

CHAPTER II

LITERATURE REVIEW

2.1 Hyrophilic Finishes on Polyester Fabrics

2.1.1 Chemical Modification

Polyester fibers generally exhibited low surface energy and limited chemical reactivity, resulting in poor wettability and weak adhesive binding. The introduction of new functional groups by means of chemical modification reactions was one possible mean for altering the physical and chemical nature of the fibers.

Polyesters are highly sensitive to bases such as sodium hydroxide and methylamine, which serve as catalysts in the hydrolysis reaction. Hydrolysis is believed to increase the number of polar functional groups at the fiber surface. The action of strong base leads to cleavage of ester linkages on the fiber surfaces. The result is the formation of hydroxyl and carboxyl groups on the fiber surface. Reaction of methylamine with an ester group of the polyester led to chain scission at the reacting site giving rise to amide formation. The presence of amide groups would also increase wettability of polyester.

The degradation of polyester fibers caused by diethyl amine treatment was studied (Bendak, 1987). Methanolic medium and higher temperature if treatment resulted in the loss in weight. Wicking properties of polyester were found to be significantly improved with increasing the percentage loss in weight of the substrate. Diethyl amine treatment caused a relatively significantly increase in the moisture regain.

Bendak *et al.* (1991) carried out treatment of polyester fabric in 25% sodium hydroxide followed by hot air drying at 60°C for 5-15 minutes and subsequent washing. Improvement in feel was observed for polyester along with wettability without affecting the strength or dimensional stability.

The reactions of semicrystalline PET film with ester-selective reagents to produce modified film samples were studied (Chen *et al.*, 1998). Hydrolysis of PET yields a surface mixture of alcohol and carboxylic acid groups.

Reduction with lithium aluminium hydride and transesterification with ethylene glycol (glycolysis) both produce surface with alcohol functionality (PET-OH^R and PET-OH^G, respectively). Each of these modification reactions involves chain cleavage and can lead to degradation; for each reaction, the conditions were optimized to maximize conversion and minimize degradation. The surface density of alcohol is higher on PET-OH^R than PET-OH^G.

Dauginet *et al.* (2001) Hydrolyzed PET film by using 2 M aqueous sodium hydroxide for 30 min at 70°C. XPS results showed that the hydrolyzed PET surface contain a mixture of carboxylic acid and alcohol functional groups due to the selective cleavage of the ester. The water contact angle measurement leads to an increase of the the hydrophilicity of PET film surfaces. The contact angle of the untreated film is 69.7°, while the contact angle of the hydrolyzed film is 58.1°.

In addition, surface modification of polyester to make it hydrophilic can be achieved by adsorbing polymers on the polyester surface. Starch is a hydrophilic polymer used in many textile applicationa that can be used to modify polyester fabric and physically modify the fabric characteristics. Cationic modification of the starch is one of facilitating the adsorption of starch on polyester is reported to be negatively charged.

The effects of charge and hydrophobicity on adsorption of modified starches on polyester were investigated (Samu *et al.*, 1999). Starch is a hydrophilic polymer used in many textile applications that can be used to modify polyester to make it hydrophilic. The degraded tapioca starch was treated with two different cationic reagents; 3-Chloro-2-hydroxypropyl-trimethyl-ammoniumchloride (CHTAC) and 3-Chloro-2-hydroxypropyl-dimethyl-dodecylammoniumchloride (CHDAC) and anionic reagent; methacrylic acid. The adsorption kinetics of the modified starch on polyester was measured by using the UV spectrophotometer. The results showed that cationic starches are easily adsorbed on the fabric due to charge interactions. The presence of hydrophobic substituents on the cationic moiety results in increased adsorption. With the same cationic moiety, an increase in charge decreases the adsorption. While the adsorption of anionic starch on polyester is lower than for the cationic starch. The starch adsorptions were qualitatively estimated by the addition of iodine. No color was seen for polyester treated with the anionic

starch. This is in contrast to the cationic starches, where the fabric shows a strong blue color, indicating adsorption of the starch.

2.1.2 Corona Discharge

Corona discharge has been proved to be a useful method for improving the polymer surface hydrophilic property, especially in the composite material strength improvement, the treatment can improve the surface affinity and the sticking strength with some hydrophilic polymers, because the treatment can lead to the increasing of the high reactive free radical oxygen in the polymer surface. The treatment is a simple and more practical than any other chemical and physical methods because the samples can be quickly treated under atmosphere pressure.

