CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

This chapter deals with the review of literatures related to this research work. It has the details of nano science and technology and their impact on textiles, different cross linking agents and their influence on fabric properties, various methods of synthesis of nano metal oxides, applications and their effect on fabric properties. It also deals with microencapsulation and its application in textiles.

2.2 FINISHING OF FABRICS

Textile finishing provides a method where by deficiencies in the textile can be corrected or specific properties can be introduced by physical finishing techniques or chemical finishing methods. Physical finishing is usually carried out on the yarn or formed textile substrate, whereas chemical finishes can be added by the solution bath.

The finisher has to design a procedure to produce a fabric that is clean and free from contaminants, has a soft handle and drape and any additional desired aesthetics, such as stretch or waterproof finish. The fabrics must be of correct dimensional stability for garment making and the correct finished width. Every finishing treatment of the fabric added certain value to the finished fabric.
Value additions could be conveniently divided into three categories.

- Improving ‘use’ value
- Enhancing ‘esteem’ value
- Imparting ‘gimmick’ value

Many finishing techniques and methods revolve around comfort properties and health care. Saravanan (2007) stated that most of the developmental works in garments/fabrics were aimed at enhancing the comfort properties along with various functional finishes.

2.3 AN INTRODUCTION TO NANO TECHNOLOGY

Nano technology employs bottom up as well as top down approaches to produce nano materials in all the three dimensions. Bhupendra Singh Butola and Swapna Mishra (2007) discussed nano technology is the art and science of manipulating matters at the nanoscale to create new and unique materials and products. Nanotechnology is defined as the utilization of structures with at least one dimension of nanometer size for the construction of materials, devices or systems with novel or significantly improved properties due to their nano-size. Nano science and technology offer great opportunities in all fields of science and technology material science, mechanical, electronics, optics, medicine, energy, aerospace and textiles (Mangala Joshi 2006). Nano technology has the potential to create new bulk materials with new bulk properties in textile coating and finishing (Michal Werner Schmitt and Yoram Benjamin 2008).

The impact of nano technology in the textile finishing area has brought up innovative finishes as well as new application technique. Ideally, discrete molecules or nano particles of finishes can be brought individually to
designated sites on textile materials in a specific orientation and trajectory through thermodynamic, electrostatic or other technical approaches (Lei Qian and Juan P. Hinestroza 2004).

Gulrajani (2006) reviewed nano technology is making significant in roads in field of textiles. The five main areas are nano finishes, nano colouration, nano fibres, nano composites and nano filtration. The types of nano finishes are given below:

i) Hydrophobic nano finishes
ii) Self cleaning nano finishes
iii) Photocatalic self cleaning
iv) Antimicrobial finishes

The use of nanotechnology in the textile industry has increased rapidly due to its unique and valuable properties. Nanotechnology also has real commercial potential for the textile industry. This is mainly due to the fact that conventional methods used to impart different properties to fabrics often do not lead to permanent effects, and will lose their functions after laundering or wearing. Nanotechnology can provide high durability for fabrics, because nano-particles have a large surface area-to-volume ratio and high surface energy, thus presenting better affinity for fabrics and leading to an increase in durability of the function. In addition, coating of nano-particles on fabrics will not affect their breathability or hand feel (Wong et al 2006).

Radhakrishnaiah (2005) noted that rapidly emerging nanotechnology offers new and improved ways of imparting a range of functional performance properties to cotton rich fabrics. In fact, textile industry is the first manufacturing industry to come up with finished products that are enhanced through nanotechnology-based functional finishing.
The enabling nano science and technology has emerged with huge potential applications in the area of textile. Nanoparticles coating on the surface of fibres/fabrics is one of the approaches to produce high active surfaces with unique properties and also to obtain high durability function for the fabrics (Yadav et al. 2006).

Various properties are imparted to textiles using nanotechnology include water repellence, soil resistance, wrinkle resistance, anti-bacteria, anti-static and UV-protection, flame retardation, improvement of dyeability photocatalic ability, electrical conductivity and photo oxidizing capacity against chemical and biological species, antimicrobial, self decontaminating and UV absorption & blocking functions for both military protection gears and civilian health products and so on. Nano metal oxides such as TiO$_2$, Al$_2$O$_3$, ZnO, MgO SiO$_2$ and ceramics are used in textile finishing for altering the surface properties and imparting functional properties (Torsten Textor et al. 2006).

### 2.3.1 Coating Technologies

Coatings are increasingly being used for outer surfaces of the fabrics/garments. This development has its roots in the invention of new water dispersed polymers. From the late 1950s to early 1960s, when polyacrylates and polyvinylacetate were supplemented by polyurethanes, coatings have become increasingly popular for fashionable garments. However the fashion is inconstant and fashionable coatings are often out of fashion soon after they have been accepted by the market. Functional coatings on the other hand are the main theme for today’s market (Kubin 2001).

A wide range of processes are available for applying the coating. The most suitable coating process is chosen depending on the substrate,
polymer and end use of the article. The coating compounds may be applied to
one or more surfaces of the textile substrate (Dipl-Ing et al 2004).

Coating is a common technique used to apply nano-particles onto
textiles. The coating compositions that can modify the surface of textiles are
usually composed of nano-particles, a surfactant, ingredients and a carrier
medium. Several methods can apply coating onto fabrics, including spraying,
transfer printing, washing, rinsing and padding. Of these methods, padding is
the most commonly used one. The nano-particles are attached to the fabrics
with the use of a padder adjusted to suitable pressure and speed, followed by
drying and curing.

2.3.2 Nano Coatings

Nano coating refers to covering materials with a layer on the nano
meter scale (10-100 nm) in thickness or covering of a nano scale entity to
form nano composite and structured materials. Materials are coated for a
number of reasons: coating can make a substance bio-compactable to increase
material’s thermal and mechanical stability, increased wear protection,
durability or life time, decrease friction or inhibit corrosion or change the
overall chemical, physio-chemical and biological surface properties of the
material in general (Deepti Gupta and Somes Bhaumik 2007).

Nano metal oxide coating on the surface of fabrics is one of the
approaches to produce high active surfaces with unique properties and also to
obtain high durability function for the fabrics (Patel and Chattopadhyay
2008).
2.3.3 Characteristics of Nano Finished Garments

- Nano processed garments have protective coating, which is water and beverage repellent.
- Their protective layer is difficult to detect with the naked eye.
- When a substance is manipulated at sizes of approximately 100 nm, the structure of the processed clothing becomes more compressed. This makes clothing stain and dirt resistible.
- Saving time and laundering cost.
- This technology embraces environmental friendly properties.
- Nano materials allow good ventilation and reduce moisture absorption, resulting in enhanced breathability while maintaining the good hand feel of ordinary material.
- The crease resistance feature keeps clothing neat.
- Nano products are toxic free.
- Garments stay bright, fresh looking and are more durable than ordinary materials.
- Manufacturing cost is low, adding value to the product.

2.3.4 Applications of Nano Materials

Nano science and nano technology have been carefully implemented in many areas of engineering to enhance the performance and quality of living condition. Proper implementation of technology needs careful assessment of the impact on environment, health hazards to the workers, users of the product and to environment (Saravanan and Ramachandran 2007).
Nylon fibre filled with ZnO nano particles can provide UV shielding function and reduce static electricity of nylon fibre. A composite fibre with nano particles of TiO$_2$/MgO can provide self sterilizing function. In a hydrophobic coating, the nano metal oxides are coated on the surface with the thickness of 500 nm instead of 1 micron, the coating will still be a hydrophobic with no actual nano-effects.

Zinc oxide nano particles, zinc metal nano particles and silver metal nano particles are used for many applications. These include antimicrobial, antibacterial, anti-biotic and antifungal agents when incorporated in coatings, fibres, polymers, first-aid bandages, plastics, soap and textiles (Babi 2006). Nano sized silver particles are mostly being used to impart antimicrobial activity to fabrics for use not only in medical textiles but also in home furnishings. Use of silver nano particles could enhance the use of alginate and chitosan in the wound dressing market by combining both the antibacterial activity and biodegradability (Sreenivasan 2006).

