic attraction between protonated $-NH_2$ of chitosan and anion of acid dye ($R\text{-}SO_3^-$)



$$\text{Chitosan-NH}_3^+\text{A}^- + \text{R-SO}_3^-\text{Na}^+ \longleftrightarrow \overset{\text{R-SO}_3^-}{\text{Chitosan-NH}_3^+} + \text{Na}^+ + \text{A}^-$$

A^- is acetate anion (from chitosan acetate) or citrate anion (from buffer solution). In the dye bath, some of the acetate anions of chitosan acetate were firstly replaced by the bigger citrate anions of buffer solution, and then these anions were replaced by the much bigger acid dye anions, which were held at the $-NH_3^+$ of chitosan by electrostatic forces. Finally, the acid dye molecules diffused from the chitosan into the silk and dyed the silk.

4.1.5 Effect of Acid Dye on Dye Exhaustion of Silk Fabric

The molecular structure of the employed dyestuffs is listed in Table 3.2.

The data from Table 4.3a to 4.3d indicated that the dye exhaustion of silk fabric decreased as the number of $-SO_3^-$ group of dye molecule increased, such as in the case of AO 10 and 12, and AR 18 and 44. This result is due to the number of absorbed acid dye molecule decreased as the $-SO_3^-$ group of dye molecules increased. For AB 129 and 25, AG 27 and 25, the same number of $-SO_3^-$ group of dye molecules resulted in similar dye exhaustion, which was not affected by the hydrophobic substituents on dye molecules.

4.1.6 Summary

Chitosans of high DD were prepared from chitin through consecutive alkaline hydrolysis. Chitosans of different DD were prepared through heating chitin and then reheating the product obtained (chitosan) in aqueous NaOH solution of different concentrations and at various lengths of time. Because the reaction is heterogeneous, we were unable to obtain a sample with DD = 100% even by treating the deacetylated chitin sample (chitosan) again and again with NaOH solution at high temperature.

The optimal experimental conditions obtained in our study of chitosan treating and dyeing silk fabric: 1. The best exhaustion time length is 30 minute period, and curing is not necessary for the chitosan treatment of silk fabric; and 2. The silk fabrics should be dyed in a dyeing bath of pH=4 adjusted using a citrate buffer solution.

Chitosan significantly improved the dye exhaustion of silk fabric dyed with acid dye without the lowering of color fastness to washing when compared with the untreated silk fabrics. The color yield (K/S value) and color difference (ΔE*) increased as the concentration of chitosan increased from 0.5% to 1.0% and the DD from 57% to 95%. The maximal gain of K/S value reached 555% (Table 4.3a) and the maximal ΔE* reached 53.4 (Table 4.3c). That was owing to the electrostatic attraction between protonated $-NH_2$ of chitosan and anion of acid dye.

The dye exhaustion of silk fabric decreased as the number of $-SO_3^-$ group of dye molecule increased, such as in the case of AO 10 and 12, and AR 18 and 44. This result was due to the decrease in the number of absorbed acid dye molecule as the $-SO_3^-$ group of dye molecule increased. For AB 129 and 25, AG 27 and 25, the same number of $-SO_3^-$ group of dye molecules resulted in similar dye exhaustion, which was not affected by the hydrophobic substituents on dye molecules.

4.2 MW and DD of Degraded Chitosans and Their Effect on the Dyeability of Silk Fabrics

4.2.1 Ultrasonic Degradation Time and MW of Degraded Chitosans

The relationship of MW of degraded chitosans and the degradation time is shown in Fig. 4.4. It showed that the MW of ultrasonically degraded chitosan decreased fast at the beginning of the operation, and then changed slowly after 24h. We were unable to obtain degraded chitosan of MW that is lower than 1.50x10^{5} by this method owing to the limited energy. The DD of degraded chitosan DCH02 derived from CH04 (MW = 11.7x10^{5}; DD = 88%) was determined using ^{1}H NMR technique and was found to be 84%. The above results indicated that ultrasonic vibration only gives rise to the cleavage of main chain of chitosan and does not affect the (de)acetylation of chitosan. The ultrasonic degradation did not change the DD of the chitosan samples much. This agrees with the result reported by other investigators. [188]

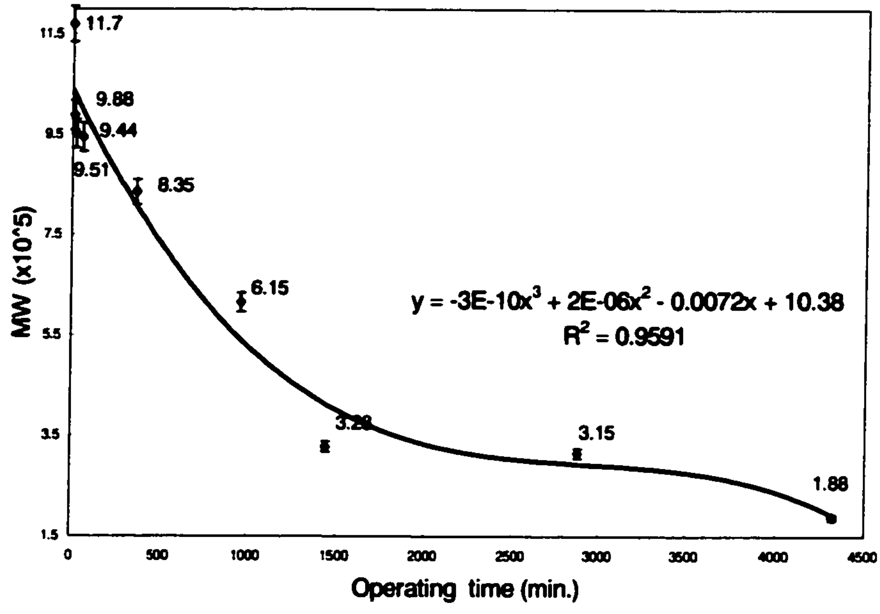


Fig.4.4 MW of degraded chitosan against the degradation time

4.2.2 Effect of Different MW of Degraded Chitosans on the Dyeability of Silk Fabrics

The color yield (K/S value), color difference (ΔE*) and color fastness to washing (grey scale) of silk fabrics dyed with acid dyes and treated with chitosans of different molecular weight are summarized in Table 4.4.

Table 4.4 Effect of different MW of chitosans on the dyeability of silk fabrics

Chitosan	MW (x10^5)	Dyestuff (C.I.)*	K/S value ± Av. Dev.	ΔE* ± Av. Dev.	Grey Scale
No		AR 44	16.8±0.2	0.00±0.00	1-2
CH04	11.7	AR 44	19.0±0.2	7.40±0.07	1-2
DCH01	6.15	AR 44	19.4±0.2	6.30±0.06	1-2
DCH02	1.88	AR 44	19.1±0.2	4.30±0.04	1-2
No		AG 25	18.8±0.2	0.00±0.00	2-3
CH04	11.7	AG 25	20.8±0.2	4.60±0.05	2-3
DCH01	6.15	AG 25	21.1±0.2	4.40±0.04	2-3
DCH02	1.88	AG 25	20.1±0.2	3.30±0.03	2-3

*For the molecular structures of dyes, see Table 3.2.

