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An Overview: Textile Surface Modification by Using Sol-gel Technology



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THE sol-gel technique is a new technique which offers an effective way of modifying fabrics, and it has been proven to be simple, effective, and has many advantages. It is interesting to explore on the viability of using sol-gel technology to modify surfaces of various fabric blends.

Keywords: Sol-gel, Surface modification, Textiles, Hybrid materials.

Introduction

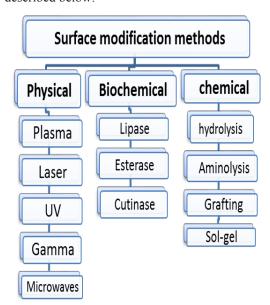
In recent decades, hi-tech textiles include innovative polymers, whose no limited uses to the textile and clothing industry. Sol-gel technology is one of importance techniques in the textile sectors. The importance of sol-gel technology is the ability to create of nano-composite polymer films on the surface of the fibres giving the textiles new mechanical, optical, electrical and biological properties that cannot be achieved using conventional finishing agents. It is of great commercial importance in the production of fabric, protective, medical and technical textiles.

Surface modifications of fabrics

Today modern textiles and woven fabrics are used throughout the world in a wide range of applications for_example, the apparel industry, household textiles and furnishings, medical substances and manufacturing uses. Many textiles properties such as wetting, adhesion, and many other performance properties all begin at the surface. Hence, the surface of textiles offers a platform for functional modifications to meet specific requirements for a variety of applications.

Surface modification of textiles refers to the use of a widespread range of technologies designed to modify the surface properties of textiles to create the surface structures that give the textile product the desired properties.

In recent years, tremendous advantages are afforded by surface modification of textile materials to enhance adhesion, wettability, chemical affinity or inertness. The surface modification of textiles may be achieved by several techniques ranging from traditional solution treatments to biological approaches. Some of the common techniques are described below:



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Physical surface modifications

Textile manufacturing is one of the most pollutant industries because of the several processes involved for instance singeing, desizing, scouring, bleaching, mercerization, dyeing etc. These processes pollute the environment and water resources. Economical and ecological pressure on textile industry includes the development of economic and environment friendly "green" processes. Therefore, one has to select a proper pretreatment for the modification of surfaces amongst the available processes (1).

Plasma treatment is one of the modifications used for surface modification of textile fabrics. It is highly surface specific; it does not affect the bulk properties of the textile fibers. Therefore, it is considered as environmentally friendly process.

Tsafack and Levolois-Grutzmacher, (2) reported the use of plasma based methods to reach a single treatment step and provide excellent properties such as flame retardant and water-repellent properties of cotton fabrics. The process of surface modification using plasma can also be used to improve hydrophilic properties of cotton fabric. Gawish et al, (3) have studied the effect of low temperature plasma for improving wool fabric properties. They have used plasma treatment to modify the surface properties of wool fabrics by partial removal of the scales and the lipid layer. Shahidi et al. (4) have studied the effect of low temperature plasma on dyeing properties of PET fibers. PET fibers were subjected to O₂ and N₂ plasma. It was observed that after the plasma treatment, PET fabrics achieve vital hydrophilicity because of incorporation of polar functional groups for example, hydroxyl, carbonyl, ester and carboxyl. Moreover, the plasma treatment significantly improved the dyeability and colorfastness properties of dyed PET fabric with an acid dyestuff. Costa et al, (5) also studied the effects of gas composition on the wettability of PET fabrics. Palaskar et al, (6). Has recommended the use of plasma induced hexamethyldisiloxane polymer on polyester/ cotton blended fabric so as to impart to it water repellent property.

A main disadvantage of plasma treatment is the aging effect of the surface modification created; often the hydrophilicity acquired is lost with time, depending on the temperature and other environmental (storage) conditions. Another drawback of simple plasma treatments is the variety of functional groups simultaneously formed on the treated polymer surface (7-8).

