
by

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June 2005, Hong Kong
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Table of Contents

Title Page ................................................................. i
Authorization Page ..................................................... ii
Signature Page .......................................................... iii
Acknowledgements ...................................................... iv
Table of Contents ....................................................... v
List of Figures and Tables ............................................. viii
Abstract ........................................................................ xiii

Chapter 1   Introduction ................................................ 1
1.1        Prologue ......................................................... 1
1.2        Objectives ....................................................... 2
1.3        Structure of Thesis ........................................... 2

Chapter 2   Literature Review ......................................... 3
2.1        Introduction .................................................... 3
2.2        Cotton fibers .................................................. 4
2.3        Durable / Permanent press ................................ 7
2.3.1     N-methylol cross-linking agents ..................... 8
2.3.2     Non-N-methylol cross-linking agents ............... 12
2.3.3     Fabric softeners or lubricants ......................... 14
2.4        Fabric finishing process ................................. 15
2.5        Application of nano-particles in textile industries 18
2.6        Emulsion Polymerization of nano-particles and characterizations 20
Chapter 3  Synthesis of and Characterization of nano-particle emulsions

3.1 Introduction ............................................. 23
3.2 Experimental Section ..................................... 24
  3.2.1 Synthesis of nano-emulsions ......................... 24
3.3 Analytical Procedures .................................... 28
3.4 Results and Discussions ................................ 31
  3.4.1 Synthesis parameters .................................. 31
  3.4.2 Effect of monomers ..................................... 35
  3.4.3 Particle size distribution and morphology .............. 37
  3.4.4 Thermal properties ..................................... 40
  3.4.5 Formation of nano-films upon heating .................. 42
  3.4.6 Surface functionalities ................................ 46
  3.4.7 Mechanical properties ................................ 51
3.5 Summary .................................................. 54

Chapter 4  Fabric treatment ................................... 55

4.1 Introduction ............................................. 55
4.2 Experimental Section .................................... 56
  4.2.1 Fabric treatment process ............................... 56
  4.2.2 Testing standards and analytical procedures ............ 57
4.3 Results and Discussion .................................. 61
  4.3.1 Cross-linking agent (DMDHEU) ......................... 61
  4.3.2 Softeners .............................................. 63
  4.3.3 MgCl2 cross-linking catalyst ......................... 64
4.3.4 Padding pressure.................................................. 65
4.3.5 Effect of moisture.................................................. 66
4.3.6 Curing............................................................... 67
4.3.7 Nano-particle effect............................................... 70
4.3.8 Implementation of nano-particles in commercial laboratory..... 84
4.4 Summary............................................................. 87

Chapter 5 Rheological studies of nano-emulsion ....................... 88
5.1 Introduction.......................................................... 89
  5.1.1 Background..................................................... 89
  5.1.2 Optical rheology............................................... 91
5.2 Experimental Section............................................... 94
5.3 Results and Discussion........................................... 96
  5.3.1 Optical rheology............................................... 98
5.4 Summary............................................................. 102

Chapter 6 Conclusions and future work................................. 103
6.1 Conclusions.......................................................... 103
6.2 Future work.......................................................... 105

References.................................................................. 106
## Lists of Figures and Tables

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Schematic diagram of cellulose fiber</td>
<td>5</td>
</tr>
<tr>
<td>2.2</td>
<td>Repeat unit for cellulose by condensation of glucose molecules</td>
<td>5</td>
</tr>
<tr>
<td>2.3</td>
<td>Preparation of DMDHEU</td>
<td>9</td>
</tr>
<tr>
<td>2.4</td>
<td>Cross-linking between DMDHEU and cellulose</td>
<td>10</td>
</tr>
<tr>
<td>2.5</td>
<td>1,2,3,4 butane tetra carboxylic acid (BTCA)</td>
<td>13</td>
</tr>
<tr>
<td>2.5</td>
<td>1,2,3-propanetricarboxylic acid (PCA)</td>
<td>13</td>
</tr>
<tr>
<td>2.6</td>
<td>Positive SIMS spectrum of polystyrene</td>
<td>22</td>
</tr>
<tr>
<td>3.1</td>
<td>Conversion of emulsion polymerization with time</td>
<td>25</td>
</tr>
<tr>
<td>3.2</td>
<td>Schematic diagram of emulsion synthesis</td>
<td>25</td>
</tr>
<tr>
<td>3.3</td>
<td>Schematic drawing of film for tensile test</td>
<td>30</td>
</tr>
<tr>
<td>3.4</td>
<td>Kinetic equations of radical polymerization</td>
<td>31</td>
</tr>
<tr>
<td>3.5</td>
<td>Particle size at different synthesis temperatures</td>
<td>32</td>
</tr>
<tr>
<td>3.6</td>
<td>Particle size at different amount of surfactants</td>
<td>34</td>
</tr>
<tr>
<td>3.7</td>
<td>Structure of 2-Hydroxyethyl methacrylate (HEMA )</td>
<td>35</td>
</tr>
<tr>
<td>3.8</td>
<td>Structure of Butyl Acrylate (BA)</td>
<td>35</td>
</tr>
<tr>
<td>3.9</td>
<td>Structure of n-Butyl Methacrylate (BMA)</td>
<td>35</td>
</tr>
<tr>
<td>3.10</td>
<td>Structure of Styrene (St)</td>
<td>36</td>
</tr>
<tr>
<td>3.11</td>
<td>Structure of Isoprene (Iso)</td>
<td>36</td>
</tr>
<tr>
<td>3.12</td>
<td>List of glass transition temperatures of individual polymers</td>
<td>36</td>
</tr>
<tr>
<td>3.13</td>
<td>Schematic diagram of nano-particles with PS/PHEMA</td>
<td>37</td>
</tr>
<tr>
<td>3.14</td>
<td>TEM image showing particles in narrow size range</td>
<td>38</td>
</tr>
</tbody>
</table>
Figure 3.15  TEM image showing particles exist in nano-sized spherical shape  38
Figure 3.16  SEM image showing regular packed particles  39
Figure 3.17  AFM image showing spherical particles in very regular packing  39
Figure 3.18  DSC plot of PS/PHEMA co-polymeric particles  41
Figure 3.19  AFM contour map of particles at 25°C  43
Figure 3.20  AFM contour map of particles at 80°C for 15 minutes  43
Figure 3.21  AFM contour map of particles at 80°C for 30 minutes  44
Figure 3.22  TGA curve of PS/PHEMA copolymer  45
Figure 3.23  Structure of repeating unit of PHEMA  46
Figure 3.24  Structure of repeating unit of PS  47
Figure 3.25  Structure of SDS  47
Figure 3.26  Mass spectrum of nano-particle of PS only by ToF-SIMS  47
Figure 3.27  Mass spectrum of nano-particle of PS/PHEMA by ToF-SIMS  49
Figure 3.28  Core-shell structure of PS/PHEMA  50
Figure 3.29  Mass spectrum of nano-particle of PS/PHEMA after heating at 80°C for half an hour by ToF-SIMS  50
Figure 3.30  Stress-strain curve for tensile modulus calculation  51
Figure 3.31  Young’s Moduli at different strain rates  52
Figure 3.32  Extrapolation of Young’s Moduli at different strain rates  53
| Figure 4.1 | Flowchart of the Pad-Dry-Cure fabric treatment process | 57 |
| Figure 4.2 | Schematic diagram of woven cotton fabric | 57 |
| Figure 4.3 | Schematic diagram of sample preparation in tensile test | 58 |
| Figure 4.4 | Schematic diagram of sample preparation in tearing test | 59 |
| Figure 4.5 | Simulation of recovery angle measurement | 60 |
| Figure 4.6 | Molecular structure of DMDHEU resin | 62 |
| Figure 4.7 | Effect of resin on the recovery angle | 62 |
| Figure 4.8 | Effect of softener amount on the mechanical strength | 63 |
| Figure 4.9 | Effect of catalyst at constant amount of resin on the mechanical strength | 64 |
| Figure 4.10 | Effect of padding pressure on the recovery angle | 65 |
| Figure 4.11 | Effect of wet-up-pick percentage | 66 |
| Figure 4.12 | Thermal degradation of cotton fabric | 67 |
| Figure 4.13 | Recovery angle of fabric treated at various curing temperatures and times | 68 |
| Figure 4.14 | Tensile strength retention on various curing temperature and time | 69 |
| Figure 4.15a | Tensile test curve of resin at 120g/L | 70 |
| Figure 4.15b | Tensile test curve of resin at 240g/L | 71 |
| Figure 4.15c | Tensile test curve of resin at 360g/L | 71 |
| Figure 4.16a | Recovery angle results of various emulsions | 72 |
| Figure 4.16b | Tensile strength results of various emulsions | 73 |
Figure 4.17a  Tearing strength results of various emulsions 73
Figure 4.17b  Tensile strength results of various emulsions 74
Figure 4.17c  Recovery angle results of various emulsions 74
Figure 4.18   Performance of copolymer St/Iso/HMA 76
Figure 4.19a  SEM micrographs of nano-particles coated yarn 77
Figure 4.19b  SEM micrographs of nano-particles coated yarn 77
Figure 4.19c  SEM micrographs of nano-particles coated yarn 78
Figure 4.20a  SEM micrographs of nano-film coated yarn     79
Figure 4.20b  SEM micrographs of nano-film coated yarn     79
Figure 4.20c  SEM micrographs of nano-film coated yarn     80
Figure 4.20d  SEM micrographs of nano-film coated yarn     80
Figure 4.21   SEM micrographs of nano-particles coated yarn (a-h) 81
Figure 4.22   Tensile result for presence of nano-particle in commercial recipe and UST recipe 84
Figure 4.23   Tearing result for presence of nano-particle in commercial recipe and UST recipe 85
Figure 4.24   DP rating result for presence of nano-particle in commercial recipe 86
Figure 4.25   DP rating result for presence of nano-particle in UST recipe 86
| Figure 5.1   | Optical train block diagram          | 94 |
| Figure 5.2  | Shearing effect on water             | 96 |
| Figure 5.3  | Viscosity of nano-particle solution under different shear rates relative to water | 97 |
| Figure 5.4  | Molecular structure of PS repeating unit | 98 |
| Figure 5.5  | Molecular structure of PHEMA repeating unit | 98 |
| Figure 5.6  | Dichroism change in solution under shear | 99 |
| Figure 5.7a | Dichroism change in solution under different shear rates | 100 |
| Figure 5.7b | Shorter time range of dichroism change | 100 |
Abstracts

This study examined the mechanical and durable press properties of cotton woven apparels by applying nano-technology. Cotton fiber is an important material in the textile industry. However, its poor smoothness performance after laundering has caused a major problem in its application. Durable press finishing process can increase wrinkle resistance but also induce deleterious loss in mechanical strength in treated fabric due to the rigid cross-linking formed on the other hand. Nano-sized polymeric particles have been synthesized and characterized to solve this problem.

A core-shell structure has been observed in the particles with functional polymer on the surface. Nano-particles exhibit functional groups such as hydroxyl and carboxylic groups will react with hydroxyl groups present in the cellulosic fiber. After curing, those particles will form a film on the fabric surface which then will help to impart the mechanical strengths. The fabric treatment process is optimized by varying different parameters such as the proportion of cross-linking reagent and catalyst as well as the curing temperature and duration time. Results indicated that application of nano-particles will improve the tensile, tearing strength as well as the abrasion resistance of the treated fabric. Both tensile and tearing strength retentions are increased by at least 20% when compared with native fabric.

Rheological studies provided useful information for the particles under shear. Shearing thickening effect indicated the formation of clusters for the particles under shear. Optical rheological result suggested that fabric treatment with nano-particles should be not done under vigorous stirring in order to prevent agglomeration of particles.
Chapter 1  Introduction

1.1 Prologue

Cotton has been one of the most widely used materials in the textile industry for several centuries. The reason that its role has not yet been replaced by synthetic fiber is mainly due to its comfort ability to users. It has good moisture absorption and quite strong in strengths. A major problem with all-cotton apparel is its undesirable wrinkle characteristic during wearing and laundering.

Durable press is the fabric finishing process, through which, the fabric is treated with reactants or resin to impart the wrinkle-resistant. However, there one of the most deleterious effects is that the treated fabric will greatly lose its mechanical strengths due to the rigid cross-linking and acid degradation through the process. Many researchers are now still focusing on reducing the strength loss in the wrinkle free cotton apparels.