The results showed that all chitosan treatment processes effectively improved the dye exhaustion of silk fabrics dyed with acid dyes without the lowering of color fastness. The K/S values were nearly constant. However, the ΔE* decreased slightly as the MW decreased. This decrease could be explained as a result of the higher water solubility of the chitosan with lower MW.

4.2.3 Summary

Ultrasonic degradation effectively degraded the chitosan of high MW, but we were unable to obtain an MW of degraded chitosan that is lower than 1.5x10^5 by this method, owing to the limited ultrasonic wave energy. The DD of chitosan samples were not affected by ultrasonic degradation.

All degraded chitosan treated processes effectively improved the dye exhaustion of silk fabrics dyed with acid dyes without the lowering of color fastness to washing. The K/S values were nearly constant. However, the ΔE^* decreased slightly as the MW decreased. This could be explained as a result of the higher water solubility of chitosan with lower MW.

4.3 Structure and Properties of O-Carboxymethyl (O-CM) Chitosans and Their Effect on the Dyeability of Silk Fabrics

4.3.1 Structure of O-CM Chitosans

Fig.4.5 below shows the FTIR spectra of the region of carbonyl and amino groups of sample OCMCH3 (DD=83.2%, DS=9.5%), which are similar to those of the other three samples OCMCH1, 2, 4 (for their DD and DS, see Table 4.5) and also similar to those reported by Park et al. [158] In the spectrum of the film prepared from acidic solution (a), the band of unionized carboxyl groups was observed at 1717 cm^{-1} (-CO_2H), and the bands at 1633 cm^{-1} and 1520 cm^{-1} are mainly due to asymmetric and symmetric N-H bend of -NH_3^+ group respectively, and overlapped with the bands of amide C=O stretch and N-H bend of -$NHCOCH_3$ group. Both curves b and c show broad absorption signals in the region and are difficult to assign. However, the C=O stretch band of ionized carboxyl group was overlapped with the bands of amide C=O stretch and N-H bend of -$NHCOCH_3$ group, and the disappearance of C=O stretch band of carboxylic acid group, due to ionization, can be seen.

Fig.4.6 represents the ^{1}H NMR (400 MHz, 1.0 wt.% of DCO_2D in D_2O) measured at 80°C for sample OCMCH4 (DD=83.1%, DS=28.7%). Fig.4.7a shows the 500 MHz ^{13}C NMR spectrum measured at 80°C for chitosan (DS=0.0%) in D_2O (+1.0 wt.% of DCO_2D). Fig.4.7b shows the 500 MHz ^{13}C NMR spectrum measured at 80°C for sample OCMCH4.

Fig.4.5 FTIR spectra of OCMCH3 films obtained from acidic solution (a), neutral solution (b) and basic solution (c)

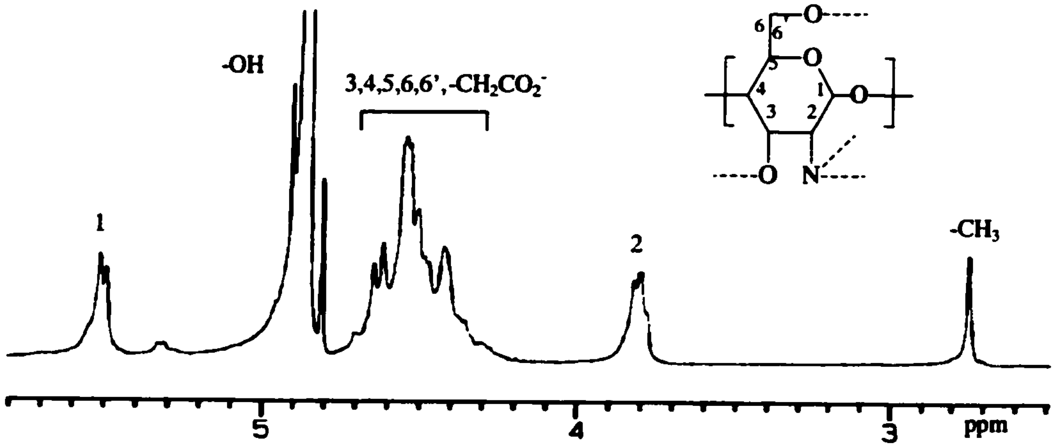


Fig.4.6 ^{1}H NMR spectrum of OCMCH4 (80°C)

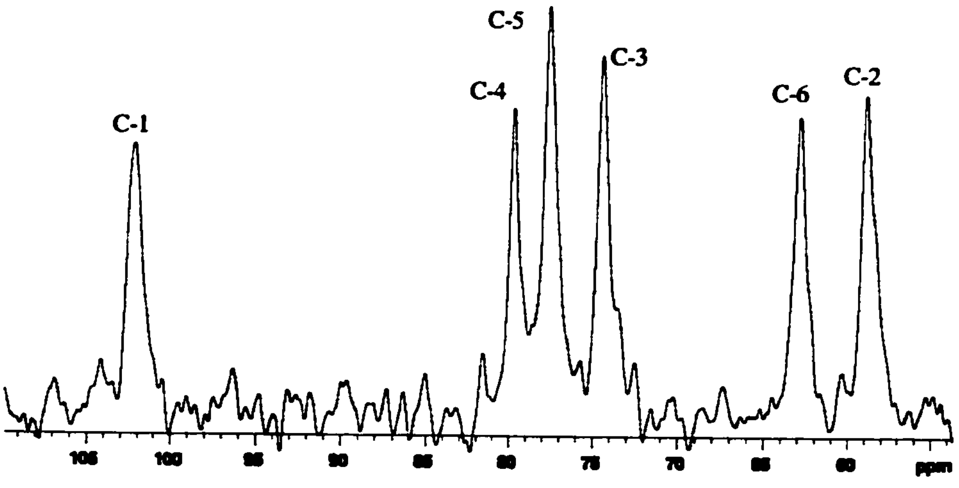


Fig.4.7a ^{13}C NMR spectrum of chitosan (80°C)

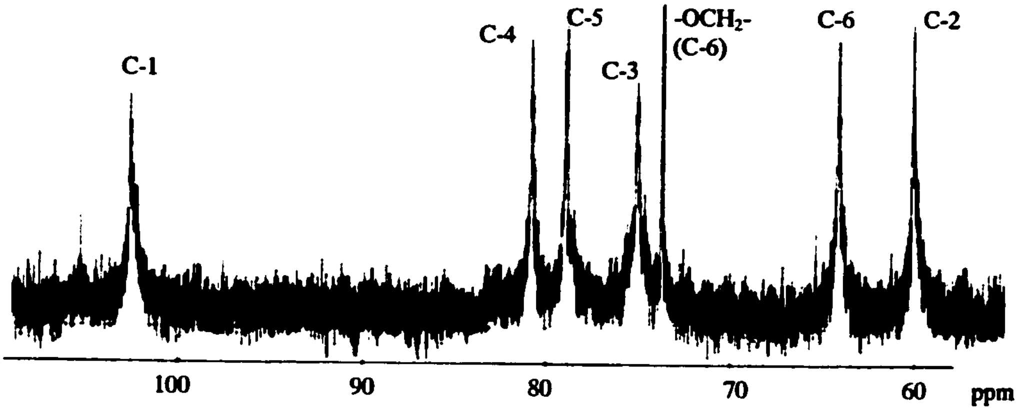


Fig.4.7b ^{13}C NMR spectrum of OCMCH4 (80°C)