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On the other hand, surface modification by the use of UV (ultraviolet radiation) is well known as one of the physical surface modification techniques. UV is electromagnetic radiation, which is emitted by the natural or artificial sources (9). The advantage of UV treatment for textiles is that the chemical changes brought about by their treatment turns out to be restricted in the uppermost layers of substrates thus preventing the fibers from undergoing mechanical loss (10). UVirradiation introduces carboxylic acid groups into the cotton and may create spaces between fiber linings, possibly due to oxidation of cellulose, thus may improve the interactions between dye molecules and cellulose functional groups. Bhatti and co-workers, (11) treated cellulose fabrics with UV rays afterward dyeing using direct dyes. They compared the results with cellulose fabrics modified by conventional mercerization technique and also dyed with direct dyes. Their study confirmed that UV irradiated cellulosic fabrics had better dye uptake as compared to the mercerized ones. Periolatto and co-workers, (12) observed that wool fabric after irradiation under certain conditions can be dyed at 80°C with total bath exhaustion and good fastness without loss of mechanical properties. Furthermore Migliavacca and co-workers,(13) examined the UV irradiation of wool fabric as pretreatment for difference dyeing with metal-complex dyes or combinations of the same with acid dyes.

The major disadvantage of the UV process lies in the use of electricity as energy source, which unfavorably influences the process economy. A further consideration is that the UV processes have more parameters to control compared to traditional processes and require hence a higher degree of automation in the process control.

Biochemical surface modification

Enzymatic surface modification of textile material includes processing of fibers to modify physical and chemical surface properties or introduction of functional groups on the surface. The advantage of enzyme technology over the other technologies is their high specificity towards a certain reaction and / or substrate (14). Nierstrasz,(15) described that the surface modification of textiles with enzymatic treatment has the potential to replace conventional wet treatment.

There are few disadvantages of enzymes application in textile processing since, some physical and chemical factors affect the

stability of enzymes, e.g. Enzyme processes can deactivate easily by increasing the pH value and/or the temperature. Another disadvantage is that, once enzymes are destroyed they cannot be reactivated.

Chemical modification

In chemical modification approach, the textile material is treated with liquid reagent to produce reactive functional groups onto the surface. The commonly used chemical processing agents are chromic acid which introduces oxygen containing functional groups on synthetic fibers for instance, polyester and nylon. Another method for chemical modification is grafting, the first step is to generate radicals on the textile to initiate copolymerization reactions with different monomers (16).

Conventional wet processes involves long residence time, high concentrations of harsh chemicals, large amount of water and are generally carried out at high temperatures leading to high energy consumption. Deo and Gotmare, (17) have carried out grafting of acrylonitrile monomer on cotton to impart high water absorbency. Tsukada et al, (18) have used ammonium peroxysulfide as an initiator to graft benzyl methacylate on wool fibers.

One of the chemical methods of surface modification is sol-gel technology. Sol-gel technology represents also a new approach to the preparation of the composite materials.

Modification of blend fabrics could be carried out by film coating either with nanosol or by deposition with silica nanoparticles.

Coatings by sol-gel process

The sol-gel approach is a versatile technique that can be employed for modification of several textile materials. In the literature one can find reports of almost every type of fiber material modified with a huge number of different sols. The main function of sol-gel technique is to combine different properties in a single coating step. The sol-gel technique has become an important tool for the preparation and application of thin layers based on either inorganic materials or inorganic—organic hybrids.

Coating by sol-gel process can be basically divided into three main steps: formation of the "sol" by hydrolysis of the precursor material and subsequent condensation reactions, the coating process, then drying or curing. This "sol" can be easily applied to textile fabrics, forming dense layers after the evaporation of the solvent. The main steps for preparing sol-gel derived coatings are depicted in Fig. (1).

According to Sakka(19) who is one of the pioneers in this new trend of technological development, the sol–gel process includes the transition of a system from a chemical solution "sol" (mostly colloidal) into an integrated network "gel". The precursors used in the preparation of the "sol" are usually inorganic metal salts or metal organic compounds such as metal alkoxide. (20-24).

Formation of the sols involves the following reactions, which are illustrated in Fig. (1).

Hydrolysis: The forward reaction in the hydrolysis is the hydrolysis of alkoxy groups into hydroxyl groups, and the reverse reaction is called esterification reaction. The complete hydrolysis reaction to form Si (OH)₄ is very difficult to achieve.