The nano-scale cerium oxide nano particles, platinum/gold/molybdenum/nickel and iridium metal nano particles have extremely high surface area. Due to this they may have found important uses in catalysts for a whole host of chemical synthesis, chemical treatment and chemical cracking applications, including automotive catalytic converters.

The German researcher Wilhelm Barthlott of Bonn institution of botany discovered, in 1990, that the lotus plant, admired for the resplendence of its flowers and leaves, owed this property of self cleaning to the high density of minute surface protrusions. These protrusions catch deposit of soil, preventing them from sticking. Using nano techniques, these tree trunks are covered in a fuzzy of minute whiskers which creates a cushion of air around the fibre. When water hits the fabric, with beads on the point of the whiskers and also it gives self cleaning effect (Parthasarathi 2007).
Nano crystalline titanium dioxide films have received much attention as a photo catalyst due to its high oxidizing ability, non toxicity and long term stability. More recent application of titanium dioxide in various fields has involved self cleaning, deodorizing, sterilization and antifouling functions (Kaihong Qi et al 2006).

Nanoparticle-embedded acrylic coatings that can absorb copious amounts of UV radiation yet scatter little were developed to protect base fabrics from sun-induced degradation (Phaneshwar Katangur et al 2006). The metal oxide nanoparticles such as SiO$_2$, TiO$_2$, ZnO and Fe$_2$O$_3$ are used as a solid sun block agent to protect the harmful UV radiation (Alterman and Chun 1978).

The nano-SiO$_2$ composite has been coated on the wool fabrics as an antibacterial agent, which provides a good antibacterial activity (Shuhua Wang et al 2007).

The mixture of TiO$_2$-SiO$_2$ coating on the fabrics has shown a high photo catalytic activity than the TiO$_2$ coating which is due to the high dispersion and structural effects of the presence of amorphous silica (Yuranova et al 2006).

2.3.5 Synthesis of Nano Particles

Different approaches have been employed to prepare a range of nano silica particles like thermal decomposition, sol-gel processing technique and vapor-phase reaction (Nittaya Thuadaij and Apinon Nuntiya 2008). In most of the techniques to synthesis the nano silica, the base material is taken from the chemically available precursors. But in the case of thermal degradation, the source material taken from rice hulls is the simplest and cost effective method for large scale production (Kalapathy et al 2000).
There are several physico-chemical methods used for the preparation of nano sized materials, which are given below:

- Vapour phase reaction
- Chemical vapour deposition
- Inert gas condensation
- Laser ablation
- Plasma spraying
- Spray conversion and
- Sputtering

Various nano metal oxides and the end uses are mentioned in Table 2.1.

Nano-particles coating may affect the other fabric properties like dyeing property, strength, bending rigidity and air permeability. The durability of coating is another one important key factor when the fabrics are coated with nano particles.
Table 2.1 Nano Metal oxides and their applications

<table>
<thead>
<tr>
<th>S.No</th>
<th>Nano particles</th>
<th>Application</th>
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<tbody>
<tr>
<td>1.</td>
<td>Silver nano particles</td>
<td>Anti-bacterial finishing</td>
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<tr>
<td>2.</td>
<td>Fe nano particles</td>
<td>Conductive magnetic properties, remote heating</td>
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<tr>
<td>3.</td>
<td>ZnO and TiO$_2$</td>
<td>UV protection, fibre protection, oxidative catalysis</td>
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<td>4.</td>
<td>TiO$_2$ and MgO</td>
<td>Chemical and biological protective performance, provide self sterilizing function</td>
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<tr>
<td>5.</td>
<td>Al$_2$O$_3$ nano particles with PP or PE coating</td>
<td>Super water repellent finishing</td>
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<tr>
<td>6.</td>
<td>Indium-tin oxide nano particles</td>
<td>EM/IR protective clothing</td>
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<tr>
<td>7.</td>
<td>Ceramic nano particles</td>
<td>Increasing resistance to abrasion</td>
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<tr>
<td>8.</td>
<td>Carbon black nano particles</td>
<td>Increasing resistance to abrasion, chemical resistance and impart electrical conductivity, colouration of some textiles</td>
</tr>
<tr>
<td>9.</td>
<td>Clay nano particles</td>
<td>High electrical, Heat and chemical resistance</td>
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<tr>
<td>10.</td>
<td>Cellulose nano-whiskers</td>
<td>Stain resistance and water repellency</td>
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2.4 CROSS LINKING AGENTS

The creasing behavior of cotton fabric is directly related to the free hydroxyl groups present in the amorphous regions. To impart cotton crease resistant finish to the cotton material, the free hydroxyl groups in the structure should be either masked or totally removed. The distance less than 0.5nm are essential to form hydrogen bond formation. In the amorphous region the hydroxyl groups of the cellulose polymer are far apart and hence hydrogen bond formation does not take place, so these hydroxyl groups remain unbound. A popular and widely used method of imparting the crease resistant
finish is the one in which the hydroxyl groups of adjacent macro molecules are reacted with bi-functional chemicals forming a cross link with elimination of water or methanol molecules (Shenai 2001).

2.4.1 Cross Linking Resins

Sivaramakrishnan (2006) explained in detail about various cross linking resins. They are used to improve the durable press rating of the cotton fabrics. Various types of cross linking resins are

- Formaldehyde type
- Melamine formaldehyde type
- Glyoxal resins
- Non-formaldehyde type

Formaldehyde has many advantages as a cross linking agent, including low chemical cost and high finish durability. The formaldehyde process is identified as notorious for its lack of control, high strength loss of treated cotton and excessive fumes around the treating range. It was found that formaldehyde and hydrochloric acid in the presence of water can form Bichloromethyl Ether (BCME), which is a human carcinogen, irritant and allergic to human being and hence cross linking process using formaldehyde has been abandoned. Some of the formaldehyde based cross linking agents are Di-methyl Urea (DMU) and Di-methyl di-hydroxyl ethylene urea (DMDHEU) (Shet and Yabani 1981).

Cellulosic fabrics are treated with formulations containing methylol crosslinking reagents and polycarboxylic acids having three or more acidic groups per molecule. The treated fabrics are cured in a flat configuration and washed. The fabric is subsequently heated in a folded configuration whereby
the folded or creased configuration is permanently imparted to the fabric. A metal salt activating catalyst included in the formulation of the textile treating solution decreases the time required to form sharp, permanent creases in the cured fabrics (Franklin and Rowland 1974).

2.4.2 Mechanism of Cross Linking of Cellulose and Polycarboxylic acids

The Figure 2.1 shows the mechanism of cross linking of cellulose and polycarboxylic acids. The mechanism of polycarboxylic acids is carried out in two steps of cellulose esterification. In the first step the formation of a cyclic anhydride intermediate by the dehydration of two carboxyl groups is carried out. In the second step the ester crosslinks are formed by the reaction between the anhydride with cellulose (Charles Q. Yang and Xilie Wang 1996). The formation of cyclic anhydrides at lower temperatures without catalyst, but the catalyst sodiumhypophosphite (SHP) accelerates the cyclic anhydride process for polycarboxylic acids (Charles Q. Yang 1991).

![Figure 2.1 Mechanism of cellulose and Polycarboxylic acids](image)

**Figure 2.1 Mechanism of cellulose and Polycarboxylic acids**
2.4.3 Methods of Cross Linking and their effects with citric acid and BTCA

Shippee and Gagliardi (1966) proposed a new mechanism to impart improved wear life in 100% cotton fabrics by treating with cross-linking agents so as to effect a differential distribution of the crosslinking agent in the fabric, yarn and fibre. The theoretical basis for this is considered and practical methods to achieve the differential distribution effects.

Kottes Andrews (1990) studied; where in 7% of citric acid was used as cross linking agent and sodium hypophosphite (NaH$_2$PO$_2$) was used as catalyst. The increase in the percentage concentration of catalyst increased the whiteness index, durable press rating (DPR), wrinkle recovery angle and breaking strength. More than 7% of citric acid reduced the whiteness Index and breaking strength. The mechanism of cross linking of cellulose and citric acid is shown in Figure 2.2.