Nano-technology has been used to modify the functionality of the fabric such as the anti-microorganism or absorption of odors in the recent researches. Now, we proposed to use nano-technology to solve the problem. Polymeric nano-particles are used to overcome the mechanical strengths loss of permanent press fabric. Nano-sized particles can be produced through emulsion synthesis by using different functional monomers. Characterizations on the particles will help to know the functionality of those particles which in turn help to interaction mechanism between the particles and the cotton fibers.
1.2 Objectives

In this study, functional polymeric nano-particles have been designed and synthesized through emulsion polymerization to overcome the loss in mechanical strength in wrinkle free cotton apparels. Also, we aim to characterize the nano-particle through its thermal properties, mechanical properties, surface analysis as well as the rheological behavior studies. This will in turn allow us to know the interaction mechanism between the functional particles with the cellulose fibers.

This project is using nano-polymeric material with functional surface to bond with the cellulosic fiber to improve the wrinkle resistance and impart mechanical strength of cotton fabric. Moreover, rheological experiment will be used to investigate the effect of particle morphology and concentration on the coalescence structure as well as the film properties in order to simulate the particle behavior on the coated fabric.

1.3 Structure of thesis

The thesis is composed of 6 chapters. Chapter 2 is a literature review on cotton apparels and durable press treatment process. Chapter 3 will illustrate how the particle is synthesized and characterization of the particles. Fabric treatment results and discussion will be founded in Chapter 4. Chapter 5 will discuss about the rheological behavior of the nano-particle solution. Finally, it comes to the conclusions in Chapter 6.
Chapter 2  Literature Review

2.1 Introduction

Cotton is still the "King" of fibers in textile industries. Cotton fabrics have been found dating back to 3500BC, but their use in the civilizations of Mesopotamia, Babylon and Egypt was not recorded until about 500BC [Munro J., 1987, Dodge B.S., 1984]. More than half of the world's cotton crops are produced in three countries: the United States of America, the Russia and the People's Republic of China.

Cotton fiber is a popular material for textile manufacturers because of its good moisture absorption and comfort to users. However, poor smooth drying properties after laundering caused limitations in applications [Norton, 1998]. Research studies on improving the wrinkle resistance of cotton have been started since early nineteenth century. Textile and apparel manufacturers spent more than US$60 billion in durable press finishing in US market [Hurwitz, 1987].

Durable press treated cotton apparels have the problem of significant loss of mechanical properties due to the rigid cross-links formed to resist the slippage of cellulose chain which in turn prevent the formation of wrinkle. Nowadays, there is still no definitely good technique in improving the mechanical properties of durable press finished material though a wide range of research efforts has been put on it. Investigations on both N-methylol and non-N-methylol cross-linking agents have been carried out in both academic and industrial fields, but there is no definite solution yet.
2.2 Cotton fibers

Cotton fiber is one kind of single-cell fibers and develops from the epidermis of the seed. The elongation period takes about 17 to 25 days after flowering [Karmakar, 1999]. Cellulosic fiber has comprised the most important segment of the textile mill and apparel industries. The cellulosic fabric provides comfort to users due to the fiber's good moisture absorption and wicking properties. However, cotton fabric has a high tendency to wrinkle badly and has poor smoothness in the dry state after laundering [Norton, 1998].

The structure of cotton fiber can be viewed in two directions: longitudinal and cross-sectional. The longitudinal view reveals that the fiber has a ribbon-like structure with twists, called convolutions, at irregular intervals along the fiber. From the cross-sectional view, cotton fiber consists of several sub-layers including the outer cuticle, primary layer, secondary layer and a hollow inner lumen as illustrated in Figure 2.1. The primary layer is made up of wax, protein and amorphous cellulose and it acts as a protective layer to the whole structure. In this regime, the cellulose chains are randomly packed together. Ninety percent of the weight of the fiber comes from the secondary layer which is made up of the semi-crystalline cellulose. Due to the regular packing of the cellulose chains, this part contributes most of the mechanical strength to the fiber. Finally, the central hollow lumen is used for transportation of water and nutrient to the plant when it is alive.
In natural cellulosic fibers, there are 3000-5000 glucose units joined together by condensation, in which cellobiose is the repeat unit as shown in Figure 2.2. There exist six hydroxyl groups per repeat unit and then throughout the cellulose chain, enabling it to react with some other chemicals by covalent bonding or hydrogen bonding.

The moisture absorption ability of the fiber comes from the presence of hydroxyl groups as well. The hydrophilic hydroxyl groups will tend to absorb sweat coming
out from the user. Removing sweat from skins makes the user feel very comfortable.

However, the poor smooth performance of cotton upon the external stress in dry state is the major obstacle for applications. Under distortion or moist conditions, the hydrogen bonds holding the cellulose chains are ruptured. In order to minimize the stress within the fiber, the cellulose chain slides. The new position of chains resulted in wrinkle formation.
2.3 Durable / Permanent press

The term permanent press refers to fabrics and resulting garments that have been treated with reactant or resin composition to impart smoothness and retention of creases in wearing and after laundering. Durable press, wrinkle resistant, crease resistant and easy care are the other terms to describe such phenomenon [Hurwitz, 1987].

Permanent press finishes involves the use of some cross-linking agents to form covalent bonds with adjacent cellulose polymer chains, these give cotton some elastic and resiliency properties. However, the early studies was well recognized the loss in physical strength on treatment with formaldehyde-containing compound. When external stress is applied to the fiber, these newly formed cross-links are able to pull the cellulose chains back into the position after the removal of force resulting in wrinkle resistance [Norton, 1998, Chen, et al., 2004]. These bonds usually take place in the amorphous region of the fiber. The rigid cross-links bound cellulose molecular segments together and block the chain slippage. The loss of chain slippage leads to stress being distributed unevenly among cellulose chains [Chen, et al., 2004]. Nevertheless, these rigid cross-links provide wrinkle resistant properties and also lower the mechanical strengths. This technology can be traced back to 1907, Eschalier treated cellulosic materials, depolymerized celluloses and specifically regenerated celluloses with formaldehyde under acidic conditions to improve strength of durable press finished fabric.
2.3.1 N-methylol cross-linking agents

Various cross-linking agents are commercially available, including N-methylol and non-N-methylol cross-linking agents. The former is of low cost and high efficiency but toxic formaldehyde molecules will be emitted during the finishing process and these molecules are unflavored as they do harm to human beings. Studies showed that formaldehyde is a carcinogen to animals. Severe irritation will be resulted to the eye, mucous membrane and skin in human beings. However, N-methylol cross-linking agent is still widely used in durable press finishes because of their low expense, easy application and excellent durable press properties. Among these, dihydroxymethyl-4,5-dihydroxyethylene urea (DMDHEU) is the most commonly used in the textile industries because of its low formaldehyde release.

Cross-linking agent dihydroxymethyl-4,5-dihydroxyethylene urea (DMDHEU) resin is prepared by reacting urea and glyoxal and then followed by two moles of formaldehyde as illustrated by the following equation Figure 2.3.
The outstanding performance of DMDHEU when compared with other similar compounds was found to be related to the activities of the 1 and 5 hydroxyl groups. Moreover, it is less sensitive to acid hydrolysis and dyes which also caused the success of DMDHEU in the durable press industry [Hurwitz, 1987]. The reaction between DMDHEU and cellulose can be simulated by Figure 2.4. However, there is a deleterious effect in mechanical strengths; more than 60% on the strength loss is resulted due to the treatment. It is found that the strength loss in the durable press finishing fabric is mainly attributed to by two factors: acid-catalysed depolymerization of cellulose molecules and cross-linking of cellulose molecules [Kang, et al., 1998].
The catalysts used in the N-methylol cross-linking agents are metal salts of mostly inorganic acids. Acid catalysts such as magnesium chloride, aluminum chloride and zinc chloride hydrates are needed for initiating the reaction. Stronger acid is a better catalyst, however, it will induce greater damage to the cellulosic fiber through hydrolysis. Blending citric acid and aluminum chloride is used in the quick catalysis for short time curing process. The wrinkle resistance of treated fabric is found to increase as the catalyst concentration increased and then came to a stabilized state as further increasing the catalyst concentration [Lickfield and Yang, 1998].
The catalyst used caused degradation of cellulose, thus reducing the mechanical strength of the cotton fabric. The magnitude of fabric strength loss is affected by the temperature, time, and concentration of the catalyst. Therefore, proper selection of catalyst is an essential factor in controlling the balance between wrinkle resistant and mechanical strength loss. Magnesium chloride is the most commonly used catalyst in the commercial world because of its better durable press performance and less degradation.
2.3.2 Non-N-methylol cross-linking agents

The emission of toxic formaldehyde molecules by using N-methylol containing cross-linking agent caused obstacles during application. Therefore, non-formaldehyde alternatives are investigated. Research studies by using some other organic acids alone or combined with DMDHEU have been carried out [Hsiung, et al., 2004, Mao and Yang, 2001].

Extensive efforts have been make to use organic acid to replace the traditional DMDHEU due to the increasing concern with the toxicity of formaldehyde [Mao and Yang, 2001]. Polycarboxylic acid is most commonly used, typically BTCA(1,2,3,4 butane tetra carboxylic acid) or citric acid, by the existence of carboxylic group to form ester with the hydroxyl groups present in the cellulose. Polycarboxylic acid has been shown to impart high level of wrinkle resistance and smooth drying properties as it contains three and six carboxylic groups per molecules [Welch, 1990]. Sodium hypophosphite is the most effective curing catalyst by using BTCA as the cross-linking agent.

Researches in using BTCA for the purpose of durable press have been widely investigated. However, BTCA is expensive to use and citric acid causes yellowing. The low yield cross-linking esterification with the cellulose fibers, higher curing temperature and time must be used to obtain wrinkle resistance. Moreover, the breaking strength and tearing strength of finished fabrics are almost 50% lower than those of untreated fabric [Norton, 1998]. One of the alternative approaches is using polymers of maleic acid to form ester cross-links, and yet another to fix a quaternary group through an epoxidation reaction to the cellulose chain to form cross-links.
[Norton M., 1998].

![Butane Tetra Carboxylic Acid (BTCA)](image)

More recent development has been carried out by using 1,2,3-propanetricarboxylic acid (PCA). It is found that PCA is more effective cross-linking agent [Mao and Yang, 2001]. Both BTCA and PCA formed a five-membered cyclic anhydride in the same temperature region but PCA is able to bond to cotton cellulose through esterification and form a second five-membered cyclic anhydride intermediate which can further esterify cotton to form cross-links.

![1,2,3-Propanetricarboxylic Acid (PCA)](image)

Organic acids such as acrylic acid and maleic acid have been tried with cotton fabric to improve the wrinkle resistance by esterification of their functional groups with hydroxyl groups on cellulose [Undomkichdecha, et al., 2003]. However it does not provide good physical properties to the fabric as well as the whiteness compared with DMDHEU.
2.3.3 Fabric softeners or lubricants

The durable press fabrics suffer from loss of mechanical strengths, poor hand feel and moisture management. Fabric softeners or lubricants may be used to mitigate these deficiencies [Hurwitz, 1987]. The softeners may have reactive functional group which provides elastomeric finishes imparting higher crease resistance, good dimensional stability (smooth drying properties) and excellent soft hand feeling with good sewability. They can also reduce free formaldehyde release by replacing part of the resin. There are four basic types of softeners: anionic, cationic, non-ionic and blended systems. Anionic softeners tend to provide inferior softness compared with others but incompatible with some resins due to their negative charge. Cationic softeners are with better compatibility with resins but they have high tendency to change the shape or affect the fastness of certain dyestuffs. The discoloration problem goes to both cationic and non-ionic softeners. Among these, blended softeners are able to optimize the softening and lubricating properties. Typically, an aminosilicone and cationic polyethylene blend is used in the durable press treatment system. Presence of softeners will increase the tearing strength, tensile strength as well as the abrasion resistance [Lee and Kim, 2004]. It is thought that the softening agent acted as a lubricant in the treated fabrics so that slippage could occur between the fibers or at points of the intersection of the warp and filling when they were stressed. However, the effect caused by softeners is not long lasting as they will be washed away.

