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The Hong Kong Polytechnic University Department of Applied Physics

Laser Surface Modifications of

Polymeric Electrets for Efficient Charge Trapping

Submitted by

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A thesis submitted in partial fulfilment of the requirements

for the Degree of Master of Philosophy

August 2005



CERTIFICATE OF ORIGINALITY

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Abstract

In this study, poly(ethylene terephthalate) (PET) films were irradiated by KrF pulsed excimer laser of wavelength 248 nm with different number of pulses at 1Hz. The PET samples were then electrified by the negative corona discharging method. The electret properties of the charged samples were studied by various techniques. A significant increase of surface potential was obtained for the PET films irradiated of more than 15 pulses with a laser fluence of 86 mJ/cm². The surface potential of those films irradiated for more than 20 pulses did not increase further but dropped to the same level as untreated films.

From the SEM pictures, melt ripple tips were observed in the laser irradiated area on the PET film surface and some of them were even fused together. This layer of melt polymer led to an increase of charge storage, which the surface potentials of the samples were enhanced. It suggested the possibility of enhancing the charge trapping capability of polymers by altering the surface morphology with the laser ablation process.

On the other hand, the charge retention capabilities of the PET films electrified with different corona voltages were studied. The results showed that the surface potential of the electrets would decay and reach a steady value whatever the initial charging condition and the corona voltage were different. This steady value was depending on the sample thickness.

Using the open-circuit Thermally Stimulated Depolarization Current (TSDC) with a Polytetrafluoroethylene (PTFE) spacer, the characteristics of the PET electrets obtained in various conditions were studied. The polarization and space charges peaks were distinguished clearly in the TSDC thermograms. TSDC with different heating rates were conducted. From the current magnitudes and peak positions obtained, the activation energy of the space charges in PET can be estimated.

Finally, a prototype electret microphone was fabricated to examine the laser irradiated PET film with respect to its frequency responses and signal sensitivity as the microphone diaphragm. It can be seen that the performance of the laser irradiated PET film was better than the untreated film and was comparable to the commercial Teflon diaphragm and even better at frequencies over 5 kHz.

Publication

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Table of Contents

Abstract	Ι
Publication	III
Acknowledgements	IV
Table of Contents	V
List of Figures	VIII

Chapter 1	Introdu	uction	1
1.1	Backgr	ound	1
1.2	Scope of	of This Study	3
1.3	Historie	cal Development of Electret	5
1.4	Review	s on Electret Materials	7
	1.4.1	Inorganic Materials	7
	1.4.2	Classical Organic Materials	9
	1.4.3	Polymeric Materials	10

Chapter 2	Theore	tical Aspec	ts and Experimental Methodology	15
2.1	More A	bout Electre	ets	15
2.2	Charact	erization Te	chniques of Electrets	16
	2.2.1	Formation	and charging of electrets	16
	2.2.2	More abou	it corona discharge	19
		2.2.2.1	Corona discharge set-up with different	19
			electrode separation	
		2.2.2.2	Corona triode set-up coped with a grid in	22
			different grid spacing	
	2.2.3	Surface po	otential measurement	27
	2.2.4	Thermally	stimulated depolarization current (TSDC)	32
2.3	Laser S	urface Mod	ification of Polymer	35

Chapter 3	Sample	e Preparat	ion and Characterizations	37
3.1	Laser I	rradiation o	on Polymer Samples	37
3.2	Electri	fication Me	thod	38
3.3	Sample	e Characteri	zation	39
	3.3.1	Surface n	norphology of the irradiated PET	39
		3.3.1.1	Optical Microscopy	39
		3.3.1.2	Scanning Electron Microscopy (SEM)	40
	3.3.2	Thermal .	Analysis	41
		3.3.2.1	Differential Scanning Calorimetry (DSC)	42
		3.3.2.2	Dynamic Mechanical Analyzer (TMA)	45
	3.3.3	Infrared a	bsorption spectra of PET	47
	3.3.4	Dielectric	e properties	50
	3.3.5	X-ray An	alysis	55
		3.3.5.1	X-ray Diffraction (XRD)	55
		3.3.5.2	X-ray Photoelectron Spectroscopy (XPS)	58

Chapter 4	Electre	et Effect of Laser Irradiated PET Films	60	
4.1	Micros	Microstructure Analysis		
	4.1.1	Optical Microscopy	61	
	4.1.2	Scanning Electron Microscopy (SEM)	69	
4.2	Surface	e Potential Measurement of Laser Irradiated PET Films	84	
4.3	Chemic	cal Properties of Laser Irradiated PET Films	88	

Chapter 5	Charge Retention Capability of PET Films	96
5.1	Charge Retention of PET Films with Different Thickness	96
5.2	Charge Retention of Laser Irradiated PET Films	102

Chapter 6	TSDC Measurement on PET Samples	107
6.1	Open Circuit TSDC with PTFE Film Spacer	107
6.2	TSDC Investigation on Laser Irradiated PET Films	111
6.3	TSDC Investigation on Ethanol Treated PET Films	115
6.4	TSDC Investigation on PET Films with Pre-annealing	123
	Treatment	
6.5	Investigation of Activation Energy of PET by TSDC	128
Chanter 7	Application of Laser Irradiated PFT Film	138
Chapter /	Application of Laser Infaulated TET Film	130
Chapter 8	Conclusions	144
-		
References		148

VII

List of Figures

Figure	Captions	Page
Figure 1.1	Chemical structures of some polymeric electrets: (a) PP; (b) PET; (c) PMMA and (d) PTFE.	14
Figure 2.1	Schematic diagram of a corona discharge set-up.	18
Figure 2.2	Schematic diagram of corona discharge set-up with varying separation.	21
Figure 2.3	Surface potentials of PET films charged at different electrode separation and corona voltage.	21
Figure 2.4	Schematic diagram of a simple version of corona triode.	22
Figure 2.5	Schematic diagram of corona triode coped with a floating metal grid in different spacing.	23
Figure 2.6	Grid voltage obtained at various corona voltages with different grid spacing.	24
Figure 2.7	Surface potential of PET films charged at -8 kV in different grid spacing.	26
Figure 2.8	Schematic diagram of a capacitive probe set-up for induced charge measurement of polymer electret.	27
Figure 2.9	The electrical parameters in the capacitive probe set-up.	29
Figure 2.10	Schematic diagram of an electrostatic sensor set-up for surface potential measurement of polymer electret.	31
Figure 2.11	Schematic diagram of an open circuit TSDC with an air gap.	34
Figure 3.1	Schematic diagram of the laser irradiation set-up.	37
Figure 3.2	Schematic diagram of corona discharging set-up.	38
Figure 3.3	DSC thermogram of the heating and cooling cycle of untreated PET.	44

Figure 3.4	Schematic diagram of DMA under vertical load with tensile mode.	46
Figure 3.5	DMA thermogram of the PET film under vertical load with tensile mode.	46
Figure 3.6	Schematic diagram to show FTIR in diffuse reflectance mode.	47
Figure 3.7	FTIR spectrum of untreated PET film.	49
Figure 3.8	FTIR spectrum of laser irradiated PET film.	49
Figure 3.9	Temperature dependence of (a) loss tangent and (b) the relative permittivity of the untreated PET.	53
Figure 3.10	Temperature dependence of (a) loss tangent and (b) the relative permittivity of the laser irradiated PET.	54
Figure 3.11	X-ray diffraction profile of untreated PET film.	57
Figure 3.12	X-ray diffraction profile of laser irradiated PET film for 18 pulses.	57
Figure 4.1	PET film irradiated by 5 shots.	62
Figure 4.2	PET film irradiated by 10 shots.	62
Figure 4.3	PET film irradiated by 15 shots.	63
Figure 4.4	PET film irradiated by 17 shots.	63
Figure 4.5	PET film irradiated by 20 shots.	64
Figure 4.6	PET film irradiated by 30 shots.	64
Figure 4.7	Polarized microscope photo of PET film irradiated for 3 shots.	66
Figure 4.8	Polarized microscope photo of PET film irradiated for 4 shots.	66
Figure 4.9	Polarized microscope photo of PET film irradiated for 6 shots.	67
Figure 4.10	Polarized microscope photo of PET film irradiated for 15 shots.	67
Figure 4.11	Polarized microscope photo of PET film irradiated for 30 shots.	68

Figure 4.12	SEM pictures of PET surface treated with the laser at 248 nm: (a) 1 pulse and (b) 2 pulses.	70
Figure 4.13	SEM pictures of PET surface irradiated for 5 pulses: (a) rod-like periodic structure observed and (b) circular pattern found.	71
Figure 4.14	SEM pictures of PET surface irradiated for 10 pulses: (a) the overall view and (b) higher magnification.	72
Figure 4.15	SEM pictures of PET surface irradiated for 15 pulses: (a) the overall view and (b) higher magnification.	73
Figure 4.16	Model structure for surface modified PET films by the irradiation of pulsed UV excimer laser.	74
Figure 4.17	SEM pictures of PET irradiated for 17 pulses: (a) an overall view and (b) a higher magnification view.	76
Figure 4.18	SEM pictures of PET irradiated for 17 pulses at side view.	77
Figure 4.19	SEM pictures of PET irradiated for 18 pulses: (a) an overall view and (b) a higher magnification view.	78
Figure 4.20	SEM pictures of PET irradiated for 18 pulses: (a) side view and (b) a close view on a tip-cut ripple.	79
Figure 4.21	SEM pictures of PET surface irradiated for 20 pulses: (a) an overall view and (b) a higher magnification.	80
Figure 4.22	SEM pictures of PET irradiated for 20 pulses: (a) a higher magnification view on the cut ripple tip (b).at side view.	81
Figure 4.23	SEM pictures of PET surface irradiated for 40 pulses: (a) an overall view and (b) a higher magnification view on the cut ripple tip.	82
Figure 4.24	SEM pictures of PET surface irradiated for 80 pulses: (a) an overall view and (b) a higher magnification view on the cut ripple tip.	83
Figure 4.25	The measured surface potentials of laser irradiated PET films plotted against the number of laser pulses.	85
Figure 4.26	Laser irradiated PET film surface after ultrasonic treatment in an ethanol bath: (a) top view and (b) side view.	87
Figure 4.27	XPS spectra of (a) C1s and (b) O1s of untreated PET surface.	90

Х

Figure 4.28	XPS spectra of (a) C1s and (b) O1s of untreated PET surface after irradiated for 5 pulses.	91
Figure 4.29	XPS spectra of (a) C1s and (b) O1s of untreated PET surface after irradiated for 10 pulses.	92
Figure 4.30	XPS spectra of (a) C1s and (b) O1s of untreated PET surface after irradiated for 15 pulses.	93
Figure 4.31	XPS spectra of (a) C1s and (b) O1s of untreated PET surface after irradiated for 17 pulses.	94
Figure 4.32	XPS spectra of (a) C1s and (b) O1s of untreated PET surface after irradiated for 20 pulses.	95
Figure 5.1	Surface potential decay of 110 μ m thick PET films charged at different corona voltages.	99
Figure 5.2	Surface potential decay of 50 μ m thick PET films charged at different corona voltages.	100
Figure 5.3	Surface potential decay of 13 μ m thick PET films charged at different corona voltages.	101
Figure 5.4	Surface potential decay of laser irradiated PET films in 110 μ m thick shot for different number of pulses: (a) after 1 hour, (b) after 63 days.	103
Figure 5.5	Surface potential decay of laser irradiated PET films in 50 μ m thick shot for different number of pulses: (a) after 1 hour, (b) after 63 days.	105
Figure 5.6	SEM photo of 50 μ m thick PET film irradiated for 14 pulses.	106
Figure 6.1	TSDC thermogram of PET film charged at -5 kV in close-circuit mode.	110
Figure 6.2	TSDC thermogram of PET film charged at -5 kV in open-circuit mode with an air gap.	110
Figure 6.3	TSDC thermogram of untreated and laser irradiated PET charged with different corona voltage at room temperature.	113
Figure 6.4	TSDC thermogram of untreated and laser irradiated PET charged with different corona voltage at 110 °C.	114
Figure 6.5	TSDC thermograms of the uncharged PET films before and after ethanol treatment.	116

Figure 6.6	TSDC thermograms of bare PET films charged at 110°C before and after ethanol treatment.		
Figure 6.7	TSDC thermograms of laser irradiated PET films charged at 110°C before and after ethanol treatment.		
Figure 6.8	Schematic diagram of the current flow of sample in TSDC set-up.		
Figure 6.9	TSDC thermogram of PET films charged at room temperature with pre-annealing treatment: (a) above 100°C and (b) below 100°C.		
Figure 6.10	TSDC thermograms of PET films with different heating rates and charged at room temperature: (a) charged at -5 kV; (b) charged at -8 kV.		
Figure 6.11	TSDC thermograms of PET films with different heating rates and charged at 110 °C under -8 kV: (a) without ethanol treatment; (b) after ethanol treatment.		
Figure 7.1	Schematic diagram to show the operational principle of an electret microphone.		
Figure 7.2	Schematic diagram of the electret microphone.		
Figure 7.3	Schematic diagram of the testing set-up for electret microphone.	141	
Figure 7.4	Frequency response of the amplifier for the electret microphone.	143	
Figure 7.5	Frequency responses of microphone using different polymer electrets.	143	

Chapter 1

Introduction

1.1 Background

An electret is a dielectric that persistently produces an external electric field. It is a result of the charge retention in the dielectric and molecular polarizations with a "quasi-permanent" stability. The term "quasi-permanent" means that the characteristic decay time of the charges or the dipoles are much longer than the time periods over which studies are performed with the electret. [Hilczer and Małecki, 1986; Sessler, 1998]

Generally, the charges in the electret consist a layer of surface charges and space charges in the bulk material. These charges have not been compensated yet after the manufacturing processes while the polarization is usually a frozen-in alignment of molecular dipoles or a layer of trapped positive and negative charges, often positioned at or near the two surfaces of the dielectric, respectively, which resemble a true dipole polarization.

Like other modern scientific disciplines, the field of electret research is in a steady transformation characterised by plenty of new developments over the past decades. These relate to materials used, measuring techniques, insights into charge storage, charge transport and retention, polarization phenomena, pseudo-piezoelectric properties, and applications of electrets [Sessler, 2001]. Valuable applications such as electret microphones, electro-acoustic transducers and xerography have already been improved by these technologies and developments. On the other hand, new applications of electret like the non-volatile digital memory storage applied for flash memory are now influencing the engineering and industrial disciplines. Obviously, the study of electret is endless and it can be revitalized with new technologies.

1.2 Scope of This Study

In this project, we will aim at the study of electrets made of polymeric materials. Among the various electret properties, pseudo-piezoelectric effect is one of which any deformation of the electret would induce change of potential of the electrodes in its proximity. The deformation of electret may be due to the change of environment or any applied stress, its sensitivity in response to the deformation depends on the charge densities and their distributions in the surface layers of the electret material, thus it can be exploited as a vibration sensor. It is evident that polymeric electrets made of polymeric materials may have superior pseudo-piezoelectric effect because of its compliant characteristics. As an example, porous polytetrafluoroethylene (PTFE, Teflon) films are found to have an extraordinarily high pseudo-piezoelectric effect, which is comparable to the conventional piezo-ceramics such as lead zircroate titanate (PZT). It is believed that the compliance as well as the large surface area of this polymer is responsible for the large sensitivity. Thus it is interesting to investigate for more potential porous polymeric electrets that may have similar sensitivity [Hillenbrand et al., 2000]. Nevertheless, porous polymers are difficult to fabricate and apply for transducer applications. Therefore, there is an urge in searching for high sensitivity electrets of reasonable stiffness.