Citric acid (CA), one of the polycarboxylic acids used as crosslinking agents for cotton, is cost-effective and environmentally friendly, but its tendency to discolor fabric is a major disadvantage for white fabrics. The author investigated that the cotton fabric yellowing caused by citric acid at elevated temperatures. They found that yellowing increases as curing temperature, curing time, and CA concentration increase. Using sodium hypophosphite as a catalyst causes less fabric yellowing than monosodium phosphate. Therefore, yellowing caused by citric acid and other hydroxyl multi functional carboxylic acids can probably be attributed to the formation of unsaturated polycarboxylic acids (Yun Lu and Charles Qixiang Yang 1999).
Figure 2.2 Mechanism of cross linking of cellulose and citric acid
Xiaohong and Charles Qixiang Yang (2000) discussed, polycarboxylic acid esterifies cellulose through the formation of a five-membered cyclic anhydride intermediate by the dehydration of two adjacent carboxyl groups. They used Fourier transform infrared spectroscopy (FTIR) to study the formation of cyclic anhydride intermediates by BTCA and poly (maleic acid) (PMA) with and without the presence of Sodium hypophosphite (NaH$_2$PO$_2$) (SHP). In the absence of SHP, BTCA forms the cyclic anhydride only when the temperature reaches the vicinity of its melting point. In the presence of SHP, however, the anhydride forms at much lower temperatures. They found that SHP weakens the hydrogen bonding between the carboxylic acid groups of BTC, contributing to accelerated anhydride formation at lower temperatures. Sodium hypophosphite also accelerates the formation of the anhydride intermediates by polycarboxylic acids in an amorphous state. Figure 2.3 shows the mechanism of cross linking of cellulose and BTCA.

The BTCA treatment increased both the dry and wet crease recovery angle, the wet WRA being higher than dry. The WRA of anionic cellulosic fabric treated with a polyanion seems to improve the crease recovery angle better than that of cationic cellulose treated with polyanion. The whiteness index of the treated fabrics seems to decrease the concentration of cross linkers increases. It was also observed that the decrease in the whiteness is higher for BTCA treatment (Bilgen et al 2006).

The most effective cross linking catalyst is sodium hypophosphite in terms of speed and completeness of cure, fabric whiteness obtained and durability of the resultant durable press finish to alkaline laundering. The use of sodium hypophosphite as a catalyst has several disadvantages such as high cost of chemical, tendency to cause shade changes in fabrics (Welch and Julie 1993).
Figure 2.3 Mechanism of cross linking of cellulose and BTCA

Cotton twill fabric was treated by a pad-dry-cure process with combinations of DMDHEU and several potycarboxytic acids. Fabrics were prepared with several ratios of catalytic carboxylic acid groups to dihydroxyethyleneurea (DHEU) residues in the modified cellulose. The wrinkle-recovery angles, durable-press appearance ratings, and strength retentions of these fabrics were equivalent to or slightly better than those imparted by the conventional DMDHEU-MgCl₂ treatment (Franklin et al 1973).

The recurable process improved the crease recovery property of the fabrics. A recurability test, consisting of a standard ironing to impart a crease, followed by laundering and visual rating of the remaining crease, was developed and applied to cotton fabrics which had been treated with
combinations of a methylol cross linking reagent and a polycarboxylic acid. These fabrics were recurable to a much greater extent than fabrics treated with a conventional metal salt catalyst. Dimethylolhydroxyethyleneurea (DMDHEU) was the best of these reagents in recurrability and wrinkle-recovery angle in the treated fabrics (Franklin et al 1972 and 1972a).

2.4.4 Different methods of cross linking

A wrinkle resistant cotton fabric was produced by photo initiated free radical reaction with N-methyl acrylamide monomer from aqueous solution to form a poly (N-methyl acrylamide) co-polymer, followed by cross linking reactions of the methylol groups of the co-polymer with cellulose (Reinhardt et al 1980).

Cotton fabrics are oxidized with nitrogen dioxide and sodium periodate and cross linked with DMU and with DMDHEU by the pad-dry-cure process. The crease recovery angle increased with degree of oxidation and further, sodium periodate oxidation caused the release of stain in cellulose structure, there by lowering the loss in tensile strength (Shet and Yabani 1981).

Frick and Harper (1982) observed that the dihydroxy imidazolidimiones as one of the cross linking agents, but they still lack in economy and effectiveness. Some of the recent innovations in textile finishing are concerned with low wet pick-up processes. In these processes, chemicals such as cellulosic cross linking agents are applied to cotton or polyester/cotton blend fabrics with wet pick ups of about 10 to 40% fogging was selected for the low wet pick-up method (Reeves and Marquette 1982).
Various types of non-formaldehyde crosslinking agents are used to impart crease recovery finish for cotton fabrics were studied by authors. Glyoxal, polyacetal, bis-β-hydroxyethyl sulfone, propylene glycol diglycidyl ether, and glyoxal adducts of urea and its derivatives were used as crosslinkers. Two crosslinking agents, 4,5-dihydroxy-1a,3-dimethylenurea and 4,5-dihydroxy-1,3-bis-(β-hydroxyethyl) ethyleneurea were the most promising ones for practical use among the many investigated (Kazuhide Yamamoto 1982).

Glyoxal was used as cross linking agent and the effect of the concentration of cross linking agents on dry crease recovery angle in degrees (DCRA) was markedly increased by increasing the concentration of cross linking agent. Finishing with buffered glyoxal cross linking resins gave a consistently better balance of durable press rating to strength than the older, less buffered ones (Jones et al 1980).

Natrium NFO is a self reactive macro cross linking non formaldehyde resin. The concentration of natrium CRA(in degrees) was thus subjected for optimization and it was found that 40 gpl was the optimum one giving the strength retention value of the order of 54.14% with an acceptable degree of crease recovery angle (231). Higher concentration could give higher crease recovery angle values (in degrees), but the strength loss was also accordingly expectationally high (Teli et al 2006).

Wrinkle resistance in cellulosic fabrics can be achieved with ionic crosslinks. Carboxymethylated woven cotton fabric treated with cationized chitosan showed significant increased in wrinkle angle recovery without strength loss (Hauser et al 2004).

Dyeing and finishing of cotton fabric in a single bath with reactive dye and citric acid increased the colour index value and breaking strength
(Youngchun Dong et al 2001). Mercerized and bleached cotton fabrics dyed with different classes of reactive dyes as well as vat, sulphur and pigment colours have been subjected to different cross-linking agents viz., BTCA, citric acid and DMDHEU using catalysts such as sodium hypophosphite and trisodium citrate under different conditions of time and temperature of curing. Resultant fabrics were analysed for changes in colour difference, fastness to various agencies, wrinkle recovery, tensile and tear strength as well as flex abrasion properties. From the study it was concluded that the BTCA treated fabric exhibits good properties in all aspects (Doshi et al 2001).

The cotton fabric was pretreated with stannus chloride or alum and dyed with Caspian dye and cross linked with different cross linking agents viz. DMDHEU, VLF, BTCA+TSC or CA+TSC., it was observed that the colour difference of different cross linked fabric was comparable or slightly higher than that for conventionally used DMDHEU cross linked fabric (Sheth et al 2003).

Other than cotton like jute fabric also finished with suitable cross linking agents to impart crease recovery finish. To impart the crease recovery of jute fabric, citric acid and BTCA with different catalysts were used with the maximum curing temperature of 160 °C (Bagchi and Saha 2002).

Sarkar et al (2003) discussed the Dimethylol Dihydroxy Ethylene Urea (DMDHEU) based inbuilt catalyst as one type of formaldehyde cross linking agents and it was used for bacterial resistance finish on cotton fabrics using natural herbal extracts. Udomkichdecha et al (2003) revealed the non formaldehyde durable press finishing of cotton fabric with the cross linking agents such as acrylic and maleic acid.
The dry wrinkle recovery angles of fabrics increased with BAP treatment alone, but the maximum attainable value can only reach the range of 180 to 190 degrees, which was less efficient than those of modified dimethyldihydroxyethyleneurea (266 degrees) and citric acid (231 degrees) (Wan-Chao Jiang et al 2005).