^{13}C NMR spectrum (Fig.4.7b) of O-carboxymethyl chitosan provides detailed information on each carbon of the carboxymethylated glucosamine unit. Our results are in good accordance with the reported data of N,O-carboxymethyl chitosans, [164, 166] except for the absence of $-OCH_2-$ carbon of C3-oxygen and C2-nitrogen. The ^{13}C NMR results of these samples indicated that chitosan derivatives obtained had carboxymethyl group substituted exclusively on the C6-oxygen of glucosamine unit (not in Fig.4.7a), not on the C3-oxygen or C2-nitrogen. The formation of this product agrees with the higher reactivity of the hydroxyl group of C6. The degree of deacetylation (DD) of all samples was evaluated using the ^{1}H NMR integral intensity of $-CH_3$ protons, I_{CH3} (δ = 2.74 ppm), of the amide group and C2-H, and I_{H2} (δ = 3.8 ppm).

$$DD\% = [1 - (I_{CH3}/3I_{H2})] \times 100$$

The DS of these O-CM chitosans was calculated using the DD value, C% and N% of the sample from their elemental analyses.

$$DS\% = [7/12 \times (C\%/N\%) + DD - 4] \times 100$$

Table 4.5 summarizes the DD and DS values calculated from the above expressions.

Table 4.5 DD, DS and water solubility at room temperature of O-CM chitosans

Sample	DD ± Av. Dev. (%)	DS ± Av. Dev. (%)	Solubility in D.I. Water (1.0 wt.%)	Solubility in 1.0 wt.% of Aqueous HAc Solution (1.0 wt.%)
Chitosan	84±1	0.00±0.00	Insoluble	Soluble
OCMCH1	84±1	1.00±0.03	Slightly Soluble	Soluble
OCMCH2	83±1	2.20±0.07	Slightly Soluble	Soluble
OCMCH3	83±1	9.50±0.29	Soluble	Soluble
OCMCH4	83±1	28.7±0.9	Soluble	Soluble

In a parallel experiment, deacetylation of chitin was conducted under the same conditions in the absence of chloroacetic acid; the DD of the chitosan sample was found to be similar to those with a small amount of chloroacetic acid. This indicated that deacetylation was not affected by the presence of a small amount of chloroacetic acid. The DS increased from 1.00% to 28.7% as the molar ratio of chloroacetic acid to chitin monomer unit increased from 0.1 to 2.0, and the DS of these O-CM chitosans was found to be far lower than the corresponding molar ratio of chloroacetic acid to chitin monomer unit due to the heterogeneous reaction.

4.3.2 MW, Water Solubility and Thermal Property

The molecular weight of the above chitosan sample (Table 4.5) was determined to be approximately 300,000 with dilute solution viscometry. Because the coefficient values (k and α) of these O-CM chitosans are unknown, their molecular weight cannot be determined with dilute solution viscometry. The molecular weight of these O-CM chitosans was hypothesized to be similar to those of the above chitosan sample if alkali degradation was not affected by the presence of a small amount of chloroacetic acid.

The aqueous solubility of these samples increased as the DS increased. Samples with DS>9.5% were quite soluble in D. I. water, and this was probably why their effect on the dyeing of silk fabrics was lowered. O-CM chitosans with DS<9.5% were soluble in aqueous HAc solution and suitable for treating the silk fabrics for dyeing.

The thermal analysis (TA) results (Fig.4.8 and 4.9) showed that the starting temperatures of thermal degradation for O-CM chitosans were lower than chitin, and chitin was lower than chitosan. This may relate to the break of carboxymethyl, acetyl and main chain of polyglucopyranose during the thermal degradation of O-CM chitosans, chitin and chitosan. Thermal degradation of these O-CM chitosans occurred at a temperature that was higher than 180°C. Therefore, they were thermally stable, and suitable for treating silk fabrics for dyeing.

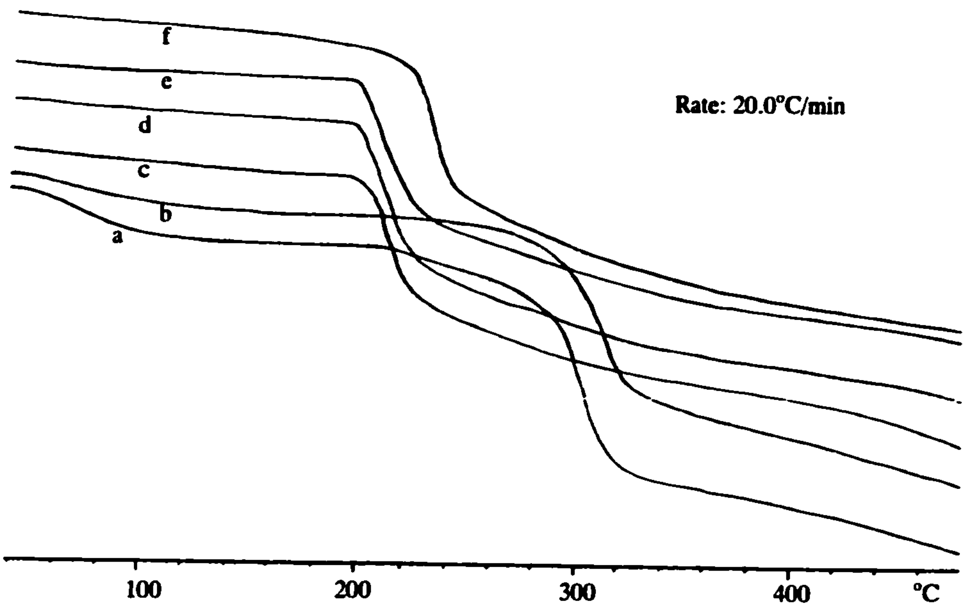


Fig.4.8 TGA curves of chitin (a), chitosan (b, DD=88.75%), OCMCH1 (c), OCMCH2 (d), OCMCH3 (e) and OCMCH4 (f)