As surface charge is important in electret, another approach to enhance the electret sensitivity will be the modification of electret surface. In this study, the laser surface treatment technique is applied to modify the surface morphology of certain conventional non-porous polymeric electrets. By the laser surface treatment, a new surface will be

produced that a considerable increase of charge trapping centres would be found, while the stiffness of modified polymer sample can still be retained. The charge retention capabilities of the polymeric electrets will be increased by this treatment. A substantial increase in sensitivity to vibration thus is expected. Finally, a microphone prototype will be fabricated using the laser modified electrets and its sensitivity will be compared with a conventional electret microphone to illustrate the effectiveness of this specifically treated polymer electret.

1.3 Historical Development of Electret

From carnauba wax to thin Teflon film, from Eguchi to Sessler, the research in electrets has been well developed in the last two centuries. In the following paragraphs, a brief history of electret and its development will be reviewed.

In 1732, electret properties were illustrated by Gray [Hilczer and Małecki, 1986] when he mentioned the "perpetual attractive power" of a number of dielectrics, such as waxes, rosins and sulphur. The static electricity of these materials had been generated by contact electrification caused by cooling of the melts in iron ladles. About a century later, Faraday proposed in 1839 that the electret properties were due to the application of an external electric field as he referred to "a dielectric which retains an electric moment after the externally applied field has been reduced to zero". In 1892, English scientist Heaviside suggested that apart from the known stable magnets, insulators which were called "electret" with permanent polarisation should also exist in nature. Debye developed the theory of dielectric polarisation in 1912, assuming the existence of permanent electric dipoles resulting from a specific space distribution of charges in molecules. These permanent dipoles form an analogy with elementary magnets in magnetic substances. Debye also described the foundations of dipolar relaxation, that is the processes responsible for the increase in dielectric polarisation in electric field and its decay after the field has been removed [Hilczer and Małecki, 1986; Sessler, 1998].

In 1919, systematic researches of electret properties were developed when Eguchi, the Japanese physicist, formed electrets with carnauba wax, by the application of an electric

Chapter 1

field to the cooling melt. He found that the dielectrics exhibited charges on their two surfaces which changed sign after a few days. These electrets exhibited polarization whose direction was opposite to the direction of the polarizing field (heterocharge). Over time the heterocharge of electrets decreased to zero following which there appeared on the electret surfaces a permanent charge whose sign agreed with the polarity of the electrodes during their formation (homocharge). In the following decades, pioneers not only explored novel materials to produce electrets, such as sulphur electret by Nadjakoff in 1937 and thermoplastic (polymeric) materials by Dickenson in 1948, but also the new principles to explain these phenomena like Boltzmann-Hopkinson superposition principle by Gross in 1937 [Hilczer and Małecki, 1986; Sessler, 1998; Sessler 1999].

1.4 Reviews on Electret Materials

From the first thermoelectret obtained by Eguchi from the carnauba wax, to the novel cellular polymeric materials like porous Teflon, electrets were put into practical use for more than 70 years. The materials applied to produce electrets have been developed into different variations. In the following paragraphs, a brief introduction will be given to describe the different types of materials used for the electrets.

1.4.1 Inorganic Materials

From the first attempt by Johnson and Carr in the 1930's, the properties of thermoelectrets made from non-polar sulphur have been studied, which also started the research of inorganic electret. On the other hand, a systematic research on the formation and properties of electret produced from ceramic materials of perovskites structure was made by the Russian scientists Gubkin and Skanavi in 1958 [Hilczer and Małecki, 1986]. Under electric fields in the range of 1-2 MV/m, the thermoelectrets, which were electrified at high temperature, can be obtained from perovskites like calcium titanate and strontium titanate. The values of electrical permittivity and resistivity for these materials are shown in Table 1.1. The stability of the electrets obtained from these ceramic materials is in the order of one year, or even more for which produced from MgTiO₃. [Hilczer and Małecki, 1986]

Today the inorganic electrets have been developed into many alternatives, such as the silicon oxide (SiO_2) and silicon nitride (Si_3N_4) etc. Submicron layers of these materials,

Chapter 1

charged on their free surface, have been examined in the past two decades and were shown to possess excellent charge stability exceeding that of the best polymer electrets [Sessler, 2001].

Material	Permittivity	Resistivity (Ω-m)
MgTiO ₃	16	$10^{11} - 10^{12}$
BaTiO ₃	1200	$10^8 - 10^{10}$
BiTiO ₃	80	$10^{10} - 10^{11}$
CaTiO ₃	150	10 ¹⁰ - 10 ¹¹
SrTiO ₃	175	$10^8 - 10^{10}$
Steatite	4-5	$10^{12} - 10^{13}$

Table 1.1Electric permittivity and resistivity at room temperature of some ceramicelectret materials [Hilczer and Małecki, 1986]

1.4.2 Classical Organic Materials

The first electrets were made by Eguchi from waxes and their mixtures with rosin. These classical electrets are still used in laboratories in basic research, and can exhibit high stability at room temperature. In short-circuited condition the lifetime of these electrets are in the order of 10^6 years. Waxes consist of fatty acid esters and alcohols of the sterol groups or aliphatic alcohols. The carboxyl groups of alcohols and esters in the wax are responsible for the heterocharge of thermoelectrets. Thermoelectrets may also be made from other organic materials which contain dipolar functional groups and of extremely low electrical conductivity [Hilczer and Małecki, 1986].

1.4.3 Polymeric Materials

Thermoelectrets which exhibit heterocharge just after electrification may also be made from polymers with dipole moment, for example, polymethylmethacrylate (PMMA) or polyvinylchloride (PVC). Homoelectrets are made from organic non-dipolar materials like naphthalene. Polymeric materials like polyolefines, including polypropylene (PP) or other similar polymers which consist of halogen, alkyl, or aromatic side groups, can store electric charges for a long time. Charge retention capability of these materials can be sustained even under conditions of considerable humidity, which is crucial for practical applications. In the following paragraphs, the electrostatic characteristics of some common solid polymeric electret materials will be introduced and their chemical structures are shown in Figure 1.1.

Polypropylene (PP)

Polypropylene thin films were studied by Dreyfus and Lewiner with corona-charging technique in 1973. From the results of open-circuit and short-circuit thermally stimulated depolarization current (TSDC), they reported that equal quantities of positive and negative charges had been injected into the samples [Dreyfus and Lewiner, 1973]. Moreover, the laser induced pressure pulse (LIPP) method was applied to study the charged PP. The results showed that the charge layer broadens towards the rear electrode with increasing injected charge density. Due to the spread charge "layer", the zero-field plane is located in the charged region, and therefore the charged PP electrets exhibit a large pseudo-piezoelectric effect [Gerhard-Multhaupt et al., 1999]. In addition, charge

distribution measurements on field-charged and electron beam charged PP samples have been used to gain information about charge transport and breakdown processes in this polymer [Sessler, 1997].

Polyethylene terephthalate (PET)

PET, commercially called Mylar, Dacron or Terylene, is a well known polyester electret with aromatic and polar group. The build-up, storage and transport of charges in this material have been studied by many research groups because of its wide electronic applications, and in particular, as diaphragm material for electret microphones [Creswell & Perlman, 1970; Hayashi et al., 1975; Schneider et al., 1983].

Practically, a charged PET sample will maintain its dipole orientation in the field due to the surface or space charges. Upon heating, the polarization in the sample will diminish together with the space charges [Sessler, 1997]. For PET, the glass transition temperature (T_g) is about 80°C, and it can be shown in the TSDC spectra as a depolarization, or so called the α peak. On the other hand, the peak related to the space charge recombination, the ρ peak, is observed at temperature higher than 110°C, which depends on sample preparations and polarizing conditions. Sessler and West discussed heterocharges and internal homocharges decay for this polyester electrets in 1968 [Sessler and West, 1968]. In 1970, Lilly et al. have studied the mechanisms of charge transport and dipole disorientation by means of TSDC under either high field at low temperature or low field at high temperature [Lilly et al., 1970]. PET can be easily electrified during the production process, which results in quasi-permanent charging of the film. To charge a PET solid film, corona-discharge treatment is commonly used. During the charging process, the charges are trapped near the surface if the temperature is below T_g . It has been reported that the rate of charge decay is enhanced by slow charge retrapping. On the other hand, if the sample temperature is greater than T_g , the mean charge depth would shift to the bulk due to the fast retrapping of the released charge carrier [Xia et al., 1992].

Polymethylmethacrylate (PMMA)

Like PET, PMMA is a polar material which shows strong dipolar peaks in the TSDC measurements. Nevertheless, unlike the PET, charge mapping methods have not been used comprehensively in PMMA for studying the interaction of real charges and dipoles. Some studies, by applying the electrically-stimulated acoustic wave (ESAW) method, have shown that heterocharge due to charge trapping appears within the bulk after the sample poled at 50°C. The dipolar charges have also been detected, however, the origin and interactions of both charges are not yet known. A strong heterocharge due to dipole orientation was found for samples poled around the T_g , at about 105°C. At a temperature of 130°C, charge injection from the cathode was dominant [Sessler, 1997].

Polytetrafluoroethylene (PTFE)

PTFE is a kind of fluoropolymer which is a member of the Teflon family. Teflon also includes fluoroethylenepropylene (FEP), perfluoroalkoxy (PFA) and a new member, the amorphous Teflon (AF) since 1992. They are non-polar polymers of very high electrical

resistivities. Due to their excellent charge storage properties they are crucial for electret applications, for example, as the diaphragms of electret microphones. Consequently, there is still a great interest in studying the charge dynamics, charge distributions, and charge stability of these materials [Gerhard-Multhaupt et al., 1999]. PTFE, in particular is one of the most important fluoropolymers which exhibits good resistance to chemically active substances and tolerance to temperature. These properties are mainly due to the high stability of the fluorine-carbon bonds in the polymer chain. Furthermore, PTFE has a low absorption of water and an extraordinarily high electrical resistivity which is greater than $10^{16} \Omega$ -m.

Electric displacement profiles of positive and negative corona charged Teflon electrets at room temperature measured by means of piezoelectrically generated pressure steps (PPS) have been reported. The results indicated some minor spreading of the charge near the injecting surface and near the back electrode. After charging at high temperature, charges in the Teflon sample would spread throughout the bulk, resulting in a quite uniform charge distribution [Gerhard-Multhaupt et al., 1992; Sessler, 1997]. From Kochervinskij reported in 1991, a decrease in crystallinity and increase of conformation defects in PTFE strongly reduced charge retention stability in negatively charged films [Kochervinskij et al., 1991]. Furthermore, the charge transport, decay and stability in Teflon have also been studied by many pioneers. In 1970's, a study of temperature dependence of surface density of corona charged samples reported that PTFE has the highest stability compared with many other polymers like polyethylene (PE) [Cresswell et al., 1972].



Figure 1.1 Chemical structures of some polymeric electrets: (a) PP; (b) PET; (c) PMMA and (d) PTFE.

Chapter 2

Theoretical Aspects and Experimental Methodology

2.1 More about Electrets

In the study of electrets, the electrical properties we concern the most are the charges retained, which include both the surface and space charges, and the dielectric polarization in the presence of an electric field. In addition, the mechanisms of charge transport and trapping as well as the polarization decay are also essential in the understanding of electrets [Hilczer and Małecki, 1986].

The first man-made electret was manufactured at elevated temperature under an electric field. Two terms had been introduced referring to the sign of charges with respect to the sign of potential on the electrodes during electret formation. For the polarity of the charges on the electret surface which were opposite to the charging electrode potential were called heterocharges, vice versa, for those charges which have the same polarity to the electrode potential were called homocharges. It is understood that heterocharge is associated with the ordering of dipolar polarization or with the separation of free charge carriers in an applied electric field, while homocharge arises as a result of the introduction of charge carriers from external sources. In order to study the dipolar polarization, homocharge and heterocharge of a polarized sample, the experimental technique - thermally stimulated depolarization current (TSDC) is commonly used [Hilczer and Małecki, 1986; Sessler, 1997].

2.2 Characterization Techniques of Electrets

2.2.1 Formation and charging of electrets

Practically, there are many ways to produce an electret. The name thermoelectrets is used to distinguish those electrets produced by thermal excitation under an external electric field and then cooling in the field. After this treatment the dipolar polarization is frozen-in and charges are injected from electrodes. For those electrets produced under an external field through optical or radiation excitation are called photoelectrets and radioelectrets respectively. The space charges of these electrets are optically or radiation excited from the valence band or trapping levels and then are frozen in the samples.

On the other hand, there are many techniques to implement electric field to electrify the electret. For example, electrically liquid contact, voltage breakdown and electron beam bombardment, or even plasma discharging. Nevertheless, corona discharge is the most commonly employed because of its simple operation and low instrumentation cost, and it is the only method that can charge up polymeric materials efficiently without damage their bulk properties. The cost-effectiveness of this method made it to be widely used in industry [Guo et al., 1999]. Moreno and Gross have improved the corona discharge setup by introducing a corona triode which consists basically of a corona tip, a metallic grid and a sample holder. By using this setup, a uniform charge distribution can be obtained [Giacometti et al., 1992]. Giacometti et al. [Giacometti, 1987; Dias et al., 1989; Ferreira, 1993] have focussed their research on the corona triode for nearly two decades, their studies mainly related to the current-density distributions, charge stability of

polymeric material such as Teflon and its current-voltage characteristics.

Corona discharge is a self-sustainable and non-disruptive electrical discharge which appears when a sufficient high potential difference exists between asymmetric electrodes such as a sharp pin point or a fine wire and a plate or cylinder [Giacometti and Jr. Oliveira, 1992]. The separation of these two electrodes is about few centimetres and the applied dc voltage can be as low as 3 kV, but most of the real application is higher because of higher efficiency. One side of the electret is metallized and in contact with the ground electrode while the non-metallized surface is exposed to the sharp point throughout charging process. Due to the high electric field near the emitting electrode (the sharp pin point), the air around this electrode that is insulating normally will become ionized and the resulting ions are driven towards the low-field electrode (the ground plate). In practical corona discharges, the negative corona is in the Trichel pulse regime where the positive one is in the continuous glow regime. Under atmospheric pressure, positive corona discharging generates positive ions like H^+ , NO^+ and NO^{2+} ion, conversely, mostly CO^{3-} ions will be produced in negative corona discharging.

The schematic setup for corona discharge is shown in Figure 2.1. Before electrifying the sample, the bottom surface is metallized with a gold layer by sputtering method. A negative voltage (4 - 9 kV) is applied to the sharp tip to produce a negative corona discharge. In the experiment, the separation between the corona tip and the sample surface is fixed at 20 mm. For preparing thermoelectret, the setup is put into an oven of which the temperature can be raised to 110° C, which is higher than the T_g of the PET sample. Then the sample was charged under this temperature for 10 minutes and the

applied electric field is maintained until the sample is cooled in the oven down to room temperature.