In both formaldehyde and non-formaldehyde releasing durable press finishing processes, there is a great loss in mechanical strength of the treated fabric due to the degradation and cross-linking cellulose [Lickfield, 2001].
2.4 Fabric finishing process

Cross-linking agents can be applied to cotton fabrics by number of ways. The Pad-dry-cure technique and the wet-fixation techniques are two most common ways. The Pad-dry-cure is the conventional technique and it is simple and easy. This technique is able to provide good wrinkle recovery angle and durable press (DP) rating to the treated sample but also with high loss in the mechanical strengths. Two major factors contributing to the loss in mechanical properties: fiber degradation caused by the acid catalyst at elevated temperatures; and the restriction of stress distribution within the fibers due to their rigid cross-linking by monomeric resins [Shin and Hollies, et al., 1989].

Wet-Fixation technique [Hollies, 1967] is able to give a good balance between the strength and wrinkle resistance by using two resin components in two steps. However, this method is very time consuming. Therefore, it is not very practical to be used in the commercial industries.

The major current application methods in applying pad-dry-cure technique are based on the following processes: pre-cure, post-cure, garment-dip, spray application and vapor phase [India Apparel Portal].

In pre-cure, the fabric is treated with resin, dried and cured in flat open-width form before it is made into garment. However, crease recovery may be decreased during the iron pressing of garment.

In order to solve the problem mentioned above, a post-cure process gives an alternative to produce a garment with smooth drying and wrinkle resistant properties.
for the service life of the garment. In this process the resin is padded onto the fabric and dried at low temperature for a mild curing before cutting and constructing into garment. Higher degree of cross-linking is formed by using high temperature cure. However this process has not been widely adopted because fabric manufacturers and garment manufacturers can hardly be the same one, which are able afford processing these two steps together.

For garment manufacturers, garment-dip method must be the best solution among all these processes. Garments are constructed from non-resinated fabric, and then it is impregnated with a resin formula similar to that used in the post-cure process. Pad-Dry-Cure process is used [Norton, 1998]. The garment is first dipped into resin together with other chemicals such as the softeners and catalyst. It is then padded through two plastic rollers to obtain a suitable wet-pick-up percentage. Tumbling drying is followed in order to get optimum moisture content before the critical curing step. Finally, it is the curing of garment inside oven at high temperature to allow the formation of cross-links between the resin and the cellulose fibers. These procedures have been widely used in the industries because they can be batch processed which save time and money.

In the spray method, the resin is applied by spraying it onto the garment during tumbling in an enclosed rotational device. A microprocessor is used to meter the exact amount of chemicals and to control the rotation time, desired wet pick-up, spray rate and process time. The garments are then pressed and cured similar to post-cure process. However, it is reported in existence of difficulties in control, potentially resulting in uneven treatments and higher strength losses.
There are patents on the durable press finishing process in investigating the optimum moisture content of the water to get better wrinkle-free performance [Payet, 2003]. Fabric treated with durable press finishing process will have unacceptable loss in tensile strength, tear strength and abrasion resistance when rigid cross-linkings are formed. Therefore, many aspects must be considered when choosing the technology. Wrinkle resistance process, time, temperature, and chemicals. For high quality pressing of 100% cotton, permanent press garments, the two most important criterions are temperature and the control of treatment cycle. This temperature is crucial as it starts the curing process and controls the overall fabric smoothness.
2.5 Application of nano-particles in textile industries

There are wide applications of polymeric material in the properties enhancement in the textile industries [Soane, et al., 2002, 2002, Payet, 2003]. Polymeric resinous additives that are capable of forming soft film such as a latex or aqueous dispersion of polyethylene, alkyl acrylate polymers, acrylonitrile-butadiene copolymers and polyurethanes, are used in textile technology. Likewise, fabric softeners or lubricants are also polymeric materials such as elastomers which can enhance the properties of textile.

Textiles treated with nano-particles exhibit a greatly improved retention or durability [Soane, et al., 2003]. The polymeric encapsulator of the payload nano-particle has a surface that includes functional groups for binding or attachment to the fibers of the textile in order to provide permanent attachment of the payload to the textile. Alternatively, the surface of the nano-particles includes functional groups that can bind to a linker molecule that will in turn bind or attach the nano-particles to the fiber. Such textiles exhibit a greatly improved retention or durability of the payload agent.

Coating of thin polymeric film onto the fabric surface is very popular in the recent years. Polymeric materials have been used to bind with textile fiber to give water or oil repellency. However, the physical and mechanical properties depend not only on the nature of the polymers but also the method of forming films [Stewards P.A., et al., 2000].

Polymer films can be made by spreading a water-based dispersion of soft particles onto a substrate, and then evaporating water until the particles come into contact and fuse together [Chevalier, et al., 1992]. The process of film formation could be
divided into four steps: Ordering of particles in concentrated solution through evaporation; contact between neighboring particle; coalescence of the particles; and finally interpenetration of the cores of the particles. It is also found that mechanical property of film would be affected by the film structure. Latex films formed by simply evaporation would have better mechanical property than solvent-casting film [Charmerau, et al., 1996].

Films made of soft particles with thin surfactant membranes have a continuous elastomer matrix with hydrophilic inclusions in it [Chevalier, et al., 1992]. The monomers, oligomers, or polymers may be copolymerized with soft or rubbery monomers to impregnate and thereby increase the durable press properties, to add to the softness, and to aid in the mechanical properties.

Textile reactive nano-particles may be applied to the fabric in conjunction with such soft or rubbery monomers or polymers. The rubbery groups will provide the necessary degree of wrinkle resistance, softness, durability, strength and abrasion resistance [Soane, et al., 2003].
2.6 Emulsion Polymerization of nano-particles and characterization

There are two classes of polymerization process by considering the underlying polymerization mechanisms, step-growth polymerization and chain-growth polymerization [Young and Lovell, 1991].

Step-growth polymerization mainly occurs between the functional groups present in monomers. Chain-growth polymerization involves the reaction of monomer with a reactive end-group on the growing chain. It usually requires an initial reaction between the monomer and an initiator to start the growth of the chain.

Free-radical polymerization in the chain-growth polymerization is the most widely practiced method, especially for monomers with general structure CH₂=CR₁R₂. Three stages are involved in this polymerization: initiation, propagation and termination. Free radicals formed in the initiation stage acts on the monomers to start up the polymerization. Propagation stage involves the rapid growth of the chain by sequential addition of monomers to the active centre. Finally, the growth of the polymer chain is terminated by combination and disproportionation.

Four commonly used methods for performing free-radical polymerizations: bulk polymerization, solution polymerization, suspension polymerization and emulsion polymerization. Bulk polymerization is simplest method involves only monomers and monomer soluble initiator. However, the viscosity of the reaction medium increases rapidly during the reactions which caused the difficulty in the heat transfer management. This problem can be solved by using solution polymerization with the using of solvent. On the other hand, the presence of solvent leads to the other complications. Suspension polymerization and emulsion polymerization are more
commonly used in industrial. The major difference between these two polymerizations is the presence of surfactant in emulsion polymerization but not in the suspension polymerization. The surfactant adsorbed in the context of emulsion polymerization can lower the interfacial tension and impart stability to the latex particles [Ali, et al., 2005]. Moreover, the size of particles from suspension polymerization is typically larger than that from emulsion polymerization. Therefore, emulsion polymerization is more suitable for nano-sized particle synthesis.

Particles made up by copolymer PS/PBA have been synthesized with the diameter of 50nm to 150nm to study the film formation structure [Chevalier Y., et al., 1992]. Multi-step emulsion polymerization is used to form particles in homogeneous composition and with only one glass transition temperature. TEM has been used to characterize the size of the particles while small-angle scattering experiment is used to examine the transformation of a dispersion into a continuous film.

Senshu [Senshu, et al., 1995] has successfully used TEM and contact angle measurement to characterize the core-shell structure of PS/PHEMA block copolymer in latex particles. It is confirmed that PS and PHEMA will appear in separated structure with either PS or PHEMA on the surface depending on the synthesis method. This is because the hydrophobic PS and hydrophilic PHEMA have different responses towards different medium. Similar techniques have been applied to prepare nano-particles of core-shell structure by using different monomers such as MMA, BMA and others [Kalinian and Kumacheva, 1999].

Secondary Ion Mass Spectrometry (SIMS) has been shown to differentiate polymers
such as polyethylene, polypropylene and polystyrene [Chan, 1993]. Positive ion spectra of different polymers have been interpreted by identifying corresponding atomic molecular unit (amu) peaks. For instance, polystyrene will give a strong intensity at 91 amu as shown in Figure 2.7. It is also reported that high resolution ToF-SIMS shows the easier of ion assignment for differentiation of the polymers.

![Positive SIMS spectrum of polystyrene](image)

**Figure 2.7 Positive SIMS spectrum of polystyrene [Chan, 1993]**

Both Atomic Force Microscope (AFM) and ToF-SIMS have been used for the surface characterization the polymer film by PS and PMMA copolymers [Bertrand 2004]. The characteristic peaks for constituent polymers are taken in the positive mode. ToF-SIMS results indicated the increase of PS concentration on the surface after annealing for copolymers. AFM result showed the surface displays some topographical features similar to islands on a matrix but the phase image showed no phase separation.

Nano-sized particles are desired because it has a larger surface to volume ratio which in turn provide higher ratio of functional groups on the surface for the bonding to the cellulose fibers. Moreover, as the surface of the cellulose fiber is very rough, smaller particles are able to be located in the “valleys” on the fiber surface.
Chapter 3  Synthesis and characterization of nano-particle emulsions

3.1 Introduction

Studies on applications of polymeric latexes have been very popular in recent years. The technique of preparing these latexes has been well-developed for various purposes. There are patents of using particles in nano-size as the encapsulator for payload reacted to the fibers of the textile to provide permanent attachment [Soane et al., 2003]. Durable press finishing treated fabric coated with polymeric material is able to provide softness, durability and better mechanical properties compare to uncoated durable press finishing treated fabric.

Nano-sized polymeric particles have been prepared by emulsion polymerization. They have large surface to volume ratio which will be more effective in surface functioning. Various functional monomers have been chosen to provide different properties. The main objective is to coat polymeric particles on the fiber surface which may form a layer of thin film. This thin film may impart better tensile strength, tearing strength as well as the abrasion resistance to the durable press finished fabric.

Core-shell structured particles consist of a co-polymer with functional groups on the surface to react with the hydroxyl groups present in the cellulose fibers to form covalent bonds. These covalent bonds will hinder the formation of rigid cross-linkings by the cross-linker. On the other hand, polymeric films coated on the fiber surface might impart better mechanical performance to the treated fabric.
3.2 Experimental Section

The chemicals for synthesis were of analytical grade, which are commercially available from SIGMA or ALDRICH. The experiment was carried out either in small scale of simple reflux setup or larger batch scale using a fermentor with 2 liters capacity under nitrogen purge.

3.2.1 Synthesis of nano-emulsions

Free radical emulsion polymerization can be divided into several stages. In the first stage, the surfactant molecules form spherical aggregates known as micelles with the hydrophilic heads pointing towards the aqueous medium with a hydrophobic core. Primary free radicals formed by initiator reacting with monomer in the aqueous phase produce oligomeric radicals, which are then diffused into the monomer-swollen micelles to initiate the polymerization (Figure 3.1 interval I). Afterwards, monomers will continue to diffuse into the micelles and eventually the monomer droplets in the aqueous phase will be exhausted (Figure 3.1 interval II). Propagation takes place inside the micelles. The monomers will attach to the active center on the oligomeric radicals to grow into long chains until all the monomers present inside are polymerized to form the polymeric particles. The reaction is terminated by the combination of chains or chain transfer to hydrogen atom from one chain to another (Figure 3.1 interval III).
Figure 3.1  Conversion of emulsion polymerization with time

Figure 3.2  Schematic diagram of emulsion synthesis
The fermentor process was started by adding the stabilizer sodium hydrogen carbonate NaHCO₃ and surfactant lauryl sulfate CH₃(CH₂)₁₁SO₄⁻Na⁺ (SDS) into 1.4L water and stirred inside the reactor with speed of 400 revolutions per minute under a nitrogen gas medium. The alkaline stabilizer NaHCO₃ provided a suitable pH medium. Presence of surfactant would prevent the agglomeration of the polymer chains during the reaction, thus allowing the formation of stable colloids in small size. Prior to reaction, a constant nitrogen purge at 500 ml/min was applied for at least 10 minutes to ensure that the top of the reactor was filled with an inert medium. Any oxygen may cause monomer oxidations at high temperatures and may inhibit further reaction.