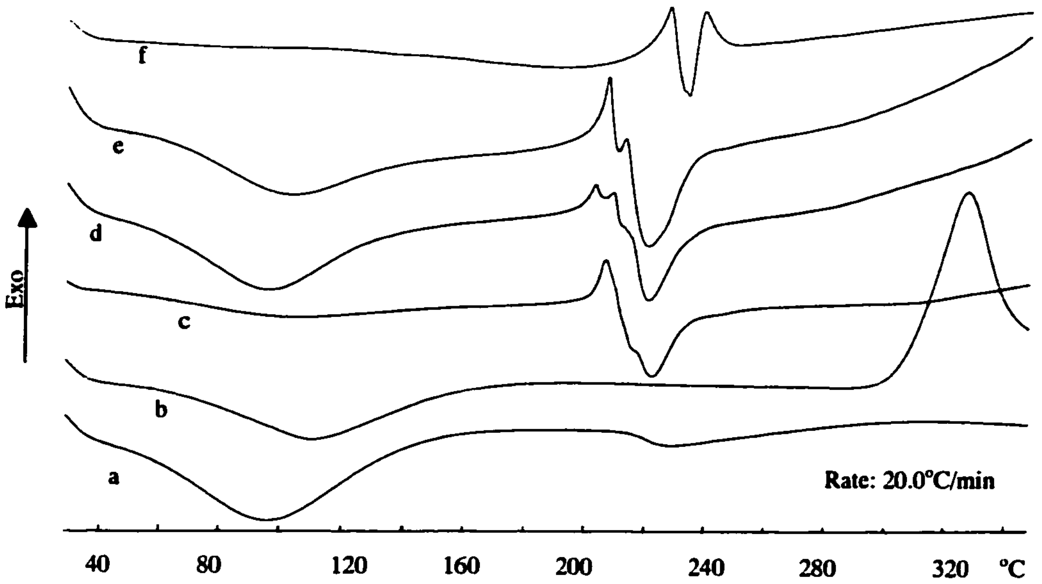


Fig.4.9 DSC curves of chitin (a), chitosan (b, DD=88.75%), OCMCH1 (c), OCMCH2 (d), OCMCH3 (e) and OCMCH4 (f)

4.3.3 Effect of O-CM Chitosans of Different DS on the Dyeability of Silk Fabrics

The color yield (K/S value), color difference (ΔE*) and colorfastness to washing (grey scale) of silk fabrics which were treated with chitosan derivatives and chitosan of same DD, and dyed with acid dyes are summarized in Table 4.6.

Table 4.6 Effect of O-CM chitosans of different DS on the dyeability of silk fabrics

Treating reagent	DS ± Av. Dev. (%)	Dyestuff (C.I.)*	K/S value ± Av. Dev.	ΔE* ± Av. Dev.	Grey Scale
No		AR 44	16.8±0.2	0.00±0.00	1-2
Chitosan	0.00±0.00	AR 44	19.0±0.2	7.40±0.07	1-2
OCMCH1	1.00±0.03	AR 44	17.8±0.2	2.70±0.03	1-2
OCMCH2	2.20±0.07	AR 44	18.8±0.2	2.40±0.02	1-2
OCMCH3	9.50±0.29	AR 44	18.2±0.2	1.90±0.02	1-2
No		AG 25	18.8±0.2	0.00±0.00	2-3
Chitosan	0.00±0.00	AG 25	20.8±0.2	4.60±0.05	2-3
OCMCH1	1.00±0.03	AG 25	20.7±0.2	3.00±0.03	2-3
OCMCH2	2.20±0.07	AG 25	20.7±0.2	2.30±0.02	2-3
OCMCH3	9.50±0.29	AG 25	20.3±0.2	2.20±0.02	2-3

*For the molecular structures of dyes, see Table 3.2.

O-carboxymethyl chitosan treatment effectively increased the dye uptake of acid dyed silk fabrics without lowering the color fastness, because of the electrostatic attraction between protonated $-NH_2$ of O-CM chitosan and anion of acid dye ($R\text{-}SO_3^-Na^+$) (see Section 4.1.4). The K/S value of silk fabric treated with O-CM chitosans slightly fluctuated. The K/S value and ΔE* of silk fabrics treated with O-CM chitosans were smaller than those treated with chitosan (same DD) because of their higher water solubility (Table 4.5). A small decrease of ΔE* was observed as the DS of O-CM chitosans increased, which meant that the dye uptake of silk fabrics treated with O-CM chitosans decreased slightly as the DS of O-CM chitosans increased. This again was due to water solubility. In general, O-CM chitosans are not as effective as chitosan in improving the color up-take of the silk fabrics. On the other hand, they have a much better effect on the silk fabric hand feel.

4.3.4 Summary

O-carboxymethyl chitosans with a low degree of substitution (DS) and a high degree of deacetylation (DD) were prepared from chitin.

Based on our NMR data, chitosan derivatives obtained had carboxymethyl group substituted exclusively on the C6-oxygen of glucosamine unit, not on the C3-oxygen or C2-nitrogen. The degree of deacetylation (DD) of all samples was evaluated using the ^1H NMR data, and the DS of the O-carboxymethyl chitosans was calculated using the DD value, C% and N% of the sample from their elemental analyses. The deacetylation was not affected by the presence of a small amount of chloroacetic acid. The DS increased from 1.00% to 28.7% as the molar ratio of chloroacetic acid to chitin monomer unit increased from 0.1 to 2.0, and the DS of these O-CM chitosans was found to be far lower than the corresponding molar ratio of chloroacetic acid to chitin monomer unit due to the heterogeneous reaction.

The aqueous solubility of these samples increased as the DS increased. O-carboxymethyl chitosans with DS<9.5% were soluble in aqueous HAc solution, and their thermal degradation occurred at the temperature that was higher than 180°C. So they were thermally stable and suitable for treating silk fabrics for dyeing.

O-carboxymethyl chitosan treatment effectively increased the dye uptake of acid dyed silk fabrics without lowering the color fastness owing to the electrostatic attraction between protonated $-NH_2$ of O-carboxymethyl chitosan and anion of acid dye. The K/S value and ΔE^* of silk fabrics treated with O-CM chitosans were smaller than those treated with chitosan (same DD) because of their higher water solubility. A small decrease in ΔE^* was observed as the DS of O-CM chitosans increased, which meant that the dye uptake of silk fabrics treated with O-CM chitosans decreased slightly as the DS of O-CM chitosans increased. This again was due to water solubility. O-carboxymethyl chitosans are not as effective as chitosan in improving the color up -take of the silk fabrics. On the other hand, they have a much better effect on the silk fabric hand feel.

4.4 Structure and Properties of N/O-(2-Hydroxy)Propyl-3-Trimethyl Ammonium Chitosan Chlorides (N/O-HTCC) and Their Effect on the Dyeability of Silk

4.4.1 Structure of N/O-HTCC

FTIR spectra of modified chitosans NQC1-NQC4 and NOQC1-NOQC4 (Table 3.5) were obtained and compared with chitosan CH05 respectively on Fig.4.10 and Fig.4.11. The spectra of modified chitosans NQC1-4 and NOQC1-4 showed two bands at 1642 and1479 cm^{-1}. These results are similar to those reported by Loubaki et al. [175] The first is a signal due to the N-H deformation vibration and the second is due to the methyl groups of the quaternary ammonium. The relative intensity of the second band to the first band increased from NQC1 to NQC4 and from NOQC1 to NOQC4, indicating that the degree of substitution of the modified chitosans increased from NQC1 to NQC4 and from NOQC1 to NOQC4. This result has been verified by the results of elemental analysis.