NAPU was used and proved to be a more effective crosslinking agent for cotton than citric acid. The whiteness of the fabrics treated with NAPU was lower than that of the untreated cotton and the fabrics treated with SDP and CA (Zheng-Rong Li et al 2007).

The steeped procedure was used to investigate the physical properties and crosslinking structure. It was found that the values of the N content, dry crease recovery angle (DCRA), and wet crease recovery angle (WCRA) of the treated fabrics with any specific steeped procedure were higher than those of normally treated fabrics (Hung-En Chen et al 2006).

An X-ray diffractometer was used to study the crystalline structure of cotton fibers after bleaching, crosslinking and a combination of bleaching and crosslinking treatments. Wet crosslinking was accomplished with formaldehyde and dry crosslinking was carried out with either dimethyldihydroxyethyleneurea (DMDHEU) or citric acid (CA). Results indicated that crosslinking of bleached cotton did not change the crystalline nature of cotton, but it increases the degree of crystallinity when crosslinked with either DMDHEU or CA; crosslinked formaldehyde was relatively less crystalline (Parikh et al 2007).

To analyse the particulate soiling properties of cellulosic fabrics durable press finished with polycarboxylic acids like citric acid, BTCA were used as crosslinking agent and SHP was used as a catalyst for both cases (Mamiko Yatagai and Yui Takahashi 2006). A new type of catalyst named
primafin NF was used as formaldehyde free cross linking agent and the results were compared with DMDHEU treated fabrics (Ramesh Kabra and Ajit Parab 2004). Sodium di hydrogen phosphate (SDP) and Sodium hypophosphite (SHP) were used as catalysts for simultaneous dyeing and finishing of cotton fabric using reactive dyes and citric acid as a cross linking agent (Malik and Sushil kumar 2005).

Enzyme washing is commonly used as a wet process technique to improve textile handle, appearance, and other surface characteristics of cottons in the industry. The authors studied the effects of cellulase treatment on tensile strength, flex abrasion resistance, and handle of cotton fabric crosslinked by a polycarboxylic acid. The fabric was first treated with cellulase (pre-curing treatment), then crosslinked by 1,2,3,4-butanetetracarboxylic acid (BTCA). The fabric was also crosslinked by BTCA first and then treated with cellulase (post-curing treatment). They compared the performance of the durable press (DP) finished cottons treated with cellulase using these two different procedures, and they found that the pre-curing cellulase treatment has a more positive influence on fabric handle than the post-curing treatment, but it also caused significantly higher fabric strength loss than the post-curing treatment (Charles Qixiang Yang et al 2003).

Polycarboxylic acids were found suitable as cellulose crosslinking in the presence of aliphatic, alicyclic and aromatic acids which contain at least three and preferably more carboxyl groups per molecule and are either olefinically saturated or unsaturated. Aliphatic, alicyclic and aromatic acids having two carboxyl groups per molecule with a carbon-carbon double bond present alpha, beta to one or both carboxyl groups (Welch and Kottes Andrews 1989).

Cotton fabric was treated in different concentrations of BTCA and SHP solutions and the results showed that BTCA is most effective for durable
press finishing at around 2%. The moisture regain of the treated fabric decreased as the weight gain increased before 10%, and then increased at high levels of weight gain. These results indicate that except for inter and intramolecular crosslinking, some side grafts were formed during the treatment, and at BTCA high concentrations, the quantity of side grafts increases. When the fabric was cured in tension, the intramolecular crosslinks can be reduced and the treated fabric's strength retention can improve from 45% to above 75% (Weilin Xu and Yi Li 2000).

Maleic acid i.e. homopolymer (PMA) and the Terpolymer (TPMA) along with citric acid were also used as cross linking agents and also they are more cost effective than BTCA. They also noticed that very less effective cross linkers than BTCA (Charles Q. Yang et al 1997 and 1998). The finishes imparted by 1,2,3,4-hutanetetracarboxylic acid (BTCA) are durable to more than 65 laundering cycles with a phosphate-built alkaline detergent at 50°C. Sodium phosphine is a toxic, spontaneously flammable gas when heated (Welch and Kottes Andrews 1989a).

Catalysts for the rapid esterification and crosslinking of fibrous cellulose in textile form by polycarboxylic acids at elevated temperatures were discussed. The catalysts are acidic or weakly basic salts selected from the alkali metal dihydrogen phosphates and alkali metal salts of phosphorous, hypophosphorous, and polyphosphoric acids. Suitable polycarboxylic acids include saturated, unsaturated and aromatic acids, as well as alpha-hydroxy acids. The textiles so treated exhibit high levels of wrinkle resistance and smooth drying properties durable to repeated laundering in alkaline detergents, and do not contain or release formaldehyde (Welch and Andrews 1990).

Dimethyloldihydroxyethyleneurea (DMDHEU) and acrylic acid cross linking agents were used to treat the cotton fabric with a pad-dry-
plasma-cure process. Rate constant and structural diffusion resistance constant for the pad-dry-plasma-cure treated fabrics were lower than those for pad-dry-cure fabrics treated at the same resin concentration, and the values of dye absorption and equilibrium absorption of plasma treated fabrics were also lower than those for non-plasma treated fabrics. However the activation energies for the pad-dry-plasma-cure process were higher than that for the pad-dry-cure process (Meng-Shung Yen et al 2006).

A multifunctional finishing was attempted to impart durable antibacterial and wrinkle resistance to all cotton and blended materials. The cross linking reactant would hook covalently the chitosan molecule to cotton cellulose in addition to imparting the wrinkle resistance. Chitosan was produced by deacetylation of chitin, a natural polymer form renewable resources (Rahman et al 2005).

Cotton fabrics treated with NMA with phosphates, NMMA with or without phosphates, and NMP-2 to lower and higher levels of DP appearance and conditioned WRA, demonstrated an overall superior balance of strength/abrasion properties (Gonzales and Rowland 1981).

The acrylamide-aldehyde adducts were tested as formaldehyde free cross linking agents for cotton. These agents were less effective in producing wrinkle resistance and durable press performance than common cross linking agents made from formaldehyde (Frick and Harper 1983).

1,2,3,4-Butanetetracarboxylic acid (BTCA) and all-cis-1,2,3,4-cyclopentanetetracarboxylic acid were studied as durable press reagents for cotton. Weak bases were proven to be active catalysts, one of the most effective being monosodium phosphate. The amount of tetracarboxylic acid required could be decreased by two-thirds by having citric or tartaric acid present as a co-reactant additive.
In the presence of polyethylene glycol (PEG), due to increased swelling of fibre and more penetrations of DMDHEU, the crease recovery, abrasion resistance and water absorbency improves (Mehdi Afsharie et al 2006).

2.4.5 Effect of cross linking agents on tensile strength

Severe tensile strength loss is the major disadvantage of crease resistance finished cotton fabrics due to acid-catalyzed depolymerization and crosslinking of cellulose molecules (In-Sook Kang et al 1998). The tensile strength loss of cross linked cotton fabric is independent of differences in the molecular structure and reactivity of the cross linking agents (Charles Q. Yang et al 2000). The cross linking of cellulose molecules by a polycarboxylic acid causes reversible fabric strength loss.

The magnitude of the tensile strength loss increased as the degree of cross linking increased (In-Sook Kang et al 1998). The gas liberated by the sodium hypophosphite was toxic nature and spontaneously flammable (Welch and Kottes Andrews 1989). The laundering durability of BTCA has maintained by the activity of the curing catalyst used. Lower concentration of catalyst, curing temperature and time affects the durable press appearance of fabric (Brodmann 1990).