Condensation: The condensation reaction can occur via two competitive mechanisms. In the forward step of first mechanism, (i) condensation may occur between two hydroxyl groups to form bridging oxygen and producing water molecule. While, in the

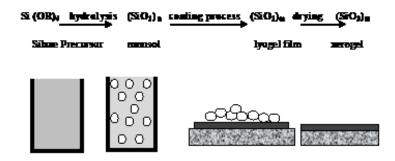


Fig. 1. Main steps for the preparation of nanosol coatings (sol-gel process), here shown for a silica coating.

reverse step of this reaction, hydrolysis may occur. Regarding to, the forward step of second mechanism, (ii) bridging oxygen may be formed by condensation of silanol groups and on alkoxy group; this reaction is accompanied by producing alcohol molecule. The reverse reaction is called alcoholysis reaction (25,26).

This type of reaction can continue to build large silicon containing polymer network with three-dimensional structure by the process of polymerization (27) Fig. (3).

The final structure of sol-gel network is determined by the relative rates of hydrolysis and condensation reactions, which are dependent upon various factors such as type of catalyst, nature of solvents, reaction temperature, alkoxide group involved and water ratio.

☐ Type of catalyst.

Hydrolysis is most rapid and complete when external catalysts, such as mineral acids or ammonia, are employed ⁽²⁸⁾. The possible mechanisms for both acid and base catalyzed reactions are discussed as follows.

• Acid catalyzed reactions.

Under acidic conditions (e.g. with mineral or organic acids), the hydrolysis reaction involves nucleophilic attack of water on silicon atoms carrying a protonated alkoxide group.

• Base catalyzed reactions.

Under basic conditions (e.g. with ammonia), water is likely to be dissociated in a rapid first step to produce nucleophilic hydroxyl ions, and hydrolysis is then initiated by the attack of this hydroxyl ion on the silicon atom(25).

□ Temperature

Temperature has a direct effect on gelation rate in a sol-gel process. The general observation is that increase in temperature accelerates the gelation time (27).

☐ Alkoxide groups

The Alkoxy group attached to the silicon atom plays an important role in the hydrolysis and condensation reactions. For more bulky group attached to a Si, the gelation time is higher.

(a) Hydrolysis:

(b) Condensation:

Fig. 2. Hydrolysis (a), water condensation (b).

■ Water ratio

Since water is a reactant in the sol-gel process, its concentration plays an important role in the reaction kinetics and final structure of the material. The overall trend which is evident from different studies (29,30,31) is that the higher the water to metal alkoxide ratio the faster is the rate of hydrolysis. As for the effects on gel structure, adding insufficient amount of water tends to promote linear structures as reported by (Sakka et al. 55) (19) who prepared a viscous, spinnable solution by combining one mole of water per mole of TEOS (Tetraethoxysilane) under acidic conditions (0.01 M HCl). Fig. shows, the different effects of water (31).

When an excess of water is present then the rate and extent of hydrolysis will be too high and self -condensation will occur and multilayer's can be formed on the surface.

The treatment of textile fibers with hybrid organic-inorganic precursors opens numerous new possibilities for the improvement of their functional and protective properties (33-38). It is worthy to mention that, the Si-OH groups of precursors can also react with the fiber surface forming hydrogen bonding Fig. (5), as well as covalent bonds Fig. (6). The latter which is formed between the precursors silanol group and the hydroxyl group of the fiber in the condensation reaction, strongly increases the adhesion of the polymer film to the textiles as well as the degree of polymer film orientation(39).

Depending on the chemical structure of the organic group, there are different applications of sol-gel technology in order to achieve improved fabric functionalities and performance properties, e.g. UV-protection, antimicrobial activity, water and oil repellency etc.., Sol-gel applications have become a very important technique in textile industry especially in textile finishing. Fig. (7) Shows applications of sol-gel technology(40,41).

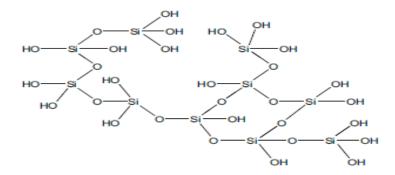


Fig. 3. Formation of polymer network with three-dimensional structure.