The polymerization between styrene and 2-hydroxyethyl methacrylate is taken as an example. In the next stage, micelles were formed and dispersed in the aqueous medium. Meanwhile, monomers such as styrene and 2-hydroxyethyl methacrylate (HEMA) in appropriate amounts and proportions were mixed together under magnetic stirring to ensure better mixing and then added into the system. Another 10 minutes was allowed in order to make sure monomer droplets were well-dispersed in the aqueous medium. Consequently, temperature was elevated for better dispersion of monomer droplets in the water and prepared for the initiation to take place before adding the initiator. Free radicals were formed once 1.5g of the water-soluble initiator potassium peroxodisulfate (KPS) was added to the system which would initiate the polymerization by reacting with monomers. Free radicals would react with the monomers first to form oligomers. These oligomers would then diffuse into the micelle, so as the monomers. Propagation took place inside the micelle and followed by termination when all monomers had been consumed. Again, the HEMA monomers would form poly-HEMA near the aqueous medium because of its
higher hydrophilicity and styrene would form polystyrene in the core as it is hydrophobic. Therefore, particles with core-shell structure were expected. Figure 3.2 illustrated the process flow of emulsion polymerization.

All the reactants solutions were colourless before the reaction taking place. After the addition of initiator and the onset of polymerization, the solution would become bluish milky in colour if the particles were in nano-size. Otherwise, large particles would appear in opaque colour. To ensure complete conversion, the reaction was maintained for at least five hours.
3.3 Analytical Procedures

Dynamic Light Scattering machine PDDSL/CoolBatch was used to measure the particle size and size distribution after each synthesis. A laser beam was transmitted through the sample vial and the reflected ray was collected. The sample solution was first diluted by de-ionized water to very low concentrations to give a scattered intensity about one million counts. The use of low concentration was essential to minimize error reading from overlapping particles.

Freeze-drying process utilized an EDWARDS Freeze Drier (Model Supermodulys 12K) at -40°C and 10⁻¹ bar for overnight to obtain powder of nano-particles without agglomeration and damaging the particles. Under these conditions, water in the emulsion solution would be sublimed. Hence particles may retain their original position with little agglomeration upon drying.

Differential Scanning Calorimetry (DSC) analysis was carried out on a Perkin-Elmer Pyris Diamond DSC. Samples were subjected to a standard heating and cooling rate of 10 °Cmin⁻¹ under a nitrogen atmosphere. In the experiment, a sample of 10mg sample has been cooled to 0°C and isothermal for 5mins before ramping up to 250°C.

Thermogravimetric analysis (TGA) was performed on a TA Instruments TGA 2950. Samples were subjected to a scanning rate of 5 °C min⁻¹ to 500°C under a nitrogen atmosphere.

Scanning Electron Microscopy (SEM) micrographs for the specimen was coated on fiber surface were taken by a JOEL 6700F at an accelerating voltage of 5 kV. Samples were then mounted on a sample stub with copper tapes and sputter coated
with ~ 150Å of gold films to minimize charging. The electron beam interacted with the specimen and signal formed an image giving the compositional and topographic contrasts.

Transmission Electron Microscopy (TEM) micrographs were taken on the Philips CM 20 with specimen illuminated in a vacuum chamber by an electron beam with accelerating voltage of 120 kV. Emulsion drops were added to copper grid and allowed for ambient evaporation before rinsing by methanol to eliminate any impurities or dust particles on the surface.

Atomic Force Microscopy (AFM) images were obtained using a NanoScope III MultiMode™ AFM (Digital Instruments) with a hot stage at temperatures 20°C and 80°C, respectively. The maximum number of tapping per line was 512. An image was produced by scanning a solid probe on the specimen surface and detecting signals from their interactions. The probe was mounted on a thin cantilever and the deflection of light from the cantilever was the detected signal, which was caused by the dragging of probe along the specimen surface. Specimen was prepared by simply drying the solution under vacuum pump to evaporate the water on the silicon wafer substrate.

Advanced Rheometric Expansion System (ARES), TA instruments, USA, was used to characterize the mechanical properties of the thin films prepared from the nano-particles. Film specimens were prepared by hot pressing of the powder of nano-particle at 140°C for half an hour at 15 to 20 tons force between two smooth
stainless steel plates. Afterwards, it was quenched in air and cooling water consequently. Tensile experiments were performed at different strain rates to investigate the solid state viscoelasticity of the films. The Young's modulus indicates the stiffness of the film. It could be calculated from the slope of elastic deformation of stress-strain curve in the tensile test. A gauge length of 10 mm and various crosshead speeds were applied. Samples with dimensions of 10 mm in length, 0.3mm in thickness and 5mm in width were used for each test. As the films prepared were too thin to be clamped securely between grips, slight modification was done. Both ends of the specimens were first stuck to paper cards at both sides with CN gauge adhesive and then the whole assembly, as illustrated in Figure 3.3, was clamped.

![Figure 3.3 Schematic drawing film for tensile test](image)

Time-of-Flight Secondary Ion Mass Spectrometer (ToF-SIMS) was used to measure the surface composition of the specimen. Pulsed liquid metals ion beams (Cs⁺ or Ga⁺) to emit molecules and fragments form the outermost surface of a sample. This surface analysis was able to provide the information of functional groups present on the particle surface.
3.4 Results and discussions

3.4.1 Synthesis parameters

Functionality of particles depends on many parameters such as the particle size, the functions of chosen monomers. Three stages are involved in free radical polymerization process: initiation, propagation and termination. The overall kinetics in the polymerization process can be illustrated by the following equations.

![Kinetic equations of radical polymerization](image)

Figure 3.4 Kinetic equations of radical polymerization

In the initiation stage, the initiator KPS was dissociated to form free radicals by thermal reaction. An active center has then created when a free radical R' generated from an initiator attacked the π-bond of monomer molecule. As a result, the monomer being attacked would yield oligomer with active center. The propagation stage involved the growth of polymer chain by rapid sequential addition of monomers to the active center. Finally, the growth of polymer chain was terminated by either the combination of two growing chains or disproportionation by abstracting a hydrogen atom from one growing chain by another one.
The degree of polymerization and rate of reaction would depend on the monomer concentration and initiator concentration. Increasing the monomer concentration might increase degree of polymerization whilst decreasing the initiator concentration would give similar result. Therefore, in order to keep the particles as small in size, the monomer and initiator concentration in the synthesis has kept at 10 wt% and 0.1 wt% respectively for all the reactions.

On the other hand, the temperature dependence of polymerization rate and degree of polymerization are very crucial as well. The rate of polymerization would increase with the temperature but the degree of polymerization would decrease with the increase in temperature. From Figure 3.5, it is observed that for this sample formulation, the increase of temperature would actually give particles in larger size and with greater particle range. This result is contradictory to the theory [Young and Lovell, 1991].

![Figure 3.5 Particle size at different synthesis temperature](image)

Figure 3.5  Particle size at different synthesis temperature
In this study, emulsion polymerization has been used because this synthesis process would give better control on the heat transfer and latex at smaller size could be prepared. Water has been used as the reaction medium which has high specific heat capacity for better heat control for the exothermic polymerization reaction. Emulsion polymerization allows user be able to control particle morphology.

By the Smith-Ewart Equation

$$\bar{x}_n = k_p [M]_p \left( \frac{N_p}{\rho_i N_A} \right)$$

$$R_p = \frac{k_p [M]_p N_p}{2}$$

where \( \bar{x}_n \) is the degree of polymerization

\( R_p \) is the propagation rate

\( k_p \) is the rate constant for the propagation stage

\([M]_p\) is the concentration of monomers

\( N_p \) is the number of latex particles per unit volume

$$\left( \frac{N_p}{\rho_i N_A} \right)$$ is the average time interval between successive entries of the radicals into the particle

The particle size will be greatly influenced by the amount of surfactant present in the system [Bechthold and Landfester, 2000]. Assuming the rate constant \( k_p \) and monomer concentration of monomers kept constant, the increase of \( N_p \) would increase the propagation rate \( R_p \) as well as the degree of polymerization \( \bar{x}_n \) in the interval II of emulsion polymerization. However, the higher the concentration of
surfactant, the larger number of particles \([N_p]\) present in the system. When the monomer concentration is kept constant, the larger number of particles would cause less amount of monomers to diffuse into one particle. Therefore, the particle size would actually decrease with the increased in surfactant concentration.

![Graph showing particle size distribution](image)

**Figure 3.6 Particle size at different amount of surfactant**

The critical micelle concentration CMC of surfactant SDS was reported to be 2.6 g/L [Suresh et al., 2004]. The amount of surfactant used must lower than its CMC as to ensure solubility of surfactant in water because of the hydrophobic tails present in SDS.
3.4.2 Effect of monomers

Various monomers have been tried out for better performance in reducing the strength loss of treated fabric. Co-polymer has been targeted so that one of the polymers were able to provide the stiffness to the fabric while the other one will be provided the resistance to tearing, thus the elasticity. Apart from these criteria, the particle must exhibit functional surface that is able to react with the hydroxyl group in the cellulose backbone.

![Structure of 2-Hydroxyethyl methacrylate (HEMA)](image)

**Figure 3.7** Structure of 2-Hydroxyethyl methacrylate (HEMA)

![Structure of Butyl Acrylate (BA)](image)

**Figure 3.8** Structure of Butyl Acrylate (BA)

![Structure of n-Butyl Methacrylate (BMA)](image)

**Figure 3.9** Structure of n-Butyl Methacrylate (BMA)
These monomers may polymerize to form polymers with different glass transition temperatures. The glass transition temperature of the polymer is critical for the mechanical properties of that polymer. Glassy polymers show rubbery responses at temperature greater than their glass transition temperatures, whilst strong and brittle response below their glass transition temperatures.

A number of emulsions with different compositions have been prepared in this study. The characterizations presented here will be focused on the copolymer of styrene and HEMA in the volume ratio of 4 : 1.

<table>
<thead>
<tr>
<th></th>
<th>PS</th>
<th>PHEMA</th>
<th>PBMA</th>
<th>PBA</th>
<th>PIso</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_g$ (°C)</td>
<td>100</td>
<td>50</td>
<td>20</td>
<td>-40</td>
<td>-73°C</td>
</tr>
</tbody>
</table>

Table 3.12  List of glass transition temperature of individual polymers [David R.Lide 1995]
3.4.3 Particle size distribution and morphology

The light scattering analysis carried out earlier (Figure 3.5) shows that nano-particles of mean diameter about 50nm with very narrow range can be obtained. In the mean time, a number of process parameters may affect the particle size and distribution, see Section 3.4.1. PS-block-PHEMA micelles with hydrodynamic radius about 30nm have been synthesized for fluorescence studies [Liu, et al., 1996]. However, detailed size and morphology studies on the block polymer have not been carried out. Anionic living polymerization has been applied to prepare PS/PHEMA block copolymer particle in nano-sized [Sensh 1995]. Characterization has been carried out by using TEM and contact angle measurement. Their TEM results of sectioning of particles show the lamellar structures. Moreover, they proved that PS and PHEMA are in separated core-shell structure.

![Diagram of nano-particles with PS/PHEMA](image)

Figure 3.13 Schematic diagram of nano-particles with PS/PHEMA

Figures 3.14 – 3.17 show the particle size and morphology characterizations by using TEM, SEM and AFM respectively. Apparently, the result is consistent with the small angle light scattering data, the particles are of uniform size of diameters about 40nm. In addition, these particles are nearly spherical in shape. Similar nano-sized particles have been also synthesized by using PS and PBA to form copolymer, though the surfactant is different [Chevalier Y., et al., 1992]. Spherical
shaped particles with uniform size are obtained as well. However, in their study, characterization of particles has not carried out as well.

Figure 3.14  TEM image showing particles in narrow size range

Figure 3.15  TEM image showing particle exists in nano-sized spherical shape
Figure 3.16  SEM image showing regular packed particles

Figure 3.17  AFM image showing spherical particles in very regular packing
3.4.4 Thermal properties

Thermal characterization in terms of phase transition temperature and film formation characterization were carried out on DSC, TGA and AFM.

DSC is used to find out the glass transition temperatures of the polymeric nano-particles. Glass transition temperature $T_g$ is the temperature at which that polymer will transform glassy state into rubbery state [Painter and Coleman, 1997]. Polymers in the rubbery state are soft and ductile. Polymers at temperature below are stiff, strong but usually brittle. The presence of thin nano-films of combined glassy and rubbery responses may be expected to impart better tearing and tensile resistance to the cotton apparels. Both properties are targeted in our study; therefore, careful decision should be make for choosing monomers.