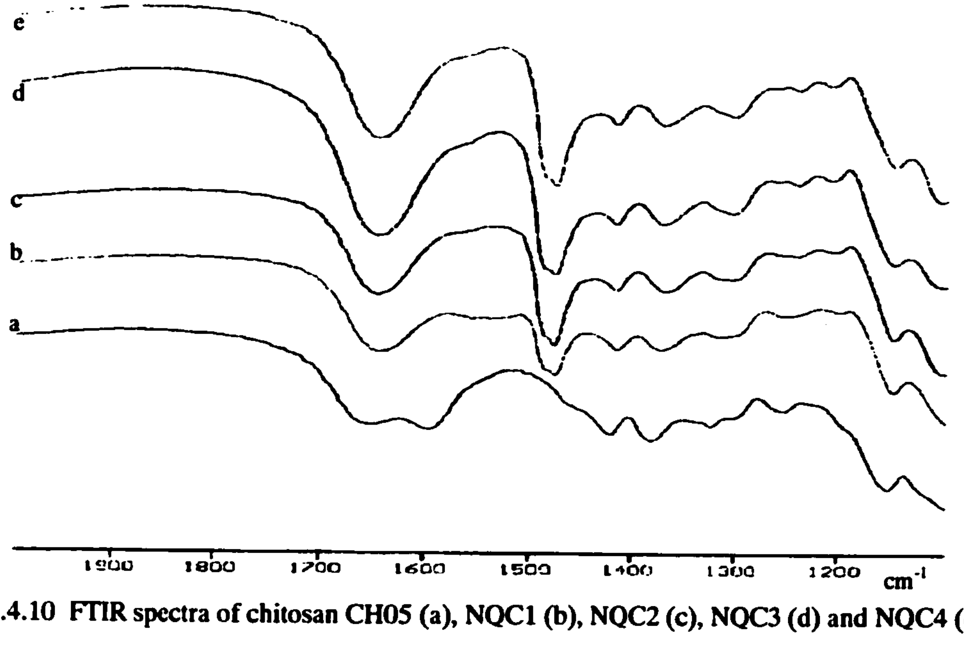


Fig.4.10 FTIR spectra of chitosan CH05 (a), NQC1 (b), NQC2 (c), NQC3 (d) and NQC4 (e)

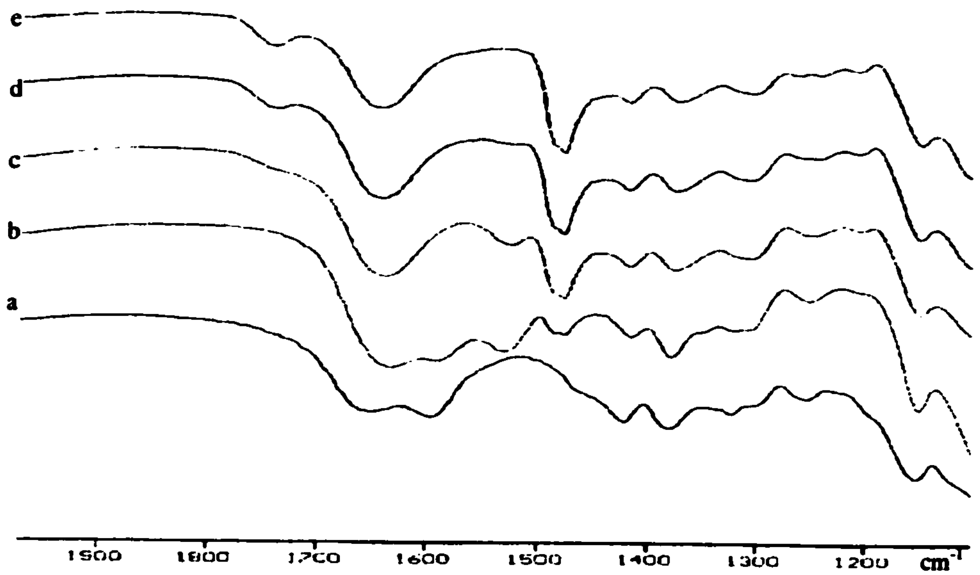


Fig.4.11 FTIR spectra of chitosan CH05 (a), NOQC1 (b), NOQC2 (c), NOQC3 (d) and NOQC4 (e)

All N/O-(2-Hydroxy)Propyl-3-Trimethyl Ammonium Chitosan Chlorides (N/O-HTCC) had similar ^1H NMR spectrum (Fig.4.12). The most important signal, at 2.9 ppm, was assigned without ambiguity to the protons of the methyl groups of the quaternary ammonium salt. All other signals assigned in Fig.4.12 were in good agreement with the NMR interpretation reported by Loubaki et al. [175]

The HTCC prepared in distilled water/acidic aqueous solution (e.g. NQC1 to NQC4) has groups substituted mainly on the C2-nitrogen of glucosamine unit (see Section 1.2.3.2), which are named N-HTCC. The HTCC prepared in alkali buffer solution at pH=10 (NOQC1 to NOQC4) has substitutions on the C2-nitrogen and on the C3/6-oxygen, which are termed N,O-HTCC. Due to the higher reactivity of the C3/6 hydroxyl group at pH=10, substitutions occurred at both N and O of the glucosamine unit. NMR cannot distinguish the difference of substituted sites between these two kinds of HTCC. This may be due to the overlapping of relative signals.

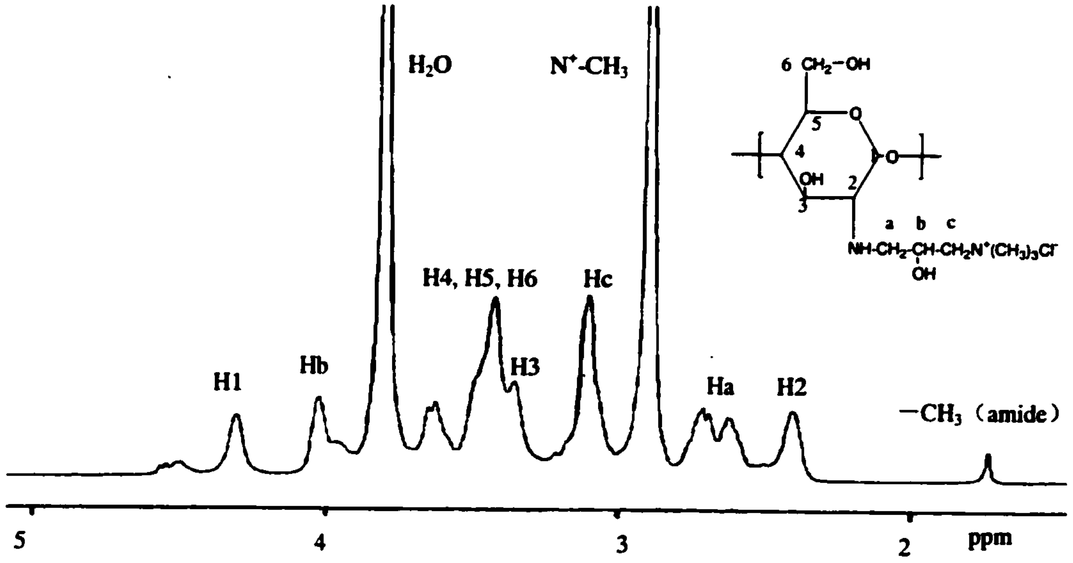


Fig.4.12 ^{1}H NMR spectrum of NQC2

The DS of the N/O-HTCC was calculated using the N% and Cl% of the sample from their elemental analyses.

$$DS = (Cl\%/N\%) / [(35.45/14.01) - (Cl\%/N\%)]$$

Table 4.7 summarizes the DS values calculated from the above expressions.

