

CHAPTER I

INTRODUCTION

In textile industry, polyester fibers are synthetic fibers in which the forming substance is a long chain polymer composed of at least 85% by weight of a dihydric alcohol and terephthalic acid. Polyester fibers found immediate acceptance in easy-care, wash-and-wash, and durable press garments. It has excellent wrinkle recovery, either wet or dry. Polyester fibers have taken a major position in textiles all over the world although they have many drawbacks, the fiber has low moisture regain and has tendency to accumulate static electricity. The cloth made up of polyester fibers picks up more soil during washing and fiber is flammable. Polyester is both hydrophobic and oleophilic. The hydrophobic nature imparts water repellency. But because of the oleophilic property, removal of oil stains is difficult. Under normal conditions, polyester fabrics have a low moisture content of around 0.4% due to its poor hydrophilic and poor wicking property so the wearer can feel damp or clammy in the presence of even only a few percent of moisture.

In general, fabric comfort-related properties are moisture vapor transport, air permeability and moisture regain. For any garment to be comfortable during wearing where liquid sweat is produced, it must wick. Wicking simply means the capillary movement of moisture within a fabric structure. Water vapor transport is related to wettability. Wettability is an important characteristic of materials indicating the hydrophobic or hydrophilic nature of the surface. To quantify wettability, one typically examines the contact angle value by any of the several techniques. A fabric that rapidly moves water from the human body makes the wearer feel more comfortable by keeping him dry. The comforts in wearing and oil removals are intimately related to the hydrophilicity of the fibers and fabrics.

Various methods have been developed to increase the hydrophilicity to polyester fabrics such as grafting copolymerization, corona discharge etc. However, most of these methods deteriorate the bulk properties of polyester or result in only temporary improvement of material performance and some of these methods have limited practical use and elevated production cost.

Admicellar polymerization has been successfully used to coat thin polymeric films on various kinds of substrates for several purposes. Examples are poly(methyl methacrylate) on cellulosic fiber (Boufi *et al.*, 2002), poly(methyl methacrylate) and polystyrene on aluminium (Materredona *et al.*, 2003), and polystyrene on cotton (Pongprayoon *et al.*, 2002). Admicellar polymerization has generally been applied to polar substrates. This technique is simple with low energy consumption and more economically than other modifying techniques.

Poly(methyl methacrylate) (PMMA) is one of the polymers that has been used by various workers to improve the properties of polyester fibers or fabrics i.e., PMMA was used to grafted with polyester fabrics to improve hydrophilic property. PMMA is an amorphous plastic with a high surface gloss, high brilliance, a clear transparency of 92 % (inorganic glass also has a transparency of 92 %), and a refractive index of 1.49. PMMA is classified as a hard, rigid, but brittle material, with a glass transition temperature of 105°C. PMMA has good mechanical strength, acceptable chemical resistance, and extremely good weather resistance.

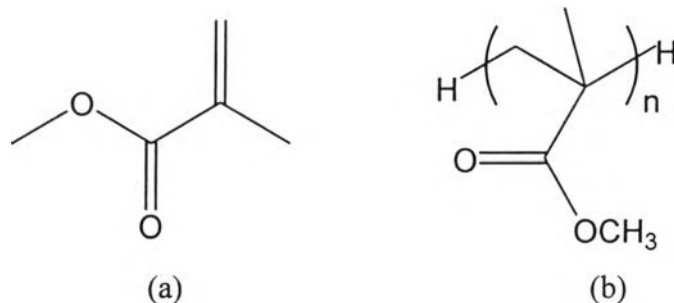


Figure 1.1 Chemical structure of (a) methyl methacrylate (MMA) (b) Poly(methyl methacrylate) (PMMA).

PMMA can be produced by using a variety of polymerization mechanisms. The most common technique is the free radical polymerization of MMA. The polymerization of MMA is most commonly initiated by thermally labile compounds, such as 2,2'-azobisisobutyronitrile (AIBN). Upon heating, the thermal initiator forms free radicals, which initiate the polymerization. Termination occurs through two mechanisms, combination and disproportionation (Figure. 1.2). With termination by combination, the resulting polymer has a head-to-head linkage, and the molecular

weight roughly doubles. With termination by disproportionation, in which a proton is abstracted from one propagating chain end to another, two different types of polymers are produced with about the same molecular weight. Combination predominates at lower temperatures. Disproportionation becomes more significant at higher temperatures.