Figure 2.1 Schematic diagram of a corona discharge set-up.

2.2.2 More about corona discharge

The corona charging of polymeric materials attracted attention, which arises from the need to electrify polymers in an open circuit configuration. In the beginning, surfaces were charged by direct exposure to a corona point or wire, but in this procedure one had little control over the potential to which the surface was charged, and over the charge uniformity. The insertion of a metal grid between the corona point and the sample changed this situation, because a better control could be achieved. This three-electrode system, now called corona triodes, were further refined so as to allow the monitoring of the charging process itself, and some of them even operate under constant charging current condition [Giacometti et al, 1992]. The constant current triodes have been extensively used in the study of charge storage and charge transport of polymers. In this part, experiments were conducted to study some interesting properties of this corona charging configuration.

2.2.2.1 Corona discharge set-up with different electrode separation

The experiments started from the simplest configuration, a point-to-plate set-up. The PET films were electrified at room temperature by a corona discharge set-up as illustrated in the previous part. However, separation between the two asymmetric electrodes was varied from 5 mm to 25 mm as shown in Figure 2.2, and the corona voltage was also varied until the surface potential became the maximum or air-breakdown were occurred.

Surface potential of PET films charged in different conditions are shown in Figure 2.3. For 5 mm separation, the surface potential of PET sample can only be charged up to a maximum -2 kV at a corona voltage of -7 kV, though as the charging voltage increases, the potential of the film still decreases. When the separation becomes wider, the endurance of PET film increases, that is, a PET sample can sustain under a higher charging voltage to obtain a higher surface potential. For example, at 10 mm separation, the potential of PET film can be charged up to -2.8 kV with corona voltage at -8 kV; in 15 mm separation; up to -4.3 kV at charging voltage -11 kV; for 20 mm, potential at -3.8kV for charging under -11 kV; and finally, charging under -14 kV with 25 mm separation results a surface potential of -4.5 kV. Nevertheless, after the separation is increased to 30 mm, the efficiency of corona discharging becomes lower and the surface potential can be obtained from the set-up is also decreased.

From these results, we can propose that there is an optimized condition to charge up a polymer sample under a point-to-plate configuration set-up. The separation of asymmetric electrodes is optimized in the range from 15 to 25 mm. Moreover, although a higher charging voltage can result a higher surface potential on the sample, if the corona discharge is occurred at room temperature under atmospheric condition, the most efficient charging voltage to obtain the highest surface potential is suggested at about -14 kV.



Figure 2.2 Schematic diagram of corona discharge set-up with varying separation.



Figure 2.3 Surface potentials of PET films charged at different electrode separation and corona voltage.
2.2.2.2 Corona triode set-up coped with a grid in different grid spacing

After the simple point-to-plate set-up, we step up to an advanced set-up, the corona triode configuration. In addition to the point-to-plate set-up, a metal grid was inserted between the asymmetric electrodes. In the past, the polymeric sample surfaces were exposed directly to a corona point or wire discharge, and higher surface charges can be achieved by using this method. However, the final sample voltage and the surface charge uniformity are not easily to control. A crucial improvement was the introduction of corona triode which included simply a corona tip, a metallic grid and a ground electrode. Using a corona triode, one can choose the potential at which the sample is to be charged, and also finally achieve a uniform charge distribution after this charging method [Giacometti et al, 1992]. As shown in Figure 2.4, the metallic corona point (sharp pin) is connected to the extra high tension to that produce corona ions which are driven towards the sample. A metal grid, biased by a voltage supply, is inserted into the point-to-plate gap. The charging current can also be measured and will decrease to zero when the sample surface is equal to the voltage supply to the grid.



Figure 2.4 Schematic diagram of a simple version of corona triode.

In the present study, we will focus on the voltage of grid when it is not connected to any voltage supply, that is, the metal grid is floating between the asymmetric electrodes. In addition, the grid spacing and surface potential of PET films charged under this configuration will also be targeted.

To investigate the effect on grid spacing, 4 metal grids with different spacing were examined in the experiments (5 mm, 2 mm, 1 mm and 0.1 mm). The metal grid was placed at 5 mm above the ground electrode as shown in Figure 2.5. Corona voltage varying from -5 kV to -10 kV was applied to the set-up, and the potential of metal grid during discharging was recorded. Figure 2.6 shows the relation between corona voltage and grid voltage. By applying corona voltage from -5 to -10 kV into the corona triode, voltage of 5 mm spacing grid increases from -0.7 to -2.4 kV. The grid potential rises from -1.1 to -3.4 kV when the grid spacing is decreased to 2 mm. In 1 mm grid spacing, the grid voltage increases from -1.1 to -3.6 kV. For the smallest spacing in 0.1 mm, the grid potential rises from -1.4 to -4.0 kV.



Figure 2.5 Schematic diagram of corona triode coped with a floating metal grid in different spacing.

From these results, we can find that the grid spacing is reversed proportional to the grid voltage. When the grid spacing decreases, or in other words, cross-points of a metallic grid intensifies, the grid potential will increase. If the separation between metal grid and ground electrode is not changed, when the grid potential increases, the sample charged under this configuration will obtain a higher surface potential depend on the grid spacing, and the uniformity of charge distribution can be enhanced.



Figure 2.6 Grid voltage obtained at various corona voltages with different grid spacing.

To study the charging effect on different grid spacing, a series of PET films charged under the same corona voltage with different grid spacing were prepared. By using the same set-up illustrated in Figure 2.5, the PET samples were electrified under a corona voltage at -8 kV with metal grid in different spacing. In Figure 2.7, the PET samples show a higher surface potential when the films are charged under a metal grid with smaller spacing. The potential of PET film charged under 0.1 mm spacing grid is 25 % higher than the sample electrified under a 5 mm spacing grid. From the result, it can attribute this significant enhancement in surface potential to the increase of cross-points on the metal grid. Since in simple point-to plate configuration, the charge distribution follows Warburg's Law which is not uniform on the polymer surface [Giacometti et al, 1992]. Nevertheless, in the case of corona triode, a metal grid is implemented. When a grid with smaller spacing is applied, the number of cross-point increases and it is similar to use a needle matrix to electrify a sample. By this configuration, the uniformity of charge distribution is improved and more charges can be accumulated on the sample surface, the total surface potential on the electrified sample surface can be measured will also increase and therefore, the average surface potential of sample is increased.

In this study, however, the simple point-to-plate configuration was applied instead of the corona triode. From the experimental result as shown before, we can see that the surface potential of PET charged by the corona triode with a 0.1 mm copper grid is -3.17 kV, and the one charged by point-to-plate configuration is about -3.08 kV, the two values were more or less at the same level. In our experiment, only a small area of PET surface was measured and the uniformity of surface potential can still be retained by using this simple setting. Therefore, for the sake of convenience, the point-to-plate configuration

was used.



Figure 2.7 Surface potential of PET films charged at -8 kV in different grid spacing.

2.2.3 Surface potential measurement

After the sample is electrified with corona discharging, it will carry space charges and being polarized. This distributed charges and polarization can be represented by an equivalent charge layer located on the sample surface, which assume that will produce an electric field same as the distributed charges and polarization. An excellent performance electret such as PTFE can store a large amount of space charges for a long time. A non-destructive method is required to measure the electric field produced externally by this charged sample. It can be accomplished by the electrostatic induction method.

Capacitive probe method as shown in Figure 2.8 is a commonly used technique [Davies, 1967; Sessler & West, 1971] to measure the equivalent surface charges of an electret. By using this typical static technique, with well-defined geometry and non-contacting measuring procedure, a great accuracy can be achieved. Also it can be easily used to determine average charge density as well as lateral charge distribution. The measuring range extends from 5×10^{-11} to about 10^{-6} C/cm² [Sessler, 1999].



Figure 2.8 Schematic diagram of a capacitive probe set-up for induced charge measurement of polymer electret.

Figure 2.9 shows the electrical parameters in the capacitive probe set-up. When the electret was electrified by corona discharging, electric field was set up in the electret. Once the electret was put in the capacitive probe set-up, charges were induced on the probe from the surface charges on the electret, and the number of charges induced was then measured by the electrometer. If the surface area of the probe is known, the equivalent surface charge density can be estimated by following equations:

$$E_1 = \frac{\sigma_1}{\varepsilon_1} = \frac{V_1}{d_1}$$
(2.1)

$$E_d = \frac{\sigma_s}{\varepsilon_d} = \frac{V_s}{d_2} \tag{2.2}$$

where E_1 and E_d are the electric field in the air gap and the electret respectively; ε_1 and ε_d are the permittivity of the air gap and the electret respectively; σ_1 and σ_s are the equivalent surface charge density on the probe surface and the electret respectively; d_1 and d_2 are the distance of the air gap and the thickness of the electret respectively; finally V_1 is the potential in the air gap and V_s is the surface potential of the electret. At equilibrium, the potential in the air gap is equal but counter-directional to the surface potential of electret,

$$E_1 d_1 + E_d d_2 = 0 (2.3)$$

and by Gauss Law, we have

$$D = \varepsilon_1 E_1 - \varepsilon_d E_d = \sigma_s \tag{2.4}$$

where *D* is the electrical displacement.

By substitute Equation (2.1) and (2.3) into (2.4), the relation between the induced charge density and the equivalent surface charge density is

$$\sigma_{s} = \sigma_{1} \left(1 + \frac{\varepsilon_{d} d_{1}}{\varepsilon_{1} d_{2}} \right)$$
(2.5)

And from Equation (2.2) and (2.5) the relation with respect to the surface potential is

$$V_s = \sigma_1 \left(\frac{d_2}{\varepsilon_d} + \frac{d_1}{\varepsilon_1} \right)$$
(2.6)



Figure 2.9 The electrical parameters in the capacitive probe set-up.

In this study, the surface charge density of the electret will be measured in an alternative way. An electrostatic sensor (Keyence SK-030/200 Series) is applied to measure the surface potential of the sample instead of using a capacitive probe. When the surface potential of a sample is equal to the voltage applied to a surface potential sensor in a fixed separation, the potential difference between the sensor and the sample is compensated by the applied voltage and becomes zero voltage. By observing this

compensation voltage, the surface potential of a sample is estimated. This is called voltage scanning search (V.S.S.) method [Keyence Corporation, 2004]. The separation between the sensor and the sample is 8 mm as shown in Figure 2.10. The surface potential measured by the sensor is the average potential of the measurement area, where the area is 20 mm in diameter. From this average surface potential, the equivalent surface charge density (σ_s) of the sample can be estimated. Based on the model proposed by Sessler and the capacitive probe method [Sessler, 1987], the equivalent voltage U_o of the electret with one sided metallized can be expressed as follow

$$U_o = \frac{1}{\varepsilon_o \varepsilon_r} \int_0^d x \rho(x) dx$$
 (2.6)

where *d* is the thickness of the electret, ε_o is the permittivity of vacuum and ε_r is the relative permittivity of the sample. $\rho(x)$ is the charge distribution as a function of *x* along the thickness direction. By integrating $\rho(x)$, the total charges in the sample can be estimated. For simplicity, we assume that the charge distribution along the sample thickness is uniform, the total charge in the sample will be the product of the equivalent surface charge density and the sample thickness, that is

$$\sigma_s = \frac{1}{d} \int_0^d x \rho(x) dx \tag{2.7}$$

Since U_o is equivalent to V_s , therefore, from Equations (2.6) & (2.7), the relation can be rewritten as

$$V_s = \sigma_s \frac{d}{\varepsilon_o \varepsilon_r} \tag{2.8}$$

For the sake of convenience, the measured surface potential V_s will be used in instead of using σ_s in the following chapters.



Figure 2.10 Schematic diagram of an electrostatic sensor set-up for surface potential measurement of polymer electret.

Chapter 2

2.2.4 Thermally stimulated depolarization current (TSDC)

Since spontaneous discharge of electrets takes several years at room temperature, Frei and Groetzinger in 1936 proposed a thermal method to stimulate the charge decay. The thermal energy will enhance the mobility of the frozen-in dipoles and charges, so that the decay experiment could be finished within a reasonable time, even for the well-known fluoropolymer Teflon, which has a long lifetime up to several tens of years. The technique involves a slowly heating of the electret between two electrodes, which is connected to a sensitive ammeter that measures the discharge current [Turnhout, 1975].

Generally, the decay of permanent electret polarization consists of several physical processes, including reorientation of ordered molecular dipoles, the motion of real charges stored in the electret, and the ohmic conductivity of the dielectric. Dipole reorientation is induced by thermal excitation, which leads to decay of the resultant dipole polarization of the electret. The motion of the charges stored in the electret is related to the charge drift in the internal field of the electret and their diffusion. When these stored charges drift with respect to the internal field, they may experience recombination with charges of opposite sign, and may recombine with compensating charges at the electrodes. Recombination of charges inside the electret or near the electrodes will not produce electric current in the external circuit. Diffusion due to the gradient of charge concentration also leads to propagation throughout the electret of the charge density $\rho(x)$ initially localized in a layer of thickness Δx . It has been found that diffusion affects the change of space charge distribution to a smaller extent than its drift in the internal electret field [Hilczer and Małecki, 1986; Turnhout; 1975].

For polar polymeric material, it is not suitable for studying the injected homocharge by TSDC. These materials can be examined with short-circuit TSDC where displacement current will be generated across the electret (the conduction current decays rapidly). The image charges from the electrodes induced by dipoles and space charge can also be measured.

For non-polar polymers, homocharges are dominant after the charging process. A non-polar polymer is thus metallized on one-side and an air gap adjacent to the non-metallized side is introduced to form an air-gap (open circuit) TSDC configuration. Only displacement current flows in the circuit since the conduction current is blocked by the air gap. The air gap TSDC may further elucidate the coexistence of a homocharge and heterocharge where their released currents have opposite signs during thermal excitation. Therefore the measurement of TSDC has been widely applied to determine the charge density and distribution of polar and non-polar polymer electrets.

In our measurement, open circuit TSDC with an air gap as shown in Figure 2.11 is employed to investigate the corona charged samples. Short circuit TSDC has also been used for comparison in some of the samples. Nevertheless, a modified configuration is applied in our measurements, a Teflon PTFE film is used as a spacer instead of an air gap in the open circuit TSDC. The sample is heated at a constant rate and the upper electrode is connected to an electrometer with high resolution up to femto-ampere (fA). The separation between the top electrode and sample surface is about 100 μ m, which is the thickness of the PTFE film. Both homocharge and heterocharge of the sample after corona charging could be detected by this technique.



Figure 2.11 Schematic diagram of an open circuit TSDC with an air gap.

2.3 Laser Surface Modification of Polymer

Besides the research on bulk polymeric materials, surface modification is also interested to many pioneers. There are several common methods to change the surface morphology of polymers, such as chemical etching, glow-discharge plasma, and radio frequency plasma. Some of these processes not only can change the surface morphology of the polymer but also alter the material properties of bulk polymer. In this study, laser irradiation is applied to change the polymer surface.