Polyester fabric was modified by using corona discharge irradiation method (Xu *et al.*, 2003). The fabric was treated at different voltages by the corona discharge irradiation. The treatment can lead to the increasing of the high reactive free radical oxygen in the polymer surface. After the treatment, the treated fabric was immersed in a water box vertically along length direction to determine the wicking property of the fabric. Wicking property was tested according to the water climbed height in the fabric at a certain time. Higher height of the water climbed with better wicking was improved when the voltage is higher than 10 kV. The treated polyester was dyed with a disperse blue HGL. Dyeing of the treated fabric showed that dyeing speed and the dye-uptake were improved. The surface affinity between the treated fabric surface and starch phosphonates sizing was tested by drawing in the length direction. The results showed that as the treated voltage increased, the affinity strength between the two fabrics improved due to the improvement of the hydrophilic property of the treated fabric produced by the corona discharge treatment.

2.1.3 Chemical Wet Oxidation Methods

In chemical wet oxidation methods, strong oxidants such as $\text{CrO}_3/\text{H}_2\text{SO}_4$, $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$, $\text{KClO}_3/\text{H}_2\text{SO}_4$, $\text{KMnO}_4/\text{H}_2\text{SO}_4$, HNO_3 and H_2SO_4 can provide an effective approach to surface modification with main drawbacks such as damages to substrates and pollution to environment. Persulfate salt aqueous solution

is a kind of milder oxidizing agents and its main drawbacks in surface modification application are slow oxidizing speed and poor modification efficiency. To overcome these problems, UV irradiation is used to enhance the oxidation ability of this system.

Yang *et al.* (2003) studied a fast surface hydrophilic modification method for polymeric materials by confined photo-catalytic oxidation. A very thin persulfate salt aqueous solution which is a kind of milder oxidizing agent was sandwiched between two polymer films. BOPP is used as the top layer because it has good ultraviolet light transmission and the bottom is a polymeric material which is prepared to be modified such as HDPE, LDPE, and PET etc. Then the assembled unit was irradiated by UV radiation from the top side at room temperature for a certain time. The effect of irradiation time, concentration of persulfate solution, the wavelength and intensity of UV radiation were investigated. The results showed that the static water contact angles of polymeric substrates decreased from 100 to 44° for LDPE, from 107 to 34° for HDPE and from 73 to 15° for PET when irradiating for 90 seconds and using 30 wt% ammonium persulfate. From the UV absorption spectrum of persulfate aqueous solution, the maximum quantum efficiency of the photolytic decomposition of persulfate was about 0.6 at $\lambda = 254$ nm. The UV irradiation intensity (at $\lambda = 254$ nm) has effect on contact angle, contact angle of the modified surface came from the formation of a sulfate salt group (SO_4NH_4^+) on the ionized surface, which was characterized by XPS and ATR-FTIR. The surface topography of the modified polymer substrates were observed by SEM and AFM, and no visible etching effect to original surface were found.

2.1.4 Plasma Treatment

Treatment of polymers by different types of plasma (microwave, radio frequency) is often used for modification of wettability, printability, adhesion etc. It is consequence of different process such as oxidation, degradation, cross-linking and structural changes, which may occur in the thin surface layer. The efficiency of these processes depends upon atmosphere, gas pressure, and temperature, kind of polymer surface, power and time of plasma action. Low

temperature plasmas are produced by electrical discharges in low pressure gases. They consist of a mixture of highly reactive species, i.e. ions, radicals, electrons photons and excited molecules, preserving electrical neutrality. Their chemical composition and physical characteristics are determined also by device parameters, such as vacuum chamber geometry, gas pressure etc. The interaction of low-temperature air plasma with polymer films or fibers causes mainly the change of surface polarity. It may be a result of the change of surface polarity. It may be a result of among others, the creation of C=O, OH and COOH groups in the oxidation process. Electron present in such plasma conditions are known to have kinetic energy sufficiently high for breaking up the covalent bonds and initiate the chemical reactions.