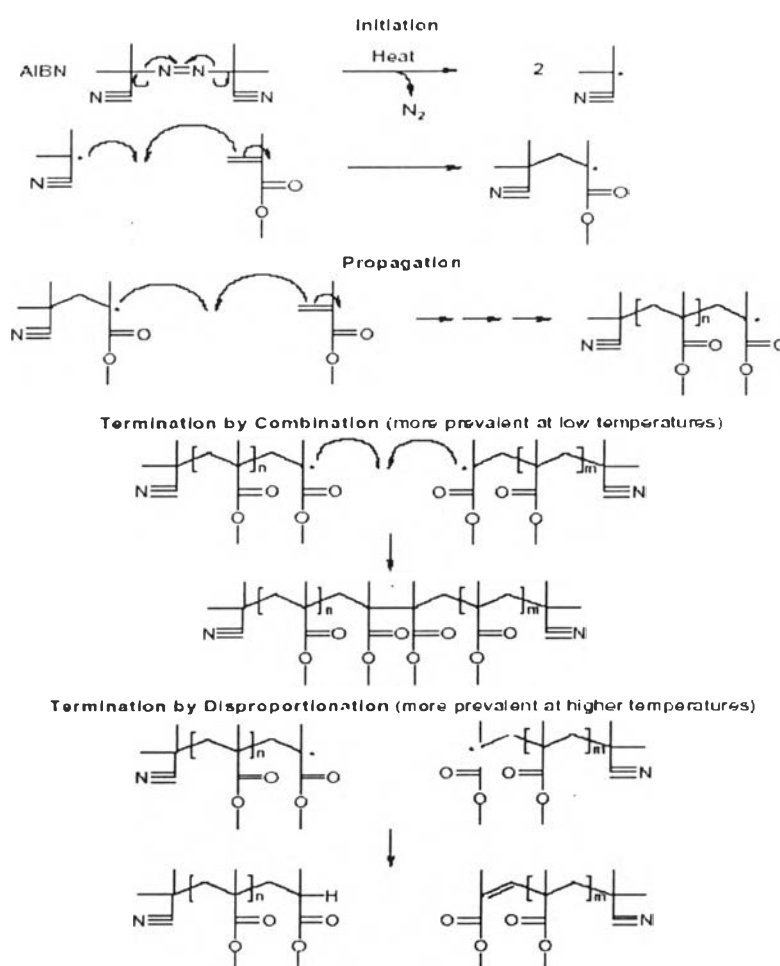


Figure 1.2 Free radical polymerization of MMA using AIBN.

In this research work, poly(methyl methacrylate) (PMMA) was coated onto the hydrophobic polyester fabric surface. The adsorbed surfactant in this case might be expected to be a monolayer with tail-down orientation, rather than a bilayer. After the polymerization reaction, the PMMA-coated polyester fabric was

hydrolyzed by acid to introduce carboxylic groups to the surface to improve the hydrophilicity of the polyester fabric. The moisture regain of the hydrolyzed PMMA-coated polyester fabric was then studied.

1.1 Admicellar Polymerization

Admicellar polymerization, a term derived from “adsorption” and “micelle”, defines a class of *in-situ* polymerization taking place inside of adsorbed surfactant bilayers on various substrates.

Admicelle is the term used when the bilayer surfactant molecules adsorbed on the solid surfaces. The word admicelle comes from “Adsorbed Micelle”, that demonstrate the properties of the adsorbed surfactant related to the micelle. For example, an ionic surfactant will tend to form aggregates at the hydrophilic surfaces in aqueous solution. To minimize the free energy, the surfactant molecules will tend to form bilayer with the hydrophilic head group facing the aqueous water and hydrophobic tails folding inside the interior at high concentration.