In 1980's, Srinivasan and Mayne-Banton have reported the so-called self-developing photoetching of polyethylene terephthalate (PET) using a 195 nm ArF excimer laser. Dyer and his research group were then working with the laser ablation on PET and polyimide (PI) by ArF laser (193 nm), KrF laser (248 nm) and XeCl laser (308 nm) [Andrew et al., 1983; Dyer and Sidhu, 1985]. Later, Srinivasan and his co-workers began to adjust the laser fluence and by using two lasers with different wavelengths to control the quality of the laser affected area [Garrison and Srinivasan, 1986; Srinivasan et al., 1990; Srinivasan and Bodil Braren, 1990].

Lazare and Srinivasan, with their pioneer research group, have investigated the surface properties of the PET film modified by UV laser for more than twenty years. In 1990's, they have concentrated their studies in periodic structure on the polymer surface induced by UV laser irradiation [Lazare et al., 1986; Srinivasan et al., 1990]. In 1991, they have discovered that the excimer laser induced periodic structures (LIPS) can be obtained in the submicron periodic pattern [Bolle et al, 1992]. And in 1995, they have identified the same pattern on other different polymeric materials [Lazare et al., 1995]. Watanabe and Yamamoto have systematically studied the physical and chemical properties of the laser ablated PET in the mid of 1990's [Watanabe, 1997 and 1999]. They used the KrF excimer laser with 248 nm in wavelength, to irradiate on the polymer surface. Both the polymer film and the material ablated out were observed and identified.

For the detail explanation on the formation of this ripple patterning, Knittel and his co-workers with their German research team have focussed on the chemical properties of the PET after laser irradiation. Besides the chemical properties, they have established a model to explain the formation of ripple pattern after the PET have been ablated by the UV laser, and the importance of threshold fluence used to ablate the materials [Bahners et al., 1990; Knittel et al., 1997a and 1998a].

In our study, the KrF excimer laser with 248 nm in wavelength is applied to ablate on the polymer surface with different number of laser pulses (0 to 40 pulses). The surface properties of the ablated samples were examined by various surface analyzing techniques.

Chapter 3

Sample Preparation and Characterizations

3.1 Laser Irradiation on Polymer Samples

Commercial Polyethylene terephthalate (PET) films of thickness 110 μ m were cut into 19 x 19 mm². The samples were irradiated under atmospheric conditions directly by a pulsed KrF excimer laser (Lambda-Physik COMP EX205) of wavelength 248 nm at a pulse rate of 1 Hz. The laser fluence was set nominally to 86 mJ/cm² without using any optical component. The irradiated area was controlled to 7 mm in diameter with a copper mask as shown in Figure 3.1. The samples were irradiated with different numbers of laser pulse varying from 0 to 40. After the laser surface treatment, different ripple patterns were induced on the laser irradiated area according to the number of laser pulses. These structures were investigated by various techniques.



Figure 3.1 Schematic diagram of the laser irradiation set-up.

3.2 Electrification Method

Corona discharge, unlike the γ -ray and glow-discharge, is an effective method to electrify polymers without any apparent change of the sample bulk properties, therefore, it was applied to charge up the laser irradiated PET. The corona voltage was set at -5 kV and the exposure time was about 10 minutes as shown in Figure 3.2. The surface potentials of the samples were measured by an electrostatic sensor (Keyence SK-030/200).



Figure 3.2 Schematic diagram of corona discharging set-up.

3.3 Sample Characterization

3.3.1 Surface morphology of the irradiated PET

After irradiated by the pulsed UV laser, the surface morphology of the PET film was changed. In order to investigate the details, microscopic imagining techniques, such as the polarized optical microscopy and Scanning Electron Microscopy (SEM) were used, and the images captured were discussed in Chapter 4 with other experimental results.

<u>3.3.1.1 Optical Microscopy</u>

To investigate the macroscopic pattern of the laser irradiated area, the polarizing optical microscope (Nikon, Microphot-FXA) was employed. This type of microscope is applicable for observing materials with birefringence.

A polarizing microscope includes two polarizers, one is placed between the light source and the condenser and the other is placed between the objective and the eyepiece, which are called polarizer and analyzer respectively. The analyzer is crossed with respect to the polarizer and so no light can reach the observer. If a specimen with birefringence properties is focussed, it will split the incident polarized light into two components, one is travelling along its principal axis and the other is perpendicular to it. As a result, the output components will have a phase difference with respect to each other due to the difference in refractive indices.

3.3.1.2 Scanning Electron Microscopy (SEM)

In this study, the surface morphology of the irradiated samples was inspected by a field-emission scanning electron microscope (JEOL JSM-6335F) by operating in the secondary electrons mode at a voltage of 3 kV. To obtain a better imaging quality, a thin layer of gold with few nanometres in thickness was sputtered on the surface of samples. This gold layer can provide a better conduction of the sample surface to avoid electrons accumulation on it, which may cause the electronic image of the sample to be blurred.

3.3.2 Thermal Analysis

Polymers are usually rigid solids at low temperature, when the temperature increases, the possibility of chain movement also increases and at high enough temperatures, polymers will behave like viscous liquids. The change of phases from solid to liquid depends on the type of chain arrangement in the polymer. If the chains are arranged randomly (i.e. amorphous polymers) then at a definite temperature, the sample will become elastic, it is known as glass transition temperature (T_g). The glass transition temperature is a crucial parameter which indicates the different molecular chains movement of the polymers below and above this temperature.

There are many ways to examine the glass transition of polymers. Over the years, thermal analytical techniques are widely used because they are powerful, high versatile tools for conducting researches in the fields of thermoplastics, thermoset and elastomer processing. In this study, some of these thermal analytical techniques will be applied to determine the glass transition temperature as well as the specific heat capacity of the PET.

Chapter 3

3.3.2.1 Differential Scanning Calorimetry (DSC)

Calorimetry is a technique for determining the quantity of heat that is either absorbed or dissipated by a substance undergoing a physical or chemical change. Such a change alters the internal energy of the substance. At constant temperature, the internal energy is known as enthalpy (*H*). For practical applications, the most interested part is the change of enthalpy ΔH between two states:

$$\Delta H = \int c_p dT \tag{3.1}$$

Processes that increase enthalpy such as melting, evaporation or glass transition are categorized as endothermic while those that lower it crystallization, progressive curing, decomposition are called exothermic.

The specific heat (c_p) is the quantity of energy needed to raise the temperature of 1 gram of material by 1°C at constant pressure. Differential Scanning Calorimetry (DSC) measures the difference of heat flow (ΔQ) between the sample and a reference at certain temperature range. Since ΔQ is directly proportional to the specific heat capacity,

$$c_p = \frac{\Delta Q}{m\Delta T} \tag{3.2}$$

where *m* is the mass of the sample and is ΔT the change of temperature. Therefore, a thermogram which is a plot of specific heat and the temperature is obtained. The glass transition (T_g) of amorphous domains of semicrystalline thermoplastics marks the

change from a glassy state to a rubbery state. The mobility of the chain segments is greater above T_g than it is below it. Because a new form of thermal mobility occurs at the T_g , a step-like change can be observed in the thermogram of c_p . By convention, T_g is the temperature at the half of the change in the thermogram. In our experiment, the heat flow of the samples against temperature was recorded by a differential scanning calorimeter (DSC, Perkin-Elmer DSC-7). 16.08 mg of sample was heated in a nitrogen filled environment, from 30°C to 250°C at a heating rate of 10°C/min. To remove the thermal history of the samples which may cause unwanted results in the measurement, only the testing data of second run will be used. Hence the glass transition temperature (T_g) of the sample was determined.

In Figure 3.3, two significant peaks are observed in the heating and cooling curves. For heating cycle, a peak at about 250°C is found; the temperature of the peak is referred to the melting temperature of the PET sample. The T_g of PET can also be estimated by finding the gradient of a step-like change in the heating cycle, from the curve, it locates at about 80°C. The peak found in the cooling cycle at about 240°C is the crystallization peak.



Figure 3.3 DSC thermogram of the heating and cooling cycle of untreated PET.

3.3.2.2 Dynamic Mechanical Analyzer (DMA)

Dynamic Mechanical Analysis yields information about the mechanical properties of a specimen placed in small sinusoidal oscillation as a function of time and temperature by subjecting it to a small sinusoidal oscillating force. The applied mechanical load elicits a corresponding strain (deformation), whose amplitude and phase shift can be determined. When the temperature is elevated towards T_g and further higher, these mechanical properties will exhibit differently, and significant changes can be observed in the thermogram. By convention, T_g is the mid-point of the largest slope of the change in the thermogram.

In our experiment, the Dynamic Mechanical Analyser (DMA, Perkin Elmer Diamond DMA Lab System) in tensile mode was applied to observe the change of mechanical properties and thus the T_g was determined. The PET film in 8 x 10 mm² with 110 µm thickness was clamped on the sample holder as shown in Figure 3.4. The sample was then heated in a nitrogen filled environment, from 30°C to 150°C at a heating rate of 5°C/min under 0.1 Hz sinusoidal oscillating force , the applied force was automatically controlled by the force motor which is not higher than 3500 mN. The mechanical properties like loss modulus (*E*") and storage modulus (*E*') were determined, and hence their ratio, the loss factor (*tan D*) was also investigated and shown in Figure 3.5.

From Figure 3.5, the T_g is estimated at about 89.8 °C, which is slightly higher than that of DSC. This small difference may due to the different heating rates of experiment and the different calibration condition of machines.



Figure 3.4 Schematic diagram of DMA under vertical load with tensile mode



Figure 3.5 DMA thermogram of the PET film under vertical load with tensile mode

3.3.3 Infrared absorption spectra of PET

Infrared spectroscopy is one of the common techniques to study the structure of a polymeric material, because it can be applied to identify the presence of functional groups in the polymer molecules.

In our study, the infrared absorption spectra of PET samples were obtained by the Fourier Transform Infra-Red spectrometer (FTIR, Nicolet, Magna-IR 760). Diffuse reflectance mode as shown in Figure 3.6 was applied in the range of wavelengths from 25 to 2.5 μ m (400 to 4000 cm⁻¹ in wave-number) in the measurement. The infrared absorption spectra of the laser irradiated samples were compared with the untreated samples.



Figure 3.6 Schematic diagram to show FTIR in diffuse reflectance mode.

Figures 3.7 and 3.8 show the FTIR absorption spectra of an untreated PET film and a laser irradiated PET film for 18 pulses, respectively. Significant peaks are observed in both spectra at about 3000 cm⁻¹ which is related to the methyl C-H group (2970 cm⁻¹)

and a small dip at about 3100 cm⁻¹ which is related to the aromatic C-H stretching.

Also, peaks are observed at about 1750 cm⁻¹ and 1300 cm⁻¹ which are related to the ester C=O stretching and C-O stretching respectively. The peaks in the range 1300 cm⁻¹ to 750 cm⁻¹ are related to the vibrational motion of the methylene C-H in the polymer.

From the results, the absorption bands of the laser irradiated PET film are more or less the same as the untreated sample and it seems that the laser irradiation did not alter the major chemical structures of the PET samples.



Figure 3.7 FTIR spectrum of untreated PET film.



Figure 3.8 FTIR spectrum of laser irradiated PET film.

3.3.4 Dielectric properties

Relative permittivity (ε_r) or dielectric constant of a polymeric material can be determined by measuring the ratio of the total charge stored on the electrode slab of the dielectric subjected to a given voltage and the charge that would be accumulated by identical electrodes separated by a vacuum at the same voltage. The relative permittivity of a dielectric can be expressed as below

$$\varepsilon_r = \frac{Cd}{\varepsilon_o A} \tag{3.6}$$

where *C* is the capacitance of parallel plate electrodes with sample, *d* is the distance between electrodes, ε_o is the dielectric permittivity of vacuum which is equal to 8.85×10^{-12} F/m and *A* is the area of the electrode.

For ac measurement, the complex frequency-dependent relative permittivity $\varepsilon_r(\omega)$ of the dielectric can be expressed as

$$\varepsilon_r(\omega) = \varepsilon'(\omega) - j\varepsilon''(\omega) \tag{3.7}$$

where $\varepsilon'(\omega)$ is the real part of the relative permittivity while $\varepsilon''(\omega)$ is the imaginary part. The dielectric loss (ε'') is related to the dissipation factor $tan\delta$ by $\varepsilon'' = \varepsilon' \tan \delta$. Measurement of the temperature dependence of the dielectric permittivity is also crucial. The dielectric permittivity can be calculated by Equation 3.6 after the capacitance and dimensions of the sample are measured.

If a polymer contains polar side groups whose moments do not cancel out, the actual value of the dielectric constant depends very strongly on these molecular arrangements, which in turn may depend on the dipoles, because strong repulsion between parallel dipoles will cause the conformation change so that the dipoles are not parallel. In practice, when the electric field is applied, the angles between the dipoles within those polar side groups can rotate independently. These angles and sections of chain that can rotate independently are temperature and frequency dependent, particularly in the region of the glass transition. In our experiment, the temperature depending dielectric properties of the untreated PET and laser irradiated PET were observed for the effect of laser irradiation on PET surface.

In the experiment the sample was placed into the temperature controlled chamber which was connected to a temperature controller. The temperature range of the dielectric measurement was taken from 25°C to 160°C, at a heating rate of 3 ~ 4°C/min. The capacitance and the loss factor were measured simultaneously from 100 Hz to 1 MHz with intervals 100 Hz, 1 kHz, 10 kHz, 100 kHz and 1MHz by an impedance analyzer (HP 4194A). The temperature scan and data acquisition were computerized and coped with a PC. Gold layers were sputtered on both side of the sample with the same overlapping area to improve the contact of sample surfaces and measuring electrodes.

The relation of temperature and relative permittivity of untreated PET upon heating is shown in Figure 3.9. The frequency spectra show the response with logarithm scale from 100 Hz to 100 kHz in 4 intervals. It is found that higher relative permittivity can be observed from lower frequency spectra, for the 100 Hz spectrum, the ε_r at room temperature (25°C) is about 3.42 and decreases to 3.28 when the frequency is 100 kHz. After the temperature reaches 80°C, the ε_r significantly increases in all frequency ranges until 140°C, and it reaches 3.75 at 160°C for 1 kHz.

In Figure 3.10, the temperature dependence frequency spectra of the laser irradiated PET are shown. Similar to untreated PET film, it is found that higher relative permittivity can be investigated from the lower frequency spectrum. For instance, ε_r at room temperature (25°C) is about 3.41 at 100 Hz where it is 3.25 at 100 kHz. After 80°C, the ε_r significantly increases in all frequency ranges until 140°C, and it reaches 3.80 at 160°C for 1 kHz spectrum. Comparing the results of untreated and laser irradiated PET, the dielectric properties of these two samples are more or less the same and the laser irradiation seems not alter the properties of PET.



Figure 3.9 Temperature dependence of (a) loss tangent and (b) the relative permittivity of the untreated PET.



Figure 3.10 Temperature dependence of (a) loss tangent and (b) the relative permittivity of the laser irradiated PET.

3.3.5 X-ray Analysis

3.3.5.1 X-ray Diffraction (XRD)

Generally, the crystallinity of a polymer will greatly affect its physical properties. In this study, the crystalline structure of the untreated and laser irradiated PET were investigated by the wide angle X-ray diffraction (XRD, Philips X'pert) method.