Table 4.7 DS values of the N/O-HTCC

Sample name	Molar ratio of GTMAC to chitosan monomer unit	N (wt. %)	Cl (wt. %)	DS ± Av. Dev.
NQC1	2	6.60	9.55	1.34±0.03
NQC2	4	6.96	11.7	1.98±0.04
NQC3	6	6.68	11.6	2.19±0.04
NQC4	8	6.68	11.8	2.31±0.05
NOQC1	2	6.73	10.8	1.73±0.03
NOQC2	4	7.37	12.5	2.03±0.04
NOQC3	6	7.48	13.4	2.42±0.05
NOQC4	8	7.53	13.7	2.56±0.05

For NQC1 to NQC4, the DS increased from 1.34 to 2.31 as the molar ratio of glycidyltrimethylammonium chloride (GTMAC) to chitosan monomer unit increased from 2 to 8. For NOQC1 to NOQC4, the DS increased from 1.73 to 2.56 as the molar ratio of

GTMAC to chitosan monomer unit increased from 2 to 8. The DS of these N/O-HTCC was lower than the corresponding molar ratio of GTMAC to chitosan monomer unit due to the heterogeneous reaction. It is impossible to obtain the N/O-HTCC of DS that is higher than 3 even when the molar ratio of GTMAC to chitosan monomer unit is very high, owing to the limited number of active functional groups of the glucosamine unit.

4.4.2 MW, Water Solubility and Thermal Property

The molecular weight of the chitosan CH05 was determined to be approximately 1,000,000 with dilute solution viscometry. Because a mild aqueous solution (even the alkaline buffer solution was at pH=10) was used during the preparation, the molecular degradation should not have happened. The molecular weight of the N/O-HTCC was considered to be the sum of MW of the chitosan added to the total weight of the GTMAC.

All N/O-HTCC were soluble in D.I. H_2O and aqueous HAc solution, and suitable for treating the silk fabrics for dyeing.

The thermal analysis (TA) results (Fig.4.13 to 4.15) showed that the starting temperatures of thermal degradation for N/O-HTCC were lower than chitosan CH05. This may be caused by the initial break of side chain (quaternary ammonium group) of N/O-HTCC during the thermal degradation. Thermal degradation of the N/O-HTCC occurred at a temperature that was higher than 180°C. Therefore, they were thermally stable, and suitable for treating silk fabrics for dyeing.

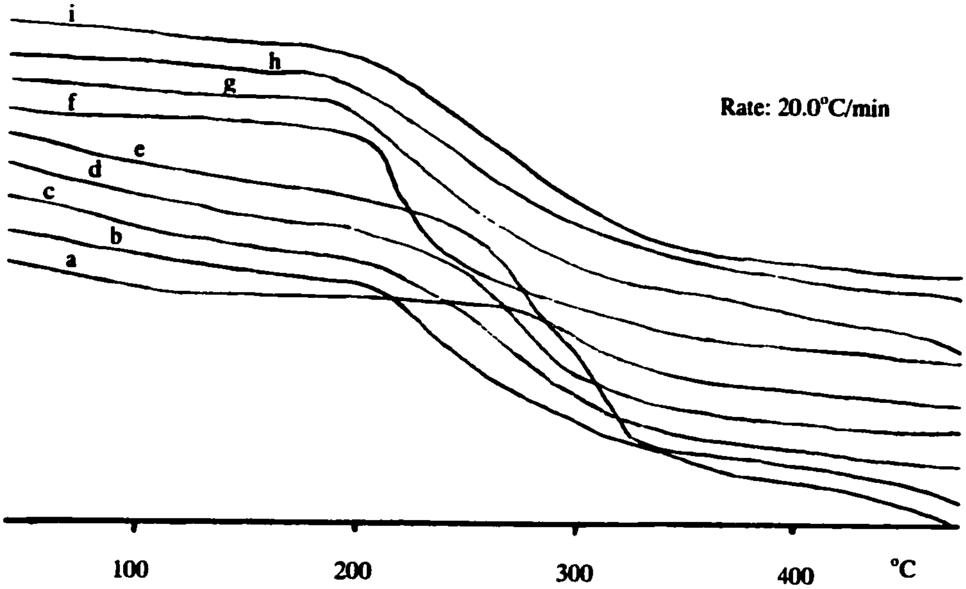


Fig.4.13 TGA curves of CH05(a),NQC1 (b),NQC2 (c), NQC3 (d), NQC4 (e), NOQC1 (f), NOQC2 (g), NOQC3 (h) and NOQC4 (i)

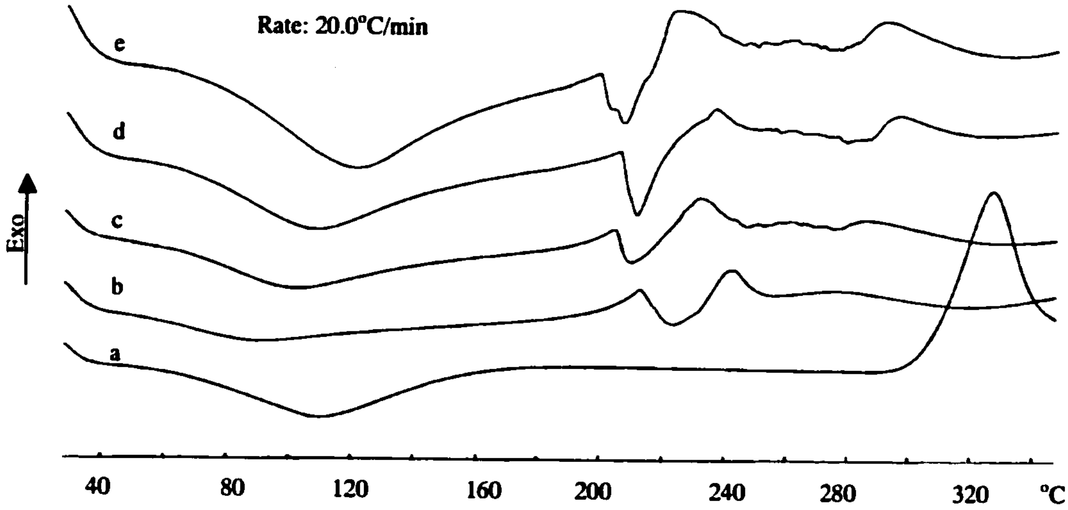


Fig.4.14 DSC curves of CH05(a),NQC1 (b),NQC2 (c), NQC3 (d) and NQC4 (e)