The catalyst monosodium phosphate results yellowness and di-sodiumphosphate was somewhat less active than sodium hypophosphite (SHP), but the quality of SHP was a remarkable factor when compared to phosphate or pyrophosphate catalyst (Brodmann 1990). High curing temperature and high BTCA concentration reduce the tensile strength and increase the WRA. 3 % of NaOH treatment recovers the tensile strength but it changed the WRA (Weilin Xu and Yi Li 2000). When the polycarboxylic acids were used in dye bath, it reduced the dye up take for certain group of
dyes (Christian Schramm et al 2002). The catalysts have more sensitivity in dyeing process. The cross linking of polycarboxylic acids significantly decreased the colour strength of prints (Hebeish et al 2006).

2.4.6 Effect of pH on cross linking

Cellulose esterification by a polycarboxylic acid proceeds in two steps: the formation of a five-member cyclic anhydride intermediate by dehydration of two adjacent carboxyl groups of the polycarboxylic acid, and the reaction between cellulosic hydroxyl and the anhydride intermediate to form an ester. The quantity of the cyclic anhydride intermediate formed in a cotton fabric increased as the pH of a finish bath was reduced from 4.5 to 1.5. Therefore, cyclic anhydride intermediate formation was accelerated by increased proton concentration of the finish bath. Anhydride intermediate formation and cellulose esterification show different pH-dependencies. When the three sodium salts of phosphoric acid were used as catalysts for the ester crosslinking of cotton cellulose, they showed different levels of effectiveness due to the different pH values of the finish baths (Charles Q. Yang 1993 and 1993a).

2.4.7 Individualized cross linking of cellulose structure

Carlisle M. Herron et al (1993) analysed the improved absorbent structure performance for structures containing individualized, crosslinked fibers obtained through the utilization of individualized, crosslinked fibers.

Carlisle et al (1996), found individualized, crosslinked fibers having an effective amount of a polyacrylic acid crosslinking agent, preferably between about 1.0 wt. % and about 10.0 wt. %, more preferably between about 3.0 wt. % and about 7.0 wt. % crosslinking agent, calculated on a dry fiber weight basis, reacted with the fibers in the form of intrafiber crosslink bonds.
2.4.8 Effect of citric acid and chitosan

Citric Acid (CA) and chitosan were used as durable press and antimicrobial finishing agents for cotton, and were applied by means of the conventional pad-dry-cure process. CA was expected to react with hydroxyl groups in cellulose and chitosan or with amino groups in chitosan to form ester cross linking or an inter-ionic attraction. Durable press appearance ratings of 3.5 to 4 were imparted with CA and chitosan treatments. The cotton fabric treated with CA alone showed antimicrobial properties. These and durable press performance were retained through twenty washing and tumble drying cycles. Strength retention improved more with CA and chitosan than with CA alone (Yong-Sik Chung et al 1998).

2.4.9 Influence of softener on crease recovery angle

The effects of an easy-care finish, namely DMeDHEU and DMeDHEU plus silicone softener, on physical properties of bleached cotton fabric have been studied. It was obvious that easy-care finish imparts marked increase in the fabric crease resistance along with the increase in static and kinetic frictions. The application of silicone softener on top of the easy-care finished fabric decreased the fabric friction and a further increase in the crease recovery angle was also observed. Easy-care finishing marginally changes the bending length, which was reduced to some extent by the application of silicone softener. The application of cross linkers improved the crease recovery angle of fabric. On the other hand the application of silicone based softeners plus DMeDHEU increased the fabric crease recovery more than that observed on treatment with DMeDHEU alone. The silicone softener treated fabric reduced the friction of the fabric. The application of silicone softener reduced the bending length of the fabric marginally (Talebpour and Holm 2006).
2.5 NANO SILICA APPLICATIONS AND VARIOUS PROPERTIES

The maintenance and improvement of current properties and the creation of new material properties are the most important reasons for the functionalisation of textiles. In this aspect nano metal oxides were incorporated with fabrics.

The solubility of amorphous Silica in water at high temperatures and high pressure was investigated using commercial scale and vitreous silica as starting materials. The maximum solubility at the vapor pressure of solution was 1660 mg/kg at 340°C and the extrapolated solubility at the critical point was 890 mg/kg (Fournier 1977).

Fibrous webs comprising fibers coated with a continuous film comprising silica have excellent absorbent and wicking properties. The fibers themselves may be hydrophilic (e.g., cellulose) or hydrophobic (e.g., a polyolefin or a polyester) (Weisman and Retzsch 1984).

Dye molecules are incorporated into silica matrices for textile dyeing. The incorporation properties were mainly influenced by the properties of the dyes, but improved wash fastness can be achieved by modifying the matrixcomposition (Mahltig et al 2004).

Structural and adsorptive characteristics of nano silica and its interaction with organics, biomacromolecules, and micro organisms were analysed to elucidate fundamentals of its application as a medicinal preparation for human protection. Nano scaled primary particles (5 to 50 nm), forming aggregates (50-1000 nm), and agglomerates (>1 micro meter), are responsible for high specific surface area (upto 500 sq.m./g), a high
adsorption capacity for proteins and micro organisms and fast adsorption of proteins or toxins (Gunko et al. 2006).

Nomex fabric composites filled with the particulates of polyfluo150 wax (PFW) and nanoparticles of SiO₂, respectively, were prepared by dip-coating of the Nomex fabric in a phenolic resin containing particulates to be incorporated and to be cured successively. The adhesion and tensile strength of the unfilled, PFW or nano-SiO₂ filled Nomex fabric composites were evaluated. The results showed that the addition of PFW and nano-SiO₂ significantly improved the wear resistance and decreased the friction coefficient (Feng-Hua Su et al. 2007).

SiO₂ thin films prepared from tetraethylorthosilicate by sol–gel method were coated on the fabric substrates of natural and synthetic fibres. The add-ons and leaching behaviors of silica xerogel coating on the surface of cotton, flax, nylon-66 and poly(ethylene terephthalate) fabrics were studied to compare the interaction and adhesion of the silica coating with different fabrics. The adhesion of silica coating on the synthetic fabric substrates was mainly a result of thermodynamic affinity by dipolar–dipolar and hydrogen bond interaction. For the cellulose fabrics, except thermodynamic affinity, there are covalent bonds formed between the end groups of silica precursor and hydroxyl groups on cellulose fibres, which made the silica coating more durable. The results show that the adhesion of silica coating on the surface of fabrics was in principle influenced by the chemical composition and structure of fabric substrates (Feneyan Li et al. 2008).

Ordered mesoporous silica particles with different morphologies were synthesized through a simple hydrothermal process. Then these silica particles were functionalized with luminescent YVO₄:Eu³⁺ layers via the Pechini sol-gel process (Piaoping Yang et al. 2008).
Many types of binders are used to apply nano particles. A coating composition that was used primarily as a clear finish over a colored or pigmented finish that are applied where as the composition contains as the film forming binder which is an acrylic polymer, a self stabilized dispersed resin formed by polymerizing in solution an acrylic solution polymer (Antonelli and Isidor Hazan 1986).

Applicability of the sol-gel method to fabricate polymer-silica composites has been briefly reviewed. The sol-gel method was used for synthesis of nanosilica in mineral and naphthenic oils and also in latexes of diene copolymers. A new silane precursor of nanosilica was prepared by transesterification of tetraethoxysilane with $n$-decyl alcohol and (aminopropyl)trimethoxysilane, in the presence of an emulsifier and a stabilizer. Transparent sols of nanosilica in oils were obtained as the main product, accompanied by few % of dispersions of $\text{SiO}_2$. Nanosilica sols were applied for modification of properties of elastomers and other polymers (Jerzy Chrusciel and Ludomir Slusarski 2003).

Nanoparticle-based silica sols produced by a novel sol-gel procedure have been deposited by dip-coating onto AISI 321 stainless-steel to improve its high temperature oxidation resistance. The oxidation rate was measured by thermogravimetry. At 500°C, the silica coating remains as a surface layer and prevents oxidation of the alloy, whereas above 700°C protective chromium oxide was formed at the surface.