Practically, the observed X-ray reflection from polymeric materials is due to the diffraction from both the crystalline regions as well as the amorphous regions. Sharp and well-defined diffraction peaks are attributed to the crystalline phase while the broad canopy is the contribution from the amorphous phase. The degree of crystallinity (χ) of a semi-crystalline polymer can be determined from the ratio of diffraction intensity (integrated over θ) of the crystalline phase to the total diffraction intensity (integrated over θ) as shown below

$$\chi = \frac{\int I_c(\theta) d\theta}{\int I_c(\theta) d\theta + \int I_a(\theta) d\theta}$$
(3.8)

where $I_c(\theta)$ and $I_a(\theta)$ are the diffraction intensity of the crystal phase and amorphous phase respectively.

The crystallinity of untreated and laser irradiated PET films were determined by this method. Since the crystalline diffraction peak and amorphous canopy appeared at

similar diffraction angles, we assumed the diffraction peaks followed Gaussian distribution, and then a de-convolution was conducted to resolve the overlapping diffraction peaks into two individual profiles. Eventually, the degree of crystallinity of the sample can be estimated from the Equation 3.8.

X-ray diffraction profiles of the untreated PET film and the PET film irradiated for 18 pulses are shown in Figure 3.11 and 3.12 respectively for the θ -2 θ scan from 2 θ = 10 to 50°. In each figure, there are two dotted-lines, which represent the de-convoluted Gaussian peaks for amorphous and crystalline phases. For the untreated PET film, the crystalline peak is observed at 2 θ = 26.1° in Figure 3.11, and the estimated corresponding crystallinity (χ) of the sample is 0.575. In contrast, the laser irradiated PET film shows a crystalline peak at 2 θ = 26.0° in Figure 3.12 and χ is 0.571. From these results, the laser irradiation on PET films does not alter the crystallinity of the whole film.

PET film with	Amorphous Peak	Crystalline Peak	Crystallinity (χ)
No laser treatment	$2\theta = 25.4^{\circ}$	$2\theta = 26.1^{\circ}$	0.575
Laser irradiated for 18 pulses	$2\theta = 25.4^{\circ}$	$2\theta = 26.0^{\circ}$	0.571

Table 3.1Summary of XRD peaks position on PET films with different treatment.



Figure 3.11 X-ray diffraction profile of untreated PET film.



Figure 3.12 X-ray diffraction profile of laser irradiated PET film for 18 pulses.
Chapter 3

3.3.5.2 X-ray Photoelectron Spectroscopy (XPS)

For nearly four decades of development, X-ray photoelectron spectroscopy (XPS) has become a powerful tool to probe the interactions of photons with atoms or molecules in solids, starting with the work of Siegbahn et al. [Agarwal, 1991]. XPS, which is also known as electron spectroscopy for chemical analysis (ESCA), is probably the most commonly used surface analysis technique.

For an electrically conductive solid, the binding energy of the core level electron (E_b) can be estimated by using the following equation:

$$E_{h} = hv - E_{k} - \phi \tag{3.9}$$

where *hv* is the x-ray photon energy, E_k and ϕ are the kinetic energy of the photoelectron and work function of the spectrometer respectively. The photon energy is known from the x-ray source employed (the two most common sources: 1486.6 eV for Al K_a and 1253.6 eV for Mg K_a), the work function of the spectrometer is about 4 ~ 5 eV and the kinetic energy can be measured by the XPS spectrometer. For insulating materials like polymers, however, surface charging has to be taken into account and the equation shown before have to be rewritten as:

$$E_b = h\nu - E_k - \phi - C \tag{3.10}$$

where C is charge constant which is unknown and varies from sample to sample.

Chapter 3

Therefore, for insulating materials the electron binding energy is usually investigated by using an internal reference peak. For instance, at 285.0 eV, the C1s peak of aliphatic carbon is often used as the internal reference for polymers.

Elements have unique electron binding energies. Therefore, examining the electron binding energy allows the identification of various elements. XPS is thus able to detect all elements except hydrogen. Furthermore, the electron binding energy is also sensitive to the electronic environment of the atom. When an atom is bonded to another atom of an element having a different electro-negativity, the electron binding energy may increase or decrease. This change in binding energy is called the chemical shift, which can be used to provide chemical information of a molecule or compound. Moreover, the XPS peak intensities after normalized by the sensitivity factors can be used to calculate the surface chemical composition by using the following equation:

$$C_{i} = \frac{\frac{I_{i}}{S_{i}}}{\sum_{i}^{m} \frac{I_{i}}{S_{i}}}$$
(3.11)

where C_i is the concentration of an element *i*, *m* is the number of elements in the sample, I_i and S_i are the peak area and the sensitivity factor of the element *i*, respectively.

In this study, XPS (Physical Electronic, multi-technique system PHI5600) was used to investigate the surface chemical composition of the untreated and laser irradiated PET films. The oxygen-carbon (O-C) ratio of sample surface was focussed to compare the change of chemical composition before and after laser irradiation.

Chapter 4

Electret Effect of Laser Irradiated PET Films

In the previous chapter, some general properties of bulk and laser irradiated PET films like IR absorption and dielectric properties have been focused. In this chapter, the differences between the bulk and laser treated PET was compared and the electret effect of this novel type material was discussed.

Charge distribution, transport, charge injection and thermally stimulated charge characteristics of most common polymeric electrets have been examined for more than half a century. Different properties of single layer polymer like PP, PET, PMMA and Teflon have been investigated by many researchers. In recent years, the focus has been targeted on the cellular or porous polymer materials such as porous PTFE and cellular PP because of their higher charge capability. Nevertheless, these types of materials are complicated to produce in industrial manufacturing. In the present study, an alternative method is introduced to achieve the similar effect.

PET films of 110 μ m thick were cut into 19 x 19 mm². They were irradiated by laser irradiation with different number of laser shots, and the surface morphology of polymer was altered. Both untreated and laser irradiated PET films were then electrified by corona discharging at room temperature under -5kV, and the surface potential of these samples were determined by electrostatic sensor as introduced in Chapter 2.

4.1 Microstructure Analysis

In the recent years, new type of polymer electrets such as porous or cellular polymer has been well developed. In this project, a new surface structure has been introduced in lieu of the complicated manufacturing of porous materials. In this section, the surface morphology of the laser irradiated PET investigated by different methods were described.

4.1.1 Optical Microscopy

From the optical microscope, the brief surface morphology of the laser irradiated PET films can be observed under a magnification of 400 times. In Figure 4.1, a shallow ripple pattern is founded on the PET film which has been irradiated for 5 shots. After the sample has been irradiated for 10 or more shots, these ripple patterns become more closely packed and some of the strips have been broken into short fragments (Figure 4.2 & 4.3), this phenomenon will be discussed in the following section. When the sample has been irradiated for 17 shots, a matrix of white spots is observed on the polymer surface, which is broken from the short fragments after excess laser pulses (Figure 4.4). As shown in Figure 4.5 and 4.6, when the PET films have been ablated for 20 and 30 times respectively, the white spots in the laser affect zone develop into bigger white stains and finally dark islands. Moreover, the background of the irradiated area becomes darker when the sample has been irradiated for higher number of pulses. It is because the PET surface has been altered and the surface roughness increases, light is scattered on the rough surface and result into this phenomenon.



Figure 4.1 PET film irradiated by 5 shots.



Figure 4.2 PET film irradiated by 10 shots.



Figure 4.3 PET film irradiated by 15 shots.



Figure 4.4 PET film irradiated by 17 shots.



Figure 4.5 PET film irradiated by 20 shots.



Figure 4.6 PET film irradiated by 30 shots.

In Table 4.1, the change of roughness of the laser irradiated PET samples with respect to the number of laser pulses was tabulated.

Number of laser pulses	0	2	5	10	20	40	80
The surface roughness	105.9	227.2	425.6	495.0	1423.3	2869.4	3280.3

Table 4.1Summary of the surface roughness of laser irradiated PET samples.

On the other hand, the polarizing microscope is applied to study the molecular change of the PET films after laser irradiation. Since the polarizer and the analyzer of the microscope are perpendicular to each other, if the molecules in the sample are aligned in one direction and it is parallel to the polarizer or analyzer, light will be blocked by them and therefore, the dark background will be observed. For the PET film irradiated for 3 shots as shown in Figure 4.7, a few white spots in the dark background are observed. When the UV laser is irradiated on the PET surface, part of the laser energy will ablate the molecules on the film surface out; however, some of the laser energy will only heat up the film surface, the heat energy will release the stress induced in the molecules and alter the orientation by randomizing these molecules, therefore, part of the light can pass through these randomized area by elliptical polarization and gives white spots in the microscope images. In Figure 4.8, when the PET film is irradiated for 4 times, the number of white spots increases because more area is affected by the laser. After 6 pulses, nearly the whole surface area is affected by the laser and white spots can be seen in the whole area (Figure 4.9). When the film is irradiated for 15 pulses and even more to 30 pulses, the white spots nearly cover the whole area (Figure 4.10 & 4.11).



Figure 4.7 Polarized microscope photo of PET film irradiated for 3 shots.



Figure 4.8 Polarized microscope photo of PET film irradiated for 4 shots.



Figure 4.9 Polarized microscope photo of PET film irradiated for 6 shots.



Figure 4.10 Polarized microscope photo of PET film irradiated for 15 shots.



Figure 4.11 Polarized microscope photo of PET film irradiated for 30 shots.

4.1.2 Scanning Electron Microscopy (SEM)

Although from the polarizing microscope, some interesting features of PET film surface after laser treatment has been revealed, the detailed surface morphology of the samples has to be investigated by the scanning electron microscope with the advantage of higher resolution than the optical microscope.

In general, the laser irradiated PET samples showed a smeared pattern at the ablated area, although in the first few pulses of irradiation, the surface of the film is not altered considerably. As shown in Figure 4.12, it has no pattern formation when PET samples were irradiated for only a very few pulses. When the PET sample was irradiated for 5 pulses, as shown in Figure 4.13, a shallow pattern with peaks-and-troughs began to occur, and it also consisted of some long thin structures.

In Figure 4.14, when the PET sample had been irradiated for 10 shots, the peaks-and-troughs pattern became more significant. For the PET samples irradiated for almost 15 pulses, rod-like structures are observed as shown in Figure 4.15, which are broken from the long thin structures found in samples irradiated with less pulses. Obviously, increasing the number of pulses produces a finer ripple structure.



Figure 4.12 SEM pictures of PET surface treated with the laser at 248 nm: (a) 1 pulse and (b) 2 pulses.



Figure 4.13 SEM pictures of PET surface irradiated for 5 pulses: (a) rod-like periodic structure observed and (b) circular pattern found.



Figure 4.14 SEM pictures of PET surface irradiated for 10 pulses: (a) the overall view and (b) higher magnification.



Figure 4.15 SEM pictures of PET surface irradiated for 15 pulses: (a) the overall view and (b) higher magnification.

Figure 4.16 is a schematic diagram to show the cross-section of an ablated surface. The ablated film surface comprises of three layers, i.e. the ablation layer, the fusion layer and the heat-affected layer. The inner depth of the film is not affected by the laser. The ablation layer is the part removed by the laser from the surface. The temperature at the fusion layer immediately below the ablation layer would be raised above the melting point of the PET film (about 300°C) because of the absorption of laser energy and the PET melts instantaneously. As it solidifies, shrinkage takes place, and the mode of stabilisation is different at each point depending on the molecular orientation and thermal properties of the materials. The peaks-and-troughs structure on the PET ablated area is produced by this difference.



Figure 4.16 Model structure for surface modified PET films by the irradiation of pulsed UV excimer laser.

Figures 4.17 to 4.20 show the features obtained by 17 & 18 pulses of irradiation. In Figure 4.17 and 4.18, when the sample was irradiated for 17 shots, the fine ripple structure is still observed, but some of the ripple tips become narrower and fused

together with the neighboring tips. A layer of polymer material is formed on the fused ripple tips. In Figure 4.19, similar morphology is observed on the PET film surface irradiated by 18 shots, but in Figure 4.20, some of the ripple tips were cut down by the excess number of laser pulses. This phenomenon can be explained in the following model.

A further irradiation for 20 pulses and more, the ripple pattern is probably destroyed by the excess laser energy. The tips of the structure are cut down and an island-like pattern is formed. The surface of the ablated area becomes relatively flatten compared with the sample of 15 pulses. This feature can be clearly seen in Figures 4.21 and 4.22, and in Figure 4.23 and 4.24, the tips were totally cut down and only an uneven surface can be found after the PET film being irradiated for 40 and 80 pulses, respectively.



Figure 4.17 SEM pictures of PET irradiated for 17 pulses: (a) an overall view and (b) a higher magnification view.



Figure 4.18 SEM pictures of PET irradiated for 17 pulses at side view.



Figure 4.19 SEM pictures of PET irradiated for 18 pulses: (a) an overall view and (b) a higher magnification view.



Figure 4.20 SEM pictures of PET irradiated for 18 pulses: (a) side view and (b) a close view on a tip-cut ripple.



Figure 4.21 SEM pictures of PET surface irradiated for 20 pulses: (a) an overall view and (b) a higher magnification.



Figure 4.22 SEM pictures of PET irradiated for 20 pulses: (a) a higher magnification view on the cut ripple tip (b).at side view.



Figure 4.23 SEM pictures of PET surface irradiated for 40 pulses: (a) an overall view and (b) a higher magnification view on the cut ripple tip.



Figure 4.24 SEM pictures of PET surface irradiated for 80 pulses: (a) an overall view and (b) a higher magnification view on the cut ripple tip.

4.2 Surface Potential Measurement of Laser Irradiated PET Films

In order to study the effect of laser irradiation on the electret property of PET, surface potentials of three series of the laser irradiated films were measured and averaged after electrified by the corona discharge method. From Figure 4.25, it can be seen that, the surface potentials of untreated films, i.e. samples of zero number of pulse, is recorded at about -1.2 kV. The surface potentials increase slightly with the number of pulses.

However, for samples irradiated for more than 15 pulses, a significant increase in surface potential is observed. It soars to nearly -1.5 kV at 18 pulses. Then the surface potentials drop dramatically to around -1.1 kV of samples shot for more than 20 times. It is most likely that the surface potential variations are correlated to the ripple pattern obtained by laser ablation as shown in the previous part (Section 4.1). We have noted earlier that at about 15 pulses, a layer of melted ripple tips are formed at the laser irradiated region, some of them will even fused together. The surface potentials of these samples are significantly higher than that of other samples. This higher surface potential can be attributed to the formation of this layer.

Nevertheless, when the PET samples were ablated for 20 pulses or more, the ripple tips have been cut down and the film surface becomes flattened. It is not surprising that the charge storage property of these samples become worse. The surface potentials of these samples are even lower than those untreated PET films. It may be due to the carburization of the surface of the PET after such high dosage of laser treatment.



Figure 4.25 The measured surface potentials of laser irradiated PET films plotted against the number of laser pulses.