*Figure 3.18* shows a typical DSC thermogram of a copolymer nano-particle of PS/PHEMA. Glass transition temperature may be identified from the slope change in the thermogram heating at 10°C per minute. Two glass transition temperatures can be identified at about 60°C and 105°C respectively. The literature glass transition temperatures of PS is reported to be 100°C [Painter and Coleman, 1997] and sub-$T_g$ $\beta$ relaxation for PHEMA is about 50°C [Mark, 1996]. Therefore, we conclude that PS and PHEMA are obtained in form of heterogeneous copolymer inside the nano-sized particles. Latex particles formed by PS/PBA shows only one glass transition temperature lies between the $T_g$ of PS and PBA indicated homogenous composition [Chevalier Y., et al., 1992]. In our case, two glass transition temperatures are observed which suggest the heterogeneous composition inside the particles.
Figure 3.18  DSC plot of PS/PHEMA co-polymeric particles

In this example, polystyrene is considered as the polymer to provide stiffness to the coated fabric because its good mechanical properties such as high tensile strength and Young’s modulus. Poly (HEMA) is regarded as the polymer which is able to provide better tearing strength to coated fabric. Moreover, the presence of hydroxyl group in PHEMA would also help the attachment to the cellulose fiber. Therefore, PHEMA is regarded as the functional part in the nano-particles.
3.4.5 Formation of nano-films upon heating

AFM was used to visualize the surface morphology of the particles under heating. In both Figure 3.17 and Figure 3.19 of AFM micrographs, the particles appeared to be very spherical and regular in the shape in the ambient temperature. However, when they are heated at 80°C for 15 minutes and 30 minutes, the particles became soft as their surface became flattened as shown in Figure 3.20 and Figure 3.21. At this temperature, which is higher than the glass transition temperature of PHEMA, PHEMA present in the particle already softened in rubbery structure. Polystyrene present in the system may not undergo glass transition in this case because its $T_g$ is higher than 80°C. Therefore, it is observed in the AFM micrographs that the core part in the particles remained at the same location after half hours of heating. This result is consistent of Bertrand’s [Bertrand, et al., 2004] observation. In which PMMA formed a continuous matrix while the PS formed the droplet-like structure.

The specimen has been subjected to higher temperature 120°C to observe the morphology change. However, the surface of the particles quickly softened once the temperature has been elevated. This disabled the functionality of the silicon probe in AFM. Hence, this provided a strong indication that tendency of the particles to form film under heating at temperature higher than 120°C.
Figure 3.19  AFM contour map of particle at 25°C

Figure 3.20  AFM contour map of particle at 80°C for 15 minutes
Apart from the glass transition temperature which tells when the particles will become soft, the thermals stability must be known as well in order to ensure the particles will be stable at high temperature. It shows the ability of a material to maintain desirable mechanical properties such as tensile strength.

The decomposition temperature of PS and PHEMA are reported to be about 300°C [Mark, 1996] and 322°C [Caykara, 2003] respectively. The TGA curve showed that the particle has good thermal stability at temperatures below 300°C, with less than 5 wt% loss up the 300°C. It may due to the presence of small amount of moisture and un-reacted chemicals. Significant weight loss after 300°C is consistent with the literature values of decomposition temperatures of PS and
PHEMA. Therefore, the above result showed that the particles were quite stable under temperature below 300°C.

![Graph showing weight loss vs. temperature](image)

**Figure 3.22 TGA curve of PS/PHEMA copolymer**

The cellulose will start decomposition at 250°C. Therefore, when the particles are applied to the cotton apparels, they will be stable enough to use as well because normal textile treatment seldom goes to such high temperature.
3.4.6 Surface functionalities

ToF-SIMS has proved to be a very useful technique for polymer surface analysis. Surface molecular structure such as branching, functional groups, end groups and molecular weight could be detected.

In order to analyze the ToF-SIMS result, the corresponding peaks of PS and PHEMA were identified according to their molecular structure first. As expected, the surfactant was also present on the surface of the particles, therefore, peaks corresponding to SDS should be considered as well. Both positive spectrum and negative spectrum are able to provide information for comparison but only positive spectra is chosen for calculation as it is more structural informative. Similar analysis has been carried out by using PS/PMMA copolymer [Bertrand 2004].

Structure of PS and PHEMA were shown in Figure 3.23 and Figure 3.24 respectively, it is quite obvious that oxygen atoms must come from the PHEMA instead of PS.

![Figure 3.23 Structure of repeat unit of PHEMA](image)

46
From the result of nano-particles synthesized by styrene only, *Figure 3.26*, it is calculated that the surface mole fraction of the surfactant SDS is ~36%, and the polystyrene is 64%. The calculation is done by the intensity ratio of some major
corresponding peaks to the total intensity. The characteristic peaks for PS at 77 amu and 91 amu observed in our spectra are consistent with the standard SIMS spectrum as reported in the literature [Chan, 1993].

On the other hand, in the copolymer result, peaks with oxygen atoms must belong to the characteristic peaks of PHEMA. Hydrophobic PS and hydrophilic PHEMA will form separate structure inside the particles as discussed elsewhere [Osawa, 1992, Kalinian and Kumacheva, 1999]. The surface mole fractions of the copolymer nano-particles obtained from SIMS spectra in Figure 3.27 are: SDS 37%, PS 33% and PHEMA 30%. The SDS composition is consistent with that in the pure PS sample. The difference of PS and PHEMA mole fraction from their initial composition of 4:1 ratio decreases. This ratio is confirmed by the X-Ray Fluorescence spectrometer (XRF) result. By calculating the ratio between carbon to oxygen mole ratio, it is showed that the PS to PHEMA in the bulk was about 3.7:1.

From the SIMS result, nearly 1:1 ratio suggests the PHEMA has higher tendency to migrate to the particle surface whereas PS is more likely stay in the core. Therefore, with this synthesis, particles with core-shell structure may be formed with PHEMA rich in shell part and PS rich in the core part. This is the desired composition and structure for fabric treatment. PHEMA exhibits functional hydroxyl group which are able to react with the cellulose fiber.
Figure 3.27  Mass spectrum by Tof-SIMS of nano-particle of PS/PHEMA

From TEM micrographs, it is known that the particles are with radius about 25nm. Assuming the total surfactant volume fraction is negligible, if polystyrene occupied four-fifth of the particle volume and it is arranged in the core part of the sphere, then it will consist about 23nm radius part. Hence, PHEMA will occupy the outer surface with 2nm thickness. The scanning depth of SIMS is about 5nm, which means it can go underneath the PHEMA layer on the surface and down to the PS layer. Theoretically, the expected volume ratio of PS : PHEMA is about 1.2 : 1 based on the ideal core : shell structure. This is very close to the observed 1.1 : 1 ratio measured. Therefore, it can be concluded that the synthesized particles were with core-shell structure as illustrated in Figure. 3.28.
After heating at 80°C for half an hour, as observed in the previous section 3.4.5, it is observed in the AFM micrographs that the shell part forming a continuous matrix of PHEMA and settled down due to gravity, while the core PS formed the droplet-like structure on the top layer because the temperature is not high enough to soften the PS part. Tof-SIM result showed in Figure 3.28 indicated the ratio of PS to PHEMA increased from 1.1 : 1 to 1.6 : 1 after heating by comparing their corresponding peak C\textsubscript{7}H\textsubscript{7} to C\textsubscript{2}H\textsubscript{5}O. This observation strongly supported the appearance of droplet-like PS core on the surface and PHEMA settled to the lower surface because the surface ratio of PS to PHEAM increased.

![Figure 3.28](image_url) Core-shell structure of PS/PHEMA

![Figure 3.29](image_url) Mass spectrum by Tof-SIMS of nano-particle of PS/PHEMA after heating at 80°C for half hour
3.4.7 Mechanical properties

The mechanical properties of the polymeric films must be investigated in order to understand the mechanism of reinforcement to the coated fiber. The tensile test was performed on ARES which is able to provide very precise control on the strain rates. However, there was also a limitation to this system, it has a maximum load of 15N only.

Stress-strain curve in the tensile test of polymer deformation can be divided into elastic deformation and plastic deformation. Due to the limitation of small load in our system, tensile test was performed in the region of elastic deformation only. In this region, when external stress was removed, the specimen would return back to its original shape. The important parameters that can be obtained directly from the tensile stress-strain curves are:

\[
\text{Young's Modulus} (E) = \frac{\text{Stress} (\sigma)}{\text{Strain} (\varepsilon)}
\]

\[
\text{Stress} (\sigma) = \frac{\text{Force Applied} (F)}{\text{Cross-sectional Area} (A)}
\]

\[
\text{Strain} (\varepsilon) = \frac{\text{Change in Length} (\Delta l)}{\text{Original Length} (l_o)}
\]

![Stress-strain curve for tensile modulus calculation](image)

**Figure 3.30** Stress-strain curve for tensile modulus calculation
The exact nature of the time dependence of the mechanical properties of a polymer sample depends upon the type of stress or strain cycle employed [Painter and Coleman, 1997]. Most polymeric materials obey time-temperature superposition principles at $T_g - 50 \leq T \leq T_g + 50$. Figure 3.30 showed an example of stress-strain curve, its slope predicted in the equation is equal to the tensile modulus. Due to the system limitation, the measured strain was only up to 1%, therefore, it was only lie on the elastic deformation region.

The response of a material to mechanical deformation reflects the microscopic deformation processes which are occurring on a molecular or atomic level.

![Figure 3.31 Young's Modulus at different strain rates](image)

$y = 15.698 \ln(x) + 928.85$

$R^2 = 0.9229$

The Young's Modulus of polystyrene was reported to be 1.4 GPa and that of pure PHEMA sol-gel was reported to be much lower value [Wei and Jin, et al., 1998]. As the four-fifth of the sample was composed of PS, a fairly good tensile modulus was also expected. However, the results showed in Figure 3.31 was with lower magnitude. Certainly, the strain rates in this system were much lower than the standard tensile test.
Therefore, an extrapolation has been done in log-log scale (Figure 3.32) to calculate the modulus at a standard strain rate (25mm/min). Therefore, by the rule of mixture, the Young’s Modulus of film formed by nano-particle should be 1.1GPa. Calculated modulus from extrapolation was about 1GPa and the experimental tensile modulus at 25mm/min strain rate was 1.02GPa by ARES. These two values were consistent with each other but they were still a bit lower than the theoretical value.
3.5 Summary

Nano-sized particles in spherical shape have been produced under free radical emulsion polymerization. TEM, SEM and AFM micrographs confirmed that particle size was about 50nm in diameter with very narrow size range.

DSC plot showed the particles were comprised of binary immiscible polymers. The glass transition temperatures were quite consistent with the constituent polymers. Particles were subjected to heating using AFM showed the tendency of forming film under heating. ToF-SIMS gave evidence of core-shell structure of the particle with functional polymer appeared on the surface.

Various kinds of monomers have been tried out for better performance on the treated fabric. Soft polymers with low T_g were targeted to provide elasticity to the coated fabric while the hard polymers were used to provide better tensile strength. On the other hand, the functionality of monomers were also considered to ensure better attachment towards cellulose fibers.

Mechanical modulus of the film formed by nano-particles was tested by using tensile test. The Young’s Modulus calculated by using strain rate extrapolation and ARES fit well with each other and indicated that its modulus was lie between two constituent polymers. This film was proved to be able to impart better mechanical strengths to the treated fabric.
Chapter 4  Fabric treatment

4.1 Introduction

Pad-Dry-Cure fabric treatment process has been adopted for this study due to its simplicity and well-developed technique in the textile industry.

Cross-linking agent dihydroxymethyl-4,5-dihydroxyethylene urea (DMDHEU) resin has been used as it has high efficiency in durable press effect and low formaldehyde release during the treatment process. The presence of the –OH group in the resin will form covalent bond with the –OH on the cellulose fiber. These cross-links provide the resistance to the slippage of chains in the fiber to external stress which in turn provides the wrinkle resistance.

Fabric treatment process has been modified to give better balance between the crease recovery and the loss of mechanical properties. Many parameters have been optimized in the process such as the padding pressure, wet-up-pick% before curing, curing time and temperature.

Nano-particles with different functional monomers has been used for the fabric treatment to investigate the effect of different polymers. Three tests, recovery angle, tensile strength and tearing strength, have been used to evaluate the performance of the treated specimen.