The authors successfully prepared transparent and durable super hydrophobic silica-coating films on cotton substrates at low temperatures. The coatings were produced via co hydrolysis and polycondensation of a hexa decyl trimethoxy silane (HDTMS), tetraethoxyorthosilicate (TEOS), and 3-glycidyl-oxypropyltrimethoxysilane (GPTMS) mixture. The hydrophobic
properties of the nanocomposite coatings were determined using contact-angle and water-gain measurements. The water contact angle for the coated substrates was 141 degrees, whereas, before coating, the contact angle was 0 degrees because of the superhydrophilic nature of cotton (Walid A. Daoud et al 2004).

Poly (vinyl alcohol)/silica organic inorganic hybrid composites were prepared by sol-gel technique. Tetraethoxysilane was used as the precursor for silica. Uniform dispersion of silica particles within the hybrid nanocomposites was also supported from the energy dispersive X-ray mapping of silicon. Dynamic mechanical properties exhibited substantial mechanical reinforcements due to the dispersion of nanosilica particles in the matrix (Bandyopadhyay et al 2005).

Multi-scale hybrid nanocomposites containing both 15 nm silica colloids and 2 nm oligosiloxanes in a methacryl polymer matrix were newly designed and fabricated. Multi-scale hybrid nanocomposites fabricated by UV and thermal curing with incorporation of silica colloids in the nano-hybrid materials show enhanced mechanical and thermal characteristics (Jeong Hwan Kim et al 2006).

Sol–gel silica coatings were deposited on soda lime glass substrates by dip-coating. The silica films were amorphous, crack free, and smooth with an average roughness of less than 3 nm and thickness of 0.8–1.2 nm. For polishing wear experiments, hardness was inversely proportional to polishing wear rate. This suggests that hardness is a good indicator for the resistance of sol–gel silica coatings to polishing (Darran R. Cairns et al 2008).

Scratch-resistance of sol-gel derived nano porous silica films were studied. It was attributed to the cross-linking of silica particles in the sols by
randomly branched or/and entangled linear chains and more Si–O–Si bonds formed by the mixture gas treatment (Jue Wang et al 2000).

The authors obtained microporous and mesoporous silica gels by sol-gel processing. Tetraethylortosilicate (TEOS) was used as precursor. Nitric acid and hydrofluoric acid were used as catalysts. The samples obtained in the presence of formamide have larger pore volume and its pore structure was in the range of mesoporosity. The samples obtained without additive were microporous. Formamide allowed the preparation of crack-free silica gels stabilized at high temperatures (Lenza and Vasconcelos 2001).

Three new processes to obtain silica having high specific surface area from burned pre-treated rice hulls were presented and discussed. These procedures allow for the simultaneous recovery of biomass energy and the production of high quality silica at thermoelectric plants, without the risk of using corrosive substances in the burning process. The first method involves treatment of the hull with hot organic acid solutions before burning, the second with boiling water, both using an autoclave at temperatures close to 150°C, while the third method renders the hull fragile by treating it at 250°C and reducing it to a fine powder before burning. The first two methods result in white amorphous silica that can show 500 m²/g of specific surface area (De Souza et al 2002).

The authors discussed a novel preparation method of silica coated organic pigment. In this approach, the surfaces of the organic pigment were first orderly modified by poly (sodium 4-styrenesulfonate) (PSS) and poly (diallyldimethylammonium chloride) (PDADMAC), then coated by silica via sol-gel process of tetraethylorthosilicate (TEOS). The results showed that PVP, pH value, water and TEOS contents had significant influence on the morphology of the silica encapsulated organic pigment. Organic pigments coated silica by this approach could scatter UV ray with a wavelength less
than 270 nm, and this scattering property increased with more silica coated (Junjie Yuan et al 2005).

Cotton fabric was successfully modified to have an antibacterial property through use of the sol-gel process. Dodecanethiol-capped silver nanoparticles, which have powerful antibacterial activity, were incorporated in silica sol. The cotton fabric was padded with dodecanethiol-capped silver nanoparticle-doped sol, dried at 60°C, and cured at 150°C. The antibacterial effects of the treated cotton fabric against *Escherichia coli* were examined and found to be excellent (Tarimala Sowmitri et al 2006).

Lightweight 100% cotton fabric was successfully modified by the sol-gel process to impart high ultraviolet radiation (UVR) scattering property to the fabric surface. Active ingredients were tetraethyl orthotitanate [Ti(OCH$_2$CH$_3$)$_4$] and tetraethyl orthosilicate [Si(OCH$_2$CH$_3$)$_4$]. The cotton fabric was padded with the nanosol solution, dried at 60°C, and cured at 150°C. Excellent UVR scattering was obtained with all treated fabrics. Increasing titania content in the nanosol solution leads to increased UVR protection (Noureddine Abidi et al 2007).

Anatase TiO$_2$/SiO$_2$ nanocomposites were prepared by a sol–gel process at a low temperature. The spherical TiO$_2$/SiO$_2$ nanocomposites were coated onto cotton fabrics by a simple dip-pad–dry-cure process. The treated cotton fabrics demonstrated higher photocatalytic activity in comparison to pure TiO$_2$ treated cotton fabrics in a typical photocatalytic test using a model compound of Neolan Blue 2G dye. The developed composite material was a step towards better self-cleaning performance of textile materials (Kaihong Qi et al 2007).

The coating of textiles with chemically or physically modified silica sols with particle diameters smaller than 50 nm (“nanosols”) enables the
manifold alteration of their physico-mechanical, optical, electrical and biological properties. Thus the protection of textiles against destruction and the creation of new advantageous functions can be realised. The prospective new products to be developed include textiles with water, oil and soil repellency and with antimicrobial properties. The authors discussed recent results from applying modified silica nanosols to the functionalisation of textiles (Mahitig Boris et al 2005).

Huang et al (2006) studied that the cotton fabrics were treated by pad-dry-cure method with an antiwrinkle finishing agent (DMEU) in combination with different concentrations of tetraethoxysilane (TEOS) and isopropanol at various volumes. It increased the crease resistance and tensile strength.

The sol-gel process is an excellent technology for coating various materials thus imparting new properties to the treated samples. 100% cotton fabric were treated in two steps with formulations containing BTCA (1,2,3,4-butanetetracarboxylic acid) and SHP (sodium hypophosphite) as catalyst and TEOS (tetraethoxysilane)/GPTMS (glycidylpropoxytrimethoxysilane)-based solutions with different amounts of GPTMS. The textile physical properties were evaluated by means of DCRA (dry crease recovery angle), and the abrasion resistance was tested with a Martindale tester. The findings make evident that the DCRA values could be moderately improved applying a two step procedure (BTCA treatment, sol-gel treatment), while the abrasion resistance was significantly increased (Schramm 2004).

The influence of the type and concentration of the acid catalyst and the gelation temperature on the structure of pores of silica gels obtained with TEOS. The values of the major structural parameters related to the pores such as volume fraction of pore (VV), surface area per unit volume (SV), the average pore size (rP) and the connectivity of pores (GV) obtained, showed
the possibility of tailoring the pore structure of silica gels by changing the processing variables. For the HF catalyzed gels, the values of average pore radius varied from 6.8 nm to 21.6 nm and the gelation time varied from 2 min to 140 min. For the gels, the activation energy for gelation (E) was found to be 11.8 kcal/mole (Silva and Vasconcelos 1999).

Spherical silica powders with uniform, submicron grain diameter have been obtained using the sol-gel technology. Subsequently, metallic silver nanoparticles have been produced on the surfaces of the grains. Silver-doped silica powders display anti-microbial capabilities and can be used to obtain doped thin-film coatings, e.g. for the production of bacteriostatic textiles (Jasiorski 2004).

Water repellent coating was prepared with the tetraethoxysilane (TEOS) and solvent ethanol, catalyzer HCl, water and modified with additives, such as Methyltriethoxysilane (MTEOS), Octyltriethoxysilane (OTEOS) and Hexadecyltrimethoxysilane (HTEOS). As a result, acceptable water repellence could only be achieved via the addition of longer chain length additives such as OTEOS, HTEOS, while the use of additives containing a shorter alkyl chain length such as MTES led to insufficient water repellence. The factors which influence contact angles were examined. Excellent water repellent properties could be achieved on the cotton fabrics treated with the silica sols by twice dip and pad and cured at 160°C. The water repellence contact angle was able to be reached around 140 degrees and the hydrostatic pressure was 46 cm (Chao-xia Wang 2007).