On the other hand, a counter experiment was conducted to examine the effectiveness for charge storages of the laser irradiated area. Samples irradiated for 17 to 19 pulses which exhibit higher surface potentials were placed in an ultrasonic bath with ethanol for 15 minutes. Then the samples were dried in air and electrified again by corona discharging. The measured surface potentials of these samples are more or less the same as the untreated PET samples. The surface morphology of the samples was inspected by SEM and is shown in Figure 4.26. It is obvious that after ultrasonic treatment, the tips of the ripple patterns on the laser irradiated PET films were destroyed and only some debris remained. It can be an evidence to verify that the higher surface potential of the laser treated films is due to formation of such ripple pattern with tips at the polymer surface. It also explains those films of more than 20 laser pulses which exhibit surface morphology similar to Figure 4.26 have lower surface potentials.

In the case porous materials like porous PTFE, a high density of micro-cavities in micron scale are contained. After electrification, charges accumulated in the pores which generate macroscopic polarization [Montanari, 2003]. Compare to the laser irradiated surface, once the ripple tips melt and fused together, voids are formed at the surface layer of the polymer. These voids resemble the pores in porous material and thus the irradiated sample can exhibit a higher surface potential.



Figure 4.26 Laser irradiated PET film surface after ultrasonic treatment in an ethanol bath: (a) top view and (b) side view.

4.3 Chemical Properties of Laser Irradiated PET Films

Besides the surface morphology and enhancement of surface potential, the chemical properties of laser irradiated PET films were also focussed. By XPS, the content of carbon (C1s) and oxygen (O1s) atoms on the PET surface after irradiated by 248 nm UV excimer laser was analyzed. C1s and O1s scanning spectra were achieved and analyzed by investigating each of peak size, intensity and position. For the C1s spectra, the peak at 284.70 eV is normalized before comparisons. Under each spectrum, either for carbon or oxygen, several peaks can be resolved by curve fitting into a sum of single-core peaks. Each peak core represents a particular chemical bond, for PET, C1s at 284.70 eV for aromatic carbon (<u>C</u>-C), 286.24 eV is for single oxygen (<u>C</u>-O-C), 288.66 eV for carboxylic carbon (<u>C</u>=O); O1s at 532.30 eV for π -bonded oxygen (C=<u>O</u>), 533.90 eV is for σ -bonded oxygen (C-<u>O</u>-C).

The changes of carbon and oxygen peak shapes due to different number of laser pulses are shown in Figures 4.27 to 4.32. For the C1s spectra, the peak intensity at 286.24 eV (<u>C</u>-O-C) decreases gradually from about 3000 to 2000 when the PET film is irradiated. Moreover, for O1s spectra, the peak intensity at 532.30 eV (C=<u>O</u>) also decreases slowly from 7000 to 6000 after ablated for 20 pulses, and this peak is fused with the peak at 529.95 eV when the number of laser irradiated pulses increases. This phenomenon indicates deoxidization reaction on the surface of PET [Watanabe et. al, 1997]. Groups such as CO, CO₂ and others may be scattered from the treated surface as a result of laser irradiation. Oxygen content of the laser irradiated zone also reflects a significant decrease after five laser shots. This shows the laser has provided a sufficiently high energy to decompose the bonds between carbon and oxygen. In Table 4.2, the atomic concentration of carbon (C1s) and oxygen (O1s) of laser irradiated PET surfaces with different number of shots is shown. Once the PET surface is irradiated, the oxygen content will decrease where carbon content will increase.

	Atomic Co		
PET film irradiated by laser for	C1s (%)	O1s (%)	C/O ratio
0 pulse	75.30 %	24.70 %	3.05
5 pulses	78.58 %	21.42 %	3.67
10 pulses	79.68 %	20.32 %	3.92
15 pulses	78.09 %	21.91 %	3.56
17 pulses	79.26 %	20.76 %	3.82
20 pulses	78.64 %	21.36 %	3.68

Table 4.2Summary of atomic concentration of laser irradiated PET surface underdifferent conditions determined by XPS.



Figure 4.27 XPS spectra of (a) C1s and (b) O1s of untreated PET surface.



Figure 4.28 XPS spectra of (a) C1s and (b) O1s of untreated PET surface after irradiated for 5 pulses.



Figure 4.29 XPS spectra of (a) C1s and (b) O1s of untreated PET surface after irradiated for 10 pulses.



Figure 4.30 XPS spectra of (a) C1s and (b) O1s of untreated PET surface after irradiated for 15 pulses.


Figure 4.31 XPS spectra of (a) C1s and (b) O1s of untreated PET surface after irradiated for 17 pulses.



Figure 4.32 XPS spectra of (a) C1s and (b) O1s of untreated PET surface after irradiated for 20 pulses.

Chapter 5

Charge Retention Capability of PET Films

Being a good electret, PET performs good charge retention to maintain its surface charges for a very long time. The charge stability of PET is already being studied in different ways by many scientists and research groups [Sessler, 1997; West et. al, 1989]. In our study, the charge retention of PET with different thickness and laser irradiation treatment was investigated.

5.1 Charge Retention of PET Films with Different Thickness

In order to study the relationship between charge retention and sample thickness, PET films in 19 x 19 mm² with three different thickness: 13 μ m, 50 μ m and 110 μ m were examined. Samples were electrified by negative corona discharge at different charging voltage varying from -5 kV to -9 kV at room temperature. The surface potentials of these films were then measured and kept in a dessicator. The surface potential measurements were carried out for about 42 days (15 days only for 13 μ m thick films) after the corona charging.

Figure 5.1 shows the surface potential decay of 110 μ m thick PET films. The surface potential of charged PET film is proportional to the charging voltage; the higher corona voltage gives a higher surface potential. In the first few hours, the surface potentials of all samples are more or less unchanged. However, the sample charged at -9 kV then

decayed more quickly than the others. The decay rate changed again after 30 hours, and the surface potentials of all samples converged to about the same value. Finally, the decay approached the same rate for all samples after 300 hours. An extrapolation of the decay curve to 3000 hours after the initial charges, all samples would remain a surface potential of about -500 V whatever are their initial surface potential.

The surface potential decay of 50 μ m PET samples is shown in Figure 5.2. In the comparison with the 110 μ m samples, the surface potentials of these films converge to the same value at a shorter time. About 40 hours after the initial charging at different corona voltages, the surface potentials of all samples approached a value about -1.4 kV. Following that time was a further decay but keeping at the same rate. Similar to the thicker samples, these samples will have a same surface potential whatever are their initial values. An estimation from the extrapolation of the decay curves, it is expected that the remaining surface potential would be about -200 V at 3000 hours after the initial charging.

Unlike the thicker films of different initial surface potentials after charging, 13 μ m PET samples can only produce a very close surface potential which was around -900 V for different corona discharge voltages. The surface potential of all samples decreased rapidly after corona charging as shown in Figure 5.3. Ten hours after the charging, the surface potentials of samples decayed to half of the initial level, and the samples can only remain about -100 V after 120 hours (5 days). Similar to the thick PET samples, the 13 μ m film charged at the highest voltage, i.e. -9 kV gave the lowest surface potential during the course of the decay process. In addition, the decay curves seem

levelling off after 100 hours. It suggests that the surface potential of these samples will keep at about -90 V for quite a long time.

In this series of experiment, several phenomena are interesting to discuss. By comparing these three sets of data, the surface potentials of PET films charged at different corona voltages will approach the same level after decaying to half of their initial values. The time to achieve this half-life depends on the thickness of the film, for 110 μ m film, it takes more than 200 hours to reach that point, for 50 μ m film, it needs several tens of hours while the 13 μ m film takes only few hours.

Moreover, it is probable that the highest surface potential for PET films can be obtained by an optimized corona voltage. Since in the decay profile of 13 μ m and 50 μ m films, though the samples are charged under the higher corona voltage at -9 kV, the surface potential of these samples are dramatically lower than that charged at lower voltage.



Figure 5.1 Surface potential decay of 110 µm thick PET films charged at different corona voltages.



Figure 5.2 Surface potential decay of 50 µm thick PET films charged at different corona voltages.



Figure 5.3 Surface potential decay of 13 µm thick PET films charged at different corona voltages.

5.2 Charge Retention of Laser Irradiated PET Films

Besides the study of the thickness dependence of untreated samples, the charge retention of laser irradiated PET films were investigated. A series of laser irradiated samples were electrified by corona discharging at -5 kV at room temperature and their surface potentials were measured. Then the PET films were stored in a dessicator for a period of time. After 63 days, the surface potentials of the samples were measured again.

In Figure 5.4, we can see that the surface potentials of the laser irradiated PET films are somewhere between -1.75 kV to -1.95 kV, and the PET films shot for 18 to 20 pulses show a higher surface potential than that of other samples. After 60 days, the surface potentials of PET films drop to around -550 V to -750 V, which is one-third of the initial values.

One crucial point is that the surface potentials of samples irradiated for 18 to 20 pulses is outstanding in the whole series, not only for the freshly charged films, but the decayed samples show the same phenomenon. For freshly charged films, the enhancement of surface potential shown by the samples is about 10 %, but after a long decay period, the irradiated samples show a better charge retention than that of untreated samples. The potential of irradiated samples in the range of 18 to 20 pulses is 35 % higher than the other films.



Figure 5.4 Surface potential decay of laser irradiated PET films in 110 µm thick shot for different number of pulses: (a) after 1 hour, (b) after 63 days.

When the experiment was repeated with 50 μ m thick PET films, the significant improvement of surface potentials are observed in Figure 5.5. The surface potential of PET film irradiated for 14 pulses is 12 % higher than that of untreated one. From the SEM picture as shown in Figure 5.6, the surface morphology of the PET film irradiated for 14 shots is similar to that of the 110 μ m thick samples, which also exhibit the same enhancement of surface potential. Nevertheless, the surface potentials of the whole series of samples decay to more or less the same level after 50 days of the initial charging.

From the previous section, we know that the thickness of samples will perform different charge retention capabilities, the thicker PET samples can provide a better charge retention capabilities. It is no doubt that the new surface morphology obtained by laser irradiation can provide the improvement of charge retention capabilities, however, the thickness of samples may also be a crucial factor to alter the charge retention capabilities of the samples.



Figure 5.5 Surface potential decay of laser irradiated PET films in 50 µm thick shot for different number of pulses: (a) after 1 hour, (b) after 63 days.



Figure 5.6 SEM photo of 50 µm thick PET film irradiated for 14 pulses.



106

Chapter 6

TSDC Measurement on PET Samples

Other than the surface potential measurements, the TSDC method is another practical technique to demonstrate electret characteristics. In an electret, dipolar polarization, homocharges and heterocharges may coexist in the same sample [Hilczer & Małecki, 1986]. The TSDC technique can be employed to study the storage mechanisms of these charges or polarization. In this chapter, the untreated and laser irradiated PET samples will be examined and their results will be discussed.

6.1 Open Circuit TSDC with PTFE Film Spacer

In our experiment, open circuit TSDC with a PTFE spacer was applied instead of using an air gap to examine the polarization and stored charges in the PET sample. This method is a modification of the ordinary open circuit TSDC. A bulk dielectric spacer with low relative permittivity, e.g. PTFE is inserted to fill the air gap. The reason of this modification is explained in the following.

The minimum corona voltage to produce a corona discharge by a point-to-plane asymmetric configuration is -3 kV. However, this corona voltage was not sufficient to charge up a polymer electret efficiently in our experiment. To achieve a better charging condition, -5 kV was applied to produce the corona in this study.

From the equations shown in Chapter 2, by rewrite the Equations 2.3 and 2.4, we have:

$$E_2 = -\frac{E_1 d_1}{d_2} = \frac{\varepsilon_1 E_1 - \sigma_s}{\varepsilon_d}$$
(6.1)

Therefore,

$$\frac{E_1 d_1}{d_2} = \frac{\sigma_s - \varepsilon_1 E_1}{\varepsilon_d} = \frac{\sigma_s}{\varepsilon_d} - E_1 \frac{\varepsilon_1}{\varepsilon_d}$$
(6.2)

and

$$E_1 = \frac{\sigma_s}{\varepsilon_d} \left/ \left(\frac{d_1}{d_2} + \frac{\varepsilon_1}{\varepsilon_d} \right) \right.$$
(6.3)

By substitute Equation 2.7 into Equation 6.3,

$$E_1 = \frac{V_s}{d_2} \left/ \left(\frac{d_1}{d_2} + \frac{\varepsilon_1}{\varepsilon_d} \right) \right.$$
(6.4)

If the surface potential of a 110 μ m thick untreated PET film (V_s) charged at -5 kV is -1.9 kV, with an air gap (d_1) of 110 μ m and the relative permittivity of PET (ε_d) is 3.4, the electric field strength in the air gap (E_1) estimated is about 13.3 MV/m.

On the other hand, the air-breakdown field between two metal plates at a separation of $200 \ \mu m$ is about 2.7 MV/m, which is much smaller than that of the sample. In the TSDC measurement, during heating up the sample, the current measured will be momentarily by the air-breakdown which eventually affects the accuracy of current induced from the sample as shown in Figure 6.1 and 6.2 respectively.

In the present study, a 100 μ m thick PTFE film was inserted between the sample surface and the upper electrode of the TSDC set-up. The current in pico-ampere range was then measured by an electrometer (Keithley, 6517A). PTFE is a good insulator and it has extremely high resistivity in the order of 10¹⁸ Ω-m. Besides the prevention of air-breakdown, the induced current is also amplified by this film, and those weak TSDC peaks can be easier to observe.



Figure 6.1 TSDC thermogram of PET film charged at -5 kV in close-circuit mode.



Figure 6.2 TSDC thermogram of PET film charged at -5 kV in open-circuit mode with an air gap.

6.2 TSDC Investigation on Laser Irradiated PET Films

TSDC is one of the common used thermal methods to characterize the dipolar polarization and free charge relaxation effect after the sample is thermally charged or polarized. The untreated and laser irradiated PET films were electrified by corona discharge at -5 kV and -8 kV at room temperature and 110°C with different combinations for 15 minutes. The electric field was maintained until the samples were cooled down to room temperature in furnace. The air gap TSDC with a 100 μ m thick PTFE film spacer was utilized to measure the current response at a heating rate of 1°C/min from 30°C to 165°C.

From Figure 6.3, two current peaks are observed in each curve. For the untreated PET, the peaks are located at about 80°C and 120°C which represent the glass transition temperature and free charge relaxation temperature, respectively. The high temperature current peak supposedly stems from the surface charge on the sample surface and charge injected during corona discharging. Laser irradiated PET shows a similar characteristic but the high temperature peak is appeared earlier at about 112°C. The current peak magnitude of PET samples charged at -8 kV is nearly double those samples charged at -5 kV. The TSDC response of charged PET samples reveals the trapping of free charge in charging. The low temperature current peak of charged polymer indicates the glass transition temperature which matches with the result of DSC and DMA.

In Figure 6.4, the thermogram shows the induced current from PET samples charged at -5 kV and -8 kV at 110°C. Similar to the samples charged at room temperature, a current peak at 120°C and 112°C is observed in the curves of untreated and laser irradiated PET films correspondingly. This peak is related to the free charge relaxation. Moreover, the magnitude of PET samples charged at -5 kV is more or less the same to those charged at room temperature, but for those samples charged at -8 kV under 110°C, the current peak is smaller than that at room temperature. Nevertheless, the low temperature peak at 80°C in all curves is diminished. This phenomenon will be explained with the results of ethanol treated and pre-annealed PET films together in the later section.