The surface properties of five polymers (HDPE, LDPE, PP, PET and PMMA) were modified by using Atmospheric Pressure Non-Equilibrium Plasma (APNEP) method (Shenton *et al.*, 1998). These polymers have been exposed to various APNEPs under a variety of gas, flow rate and geometric conditions. XPS has been used to measure the surface chemical composition of standards and plasma modified polymers to a depth 5-30 nm. The XP-spectra indicated that surface oxygen enhancement had occurred in the cases of HDPE, LDPE, PP, PET. For PMMA, removal of oxygen species was detected indicating the loss of the acrylate side group and surface cross-linking. By varying the APNEP conditions (source gas, flow rate, substrate position and reactor geometry), the rate and degree of surface modification can be controlled. Increases in the surface energy of APNEP treated polymers have been measured. The change in the chemical structure (as indicated by the XPS data) and surface energies result in enhanced surface properties. For example, the polymer-polymer adhesion of polyolefins (using an epoxy adhesive) has been shown to be enhanced. The other surface property changes include a change in wettability (all five substrates) and increased surface hardness (PMMA).

Kaminska *et al.* (2002) studied the influences of side groups and polarity of polymers on the kind and effectiveness of their surface modification by air plasma action. The polymers of different chemical structure and polarity (PE, PP, PET and PMMA) are treated under low-temperature air plasma. The interactions of low-temperature air plasma with PE, PP, PET and PMMA cause some decrease of

the liquid contact angle (θ), and the increase of surface free energy (γ_s), including its polar component (γ_s^d). It means that the amount of polarity groups on polymer surface increases significantly after plasma treatment. Electrons present in such plasma conditions are known to have kinetic energy sufficiently high for breaking up the covalent bonds and may be a result of, among others, the creation of carbonyl, hydroxyl and carboxylic groups in the oxidation process. The observed changes are depending on chemical structure of polymer, highest increase of γ_s appeared in polar polymers (PET and PMMA), where as $\Delta\gamma_s$ is lower in nonpolar PE and PP. It was proved that side group in the main chain of polymers restrain the processes caused by plasma action.

The surface modifications of PET fibers induced by RF air plasma treatment was investigated (Riccardi *et al.*, 2003). PET fabrics were treated to RF air plasma under different operating conditions. Treated polymer surfaces were characterized by water droplet absorption time measurements, XPS and AFM analysis. All of the plasma-treated PET specimens exhibited a marked increase of hydrophilicity, the absorption time t_{abs} measured immediate after the treatment was always lower than 10 s, to be compared with $t_{abs} \sim 350$ s for untreated PET. Excellent durability of wettability properties was achieved by using of a relatively long treatment time and high RF power. XPS results showed that there was the formation of C-O, C=O, C-N bonds in the surface layer which making the surface hydrophilic. These polar groups is accompanied by etching and possibly cross-linking between activated species. Etching was mainly a consequence of ion bombardment, yielding low molecular weight, water soluble oxidation products. Surface etching evidenced by AFM analysis and by the weight loss of treated samples.

Cheng *et al.* (2004) used low-temperature CF_4 plasma in a roll-to-roll double-sided treated system to modify surface of PET. PET film was exposed to radio frequency (RF) CF_4 plasma at web speed 0.5 ft/min and the RF plasma was controlled on 600 W. The surface properties of the modified polymers are characterized by XPS and water contact angle. XPS spectra showed that CF_4 plasma treatments of PET result in large amount of fluorine incorporation at the surface.

There are the formations of fluorine carbon functionalities: C-CF_n at 286.6 eV, CF at 287.8 eV, CF-CF_n at 289.3 eV, CF₂ at 291.1 eV and CF₃ at 293.6 eV. The wettability of the PET surface shows two opposite extremes. The contact angle on one side of the PET film is super-hydrophilic, 7.56°, and the other side of is hydrophobic, 108.63°. The XPS analysis measurement results also show different functional groups on the both sides of PET surfaces. The CF₃ in C(1s) spectrum can rather enhance the hydrophobic surface which only occurred in the C(1s) spectrum of plasma treated the front side (contact angle = 108.63°).

2.1.5 Grafting Polymerization

Surface graft polymerization of vinyl monomers (i.e. vinyl acetate, 2-methyl-5-vinyl pyridine, acrylic acid and methyl methacrylate) has proved to be an effective alternative way to modify surface property of polyester. Introduction of carboxylic groups on the polyester surface is very effective for increasing wettability and adhesion force. However, there is some difficulty in increasing graft density due to the simultaneous production of homopolymer.