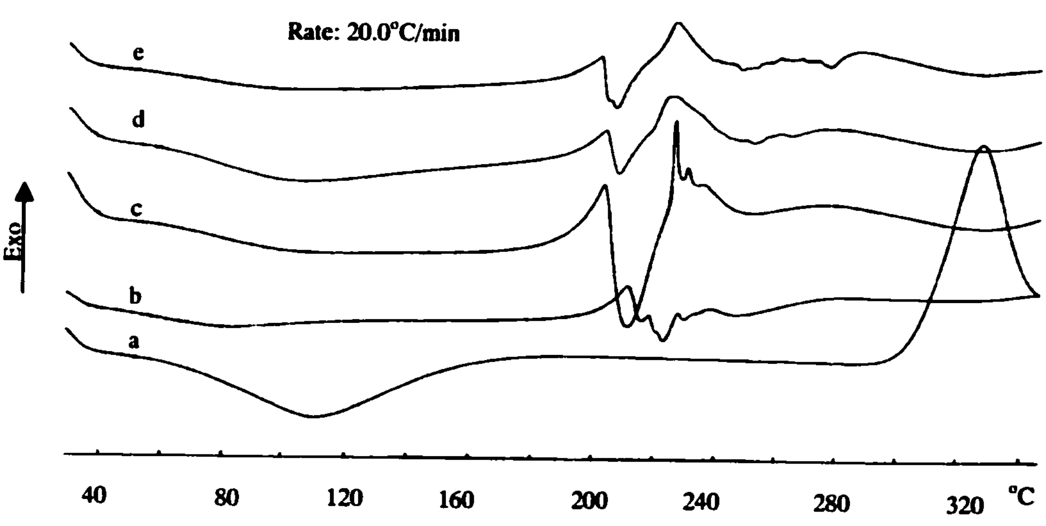


Fig.4.15 DSC curves of CH05(a),NOQC1 (b),NOQC2 (c), NOQC3 (d) and NOQC4 (e)

4.4.3 Effect of N/O-HTCC of Different DS on the Dyeability of Silk Fabrics

The color yield (K/S value), color difference (ΔE*) and colorfastness to washing (grey scale) of silk fabrics which were treated with N/O-HTCC and chitosan CH05, and dyed with acid dyes are summarized in Table 4.8.

N/O-HTCC treatment effectively increased the dye uptake of acid dyed silk fabrics without lowering the color fastness owing to the strong electrostatic attraction between quaternary ammonium salt and acid dye. The K/S value and ΔE* of silk fabrics treated with N/O-HTCC are smaller than those treated with chitosan CH05 because of their high water solubility. For series of NQC or NOQC, a small decrease of K/S value and ΔE* were observed as the DS of N/O-HTCC increased, which meant that the dye uptake of silk fabrics treated with N/O-HTCC decreased slightly as the DS of N/O-HTCC increased. This again was due to water solubility. In general, similar to O-carboxymethyl chitosans, the N/O-HTCC is not as effective as chitosan in improving the color up-take of the silk fabrics; on the other hand, it has a much better effect on the silk fabric hand feel.

Table 4.8 Effect of N/O-HTCC of different DS on the dyeability of silk fabrics

Treating Reagent	DS ± Av. Dev.	Dyestuff (C.I.)*	K/S value ± Av. Dev.	ΔE^* ± Av. Dev.	Grey Scale
No		AR 44	17.1±0.2	0.00±0.00	1-2
CH05		AR 44	20.9±0.2	10.7±0.1	1-2
NQC1	1.34±0.03	AR 44	20.7±0.2	7.26±0.07	1-2
NQC2	1.98±0.04	AR 44	20.1±0.2	6.84±0.07	1-2
NQC3	2.19±0.04	AR 44	20.0±0.2	5.50±0.06	1-2
NQC4	2.31±0.05	AR 44	19.5±0.2	4.20±0.04	1-2
NOQC1	1.73±0.03	AR 44	20.9±0.2	6.40±0.06	1-2
NOQC2	2.03±0.04	AR 44	20.9±0.2	6.19±0.06	1-2
NOQC3	2.42±0.05	AR 44	19.2±0.2	3.81±0.04	1-2
NOQC4	2.56±0.05	AR 44	18.5±0.2	3.49±0.03	1-2
No		AB 25	16.3±0.2	0.00±0.00	1-2
CH05		AB 25	18.9±0.2	4.04±0.04	1-2
NQC1	1.34±0.03	AB 25	17.8±0.2	2.09±0.02	1-2
NQC2	1.98±0.04	AB 25	17.7±0.2	1.91±0.02	1-2
NQC3	2.19±0.04	AB 25	17.3±0.2	1.87±0.02	1-2
NQC4	2.31±0.05	AB 25	16.7±0.2	1.56±0.02	1-2
NOQC1	1.73±0.03	AB 25	18.0±0.2	2.36±0.02	1-2
NOQC2	2.03±0.04	AB 25	18.0±0.2	1.86±0.02	1-2
NOQC3	2.42±0.05	AB 25	18.0±0.2	1.65±0.02	1-2
NOQC4	2.56±0.05	AB 25	17.7±0.2	1.64±0.02	1-2

*For the molecular structures of dyes, see Table 3.2.

4.4.4 Summary

N/O-(2-Hydroxy)Propyl-3-Trimethyl Ammonium Chitosan Chlorides (N/O-HTCC) of different DS can be obtained simply from chitosan and glycidyltrimethylammonium chloride (GTMAC) by heterogeneous reaction.

NMR cannot distinguish the difference of substituted sites between N-HTCC and O-HTCC. This may be due to the overlapping of relative signals.

The DS of the N/O-HTCC was calculated using the N% and Cl% of the sample from their elemental analyses. For NQC1 to NQC4, the DS increased from 1.34 to 2.31 as the molar ratio of GTMAC to chitosan monomer unit increased from 2 to 8. For NOQC1 to NOQC4, the DS increased from 1.73 to 2.56 as the molar ratio of GTMAC to chitosan monomer unit increased from 2 to 8.

All N/O-HTCC were soluble in D.I. H_2O and aqueous HAc solution, and their thermal degradation occurred at temperatures higher than 180°C. So they were thermally stable, and suitable for treating silk fabrics for dyeing.