Figure 6.3 TSDC thermograms of untreated and laser irradiated PET charged with different corona voltage at room temperature.



Figure 6.4 TSDC thermograms of untreated and laser irradiated PET charged with different corona voltage at 110 °C.

6.3 TSDC Investigation on Ethanol Treated PET Films

During corona discharging, not only the dipole in the PET sample is aligned, but also charges are injected into the sample and accumulated on the surface layer. As a result, the PET samples appear to have a surface potential which reflects the charges stored in the samples. Nevertheless, the freshly charged PET films need a long time to decay to a steady state for studying the polarization of samples. In the present study, the PET samples were immersed into different solvents to neutralize the surface charges in a very short time, then the polarization of samples were investigated by the TSDC.

Untreated PET films were corona charged at room temperature with -5 kV, and the surface potential of these films were measured. The samples were then immersed into three different solvents: acetone, ethanol and de-ionized water for 5 minutes. Since PET is a poor liquid absorption material, the immersion will not induce swelling effect on the samples. After immersion the samples were dried in still air at room temperature, and the surface potential of PET films were recorded again. The summary of these results are tabulated in Table 6.1.

PET Surface potential	Acetone	Ethanol	De-ionized Water
Before treatment	-1.63 kV	-1.60 kV	-1.62 kV
After treatment	0 kV	0 kV	0 kV

Table 6.1Summary of corona charged PET films immersed in different solvents.

Before immersion, the surface potentials of PET films are around -1.62 kV, when the samples are immersed into the solvents, the surface charges are neutralized by these solvents. To prove this phenomenon, the ethanol treated PET film was examined by TSDC to study its polarization and charge properties.

In Figure 6.5, the untreated PET film charged at room temperature under -5 kV shows two significant peaks in the TSDC thermogram. The high temperature peak located at about 120°C is the related to free charge relaxation, where the low temperature peak at 82°C shows the glass transition temperature of the PET film.



Figure 6.5 TSDC thermograms of the uncharged PET films before and after ethanol treatment.

Traditionally, many experiments and scientists reported that the low temperature peak represents the depolarization of dipoles in the polar dielectrics and so called α -peak. However, after the -5 kV charged PET film is being treated by ethanol, the surface potential shows zero; and from Figure 6.5, the TSDC thermogram gives a nearly flatten profile at zero level.

Comparing the two TSDC curves, it is no doubt that ethanol treatment can neutralize the free charges accumulated on the charged PET surface. Also exposed from the thermogram of ethanol treated sample, the two current peaks of untreated PET film at 82°C and 120°C are mainly contributed by the surface charges instead of space charges and disorder of dipoles. At room temperature, corona discharge can only electrify the sample by accumulating excess charges on the surface, because this temperature is so far away from the glass transition temperature [Xia et al., 1992]. From the thermogram, it seems that space charges and polarization are not significant during corona charging. Moreover, the low temperature current peak is a resultant of depolarization of molecules and surface charges of the sample.

Besides the PET films electrified at room temperature, the TSDC thermogram of classical electrets – thermoelectrets was also studied. The two sets of untreated and laser irradiated PET films were annealed for 1 hour, and were corona charged under -5 kV and -8 kV at 110°C for 15 minutes. The electric field was kept throughout the cooling process until it reached room temperature. One set of samples were then immersed into ethanol to neutralize the surface charges on the PET films, and the electrical properties of both sets of samplers were examined by TSDC.

Figure 6.6 shows the TSDC thermogram of bare PET films charged at -5 kV and -8 kV, and the responses before and after ethanol treatment. From the TSDC curves, the higher temperature peak for both untreated and ethanol treated bare PET films charged at -5 kV and -8 kV is located at about 120°C, again this peak represents the charge relaxation of the dielectric, but the magnitude of ethanol treated films are only one-fourth of untreated samples. However, the lower temperature peak at 82°C in all cases is diminished and shift to the negative current side. One interesting point observed is the peak magnitude of ethanol treated samples is double to that of non-treated samples.



Figure 6.6 TSDC thermograms of bare PET films charged at 110°C before and after ethanol treatment.

In Figure 6.7, the TSDC thermogram of laser irradiated PET films shows the different between untreated and ethanol treated samples. Compare to the bare films, the higher temperature peak is shifted from 120°C to about 115°C in all cases, and this peak represents the charge relaxation of the dielectric, the magnitude of ethanol treated films are around one-third to one-fourth of untreated samples. Similar to bare samples, the lower temperature peak at 82°C in all cases is diminished and shift to the negative current side. It is observed that the peak magnitude of ethanol treated samples is more than double than that of non-treated samples.



Figure 6.7 TSDC thermograms of laser irradiated PET films charged at 110°C before and after ethanol treatment.

Under conditions of thermal equilibrium in a dipolar dielectric, the dipole moments of the different molecules or fragments of molecules are randomly oriented and the resultant dipole moment for the entire sample is equal to zero. In the experiment, when samples are annealed at 110°C, which is higher than the glass transition temperature (T_g) of PET at 82°C, transition occurs from the glassy state to highly elastic state. At this temperature high electric field is applied to the PET samples, the polar groups in the bulk may become oriented. Then the samples are cooled in the presence of electric field, the ordering of activated molecular dipoles and electric charges in the bulk are frozen in. Eventually the electric field is switched off and a process of spontaneous depolarization of the electret sets in. Hence, from the TSDC thermograms, we can find that the thermoelectrets prepared in this experiment perform different electric properties compare with charging at room temperature.

At room temperature, the field of real charges during and after corona charging cannot order the dipoles frozen in disordered state in the PET bulk. However, when the temperature is higher than T_g during TSDC after corona charging at room temperature, dipoles become movable and are oriented by the real charge field in the sample, which forms the peak of TSDC spectrum at about 82°C. Therefore, this peak is due to the field of the real charge during TSDC, but not a disorder peak of oriented dipoles which should have existed before TSDC. On the other hand, when the charging temperature is at 110°C, which is higher than T_g of PET, the dipole orientation has achieved during charging. Obviously, the peak at 82 °C becomes diminished during TSDC (Figure 6.6 & 6.7). Since the oriented dipoles are bounded by the field of real charge deposited on the sample, these dipoles are always kept in the sample so long as the field is existed. Thus, by increasing temperature during TSDC, the real charges on the sample are released by thermal excitation and the field decreases gradually, and it results the depolarization of oriented dipoles. Evidently, the current peak of TSDC at about 120°C contains both relaxation of real charges and reorientation of dipoles [Xia et al., 1992].

Moreover, the direction of current peak near the glass transition temperature is different in samples charged at room temperature without ethanol treatment, and electrified under 110° C with ethanol treatment. The direction of this peak can be probably used to study the effect between depolarization of dipoles and charge relaxation on the PET films. Figure 6.8 shows the configuration of sample and TSDC set-up with current direction flow of the electrometer. For those samples charged at room temperature, since charges can only be accumulated on the sample surface, as discussed before, when the temperature is at about T_g during TSDC, dipoles in the bulk are activated by the thermal energy and become movable.



Figure 6.8 Schematic diagram of the current flow of sample in TSDC set-up.

When the dipoles move and align with the field established by the real charge as shown in Figure 6.8, the bottom of the PET bulk becomes more electronegative, to achieve an equilibrium state, more positive charges rush to the bottom electrode of the TSDC set-up. Therefore, the current flow shown on the electrometer is in positive side.

However, in the case of PET films charged at 110°C with ethanol treatment, while the charging temperature is higher than T_g of PET (82°C), the dipole orientation has achieved during charging. Therefore, the oriented dipoles are bounded by the field of real charge deposited on the sample, and these dipoles are always kept in the sample so long as the external field is not existed. Once the sample has been treated by ethanol, nearly most of the surface charges have been neutralized, only a small portion of charges which bounded with the frozen-in dipoles can be sustained. So when the sample is measured by the electrostatic sensor, a zero surface potential is observed. Thus, by increasing temperature during TSDC, the field established by frozen-in dipoles decreases gradually, the bottom of PET bulk becomes less negative and electrons flow from the upper electrode to the bottom electrode of TSDC set-up for equilibrium, it results the depolarization of oriented dipoles and a negative current peak in the TSDC thermogram.

Obviously, the current peak of TSDC at about 120°C in all cases is mainly contributed by relaxation of real charges, positive charges induced on the upper electrode of the set-up increases, and electrons flow to there for equilibrium, therefore a positive current flow is observed.

6.4 TSDC Investigation on PET Films with Pre-annealing Treatment

In the previous section, the differences in charge relaxation and dipole orientation of PET films electrified at different temperature have been illustrated. In this part, PET films will be pre-annealed before charging to release the stresses induced in the samples during manufacturing. Theoretically, the dipole orientation is mainly contributed by the electrical effect during charging or heating. However, in the manufacturing of commercial PET films, stresses may be induced into the polymer bulk by biaxial drawing of thin polymer films. These disordering of dipoles may affect the further charging process in electrification. In this experiment, the pre-annealing temperature is varied to investigate the relation between this temperature and the relaxation of PET films.

The PET films were annealed at temperature varying from 83°C to 130°C for 12 hours. The annealed samples were then cooled down in the furnace until it returned back to room temperature. After annealing, the PET samples were electrified by corona discharging under -5 kV at room temperature, and TSDC measurement was processed.

From Figure 6.9, the TSDC spectrum of untreated PET film shows two significant peaks at 82°C and 119°C, which are related to the polarization established by real charges and the relaxation of free charges, respectively. However, after the PET samples have been pre-annealed higher than 82°C, that is, the glass transition temperature of PET, the lower temperature peak is diminished. Moreover, the position of higher temperature peak at 120°C has been shifted to a higher temperature according to the pre-annealing temperature. The relation between pre-annealing temperature and peak position is tabulated below:

Pre-annealing Temperature (°C)	~ 25	83	96	105	117	130
Peak Position (°C)	119	120	122	123	126	128

Table 6.2Relation between pre-annealing temperature and current peak position

Here, the phenomena on the peaks of TSDC thermograms of PET samples with different charging conditions, ethanol treatment and pre-annealing treatment are discussed together. In the beginning, to manufacture the PET film, it is drawn out from the raw materials and is hot-rolled to make the film in the particular thin dimension. Throughout the manufacturing process, the molecules in the PET film are aligned in the direction of drawing and rolling, and therefore, the film is oriented.

When the PET film is heated up upon the glass transition temperature (T_g) during TSDC, the aligned molecules are reoriented back to its original state due to the thermal activation. On the other hand, the polarized dipoles in the sample are also depolarized.

In the case of PET films with pre-anneal treatment, the untreated sample shows a positive peak at T_g , this peak is due to the polarization of dipoles. When the sample is electrified, the charges accumulated on the film surface. Once the sample is heated up to T_g the dipoles become mobilized and the polarization occurs due to the surface charges. Since the molecular chains in the sample are well aligned that is benefit for dipole

polarization, therefore, the resultant polarization become higher and shows a significant peak. However, when the temperature still increases, the thermal energy activates the molecules in the sample to reorient and so the current drops quickly after 90°C. For the sample pre-annealed higher than the T_g , the molecules in the sample are reoriented before charging, the polarizations of dipoles are hindered by the randomized molecules. Therefore, this peak is only the contribution of dipole polarization due to the surface charges accumulated during charging and only a broaden shoulder can be observed.

It is similar to the case of PET films charged at different temperature. The positive peak at T_g for room temperature charged sample is resulted from the dipole polarization on the well aligned molecular chains. For the sample charged at 110°C, since the molecules in the sample are reoriented due to the temperature elevated before charging, once the electric field is applied, the dipole polarizations occur but are hindered by the randomized molecules. While the electric field is removed after the temperature is dropped back to room temperature, the dipole polarizations are frozen-in. When the temperature is raised again to T_g during TSDC measurement, the depolarization of frozen-in dipoles and polarization due to surface charges occur simultaneously. The current magnitudes with respect to these two mechanisms are more or less the same but counter direction to each other, therefore a flat profile can be observed near the T_g . After the temperature increases upon 90°C, the polarizations due to surface charges become dominant in measurement and hence a rise of current peak is being observed.

The above phenomenon can be revealed by the case of PET films treated by ethanol. When the sample is treated by ethanol, the surface charges on the PET film are neutralized and the surface potential becomes zero. Since the surface charges are removed, polarizations due to surface charges will not occur when the temperature increases upon T_g during TSDC measurement. Therefore, only the dipole relaxation occurs and a negative current peak is observed in the TSDC thermogram. While the temperature further increases, the space charges injected into the sample will release out and therefore the current peak flips to the positive side.



Figure 6.9 TSDC thermogram of PET films charged at room temperature with pre-annealing treatment: (a) above $100^{\circ}C$ and (b) below $100^{\circ}C$.

6.5 Investigation of Activation Energy of PET by TSDC

After processing the TSDC, different thermograms have been obtained and these data can be evaluated to derive the magnitude of molecular parameters responsible for the TSDC. Since during TSDC, several decay processes may coexist, and there is a wealth of information to be gained. For dipoles, the temperature shift or activation energy, the natural orientation frequency, the relaxation strength and the distribution function are focused; while for space-charge-limited (SCL) drift the relevant quantities are the mobility, the spatial distribution and the penetration depth of the carriers. Finally, for trapped carriers, the trapping parameters are interested [Turnhout, 1975].

The evaluation methods elaborated are similar to those applied in isothermal dielectric measurements. However, there is a fundamental difference, in that for TSDC there is one recorded curve, while in isothermal measurements many curves are available for different frequencies and temperatures. Now there are two unknowns, the distribution function and the activation energy, and it is a complicated problem to evaluate these from a single TSDC curve. These complications can be avoided by prescribing the distribution function and calculating the activation energy, or vice versa. The simplest way to evaluate the data is calculating these parameters of the Debye relaxation, and there are several methods to estimate the activation energy of dipoles with a single frequency. In the following, these methods will be discussed briefly.

First of all, during the subsequent TSDC, the aligned dipoles will randomly disorient at a rate proportional to the number of dipoles still aligned. The polarization (P) will then decay according to the Debye rate equation,

$$\frac{dP(t)}{dt} + \alpha(T)P(t) = 0 \tag{6.5}$$

where t is time and $\alpha(T)$ is the reciprocal relaxation time, or relaxation frequency with respect to temperature, which is assumed to be the same for all dipoles. It should be noted that α depends not only on T but, virtue of the T-t heating programme, also implicitly on t. Nevertheless, for the sake of convenience, $\alpha\{T(t)\}$ is written in the form of $\alpha(T)$. On the other hand, the current density i(t) generated by the decay in polarization equals

$$i(t) = \frac{dP(t)}{dt} = -\alpha(T)P(t)$$
(6.6)

where P(t) follows from (6.5) after integration,

$$P(t) = P_o \exp\left[-\int_0^t \alpha(T)dt\right]$$
(6.7)

Since in the typical TSDC thermogram, temperature is raised linearly with time, the current density can also be written as function of temperature,

$$i(T) = -\alpha(T)P_o \exp\left[-h\int_{T_o}^T \alpha(T)dT\right]$$
(6.8)

where *h* is the inverse heating rate dt/dT.
By differentiating Equation 6.8 with respect to 1/T, the initial current rise can be obtained when $h_0^T \alpha(T) dT \approx 0$, hence by plotting $\ln i$ versus 1/T, the activation energy

(*A*) can be estimated by the following equation:

$$\frac{d}{d(1/T)}\ln i(T) = \frac{-A}{k} \tag{6.9}$$

where *k* is the Boltzmann's constant.