Kawase et al. (1992) studied the effects of modifying textiles for soil release properties, polyester fabrics were grafted with acrylic acid. The surface free energies of grafted polyester fabrics were investigated by using the relationship between the polar component of surface energies γ_s and the peak ratios of COONa (1580 cm⁻¹) to COOR (1250 cm⁻¹) by FTIR measurement. FTIR-spectra showed a new peak clearly appears at 1691 cm⁻¹. This peak is attributed to the C=O stretching of grafted COOH groups. The effects of grafting on soil release were also investigated with washing experiments using squalene, triolein and oleic acid as oily soil. The effects of grafting on oily soil removal varied depending on the polarity of soil. Removals of squalene (nonpolar soil) and triolein (somewhat polar) improved by grafting. While removals of oleic acid decreased along with the grafting degree.

The grafting of methyl methacrylate onto PET fibers by using azobisbutyronitrile as an initiator was investigated (Sacak *et al.*, 1993). The effects of temperature, time, monomer and initiator concentrations were studied. The results showed that an increase in temperature and monomer concentration was

found to increase the graft yield. The graft yield increased up to an initiator concentration of 0.90×10^{-2} mol/L and decreased at higher initiator concentrations. As the graft yield increased, the fiber densities decreased, and the fiber diameters and intrinsic viscosities increased. The grafting of MMA affects some properties of PET fibers. Moisture regain showed a slight increase with the grafting.

Abdel-Bary *et al.* (1988) studied the effect of graft polymerization of 2-hydroxyethyl methacrylate on the properties of polyester fibers and fabric. Graft copolymerization of HEMA onto PET fibers and fabric using benzoyl peroxide (BP) as an initiator was carried out. The moisture regains of the polyester and grafted polyester was evaluated. The results showed that HEMA increases hydrophilicity of the polyester. This shift toward a hydrophilic nature is responsible for the increase in moisture regain from 0.6 to 12% as graft percentage of HEMA is increased steadily up to 125%.

Nonwoven PET was modified by using UV-induced surface graft polymerization of acrylamide acid onto the surface (Yang *et al.*, 2002). The surface wettability was verified by the water adsorption capability and wicking time, the results showed that the %water absorption was observed to increase from 387 for the untreated PET to 606 for the treated PET. The wicking time was also decreased from 6900 s for the untreated PET to 2 s for the grafted PET. These results indicated that the surface hydrophilicity of nonwoven PET was improved.

Gupta *et al.* (2002) used plasma-induced graft polymerization of acrylic acid onto PET film to develop surface for protein immobilization and smooth muscle cell seeding. PET film were treated with argon RF plasma reactor then graft polymerization of acrylic acid onto the plasma treated PET film was carried out under nitrogen. The contact angle of AA-grafted PET film was observed to decrease from 72.9° for the untreated PET film to between 26° and 33° depending on the grafted density. A decreasing in the contact angle by plasma-induced graft polymerization of acrylic acid onto PET films due to the introduction of $-\text{COOH}$ group at the surface.

Uchida *et al.* (2002) immobilized poly(methacrylic acid) (PMAAc) chains onto the surface of PET film by graft polymerization induced by light

irradiation was investigated (Uchida *et al.*, 2002). Monomer conversion and density of grafted PMAAc increased linearly with irradiation time and monomer concentration. AFM image of the grafted polymer chains were found to form a cluster structure. New peaks appeared in the C(1s) and O(1s) XPS spectra of the PMAAc grafted surface assigned to the carboxylic group of PMAAc in which improved the hydrophilicity of PET.

He *et al.* (2003) studied the electron beam irradiated and acrylic acid graft PET film. PET film was preirradiated with electron beam and then grafted by acrylic acid (AA). After the irradiation, the AA-grafted PET films were characterized by FTIR, SEM, ESCA, and water contact angle. The results showed that the contact angle decreases with the increased dose of irradiation, indicating that the hydrophilicity of the surface of PET film is improved. This is caused by the introduction of polar groups such as hydroxy, carboxy and peroxide onto the macromolecules of PET. FTIR spectrum of the AA-grafted PET film showed a new band at 1552 cm^{-1} which is responded for the COO^- group. That verifies that AA has been grafted onto the chains of PET film. The SEM image showed that the surface of grafted PET film presents a wave-like morphology. The water uptake of the grafted samples increases with increasing grafting yield. This is because the water molecules can bond easily with groups on the polar grafted chains.