Nano-particle solution has been sent to commercial test in order to compare the effect of presence of nano-particle to commercial formulations.
4.2 Experimental Section

Chemicals such as the cross-linking agent DMDHEU, softeners and fabrics were supplied by commercial company. Fabric used here was 100% Cotton Pinpoint Oxford 160x72 80/2//x80/2 in White 70 yds.

4.2.1 Fabric treatment process

Apart from the cross-linking agent, cross-linking catalyst magnesium chloride MgCl₂ and softener were also used in the treatment. Presence of the cross-linking catalyst would enhance the efficiency of the resin but also caused acid degradation to the fiber. Therefore, an appropriate amount of the resin and catalyst should cause significant effect on both the wrinkle resistance as well as the loss in the strengths. Two kinds of softeners were used in this study: cationic polythene softeners and no-ionic silicon softeners. Presence of the softener would impart the tearing strength as well as the hand feel to the treated sample as they acted as a lubricant between the cellulose fibers.

The fabric was cut to 30cm x 20cm size along the yarn direction. The sample was rinsed with acetone to remove the impurities on the surface which may cause experimental errors. Then the sample was dipped into the mixed chemicals for certain period of time for the absorption and diffusion of the chemicals. Padding the sample through two rollers at certain controlled pressure would squeeze the excess amount of chemical, which would then help to control the amount of uptake of chemicals. Afterwards, the sample was tumble dried to remove the excess amount of water. This procedure would help to keep the percentage of moisture of the sample before curing. Curing is the finally step but also is the most important step in the treatment. All these steps were to influence the result but controlling the
curing temperature and time was the most critical step.

![Flowchart](image)

Figure 4.1  Flowchart of the Pad-Dry-Cure fabric treatment process

4.2.2  Testing standards and analytical procedures

The treated fabric was examined according to the international standard in the commercial testing laboratory. The testing room was kept at $65 \pm 2\%$ relative humidity and $21 \pm 1\, ^\circ C$. All specimens would be conditioned for at least four hours to reach a moisture and temperature equilibrium.

As the yarn density of fabric in vertical (wrap) and horizontal (weft) directions were different, strength measurement should be performed on both sides. However, as the strength in warp direction is always greater than the other side because of the high yarn density, we only performed the test on the weaker weft direction.

![Schematic Diagram](image)

Figure 4.2  Schematic diagram of woven cotton fabric
Tensile strength test by American Society for Testing and Material (ASTM-D5034)

A four-inch wide specimen was mounted in the center of upper and lower clamps of the tensile testing machine and a force was applied until the specimen broke. Tensile test was performed by using grab method under constant-rate-of-transverse (CRT) with two pulling clamps at uniform rate $300 \pm 10$ mm/min and obtained the $20 \pm 3$ s time-to-break. The grab test measured the breaking force as well as the elongation of the specimen. The clamping area was located in the middle of the specimen so that the edge effect would not be minimized. Moreover, clamping was done along the lines drawn parallel to the yarn to ensure the number of yarns held by the clamps was consistent. Normally, the breaking force of cotton must be above 25 pound force to reach the minimum requirement in the commercial world.

![Schematic diagram of sample preparation in tensile test](image)

Figure 4.3  Schematic diagram of sample preparation in tensile test

Tearing strength test by American Society for Testing and Material (ASTM-D1424)

A four-inch wide specimen was mounted on the Falling-Pendulum type tester and which measured the force required to propagate a single-rip tearing starting from a
cut in the fabric. Put the pendulum to staring position. Tightened the clamps and made sure the specimen was mounted horizontally. A knife mounted on the stationary post was used for initial slitting about 20mm. Falling pendulum would give a deflection of the pointer which thus gave a reading of force. The minimum tearing strength of cotton must be above 1.5 pound force to reach the commercial requirement.

![Diagram of sample preparation in tearing test](image)

Figure 4.4 Schematic diagram of sample preparation in tearing test

Two tests were performed to examine the wrinkle-resistance of the fabric which included Recovery Angle test and Durable-Press rating test according to American Association of Textile for Chemist and Colourist (AATCC) 66 and 143 respectively. In the Recovery Angle test, treated samples were cut into six rectangular specimens in the size of 4cm by 1.5cm in the weft direction. These specimens were then divided into two groups according to how they were folded in the experiment: Face-to-Face and Back-to-Back. The folded sample was put under load of 500g for 5 minutes before putting on the recovery angle tester. The recovery angle actually measured the angle restored between two folded sides as illustrated in Figure 4.5. After 5 minutes, the finally reading in the tester was recorded. For the perfectly smooth sample, the recovery angle is 180°.
Figure 4.5  Simulation of recovery angle measurement

Durable Press rating or appearance of garment on laundering was carried out by using the visual method compared with standard surfaces. The treated sample was washed under the standard method and let it naturally dry. It was then observed in the standard elevated angle and distance of lamp light with the comparison with the picture for grading. Grade 0 to 5 would be scored, the higher the score, the better the wrinkle resistance of the fabric. Commercially, 3.25 is the minimum grade for the fabric to be labeled as durable press. It will be equivalent to recovery angle about 120° to 130°.

SEM micrographs for the nano-particles coated surface were taken by a JOEL 6700F at low accelerating voltage of 5 kV to minimize surface heating effect. The twisted yarns were separated by forceps and were then mounted on a sample stand by copper tapes and sputter coated with ~ 150Å of gold films to minimize charging.
4.3 Results and discussion

The fabric treatment process was first modified to optimize the various parameters in order to achieve a better balance between the wrinkle resistance and the loss in mechanical strengths.

Pad-Dry-Cure process

Though this method has been widely used in the industries, investigation about different parameters have been carried out because better control in the degree of cross-linking was aimed.

4.3.1 Cross-linking agent (DMDHEU)

The improvement in durable press rating and the deterioration of mechanical strengths will depend on the degree of cross-linking between the resin and the cotton fiber. The higher the degree of cross-linking, the better the wrinkle resistance because there are more bonds formed between the resin and the fiber. This will then help the fiber upon the distortion. However, rigid bonds between the fiber and resin will destroy the bonds between the fibers themselves which will then reduce the natural strength. The degree of curing refers to the percentage of applied chemicals cross-linked with cellulose. Nevertheless, the degree of curing depends on the amount of resin and catalyst absorbed as well as the curing conditions.
Increase in resin concentration increases cross-links density, thus the degree of curing. Therefore, when a larger amount of resin present, the recovery angle will increase as shown Figure 4.7. Research [Yen and Chen, 2004] also shows similar result, the recovery angle will increase as resin concentration increases because the density of cross-linking increases.

Figure 4.6 Molecular structure of DMDHEU resin

Figure 4.7 Effect of resin on the recovery angle
4.3.2 Softeners

Besides, the presence of softeners will also improve the recovery angle because the softeners are actually oligomers, which will have higher elasticity when compared with that of cotton fiber. Softeners act as a lubricant in the treated fabrics so that slippage could occur between the fibers or at points of the intersection of the warp and filling when they were stressed. The elastomic finishing is able to impart stronger tearing strength to the treated fabric. The softeners that were used here were polyethylene and polysilicon blend in equal proportion.

It is observed that in Figure 4.8, the increase of softener present increased the tearing strength of the treated fabric. This observation is consistent with Blanch's studies in 1997 [Blanch, 1997]. In his study, high density polyethylene softeners was able to increase the tearing strength in both initially and after laundering. However, it is known that the effect of softener will fade out after several washing as they are only surface functioning. As this effect is not permanent, permanent effect of imparting the mechanical strengths to the treated fabric is targeted by using the nano-particles.

![Figure 4.8 Effect of softener amount on the mechanical strength](image_url)

4.3.3 MgCl₂ cross-linking catalyst
Acid catalyst will enhance the rate of curing process. The stronger the acid is, the faster the rate but also the greater the acid degradation caused to cotton fiber through hydrolysis. Magnesium chloride (MgCl$_2$) is the most commonly used catalyst which has mild degradation and no yellowing effect compared with other catalysts such zinc nitrate and citric acid. Result shown in Figure 4.9 shows increasing catalyst concentration also increases the degree of cross-links, hence the recovery angle. This result is consistent with the other research [Lickfield and Yang 1998], which also shows the increase of the MgCl$_2$ catalyst will increase the recovery angle while reducing the tensile strength.

![Graph showing the effect of MgCl$_2$ concentration on recovery angle](image)

**Figure 4.9** Effect of catalyst at constant amount of resin on the mechanical strength
4.3.4 Padding pressure

The amount of chemical picked up by the fabric is controlled by two factors, the dipping time and padding pressure. If the later is well-controlled, then the former parameters will not affect much as long as enough time is allowed for dipping. The pressure is controlled by the padder, which consists of two plastic rolls. When the wet specimen is rolled through the machine, the pressure exerts by the rolls will squeeze away the excess chemicals, thus control the wet-up-pick chemical percentage. The higher the padding pressure, the larger amount of chemicals will be squeezed away. Moreover, padding will enhance the uniform distribution of chemicals on the surface, which in turn improve the physical properties of treated fabric [Yen and Chen 2004].

*Figure 4.10* shows the recovery angle result of samples padded at different pressures. It is expected that smaller pressure will give better recovery angle result because a larger amount of resin present will cause higher degree of cross-links in the treated sample. However, at very low pressures, the excess solution present in the fabric will require a larger amount of heat energy to evaporate the water before providing energy for cross-linking. Therefore, it is concluded that 1.5 kg/cm² should be the optimum padding pressure for this system.

![Figure 4.10 Effect of padding pressure on the recovery angle](image-url)
4.3.5 Effect of moisture

It is reported that the moisture content of treated fabric before curing is another key factor in controlling the degree of cross-linking. Therefore, the percentage of wet-up-pick for the specimen before going through the high temperature curing must be well-controlled.

*Figure 4.11* shows the effect of wet-up-pick% (WUP%) on the mechanical properties and the recovery angle result. For WUP% varies from about 12% to 54%, the recovery angle changes within 140 degree to 144 degree. We could assume the recovery angle kept almost constant as the range was within human error in taking the reading. On the one hand, the tensile strength and tearing strength retentions also changed though it was insignificant. However, it can be also concluded that WUP% kept at a range of about 10% to 20% would able to give better performance in all properties.

![Figure 4.11 Effect of wet-up-pick percentage](image_url)
4.3.6 Curing

Curing time and temperature are the most essential factors that influence the degree of cross-linking. Experiment shows that for the native fabric without any chemical treatment, it will undergo thermal degradation and will cause the loss in mechanical strengths especially tearing strength. Figure 4.12 shows the effect of thermal degradation on curing native fabric at 130°C for 10mins. Thermal degradation is due to the breaking of covalent bonds in the cellulose fiber.

![Graph showing thermal degradation of cotton fabric](image)

**Figure 4.12** Thermal degradation of cotton fabric

Using DMDHEU as the cross-linking agent which belongs to the hard-to-cure category, the curing temperature must high enough to ensure the bonding to take place. Certainly, with higher curing temperature, the reaction will take place more easily and to larger extent. Moreover, if longer curing time is allowed, the higher percentage of cross-links will form. Therefore, experimental results shown in Figure 4.13 also indicates the increase of curing temperature as well as the curing time will increase the recovery angle.
Figure 4.13  Recovery angle of fabric treated at various curing temperatures and times

On the other hand, the curves showing the tensile strength retention in Figure 4.14 appeared to have exactly opposite trend with the previous figure. Thus, the increase of curing temperature and time would greatly reduce the tensile strength retention. Therefore, 130°C for 10 minutes was chosen for the balance between the recovery angle and tensile strength.
Therefore, based on the above results, the optimum value of the resin concentration, catalyst concentration, softener concentration, curing temperature and time were chosen for the later treatment.
4.3.7 Nano-particle effect

In order to know the presence of nano-particle in the fabric treatment process, fixed amount of emulsion was added to different amount of DMDHEU resin. The tensile test results on different amount of resin present have shown that the higher the concentration of resin, the lower would be the breaking force. This was explained in the section 4.3.1, as the degree of cross-links increases as higher concentrations of resin present. According to the reasons mentioned, the breaking force decreased as the concentration of resin increased. In Figure 4.15a, Figure 4.15b and Figure 4.15c, the pink curves present the presence of emulsion whilst the blue curves were without emulsion. All these curves showed that the presence of nano-particles will enhance the ductility of the treated samples. Ductility indicates the ability to resist external force, thus the elasticity. Therefore, it is concluded that presence of emulsion would able to enhance the tearing strength.