Admicellar polymerization is a four-step chemical process shown schematically in Figure 1.3

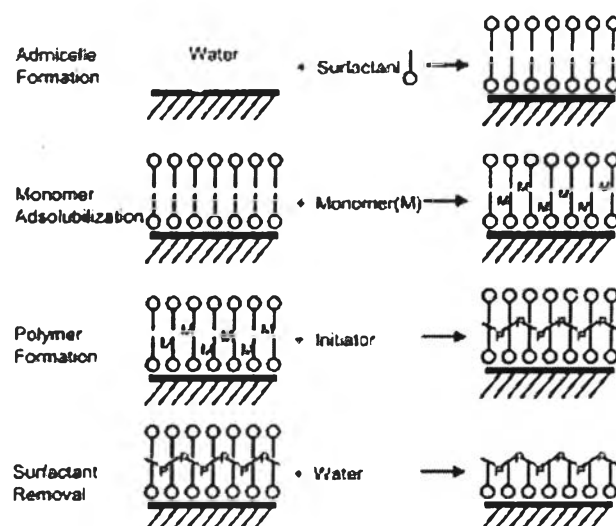


Figure 1.3 Schematic of the four step admicellar polymerization.

Step 1: Admicellar Formation. Surfactants are adsorbed on the substrate surface to form a bilayer structure or admicelle. The adsorption isotherm of ionic surfactants onto a substrate surface can be divided into four regions as shown in Figure 1.4.

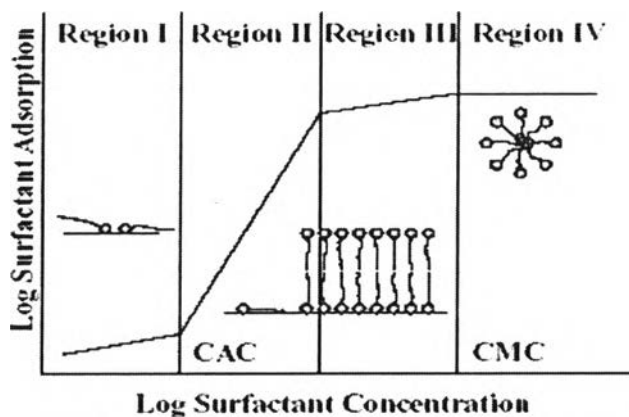


Figure 1.4 Adsorption isotherm of surfactants on a solid surface.

This curve is plotting between the log of adsorbed surfactant versus the log of equilibrium surfactant concentration which can be used to obtain the appropriate concentration of surfactant for admicellar polymerization process. This concentration is slightly below the critical micelle concentration or CMC to avoid emulsion polymerization. The electrochemical nature of the substrate, the type of surfactant molecule, the pH of solution, and added counterion control the adsorption of the surfactant on the substrate surface. At pH values below the PZC (point of zero charge), the surface is positively charged; above the PZC, the surface is negatively charged. Consequently, anionic surfactants adsorb well below the PZC and cationic surfactants above the PZC. An electrolyte is added to reduce the charge on the surface, which may affect the adsorption of ionic surfactants. The important parameters that need to be manipulated are pH value and counterion concentration. Counterions help to reduce the electrostatic repulsion between the incoming ions and the like-charged head groups of surfactants on the surface to promote the dense adsorption of surfactants.

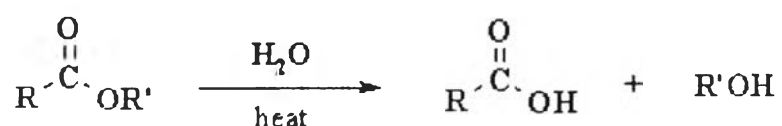
Step 2: Monomer Adsolubilization. The relatively hydrophobic monomers preferentially partition into the hydrophobic interior of the admicelle in the process called “adsolubilization”.

Step 3: Polymer Formation. The admicellar polymerization is started by addition of an initiator. Polymerization occurs in the admicelle bilayer with reaction similar to the emulsion polymerization.

Step 4: Surfactant Desorption. Surfactant is removed by washing with water, exposing the polymer film on the substrate surface.

1.2 Hydrolysis: Conversion of Esters into Carboxylic Acids

Esters undergo the same kinds of reactions for other carboxylic acid derivatives, but they are less reactive toward nucleophiles than either acid chlorides or anhydrides. Esters are hydrolyzed, either by aqueous base or by aqueous acid, to yield carboxylic acids plus alcohols:



Acid-catalyzed hydrolysis of esters can occur by more than one mechanism, depending on the structure of substrate. The usual pathway, however, is just the reverse of the Fisher esterification reaction. The ester is first activated toward nucleophilic attack by protonation of the carboxyl oxygen atom, and nucleophilic attack by water then occurs. Transfer of a proton and elimination of alcohol yields the carboxylic acid. This hydrolysis reaction is the reverse of a Fisher esterification reaction.