On the other hand, with the relation mentioned above, the activation energy can also be calculated in the second way if the natural relaxation frequency α_o is known. By substituting Equation 6.7 into Equation 6.8, we have,

$$\alpha(T) = \frac{i(T)}{P(T)} = i(T) / h \int_{T}^{\infty} i(T) dT$$
(6.10)

This equation was suggested as early as 1930 by Urbach, however it is now often credited to Fieschi and co-workers [Turnhout, 1975].

From the some of TSDC thermograms shown before, the polarization is observed to decrease gradually to zero. The current shows more structure: it first increases when the dipoles regain their mobility, passes through a maximum, and then drops sharply when the disorientation rate become high and the number of oriented dipoles becomes exhausted. The bell-shape current peak is thus asymmetric, the dipoles bound with

lower activation energy disorient at a lower temperature. Moreover such dipoles produce a stronger current, because they disorient more or less all together in a smaller temperature interval. When the dipoles react more quickly, that is, when α_o is higher, the current maximum likewise appears at a lower temperature.

Since at low temperature, $\alpha(T)$ is small and electrets will retain their charge for a long time when stored at room temperature, thus, $\alpha(T)$ increases vigorously during heating. This increase often obeys an Arrhenius equation

$$\alpha(T) = \alpha_o \exp\left(\frac{-A}{kT}\right) \tag{6.11}$$

where α_o is the natural relaxation frequency and *A* is the activation energy needed to disorient a dipole. The energy *A* can be seen as a potential barrier, which the dipole has to surmount before it can readjust its direction. Equation 6.11 broadly applies to relaxations involving the rotation of small molecular groups. It does not apply to the major relaxation in polymers, which occurs when they pass from the glassy to the rubbery state. This glass-rubber transition involves the structural rearrangement of parts of the long main chains, which in view of their bulkiness require some space to move.

For the third method, it is based on measurement of TSDC currents at two different heating rates $(h_{1,2}^{-1})$ and integration of the currents to calculate the course of the corresponding polarizations. Then a set of temperatures T_{1n} and T_{2n} is collected, in such a way that the two polarizations at these temperatures are equal. For this to be true we must have, according to Equation 6.7,

$$h_{1} \int_{0}^{T_{1n}} \exp(-A/kT) dT = h_{2} \int_{0}^{T_{2n}} \exp(-A/kT) dT$$
(6.12)

or approximately,

$$h_1 T_{1n}^2 \exp(-A/kT_{1n}) \approx h_2 T_{2n}^2 \exp(-A/kT_{2n})$$
 (6.13)

For the ratio of currents at $T_{1,2n}$, we have

$$i(T_{1n})/i(T_{2n}) = \exp(-A/kT_{1n} + A/kT_{2n})$$
(6.14)

From Equation 6.13 and 6.14, the activation energy of the α_o distribution can be calculated, provided that $T_{1,2n}$ can be determined accurately. The latter requirement is the main limitation of this method.

Optionally, the equality shown below can be applied to check the assumption of a distribution in α_o is correct or not,

$$h_1 T_{1n}^2 i(T_{1n}) = h_2 T_{2n}^2 i(T_{2n})$$
(6.15)

which results from substitution of Equation 6.13 and 6.14. Thus, when $hT^2i(T)$ versus P(T) is plotted for the two heating rates, the resulting curves should coincide if the distribution is one in α_o .

In this study, the activation energy of PET was estimated by TSDC in different heating rates because of its convenience, and no fundamental data was needed in this method, such as natural relaxation frequency. Since in the previous TSDC thermograms, the spectra of untreated and laser irradiated PET films were similar, therefore, in the following experiment, only bare PET films with different treatment will be focussed.

Bare PET samples were first electrified under different corona voltages at different temperatures listed in Table 6.3. Some of the samples were treated by ethanol to neutralize the excess surface charges for further comparison. Then the samples were examined by TSDC with different heating rate at 1°C/min, 3°C/min and 5°C/min. The corresponding current magnitudes and peak positions of α -peak and ρ -peak were recorded and tabulated in Table 6.3.

Charging condition	Ethanol	Heat rate	α-peak		ρ-peak	
(- <i>kV</i> , • <i>C</i>)	Treatment	(•C/min)	• <i>C</i>	I (pA)	• <i>C</i>	I (pA)
-5 kV, RT°C	Nil	1	82.60	5.30	119.00	20.30
		3	81.27	14.58	116.58	56.14
		5	89.69	23.39	134.38	98.02
-8 kV, RT°C	Nil	1	81.30	9.69	119.50	39.70
		3	81.81	25.82	118.66	112.04
		5	88.77	40.91	131.46	159.82
-8 kV, 110°C	Nil	1	80.20	-1.17	120.40	18.16
		3	73.80	-6.39	116.07	86.36
		5	80.20	-9.45	131.07	142.60
-8 kV, 110°C	Treated	1	81.90	-3.05	122.10	7.75
		3	83.49	-9.73	124.62	25.98
		5	91.26	-12.93	141.93	32.82

Table 6.3Summary of current magnitudes and peak positions of PET films withdifferent treatments examined by TSDC in different heating rates.

From Figure 6.10 and 6.11, thermograms of PET samples with different heating rates and treatment are illustrated. It is no doubt that the thermogram obtained from ethanol treated PET films is less fluctuation than that of untreated samples because the excess surface charges are neutralized by the solvent, Not only current magnitudes of the peak in spectra are increased, but also the peak positions of α -peak and ρ -peak shift to higher temperature when the heating rate is increased. When the heating rate increases, the sample temperature is lagging to the furnace temperature since the heat transfer rate is saturated in the samples. Therefore, the responses of dipole polarization and charge relaxation are delayed and shifted to a higher temperature. Moreover, in the thermograms, the α -peak of PET films with heating rate 1°C/min and 3°C/min are too close, for the ease of estimation, the activation energy is calculated by peaks obtained from thermograms with heating rate of 3°C/min and 5°C/min.

From Table 6.4, the activation energy of PET films charged at different corona voltages and temperatures are distributed in the range from 0.62 to 0.73 eV without any special treatment, the average is about 0.67 eV. However, after ethanol treatment, the estimated activation energy shows a smaller value at 0.41 eV.

Charging condition (-kV, •C)	Ethanol Treatment	Activation Energy (eV)
-5 kV, RT°C	Nil	0.62
-8 kV, RT°C	Nil	0.73
-8 kV, 110°C	Nil	0.65
-8 kV, 110°C	Treated	0.41

Table 6.4Summary of Activation energy estimated from PET samples with differentcharging condition and treatment.



Figure 6.10 TSDC thermograms of PET films with different heating rates and charged at room temperature: (a) charged at -5 kV; (b) charged at -8 kV.



Figure 6.11 TSDC thermograms of PET films with different heating rates and charged at 110 °C under -8 kV: (a) without ethanol treatment; (b) after ethanol treatment.

Chapter 7

Application of Laser Irradiated PET Film

Polymeric electrets are widely used for many applications like electret microphones and electro-acoustic transducers because of its flexibility, low cost and light-in-weight. To demonstrate the enhancement on electret property of the laser irradiated PET films, a prototype of electret microphone was fabricated. The diaphragm of microphone was interchangeable so that different polymeric electrets can be placed in the device for comparison.

The electret microphone was a simple device consisted of two parallel flat electrodes, of which one was fixed and the other served as the diaphragm was made of polymeric electret metallized on one of the surface. The electret produced an electric field in the air gap between the electrodes. The schematic diagram of the microphone is shown in Figure 7.1.



Figure 7.1 Schematic diagram to show the operational principle of an electret microphone.

Sound pressure change produced by the external acoustic wave causes the diaphragm to move which leads to a potential change between the electrodes. In the electret microphone, the potential difference (U) between the backing electrode, air gap and the metallized electret is equal to

$$U = E_d x_d + E_g x_g \tag{7.1}$$

where E_d and E_g are the electric field strength in the electret and air gap, x_d and x_g are the thickness of the electret and the separation of the air gap. Since we assume that the electric field strength and thickness of the electret are not changed in the operation, therefore, the magnitude of that potential change (ΔU) is simply a product of electric field strength in the gap (E_a) and the amplitude change of diaphragm (x_a) during vibrations, and it has already been illustrated by Hilczer and Małecki [Hilczer and Małecki, 1986]:

$$\Delta U = E_a x_a \tag{7.2}$$

In the present study, an untreated and a laser irradiated PET film was tailored into a small round disc with 7 mm in diameter which was used to compare with a commercial electret microphone, that is, a 9 μ m thick Teflon round electret with one-side metallized. The PET samples were metallized with a layer of gold by sputtering. They were then electrified by corona discharging under -5 kV.

After the polymer electret had been installed into the microphone as shown in Figure 7.2, the electret microphone was examined by a testing kit coped with amplifiers and a speaker as illustrated in Figure 7.3. The sinusoidal signal with a peak-to-peak voltage of 1 V was generated by a signal generator, the signal was then amplified by a Class-A amplifier which was output to a loudspeaker with 7.5 cm in diameter. The transmitted audio signal was received by the microphone placed at 9 cm from the loudspeaker.

The microphone converted this audio signal to electrical signal through a pre-amplifier and its peak-to-peak voltage was measured by a digital storage oscilloscope. The signal gain at different frequencies were calculated by the following equation which is the voltage ratio of the output signal from the speaker (V_o) and the input signal from the microphone after passing the pre-amplifier (V_i):

$$Gain = 20\log_{10}\left(\frac{V_o}{V_i}\right)$$
(7.3)



Figure 7.2 Schematic diagram of the electret microphone



Figure 7.3 Schematic diagram of the testing set-up for electret microphone

Figure 7.4 shows the frequency response of the amplifier used to amplify the signal input from the signal generator. The amplifier performs a steady gain level higher than 200 Hz up to 100 kHz, which covers the human vocal frequency range (300 Hz to 3400 Hz) and the audio frequency range (20 Hz to 20 kHz). In the measurement, different polymer electrets were tested with frequency range varying from 100 Hz to 20 kHz in logarithmic scale as shown in Figure 7.5. From the frequency responses shown in the figure, all three samples perform have steady gain level below 1 kHz, and the signal gains then increase until the frequency reaches 5 kHz, then the gains drop at higher frequencies. Though the three samples exhibit similar frequency response, the untreated PET film performs worse than that the other two samples. It is not surprising that the gain of laser irradiated PET film is competitive to the commercial Teflon film and even better at frequency below 5 kHz.

From this result, we can see that the laser irradiated PET can perform like a Teflon film, even it is well known that Teflon is one of the best polymeric electret. If this surface morphology treatment can be applied to other polymeric electret which performs better than PET, the enhancement on the sensitivity of these materials may even be more significant.



Figure 7.4 Frequency response of the amplifier for the electret microphone



Figure 7.5 Frequency responses of microphone using different polymer electrets

Chapter 8

Conclusions

In this study, PET films were treated by laser irradiation to modify the surface morphology. The surface structures, electret effects and some related properties of these irradiated samples were studied by various techniques.

PET films were irradiated by UV excimer pulsed laser in 248 nm wavelength with different number of shots. From the investigation of surface morphology by polarized microscope and SEM, it was observed that the sub-micron scale ripple pattern was induced on the PET film surface by the laser pulses. When the number of laser shot increased, the ripples structure became finer. Until the sample was irradiated for about 17 & 18 pulses, some of the ripple tips became narrower and fused together with the neighboring tips, and a layer of polymer material was formed on the fused ripple tips. The surface potentials of these samples were significantly higher than that of other samples. However, by comparing to the films that treated by ultrasound, this layer of polymer melt was destroyed and no enhancement can be found. This higher surface potential can be attributed to the formation of this layer. Compare to the porous materials like porous PTFE, once the ripple tips melt and fused together, voids were formed at the surface layer of the laser irradiated polymer. These voids resembled the pores in porous material and thus the irradiated sample exhibited a higher surface potential.

The charge retention capability of both untreated and laser irradiated films PET were studied. For untreated PET films, three different thickness of 13, 50 and 110 μ m were examined, the charge retention capability of the thicker sample in 110 μ m performed a better retention to maintain its charges than the thinner samples. On the other hand, the surface potentials of PET films in different thickness, charged at different corona voltages would be approached to the same level after decaying to half of their initial values. Moreover, it was probable that the highest surface potential for PET films can be obtained by an optimized corona voltage. Since in the decay profile of 13 μ m and 50 μ m films, though the samples were charged under the higher corona voltage at -9 kV, the surface potential of these samples were dramatically lower than that charged at lower voltage.

For the laser irradiated PET films, the surface potentials of samples irradiated for 18 to 20 pulses was outstanding in the whole series, not only for the freshly charged films, but the decayed samples showed the same phenomenon. For freshly charged films, the enhancement of surface potential shown by the samples was about 10 %, but after a long decay period, the irradiated samples showed a better charge retention than that of untreated samples. The potential of irradiated samples in the range of 18 to 20 pulses was 35 % higher than the other films.

By summarizing the results of laser surface modification and charge retention capability explained before, a better charge retention capabilities can be provided by the thicker PET samples. It was no doubt that the improvement of charge retention capability could be provided by the new surface morphology obtained from laser irradiation. However, the thickness of samples may also be a crucial factor to alter the charge retention capabilities of the samples.

TSDC was employed in this study to examine the dipole re-orientation and charge relaxation of the corona charged PET samples. Since the electric field inside the corona charged PET films (17 MV/m) were much higher than that of the air-breakdown field (2.7 MV/m), the open-circuit TSDC mode with a 100 μ m PTFE spacer was introduced.

For the samples electrified at room temperature, the α -peak and the ρ -peak of the untreated PET film were located at about 80°C and 120°C respectively. Laser irradiated PET film showed a similar characteristic but the ρ -peak was appeared earlier at about 112°C. For those 110°C charged samples, the ρ -peaks of untreated and laser irradiated PET films were appeared at 120°C and 112°C respectively. Nevertheless, the low temperature peaks at 80°C in both cases were diminished.

Moreover, the PET films pre-annealed at different temperatures which were higher than that of the glass transition temperature were studied. From the experimental results, the α -peak was diminished and the ρ -peak was shifted to higher temperature when the pre-annealing temperature was increased.

By ethanol treatment, the excess charges on the PET film surface were neutralized and the surface potential measured by the electrostatic sensor was dropped to zero, and the equilibrium state was reached in a very short time. The investigation of the depolarization peak position of the PET sample electrified at elevated temperature can be aided by this method. In addition, the activation energy of the PET was estimated by the current magnitudes and peak positions obtained form the TSDC processing at different heating rates. The estimated activation energy of PET was about 0.67 eV.

Eventually, to demonstrate the advantage of the laser irradiated PET film, a prototype electret microphone was fabricated. The frequency responses of the laser irradiated PET performed like a Teflon film, even it is well known that Teflon is one of the best polymeric electret. If this surface morphology treatment can be applied to other polymeric electret which performs better than PET, the enhancement on the sensitivity of these materials may even be more significant.

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