Nanosilica was prepared by precipitation method and characterized by various analytical techniques. From the experimental results, it was found
that the incorporation of the nanosilica in the cement paste increase the compressive strength when compared with that of the portland cement paste (Nittaya Thudaij 2008a).

In order to investigate the effect of silica size on the friction and wear behaviors of PI hybrids, polyimide/silica (PI/SiO2) hybrids with different size of silica were successfully synthesized through an in situ sol-gel reaction from pyromellitic dianhydride-4,4-oxydianiline (PMDA-ODA) and tetraethoxysilane (TEOS). The size of silica in the hybrids was 100–800 nm. Tensile tests on the PI/SiO2 hybrids showed that the strength and toughness of PI/SiO2 hybrids were improved simultaneously when the size of silica was less than 300 nm. The friction coefficient and wear rate of the PI hybrids firstly decreased and then increased with increasing the size of silica. The friction coefficient of the hybrid with 100 nm SiO2 was the lowest and Ca 20% lower in contrast with that of pure PI. However, the lowest wear rate was recorded for the hybrid with 300 nm SiO2, Ca 20% lower than that of neat PI. These behaviors were attributed to the size effect of silica in PI matrix. Scanning electron microscopy (SEM) revealed that an appropriate size of silica in PI matrix could effectively reduce adhesive wear of PI and restrain the formation of bigger debris (Shi-Quan Lai 2007).

The authors aimed to improve wear resistance of composite fabrics via nano-silica-fused whiskers. It was hypothesized that nano-silicafused whiskers would significantly improve composite mechanical properties and wear resistance. Nano-silicas were fused onto whiskers and incorporated into a resin at mass fractions of 0 to 4%. Linear correlations were established between wear and hardness, modulus, strength, and toughness. Novel nano-silica-fused whisker composites possessed high toughness and wear resistance with smooth worn surfaces, and may be useful in large stress-bearing restorations (Xu 2004).
2.6 MICROENCAPSULATION

Micro-encapsulation is a very important growing technique which finds applications in many industries like agricultural, medical and textiles. Micro-encapsulation technologies offer many opportunities to improve the properties of fabrics to obtain and enhance new functionalities (Sudha et al 2006).

The textile roots of yeast microencapsulation technology were introduced as were the wide range of applications in food and other business sectors. In microencapsulation, in general the number of commercial applications in the textile industry continues to grow, particularly in the textile industries of Western Europe, Japan and North America. The move by the more developed countries into textiles with new properties and added value, into medical textile and technical textiles for example has encouraged the industry to use microencapsulation processes as a means of imparting finishes and properties on textiles which were not possible or cost-effective using other technology. Textile manufacturers are demonstrating increasing interest in the application of durable fragrances to textile as well as skin softeners. Other potential applications include, insect repellents, dyes, vitamins, antimicrobials, phase change materials and in specific medical applications, antibiotics, hormones and other drugs (Gordon Nelson 2002).

Micro-encapsulation is the packaging of materials in the form of capsules, ranging in size from 1µm to less than 1000 µm (Ya-I Hung et al 2007). Uniqueness of micro-encapsulation leads to several advantages in practical applications and it provides a means of packaging, separating and storing active materials on a microscopic scale, and then later to release under controlled conditions (Thilagavathi et al 2007).
Harris and Blevins (2002) discussed a process for applying microcapsules to a textile material comprising, contacting the textile material with the microcapsules, dispersing around and through the textile material with a dispersant, and adhering the dispersed microcapsules to the textile material with a binder.

The authors presented a process for the preparation of microcapsule compositions, methods for using those microcapsule compositions, compositions containing those microcapsule compositions and microcapsules prepared by the process. (Brian Eric Benoff and Robin William Dexter 1998).

Microencapsulation is the envelopment of small solid particles, liquid droplets or gas bubbles with a coating. Microcapsules preserve a substance in a finally divided state and release the substance from the enclosed capsules as required (Amit Dayal et al 1999).

Micro-encapsulation of nano metal oxide particles in a polymer shell, helps to avoid undesirable aggregation. Thus, the preparation of microcapsules by encapsulating nanoparticles in to the polymer matrix has been attracted in recent years. Various kinds of encapsulation techniques like solvent dispersion, coacervation, co-crystallization, interfacial polymerization and spray-drying have been developed for coating applications (Su et al 2008).

Georg Horger (1975) and Gunther Baatz et al (1978) discussed, a process which has disclosed a liquid-liquid phase separation utilizing certain inorganic polymeric materials as phase-separation-inducing materials. The Liquid-liquid phase separation of this disclosure is of the type generally named "simple" coacervation wherein a major portion of the organic hydrophilic polymeric material was included in the separated, emergent, liquid phase and the phase-separation-inducing material was substantially
evenly distributed, as to concentration, between the separated phase and the manufacturing vehicle. Gelatin as the organic hydrophilic polymeric material and polysilicates and polyphosphates as the inorganic polymeric phase-separation-inducing materials were used. The liquid-liquid phase separation was useful for, among other things, manufacturing, minute capsules having the organic and inorganic hydrophilic polymeric material as capsule wall material.

Microcapsules were formed in the absence of coacervation by providing an oil-in-water emulsion containing a polymeric, emulsifying agent having cross-linkable groups or complexing sites and admixing with the emulsion a cross-linking agent or a complexing agent, which forms an impermeable coating around the dispersed oil droplets. The emulsifying agent may be non-proteinaceous or the protein, gelatin. Impermeable capsule walls were formed solely by the addition of the cross-linking or complexing agent and extraneous hardening agents were obviated. Moreover, the emulsifying agent may be a preformed, polymeric, cross-linking agent which eliminates the need for any separate cross-linking agent (Vassiliades 1981).

A microcapsule containing hydrous composition containing an electrolyte and microcapsules coated with a water-soluble polymer which undergoes phase separation by the action of the electrolyte. The electrolyte causes the above-mentioned phase separation comprising 5% to 80% by weight of water and water-soluble components (Masahiro Takizawa and Hideyuki Takahashi 1990).

A fragrant fibrous structure, such as fabrics, apparels or the like, provided with microcapsules encapsulating a perfume and a resinous binder, preferably a silicone resin. The process for preparing the above fibrous structures comprises applying a treating liquid, comprising microcapsules composed of an external wall of a formaldehyde based resin enclosing a
perfume and a resinous binder, preferably a low temperature reactive organopolysiloxane prepolymer emulsion, preferably together with a pressure absorbing agent, to at least a part of a fibrous structure and then drying the fibrous structure at a temperature of less than 150°C to fix said microcapsules on the fibre surfaces of the fibrous structure (Akira Ono et al 1989).

Molten, a water soluble polymer was used as a binder for agriculturally effective active ingredients in a water free encapsulation process. For finely divided solid active ingredients, a solvent for the binder can be used to increase the amount of bound active ingredient. For water insoluble active ingredients, the binder provides a method for rendering the active ingredient dispersable in water (Lew et al 1997).

Coating or encapsulation processes provide good durability for finishing. The encapsulation process enable aqueous dispersions of particles for which dispersions have been stabilized with basic dispersant, to be used without undue reduction in encapsulation efficiency due to the presence of the basic dispersant. In the processes, ethylenically-unsaturated carboxylic acid was used to treat the stabilized aqueous dispersion prior to the encapsulation or coating of the particles with polymer (Smith and Hoy 1991).