![Resin = 120 g/L](image)

Figure 4.15a Tensile test curve of resin at 120g/L
In the first batch of fabric treatment with nano-particle, the functional polymer on the surface of the nano-particles are varied by using PAA, PHBMA, PMA, PHEMA, PAMS and so on.

The glass transition temperature of individual polymer must be known because polymer exists at temperature higher than its Tg will behave like rubber. On the other side, it will be brittle. As the mechanical property is greatly depend on the
glass transition temperature, polymers with glass transition temperature below or above the ambient temperature are very important in this system. Polymers with $T_g$ lower than ambient temperature are considered as soft polymers which are able to increase the elasticity of the coated sample. On the hand, polymers with $T_g$ higher than ambient temperature will be regarded as hard polymers which are able to increase the tensile strength upon external force.

On the other hand, the function groups present in the polymer are also crucial as they must able to react with hydroxyl group in the cellulose fiber. Functional monomers are chosen to contain either hydroxyl group or carboxylic acid group so that they are able to produce polymer that can react with the hydroxyl group.

![Graph showing recovery angle results of various emulsions](image)

**Figure 4.16a** Recovery angle results of various emulsions
Figure 4.16b  Tensile strength results of various emulsions

Figure 4.17a  Tearing strength results of various emulsions
Figure 4.17b  Tensile strength results of various emulsions

Figure 4.17c  Recovery angle results of various emulsions
From the above result of recovery angle, tensile strength and tearing strength retentions of various polymers synthesized by different monomers. Results indicated that the presence of the polymer with better strength will improve the tensile strength while elastic polymer will provide better tearing strength. The polymers with high glass transition temperatures will be regarded as hard polymers such as polymers consist of St and AMS. While those with low glass transition temperatures will be regarded as soft polymers such as polymers consist of BA, BMA, HEMA or isoprene. Moreover, most of the soft polymers also consisted of reactive functional groups for attachment to the cellulose fiber.

Usually, the particles with larger portion of hard polymer will be able to give better tensile strength retention while those with larger portion of soft polymer will impart better tearing strength retention. Among the nano-particles, particles made of St/HEMA are able to give the best performance.

*Figure 4.18 showed the result of one of nano-particle solutions consisted of Styrne/Isopren/HydroxylMethacrylate. Fabric treated with this kind of nano-particle together with resin is able to provide good recovery angle over 140 degree, and the tensile strength retention and tearing strength retention over 60% and 50% respectively.*
Specimens of fabric treated with emulsion only will allow us to know more about the interaction between nano-particle and the cellulose fiber. Morphological studies were carried out by using SEM. Spherical particles in nano-size will be able to coat on the surface of yarn. Especially because of the rough surface of the yarn which made the particles easier to fit into the “valleys” on the surface. However, it was found that controlling the coverage of particle on the yarn surface was very important. If the amount of particles is not enough, then it is not able to cover all the area. On the other hand, too many particles present in the treatment will cause agglomeration between particles. Functionalized nano-particles used for improvement of fabric have been widely carried out and patented [Soane, 2002, 2003]. However, no much information has been provide for the morphology of nano-particles coated on cotton fiber. *Figure 19a* to *Figure 19c* are showing how these nano-particles are attaching towards the fiber surface.
Figure 4.19a  SEM micrographs of nano-particles coated yarn

Figure 4.19b  SEM micrographs of nano-particles coated yarn
Figure 4.19c  SEM micrographs of nano-particles coated yarn

As mentioned in the previous chapter, our target is forming a layer of polymeric thin film on the surface of the yarn which is able to impart better mechanical properties to the durable press finished fabric. Therefore, the morphology of nano-particle coated fabric after higher temperature ironing is studied as well. Formation of film from polymeric particles has been reported in earlier researches [Chevalier, et al., 1992]. SEM micrographs also prove the formation of film on the fabric surface.
Figure 4.20a  SEM micrographs of nano-film coated yarn

Figure 4.20b  SEM micrographs of nano-film coated yarn
Figure 4.20c  SEM micrographs of nano-film coated yarn

Figure 4.20d  SEM micrographs of nano-film coated yarn
With the presence of all chemicals including resin, resin catalyst, softeners together with nano-particles coated on the fiber surface. The morphology of coated fabric under different concentrations of nano-particles has been studied. The concentration of nano-particles increases from solid content of polymer 0.1 v/v% to 1 v/v% in the treatment. From Figure 4.20a to Figure 4.20d, it is observed that the amount of nano-particles is not enough in order to coat the yarn surface.

Figure 4.21a  SEM micrographs of nano-particles coated yarn (0.1v/v%)  
Figure 4.21b  SEM micrographs of nano-particles coated yarn (0.1v/v%)
From Figure 4.21a to Figure 4.21d, the micrographs show the optimum amount of nano-particles to coat on the yarn surface without agglomeration is about 0.5 v/v% in polymer solid content. Agglomeration would take place for higher concentration. This result is actually matched well with the experiment result in the mechanical test. In previous section, it also shows that this concentration will give the best performance among all.
Figure 4.21e  SEM micrographs of nano-particles coated yarn (0.5v/v\%)  

Figure 4.21f  SEM micrographs of nano-particles coated yarn (0.5v/v\%)  

Figure 4.21g  SEM micrographs of nano-particles coated yarn (1v/v\%)  

Figure 4.21h  SEM micrographs of nano-particles coated yarn (1v/v\%)
4.3.8 Implementation of nano-particles in commercial laboratory

After series of test carried out in the laboratory, implementation of the application of the nano-particles in the commercial industries was carried out as well.

In the first test, it was the addition of nano-particle in the commercial recipes of the fabric treatment and following their own durable press finishing process. In the second test, it was the test following our modified treatment process.

First, when comparing the results with absence of emulsion in the commercial formulation and our modified formulation. There is an increase in tearing and tensile strength retention of more than 10% and 20% respectively. When the emulsion is present at 0.1v/v% solid content, there is more than 20% improvement in both tearing and tensile strengths.

![Tensile strength retention graph](image)

**Figure 4.22 Tensile result for presence of nano-particle in commercial recipe and UST recipe**
Figure 4.23  Tearing result for presence of nano-particle in commercial recipe and UST recipe

From the results of tensile and tearing strengths in the above graphs, it is concluded that the presence of small amount of nano-particles is able improved the mechanical properties. On the other hand, the results of DP rating that indicated the wrinkle resistant of the treated sample also proves the presence of nano-particle would not decrease the wrinkle resistant. The DP rating of 1 time wash, 3 times wash and 5 times wash all showed similar results in commercial formulation and the modified formulation with or without the presence of nano-particle.
Figure 4.24  DP rating result for presence of nano-particle in commercial recipe

Figure 4.25  DP rating result for presence of nano-particle in UST recipe
4.4 Summary

Pad-dry-cure durable press finishing process has been optimized by varying different parameters such as chemicals and operating conditions. The resin concentration, catalyst concentration and softener concentration have been adjusted to give a better balance between the wrinkle resistant and mechanical strength loss. Moreover, the most critical step, the curing condition has been optimized by varying the curing time and temperature.

Nano-particles made by different monomers in different proportions have been investigated for the performance in treated fabric. Usually, particles in larger portion of hard polymer would able to provide better tensile strength. Better tearing strength would be imparted by using particles with larger portion of soft polymer. The optimum performance would able to give good wrinkle recovery angle rest over 140 degree, tensile strength and tearing strength retention higher than 60% and 50% respectively.

Further confirmation of the effect of nano-particle has been done by implementation of nano-particle in commercial laboratory test. Results showed that modified pad-dry-cure process has imparted more than 10% the mechanical strengths retention. Under the presence of nano-particles at suitable amount, the improvement could be as high as greater than 20% in both tensile and tearing strengths.
Chapter 5  Rheological studies of nano-emulsion

5.1 Introduction

Rheology is recognized as an important field of research and application in industries, especially in polymers. It is a science that deals with the deformation of materials as a result of an applied stress [Carreua, et al., 1997]. In durable press finishing process, the nano-particles have undergone deformation process. Rheological studies are carried out to visualize the performance of those nano-particles in the finishing process.

Addition of particles in the system will not only change the magnitude of viscosity but also other deviations from the Newtonian behavior [Christopher, et al., 1994]. Rheological studies in the suspension are able to show how interfacial tension between particles exists. Investigation of shear induced alignment of particle was carried out. The interaction between particles with effect of hydrodynamic forces and Brownian motion was studied by using optical rheology.

The optical rheology indicates the anisotropy change of the particles is present in the system. Shearing will induce the orientation of particles inside this system, and hence anisotropy change as indicted by the dichroism change. Therefore, measuring the optical dichroism of polymer solution will provide a direct measure of the shear stresses due to the thermodynamic forces.
5.1.1 Background

In 1906 and 1911, Einstein has published his classical paper in the analysis of the particles suspended in Newtonian fluid. Presence of particles will modify the velocity distribution in a flowing liquid. Extra energy dissipation will arise because of this and will be reflected in a proportional increase in the viscosity. Einstein derived his famous relationship describing the viscosity for dilute suspension of rigid spheres in Newtonian fluid in 1905.

\[ \eta_s = \eta_m (1 + \frac{5}{2} \phi) \]

In this equation, the subscription \( \eta_s \) refers to the viscosity of suspension, \( \eta_m \) refers to the viscosity of the fluid and \( \phi \) is the volume fraction of suspension. However, this relation is only valid for rigid spheres of narrow size distribution in Newtonian fluids. Nevertheless, this theoretical result is only applicable to very low concentration with volume fraction < 0.01 only [Carreau, et al., 1997]. However, this equation is re-modified to determine the zero-shear viscosity by Batchelor 1977.

\[ \frac{\eta_o}{\eta_m} = 1 + 2.5\phi_{eff} + 5.9\phi_{eff}^2 \]

The response of the suspension to deformation and flow is very important. Therefore, knowing the viscosity change is very desirable.

For particles suspended in solution, the stresses present will be provided by Brownian motion and hydrodynamic forces. Researches [J.F.Brady and G.Gossis 1989] has done to prove the theory for viscoelastic behaviour of ideal, hard-core Brownian particle. The theory expressed the hydrodynamic and Brownian stresses in terms of pair-wise particle distribution and the hydrodynamic mobility to describe linear viscoelastic quantities for \( \phi < \phi_m = 0.63 \) where the \( \phi_m \) is the volume fraction for
maximum random packing.

\[
\frac{\eta_0}{\eta_m} = (1 - \frac{\phi}{\phi_m})^{-2} \quad \text{for} \quad \phi \rightarrow \phi_m
\]

In dilute solutions, the rheological properties of such hard sphere suspended in Newtonian fluid is independent of the shear rate [Peason and Shikata, 1994]. Instead the viscosity is increased with the volume fraction of particles. However, if the particles are small enough, it will be hardly depended on the shear rate and frequency even in the concentrated concentration. It is because Brownian forces contribute to the stress dominates in such small particles.

Experiments have demonstrated that shear thinning is due to changes in the thermodynamic contribution to the viscosity [Wagner and Bender, 1995]. Meanwhile, the hydrodynamic contribution remains relatively constant throughout the shear thinning regime. However, shear thickening is observed at higher shear rates due to the formation of hydrodynamic clusters. Result shows that at low shear rates, the thermodynamic (Brownian) stresses dominate the hydrodynamic stress while the later one becomes more significant at higher shear rate.

On the other hand, Meeker [Meeker, et al., 1997] stated that the viscosity is not only dependent on the volume fraction but also the dimensionless stress for non-dilute solution. It is found that at very low shear stresses, the viscosity is independent of the volume fraction as well as the shear rate, which is known as the Newtonian regime. At higher stress, the viscosity decreases with increasing shear rates and then eventually reaches a Newtonian plateau. This is so called shear thinning effect. Finally, at concentrated condition, the solution exhibits shear thickening effect as the
shear stress increased. Relaxation mechanism of the suspension was suggested with the influence of volume fraction [Horigome, et al., 2002]. Moreover, for concentrated suspensions at higher shear rates, the shear thickening effect is quite significant due to the shear-induced dynamic clustering of the particles.