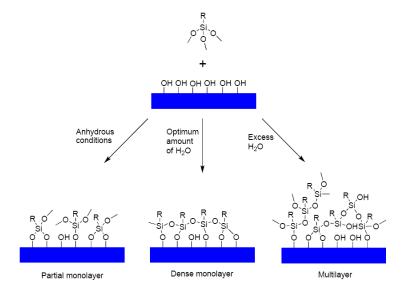


Fig. 4. Illustration showing the effects of no, optimum, and excess water on the formation of monolayers from silanes.

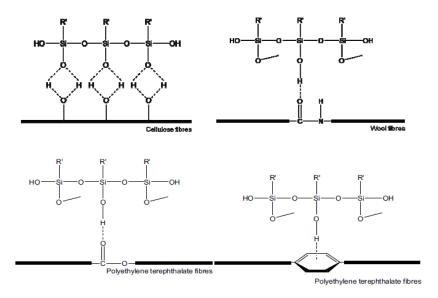


Fig. 5. Hydrogen binding of the precursor silanol group to the fiber surface.

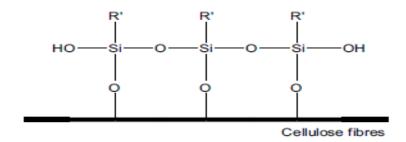


Fig. 6. Covalent binding of the precursor silanol group to the hydroxyl group of the textile fiber in the reaction of condensation.

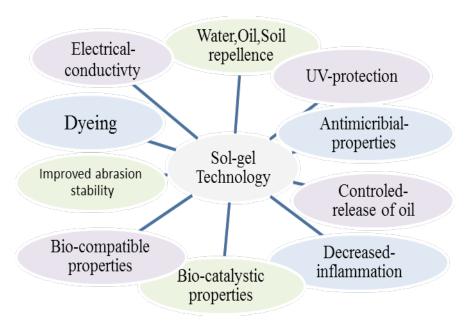


Fig. 7. Different applications of sol-gel coating on textiles.

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Improved dyeing properties using sol-gel technology

Mahltig et al. (42) investigated the role of solgel coating in improving the fastness properties of dyes on textiles. Sol-gel coating is one of the useful ways for embedding the organic dyes and applying it to different type of substrates like glass, paper, or textile (43) Fig. (15) shows the illustration of different schemes for coating solgel on the dyed fabric.

☐ Improved antibacterial activity

Textiles are an excellent substrate for bacterial growth and microbial proliferation under appropriate moisture, nutrients and temperature conditions (44-46).

The number of bio-functional textiles with an antimicrobial activity has increased significantly over the last few years (44,47). Application is nowadays extended to underwear, sportswear, home furnishing and protective clothing in areas with high risk of infection by pathogens (hospitals, schools and hotels) (47,48); and because they are able to absorb substances from the skin and can release therapeutic compounds to the skin, they find applications for prevention, as surgical lab coats, or therapy, as wound dressings (44,49). Therefore, biomedical products will perhaps be the largest application of antimicrobial textiles (48,49).

It was found that, modified knitted cotton fabrics with GPTMS and TEOS were examined

for antibacterial activities against S. aureus bacteria and E. coli bacteria according to the AATCC 100-2004 standard method exhibited the satisfactory antibacterial activity (49).

Synthesis of silica nanoparticles by sol-gel method

In the last two decades, material science and engineering has come out with some excellent nanomaterials exhibiting novel features due to their unique physio-chemical properties(50,51). Recently, silica nanoparticles (SNPs) have drawn widespread attention due to their applications in many emerging areas because of their tailorable morphology. A number of techniques available for preparing SNPs namely, flame spray pyrolysis, chemical vapor deposition, micro-emulsion, ball milling, sol-gel etc. However, among these solgel process remains the most popular one, due to its ability to control the size, distribution and morphology of their action parameters (52).

The manufacturing of nanomaterials can be classified as bottom-up and top-down approaches Fig. (9). The bottom-up approach involves building up from atomic or molecular scale and top-down approach involves making smaller sizes through etching or grinding from the bulk materials. Sol-gel, for the preparation of SNPs, is an extensively used bottom-up approach. This approach has some advantages such as low cost, higher productivity, environmentally benign etc.

A Cotton fabric silica sol coated fabrics dye solution dye & coated fabrics

B Cotton fabric dye solution colored fabrics silica sol dye & coated fabrics.