Microcapsules were prepared by encapsulating a core material with a capsule shell wall containing glutaraldehyde crosslinked gelatin and at least one water soluble plasticizer that reduced the permeability of the crosslinked gelatin. Optionally, the capsule shell wall also contains a feeding deterrent that dissuades accidental ingestion of the microcapsule. Upon exposing the microcapsules to water, the plasticizer was removed making the shell wall permeable whereby the encapsulated core material is released. Materials such as insecticides, herbicides, plant growth regulating agents, and fungicides may be encapsulated and released at a controlled location, time and rate (Mcmahon et al 1995).
2.6.1 Application of microencapsulated silica

Richard Billings and Lyle D Burns (1997) explained a method for cleaning contaminated surfaces or for cleaning bulk contamination of hydrocarbons or chemicals. To clean hydrocarbon or chemical contaminated surfaces, a basic aqueous silica solution was sprayed onto the contaminated surface and allowed to dry. The resulting dry material will flake off, leaving a cleaned surface, without damaging the surface. To clean bulk contamination of hydrocarbons or chemicals, the basic silica solution was mixed with hydrocarbons or chemicals and then an acidic aqueous polymer solution was added and mixed. An amorphous silica material was immediately formed which permanently encapsulates the hydrocarbons or chemicals and which dries to an inert powder.

The microencapsulation of l-menthol was studied by spray drying, using gum arabic and modified starch as capsule materials. The release characteristics of l-menthol were also analysed and the release rate increased upon elevation of relative humidity and temperature. The activation energies of the release of l-menthol from GA wall matrices at 75 and 83%RH were 140 and 48 kJ/mol, respectively (Apinan Soottitantawat et al 2005).

2.6.2 Microencapsulated fire retardant fabric

Two types of microcapsules of di-ammonium hydrogen phosphate (DAHP) with respectively polyether-polyurethane shell and polyester-polyurethane shell were evaluated as intumescent flame retardant (FR) in a commercial polyurea coating for textiles. The expected advantages of this new concept of encapsulated FR agent are to be compatible with a polymeric matrix in order to give a permanent FR effect and to be itself an efficient FR intumescent formulation for many materials. The thermal degradation for the two types of DAHP microcapsules shows characteristics of an intumescent
formulation. The reaction to fire of cotton fabrics coated by FR polyurea loaded with neat or microencapsulated DAHP was studied with the cone calorimeter as the fire model. Both types of DAHP microcapsule present in the polyurea coatings on cotton fabric give an efficient FR effect, although the char developed with microcapsules was a little less heat resistant than that developed with the pure DAHP. Coatings containing microcapsules with polyester-polyurethane shells evolve the smallest quantity of smoke and CO (Stephane Giraud et al 2005).

Polyurethane-phosphates combination was known to form a flame retardant (FR) intumescent system. The intumescent formulation could not be permanent because of the water solubility of the phosphate. This problem could be solved by the technique of microencapsulation. Di-ammonium hydrogen phosphate (DAHP) was microencapsulated with a polyurethane (PU) shell. Polyurethane for textile coating was loaded with neat or microencapsulated DAHP. Thermal degradation behaviour of DAHP microcapsules, PU loaded formulations and cotton coated by these PU formulations. Improvement of the thermal stability for PU textile coating was observed with neat and microencapsulated DAHP. The flame retarding behaviour of these coated cotton fabrics was also valued with the cone calorimeter. This new concept of phosphate encapsulated by PU shell showed a significant FR effect. (Stephane Giraud et al 2002).

2.6.3 Advantages of Microencapsulation

It was clear that microencapsulation systems have many advantages such as controlled release behaviour, protection of agents from hazardous environments, increasing the surface area, allows the specific applications. Although textile manufacturers and scientists will investigate the potential applications of microencapsulation in textiles, the consumers’ demands will
play a major role (Gohhanerloan and Marihsuwtish 2004).

Encapsulation of a dispersed oil phase (hexadecane) was realized by simple coacervation method. The authors used soy glycinin as the wall forming material. In simple coacervation method suitable emulsification and conditions, that favor the formation of microcapsules wall were identified. The glycinin-hexadecane couple microencapsulation feasibility, the appropriate choice of the emulsification parameters allowed a significant improvement of the protein deposition around oil droplets during the coacervation (Lazko et al 2004 and Bojana Boh and Emil Knez 2006).

Lycopene microcapsules were prepared by a spray-drying method using a wall system consisting of gelatin and sucrose. The effects of technological parameters including the ratio of core and wall materials, ratio of gelatin and sucrose, homogenization pressure, inlet temperature, feed temperature, and lycopene purity on encapsulation yield (EY), encapsulation efficiency (EE) were analysed (Bo Shu et al 2006).

2.7 MICROENCAPSULATION OF NANO MATERIALS

Nanotechnology processes have recently been introduced into the textile field. One of these processes involves encapsulated nanoparticles or nanoproducts, known as microcapsules. They are available with a wide range of products which confer different properties related to the nature of the encapsulated product. The composition of the wall material determines the release of the product into the fabric. The behaviour of microencapsulated peppermint was analyzed on cotton fabrics. Different application methods have been tested, impregnation versus bath exhaustion. As impregnation turned out to be the most efficient, some recipes were assayed and the effect
of microcapsules on maintenance conditions was evaluated in order to
determine the most suitable method with the longest lasting effect on fabrics.
The effect of microcapsules was usually measured by the presence of the property such as odour measurements when flavours are encapsulated (Pablo Monllor et al 2007).

Because of their perceived health benefits, probiotics have been incorporated into a range of dairy products, including yoghurts, soft, semi-hard and hard cheeses, ice cream, milk powders and frozen dairy desserts. However, there are still several problems with respect to the low viability of probiotic bacteria in dairy foods. This review focuses mainly on current knowledge and techniques used in the microencapsulation of probiotic microorganisms to enhance their viability during fermentation, processing and utilization in commercial products. Microencapsulation of probiotic bacteria can be used to enhance the viability during processing, and also for the targeted delivery in gastrointestinal tract.

Sophisticated shell materials and technologies have been developed and an extremely wide variety of functionalities can now be achieved through microencapsulation. Any type of triggers can be used to prompt the release of the encapsulated ingredients, such as pH changes, mechanical stress, temperature, enzymatic activity, time, osmotic force, etc. Encapsulated probiotic bacteria can be used in many fermented dairy products, such as yoghurt, cheese, cultured cream and frozen dairy desserts, and for biomass production. In the encapsulated form, the probiotics are protected from bacteriophage and harsh environments, such as freezing and gastric solutions. Thus, encapsulation facilitates the manufacture of fermented dairy products in which the bacteria have consistent characteristics and higher stability during
storage and higher productivity than nonencapsulated bacteria. With the encapsulated products, the residence time, acidity and continuous inoculation of milk with a constant bacilli/cocci ratio can be controlled at a desired pH (Anil Kumar Anal and Harjinder Singh 2007).

The initial burst release was one of the major problems in the development of controlled release formulations including drug-loaded micro and nanoparticles, especially with low molecular weight drugs. They aimed to encapsulate, by the W/O/W emulsion, polymeric nanoparticles into polymeric microparticles by using non-water soluble polymers and appropriate organic solvents for the preparation of these composite microparticles (Sheikh Hasan et al 2007).

Human retinal pigment epithelial cell line (ARPE-19) for cell encapsulation was obtained and optimized through alginate-based microencapsulation. They used immortalized ARPE-19 cells and the transfected sub-line that expresses secreted alkaline phosphatase (SEAP) reporter enzyme. Alginate was cross-linked with different divalent cations (Ca$^{2+}$, Ba$^{2+}$, Sr$^{2+}$ and the combination of Ca$^{2+}$ and Ba$^{2+}$) was coated first with poly-L-lysine (PLL), and then with alginate. Microcapsules with different pore sizes and stability were generated. The pore size of the microcapsules was assessed by the release of encapsulated fluorescein isothiocyanate (FITC)-dextrans. The viability of the cells in the microcapsules was studied in vitro by assessing the secretion rates of SEAP and oxygen consumption by the cells. The best microcapsule morphology, durability and cellular viability were obtained with alginate microcapsules that were crosslinked with Ca$^{2+}$ and Ba$^{2+}$ ions and then coated with PLL and alginate (Jonna Wikstrom et al 2008).
An organic pigment was coated with nano-silica particles via layer-by-layer self-assembly technique and some properties were investigated. The results revealed that the coating of nano-silica on the surfaces of pigments could improve the thermal stability, wettability, acid and alkali resistance, and weatherability of the organic pigment (Junjie Yuan et al 2005).