It is reported that shear thickening effect is due to the increase of Reynolds number, competition between conservative repulsive forces and hydrodynamic force, or divergent lubrication interactions. Studies also showed the fundamental origin of thickening or clustering is evident in the behavior of particle systems with only dissipative interactions [Melros, et al., 1996].

5.1.2 Optical rheology

In general, rheological experiment is measuring force, displacement or velocity. In a rheo-optical experiment, the measurement of force is replaced by the measure of some optical property of the sample. Birefringence is based on a change in its state of polarization. The light can propagate through the material with no change in direction or energy. Dichroism is an absorption process very closely coupled to birefringence.

The phenomenon of dichroism occurs when the wavelength of light entering a macroscopically anisotropic material is such that it will be absorbed to some extent. The value of the molar absorptivity also depends on the relative orientation of the light polarization and the so-called transition dipole of the molecules. The resulting variation in absorption with polarization orientation is referred to as dichroism. A dichroic sample will preferentially scatter or absorb light of a particular polarization state, resulting in measurable variations in emerging intensity.
A new design of optical rheometer was developed by rotary polarization modulator [Fuller, 1989]. This technique has been applied to suspension of colloidal iron oxide particle at Newtonian solvent. Taking the dichroism measurement in a transient simple shear flow using a Couette cell, results show a behavior of typical colloidal particles in time-dependent shear flow. The dichroism and orientation angle oscillate in time which indicate the rotation of particle. The dichroism relaxes to zero and orientation angle as well.

Measuring the optical birefringence of polymer solution provides a direct measure of the shear stresses due to the thermodynamic force because a stress-optical law exists [Wagner and Bender 1995]. Combined rheological and flow dichroism measurement enable us to distinguish between the thermodynamic and hydrodynamic contributions to the total stress and to test the microstructure as well. According to the stress-optical relation, the low shear rate limit the dichroism is then proportional to the total shear stress. \[
\eta_{\text{total}} = \eta_{\text{thermo}} + \eta_{\text{hydro}} = \frac{1}{C} \left( \frac{\Delta n''}{45^\circ} \right) \gamma + \eta_{\text{hydro}}
\]

Studies indicated that in the low shearing rate, the thermodynamic stress (Brownian motion) dominates such that hydrodynamic viscosity is constant throughout the shearing thinning regime. And the dichroism related to the thermodynamic stress is independent of shear rate.

Puyvelde [2001, 2002, 2003] pointed out that the morphology of polymeric blends in aqueous phase can govern the sensorial properties and the ability of simulating the process conditions. Small angle light scattering experiments (SALS) have been used on a water/gelatin/dextran emulsion on the Rheometrics Optical Analyzer to
find out the interfacial tension. Two methods have been applied: one is based on the patterns observed by the optical microscope; and the other one is to use anisotropy patterns during relaxation after steady state shearing. The anisotropy curve shows that at low shear rates, the emulsion just deforms as conventional emulsion. Initially, there is large deformation of the droplet as reflected in the increasing the anisotropy. Then, when steady state is reached, the droplet returned to elliptic structure. At higher shear rate, the shear flow can homogenize the structure as observed in the scattering pattern. This result show that shear flow can homogenize the structure.
5.2 Experimental Section

Nano-emulsion is synthesized with monomer solid content of 10 v/v% as described in Chapter 3.

Advanced Rheometric Expansion System (ARES) in concentric cylinder rheometer (Couette) with length 20mm, cup internal diameter 34mm, bob outer diameter 30mm and bob length of 20mm. Solutions for test were diluted into different concentrations using de-ionized water. Concentrated solution was prepared by centrifugation at 15K rounds per minutes for two hours. Gelation took place with the gel in solid content of 53 wt%. Then it was further diluted into solution with higher concentration when compared with the mother solution.

![Optical train block diagram](image)

*Figure 5.1 Optical train block diagram*
Laser light passes through the first polarizer and outputs linearly polarized light. Transmission through the rotating half-wave plate, the light remains linearly polarized but rotates at a certain frequency. Laser light then passes through a nono-polarizing beam splitter and sent to a pair of prisms that are arranged so the light is deflected 90° toward the sample. This patented arrangements of prisms has the special property of deflecting the beam without changing its polarization properties.

The beam that is split at the non-polarizing beam splitter is sent through a modulation polarizer, then to the reference detector. The modulation polarizer causes the light to undergo a sinusoidal attenuation. The reference detector produces a reference signal that tracks the polarization modulation of the light that is sent to the sample.

Linearly polarized light is sent to the sample senses optical anisotropy in the material through the rotation of its polarization, which is continuously projected onto the refractive index tensor of the sample. The presence of either dichroism or birefringence in the sample will cause the polarization of the light to be altered from linearly polarized to elliptically polarized. The transmitted light then passes the detector. The signal consists of a DC time-independent value (IDC) and two components at a frequency 4ω: an in-phase sine(SIN) components, and an out-of-phase cosine (COS) component.

Couette geometry is applied for flow birefringence measurement because with which the optical beam can be introduced into the experiment. Moreover, the wide range of shear rate is available and very well-characterized flow profile is developed.
5.3 Results and discussion

Concentric cylinders (Coutte) was used to study the shearing effect on the viscosity change. Experiments were carried out on pure water to check the shearing effect on water first, result is shown in Figure 5.2. The viscosity of pure water increases with the shear rate and it indicated the inertia effect present in the system at such high shear rate. Therefore, for the result following, the viscosity presented will be subtracted by the corresponding viscosity of water under that shear rate. Moreover, it is observed that for very dilute solution, the viscosity is independent with the shear rates. This observation is consistent with the result in many studies.

![Figure 5.2 Shearing effect on water](image)

Figure 5.2 Shearing effect on water
For solutions in higher concentrations, it is found that shear thickening also occurs at low concentration about 9wt% of polymer solid content in Figure 5.3. Studies elucidated shear thickening the concentrated non-interactive colloids with volume fraction greater than 0.4. However, in our system, shear thickening effect took place even at volume fraction less than 0.1. Therefore, we may conclude the nano-particle tend to form clusters.

![Graph showing Viscosity difference (P-μ) vs Shear rate (1/s)](image)

**Figure 5.3** Viscosity of nano-particle solution under different shear rates relative to water

Concentrated solution will undergo jamming transition at a volume fraction below close packing is reported [Melroso, et al., 1996]. This might help to explain why the nano-emulsion also undergone gelation after centrifugation and forming gel at about 53wt% of solid. This value is a slightly lower than maximum packing volume fraction 0.6 as reported. The onset of shear thickening in colloidal dispersion is predicted to occur when the compressive hydrodynamic force between two particles in the suspension become larger than the total repulsive force between particles, leading to the formation of hydroclustered state [Wagner, et al., 2001].
5.3.1 Optical rheology

The molecular structure of PS and PHEMA were illustrated in Figure 5.4 and Figure 5.5. For the measurement of dichroism, the specimen must exhibit some degree of optical anisotropy which will directly relate to their chemical structure. Both PS and PHEMA are suitable in this case. Therefore, when the molecule is orientated preferentially in one direction, it will cause a change in the dichroism measurement.

![Molecular structure of PS repeating unit](image1)

*Figure 5.4  Molecular structure of PS repeating unit*

![Molecular structure of PHEMA repeating unit](image2)

*Figure 5.5  Molecular structure of PHEMA repeating unit*

When shearing is applied to the solution, it will introduce the thermodynamic effect to the particle which caused the ordering to the particles. Therefore, the anisotropy of the system increases. However, as time went on, the kinetic effect (Brownian motion) became dominant and caused disorder to the system. There will be a decrease in the anisotropy. *Figure 5.6* shows the dichroism changes of solution under shearing.
Figure 5.6 Dichroism change in solution under shearing

After repeating experiments at different shearing rates, a conclusion could be drawn is that the nano-particles would orientate due to shearing. For instance, the following graph showed that the anisotropy change of the emulsion at fabric treatment concentration at different shear rates. Shearing induced hydrodynamic force which caused the particles to rotate. In turn, this caused a rise in anisotropy recorded by the dichroism. A pseudo steady state was reached. However, the Brownian force was then taken part which induced the disorderness of the particles and resulting the drop in anisotropy. This period of this loop would be shortened by the increasing in shear rates.
Figure 5.7a  Dichroism change in solution under different shear rates

Figure 5.7b  Shorter time range of dichroism change
From the change in anisotropy indicated by Figure 5.7b above, it is shown that under small shear rate, the increase in anisotropy was small in short period of shearing time. In the fabric treatment process, in order to prevent the agglomeration between particles, slow stirring or slow picking up process must be applied in order to ensure a slow shear rate that prevent the clustering effect.
5.4 Summary

Rheological studies in the nano-emulsion solution through conventional rheology test together with optical rheological test provide useful information for the particles under shear.

The effect of shearing to viscosity experiment indicates that viscosity is independent of shear rate under very dilute condition because Brownian force was dominant in this case. However, shear thickening effect took place at higher concentration due to hydrodynamic force dominant situation. Under such conditions, clusters may form which thus increases the viscosity of the system.

Optical rheological result proved the orientation of particles under shear. Shear induced rotation would be overcome by the disorderness of particles again due to the Brownian motion of particles in nano-size. Higher shearing rate would cause the particles to response more quickly and dichroism relaxation came faster. Therefore, this result suggested that fabric treatment with nano-particles should not be done under vigorous stirring.
Chapter 6  Conclusions and future work

6.1 Conclusions

In this research, nano-sized polymeric particles have been synthesized by using free radical emulsion polymerization method to impart better mechanical properties to the durable press finishing treated cotton fabric. Wrinkle-free apparels usually exhibit poor mechanical properties because of the rigid cross-linkings and degradation during the finishing process. In order to overcome the large extent of loss in mechanical strength, nano-particles with functional surface were used to attach to the cellulose fiber to prohibit the extensive rigid network formed by cross-linking agents. Moreover, particles would form films on the surface of the fiber to impart better strengths.

Investigation on the nano-particles which includes the synthesis parameters such as the reaction temperature and surfactant amount has been performed. Decreasing temperature and increasing the amount of surfactant would reduce the particle size, which would promote easier allocation of particles onto the rough yarn surface. Monomers with different properties have been tried for a better interaction with the cellulose fiber. The glass transition temperature of a polymer would greatly affect its mechanical properties. Particles were synthesized into copolymer with constituent polymers having both high and low glass transition temperatures to provide better stiffness and elasticity to the coated fabric.

Characterizations of the particles have been done using SEM, TEM and AFM to visualize the particle morphology. Results confirmed that the particle size was about 50nm in diameter with very narrow size range. Thermal analysis using DSC
showed the presence of heterogeneous structure copolymer inside the particles. The glass transition temperatures were consistent with the constituent polymers. Particles subjected to heating using AFM showed the tendency of forming film under heating. ToF-SIMS gave evidence of core-shell structure of the particle with functional polymer appeared on the surface. The film formed by nano-particles was proved to be able to impart better mechanical strengths to the treated fabric.

Optimizing the pad-dry-cure durable press finishing process has been done by varying different parameters such as resin concentration, catalyst concentration, softener concentration as well as the curing time and temperature.

Nano-particles made by different monomers in different proportions have been investigated for their performance in treated fabric. Particles in larger portion of hard polymer would usually be able to provide better tensile strength. Better tearing strength would be imparted by using particles with larger portion of soft polymer. The optimum performance would be able to give good wrinkle recovery angles over 140 degree, tensile strength and tearing strength retention higher than 60% and 50% respectively.

Further confirmation of the effect of nano-particle was done by implementation of nano-particle in commercial laboratory test. Results showed that modified pad-dry-cure process has imparted 10% more than the mechanical strengths retention. Under the presence of nano-particles at suitable amount, the improvement could be as high as 20% in both tensile and tearing strengths.
Rheological studies in the nano-emulsion solution through conventional rheology test together with optical rheological test provide useful information for the particles under shear. Shearing thickening effect indicated the formation of clusters for the particles under shear. Optical rheological result suggested that fabric treatment with nano-particles should be not done under vigorous stirring in order to prevent agglomeration between particles.

6.2 Future work

The use of surfactant may limit the reactivity of the nano-particles on cotton surfaces. Its intrinsically ionic structure may also render the nano-particles having charges on the surface. This will in turn make the synthesized particles exhibit charge on the surface. Therefore, surfactant-free nano-particles are desired to minimize these potential problems. Small scale surfactant free synthesis has been carried out in this work. Scaling up of reactions and applications of these surfactant free particles for fabric/garment treatment remain to be further studied.
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