C Cotton fabric dyed silica sol coated & dyed fabrics.

Fig. 8. Different schemes of sol-gel coating on dyed fabric.

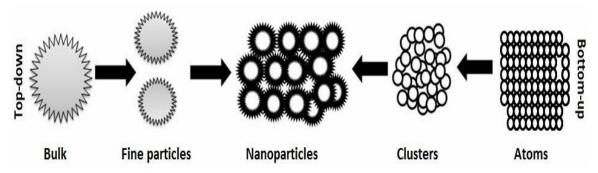


Fig. 9. Approaches for the preparation of nanoparticles.

A pioneer works on the synthesis of spherical and mono-dispersed silica particles were reported by Stöber et al. (53, 54, 55). Silica particles with the size ranging from 5 to 2000 nm from aqueous alcohol solutions of silica alkoxides in presence of ammonia as catalyst (basic condition) have been produced. Following that many contemporary research works describing the synthesis of nanosilica particles are indeed evolved from the Stöber method. The main advantage of Stöber method is the ability to form mono-dispersed spherical silica particles compared to the acid-catalyzed systems which usually produce gel structures.

Models proposed for the synthesis of SNPs

Hydrolysis and polymerization of silicon alkoxides in the presence of ammonia lead to the formation of a stable suspension of particles. Two models have been proposed to describe the growth mechanism of silica namely monomer addition(56,57) and controlled aggregation (58).

The monomer addition model describes that, after an initial nucleation, the particle growth occurs through the addition of hydrolyzed monomers, the (primary particle surface). By contrast, the aggregation model elaborates that the nucleation occurs continuously throughout the reaction and the resulting nuclei (primary

particles) will aggregate together to form dimmer, trimmer, and larger particles (secondary particles). Both models lead to the formation of either spherical or gel network depending on the reaction conditions.

Coating of textile materials with silica nanoparticles

Extensive research has recently been conducted to use silica nanoparticles for the functional textiles, including improved stability against mechanical or thermal destruction, improved water, oil and soil repellence, changing of light absorption of textiles, improved electric conductivity of textiles, immobilization and controlled release of bioactive species, oils and flavors (42).

For example, Jain Swapnal et al. (59) treated polyester blended fabrics with the silica nanoparticles and commercially available water repellent agent to impart super hydrophobicity. Hongxia Wang et al. (60) produced super hydrophobic surfaces with water contact angles over 170 degrees by a particulate silica sol solution of co-hydrolyzed TEOS/fluorinated alkyl silane with NH₃.H₂O on various substrates, including textile fabrics (e.g. polyester, wool and cotton), electrospunnanofibre materials, filter papers, glass slides, and silicon wafers.

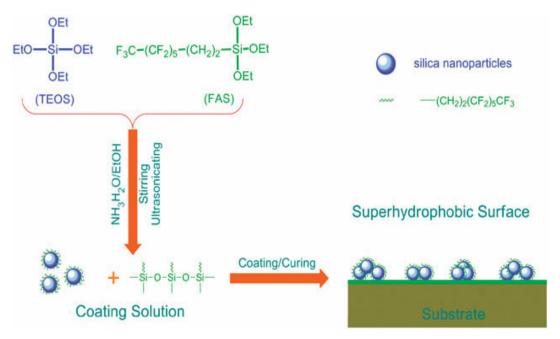


Fig. 10. Reaction route of silica sol preparation and coating procedure (60).

Conclusion

The maintenance and improvement of current properties and the creation of new material properties are the most important reasons for the functionalization of textiles. The sol-gel technique is one of the modern methods to create new advantageous functions materials. The coating of textiles with chemically or physically modified silica sols produced new products to be developed include textiles with water, oil and soil repellency and with antimicrobial properties. This article review discusses recent results from applying modified silica to the functionalization of textiles.

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مقاله: التحوير السطحي للاقمشه باستخدام تكنولوجيا السول- جل

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تقنية السول- جل هي تقنية جديدة توفر طريقة فعالة لتعديل الأقمشة ، وقد ثبت أنها بسيطة وفعالة ولديها العديد من المزايا. من المثير للاهتمام استكشاف مدى قابلية استخدام تقنية السول-جل لتحوير الأسطح الأقمشة المخلوطه المختلفة.