However some of these methods have limited practical use, and are frequently accompanied by the hardening of the touch of polymer or elevated production cost. Accordingly there has been great demand for the finishing technology that could be applied to polyester fiber more easily and efficiently.

Surface modification of polyester can be carried out by using nonionic surfactant type organic compounds for the surface modification of polyester, where the hydrophobic moiety of the compounds could anchor on polyester surface and the hydrophilic groups orientate outward.

The surface modifications of PET films were investigated by treatment with ethoxylated hexylaminoanthraquinones (Cui *et al.*, 2003). The ethoxylated hexylaminoanthraquinones shown nonionic surfactants nature with definite cloud points, and were applied onto PET by exhaustion method as in dyeing. PET films were dyed with ethoxylated hexylaminoanthraquinones at 130° for 10

hours under the bath ratio of 5000:1. The surface analysis of PET films treated with ethoxylated hexylaminoanthraquinones by XPS showed that the surface of treated PET films has relatively high oxygen content of ethoxylated groups compared either untreated PET. XPS analysis was also proved that the ethoxylated hexylaminoanthraquinones are adsorbed only onto the surface of PET. Water contact angle of the treated PET films was decreased as the adsorbed amount of ethoxylated hexylaminoanthraquinones increase. These results indicated that the ethoxylated hexylaminoanthraquinones anchor on PET surface with ethoxylated hydrophilic parts orientate outwards which make the surface hydrophilic.

2.1.6 Admicellar Polymerization

Admicellar polymerization is applicable for applying thin polymeric film on a substrate surface. A monomer is induced to undergo a polymerization reaction in a surfactant bilayer adsorbed on the substrate surface. The reaction leaves a very thin film coated on the substrate. Therefore, this technique can be used to introduce hydrophilicity to the polyester fabrics. A method for coating a thin film of polymer on various substrates by using admicellar polymerization has been widely studied.

Pisuntornsug *et al.* (2002) used admicellar polymerization to modify the surface of cotton fabric. Sodium styrene sulphonate, a polymerizable anionic surfactant, was polymerized on cotton to impart a negative charge on the fiber surface so the fiber surface can be dyed with cationic dye with no addition of salt. The amount and uniformity of the coating was determined by dyeing the treated cotton with a cationic dye. The results showed that the dyed treated gives good washing fastness at 30°C and excellent dry rub fastness.

The cotton fabric was also modified to increase its hydrophobicity by coating a thin film of styrene using admicellar polymerization method (Pongprayoon *et al.*, 2002). The polystyrene film formed was characterized by SEM, FTIR, and GPC. The increase in the hydrophobicity of treated cotton surface was determined by the drop test. The result showed that the clear evidence of a layer of coating polystyrene thin film on the fiber surface, and the coated cotton fabric can resist by a water droplet for longer than 30 minutes.

Boufi *et al.* (2002) studied the formation of polymeric films on cellulosic surfaces by admicellar polymerization. Cellulosic fibers were placed in contact with cationic or an anionic surfactant. Only the cationic surfactant was adsorbed on the cellulosic surface and forming admicelle morphologies. After that styrene, methacrylate and 2-ethylhexylacrylate monomers were added to these systems. The initiator was added to start polymerization resulted in the formation of polymer both in the aqueous medium and around the fibers. SEM images showed the uniformity of the film on the fiber surface. This treatment brought about a modification of the hydrophilic character of the cellulosic fibers, as shown by contact angle measurement.

Admicellar polymerization was used to deposit polystyrene and poly(methyl methacrylate) onto aluminium surfaces in order to mitigate corrosion caused by water (Materredona *et al.*, 2003). The films on aluminium surfaces were characterized by FTIR, SEM, and AFM. Dynamic contact angles indicated that the modified aluminium substrates showed the hydrophobic nature. Water uptake measurements showed that PS delayed water penetration for almost 4 h. Accelerated corrosion tests revealed the protective characteristics of poly(methyl methacrylate).