N/O-HTCC treatment effectively increased the dye uptake of acid dyed silk fabrics without lowering the color fastness owing to the strong electrostatic attraction between quaternary ammonium salt and acid dye. The K/S value and ΔE^* of silk fabrics treated with N/O-HTCC were smaller than those treated with chitosan CH05 because of their high water solubility. For series of NQC or NOQC, a small decrease of K/S value and ΔE^* were observed as the DS of N/O-HTCC increased, which meant that the dye uptake of silk fabrics treated with N/O-HTCC decreased slightly as the DS of N/O-HTCC increased. This again was due to water solubility. Like the O-carboxymethyl chitosans, the N/O-HTCC is not as effective as chitosan in improving the color up-take of the silk fabrics; however, it has a much better effect on the silk fabric hand feel.

Conclusions and Suggestions

Chitosans of Different DD

Chitosans of high DD were prepared from chitin through consecutive alkaline hydrolysis. Chitosans of different DD were prepared through heating chitin and then reheating the product obtained (chitosan) in aqueous NaOH solution of different concentrations and at various lengths of time. Because the reaction is heterogeneous, we were unable to obtain a sample with DD = 100% even by treating the deacetylated chitin sample (chitosan) again and again with NaOH solution at high temperature.

The optimal experimental conditions obtained in our study of chitosan treating and dyeing silk fabric: 1. The best exhaustion time length is 30 minute period, and curing is not necessary for the chitosan treatment of silk fabric; and 2. The silk fabrics should be dyed in a dyeing bath of pH=4 adjusted using a citrate buffer solution.

Chitosan significantly improved the dye exhaustion of silk fabric dyed with acid dye without the lowering of color fastness to washing when compared with the untreated silk fabrics. The color yield (K/S value) and color difference (ΔE^*) increased as the concentration of chitosan increased from 0.5% to 1.0% and the DD from 57% to 95%. The maximal gain of K/S value reached 555% (Table 4.3a) and the maximal ΔE^* reached 53.4 (Table 4.3c). That was owing to the electrostatic attraction between protonated $-NH_2$ of chitosan and anion of acid dye.

The dye exhaustion of silk fabric decreased as the number of $-SO_3^-$ group of dye molecule increased, such as in the case of AO 10 and 12, and AR 18 and 44. This result was due to the decrease in the number of absorbed acid dye molecule as the $-SO_3^-$ group of dye molecule increased. For AB 129 and 25, AG 27 and 25, the same number of $-SO_3^-$ group of dye molecules resulted in similar dye exhaustion, which was not affected by the hydrophobic substituents on dye molecules.

Chitosans of Same DD, Different MW

Ultrasonic degradation effectively degraded the chitosan of high MW, but we were unable to obtain an MW of degraded chitosan that is lower than 1.5×10^5 by this method, owing to the limited ultrasonic wave energy. The DD of chitosan samples were not affected by ultrasonic degradation.

All degraded chitosan treated processes effectively improved the dye exhaustion of silk fabrics dyed with acid dyes without the lowering of color fastness to washing. The K/S values were nearly constant. However, the ΔE* decreased slightly as the MW decreased. This could be explained as a result of the higher water solubility of chitosan with lower MW.

O-Carboxymethyl Chitosans

O-carboxymethyl chitosans with a low degree of substitution (DS) and a high degree of deacetylation (DD) were prepared from chitin.

Based on our NMR data, chitosan derivatives obtained had carboxymethyl group substituted exclusively on the C6-oxygen of glucosamine unit, not on the C3-oxygen or C2-nitrogen. The degree of deacetylation (DD) of all samples was evaluated using the ^1H NMR data, and the DS of the O-carboxymethyl chitosans was calculated using the DD value, C% and N% of the sample from their elemental analyses. The deacetylation was not affected by the presence of a small amount of chloroacetic acid. The DS increased from 1.00% to 28.7% as the molar ratio of chloroacetic acid to chitin monomer unit increased from 0.1 to 2.0, and the DS of these O-CM chitosans was found to be far lower than the corresponding molar ratio of chloroacetic acid to chitin monomer unit due to the heterogeneous reaction.

The aqueous solubility of these samples increased as the DS increased. O-carboxymethyl chitosans with DS<9.5% were soluble in aqueous HAc solution, and their thermal degradation occurred at the temperature that was higher than 180°C. So they were thermally stable and suitable for treating silk fabrics for dyeing.

O-carboxymethyl chitosan treatment effectively increased the dye uptake of acid dyed silk fabrics without lowering the color fastness owing to the electrostatic attraction between protonated $-NH_2$ of O-carboxymethyl chitosan and anion of acid dye. The K/S value and ΔE* of silk fabrics treated with O-CM chitosans were smaller than those treated with chitosan (same DD) because of their higher water solubility. A small decrease in ΔE* was observed as the DS of O-CM chitosans increased, which meant that the dye uptake of silk fabrics treated with O-CM chitosans decreased slightly as the DS of O-CM chitosans increased. This again was due to water solubility. O-carboxymethyl chitosans are not as effective as chitosan in improving the color up-take of the silk fabrics. On the other hand, they have a much better effect on the silk fabric hand feel.

N/O-(2-Hydroxy)Propyl-3-Trimethyl Ammonium Chitosan Chlorides

N/O-(2-Hydroxy)Propyl-3-Trimethyl Ammonium Chitosan Chlorides (N/O-HTCC) of different DS can be obtained simply from chitosan and glycidyltrimethylammonium chloride (GTMAC) by heterogeneous reaction.

NMR cannot distinguish the difference of substituted sites between N-HTCC and O-HTCC. This may be due to the overlapping of relative signals.

The DS of the N/O-HTCC was calculated using the N% and Cl% of the sample from their elemental analyses. For NQC1 to NQC4, the DS increased from 1.34 to 2.31 as the molar ratio of GTMAC to chitosan monomer unit increased from 2 to 8. For NOQC1 to NOQC4, the DS increased from 1.73 to 2.56 as the molar ratio of GTMAC to chitosan monomer unit increased from 2 to 8.

All N/O-HTCC were soluble in D.I. H_2O and aqueous HAc solution, and their thermal degradation occurred at temperatures higher than 180°C. So they were thermally stable, and suitable for treating silk fabrics for dyeing.

N/O-HTCC treatment effectively increased the dye uptake of acid dyed silk fabrics without lowering the color fastness owing to the strong electrostatic attraction between quaternary ammonium salt and acid dye. The K/S value and ΔE^* of silk fabrics treated with N/O-HTCC were smaller than those treated with chitosan CH05 because of their high water solubility. For series of NQC or NOQC, a small decrease of K/S value and ΔE^* were observed as the DS of N/O-HTCC increased, which meant that the dye uptake of silk fabrics treated with N/O-HTCC decreased slightly as the DS of N/O-HTCC increased. This again was due to water solubility. Like the O-carboxymethyl chitosans, the N/O-HTCC is not as effective as chitosan in improving the color up-take of the silk fabrics; however, it has a much better effect on the silk fabric hand feel.

Suggested Future Works

Study on the rate of dye uptake and isothermal conditions for dyeing of silk is helpful for finding out the shortest time required for optimal dye absorption.

Research on the chemical modification of chitosan with different length of alkyl chain substituents can lead to a more in depth understanding of the hydrophobic attraction effect on the dyeing of silk.

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