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Preparation of crosslinked polysiloxane/SiO_2 nanocomposite via in-situ condensation and its surface modification on cotton fabrics

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ABSTRACT

Novel crosslinked polysiloxane/SiO_2 nanocomposite (CLPS-SiO_2) was successfully prepared via the in-situ condensation reaction of silica sols and crosslinked polysiloxane with end-capped triethoxysilane in solvent, which was firstly fabricated through the modification of our previously developed crosslinked polysiloxane with end-capped epoxy groups using aminopropyltriethoxysilane (APTES) and noted as APTES-CLPS. Chemical structures and thermal properties of the as-prepared resultants were characterized by Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance spectra ($^1H/^{13}C$ NMR) and thermogravimetric analysis (TGA). CLPS-SiO_2 was applied as surface modification agent to treat cotton fabrics. Film morphologies and surface properties were examined with scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), contact angle measurements, and other instruments. FTIR and NMR confirmed structure of the products. CLPS-SiO_2 showed better thermal stability than APTES-CLPS due to anchor of the nanosilica. APTES-CLPS could deposit a smooth film on cotton fiber surface. Besides, CLPS-SiO_2 also coated the fibers with many nano-scaled tubercles beneath this smooth film by SEM. However, the APTES-CLPS film and the CLPS-SiO_2 film on silicon-wafer were never homogeneous and had a few low or high peaks. The root mean square roughness (Rq) of APTES-CLPS film reached to 0.441 nm in $2 \times 2\,\mu m^2$ scanning field and at 5 nm data scale. Owing to the incorporation of nanosilica, that of CLPS-SiO_2 film continuously increased and could attain 4.528 nm in $2 \times 2\,\mu m^2$ scanning field and at 20 nm data scale. XPS analysis further demonstrates that there was a CLPS-SiO_2 film covered on the cotton surface and the silyl groups had the tendency to enrich at the film–air interface. In addition, hydrophobicity of the CLPS-SiO_2 treated fabric would be enhanced with augment of the amount of nanocomposite. Water contact angle of this fabric could finally attain 158.0°. But most of all, its color and softness would not be influenced instead. The CLPS-SiO_2 treated fabric possessed good washing durability.

1. Introduction

Nowadays, polysiloxanes have been well known as textile finishes to endow with fabrics desirable properties such as softness, wrinkle and crease resistance and particularly water repellency [1–5]. Thus, it has attracted much attention. Because of the inherent characteristics of softness, comfort, warmness and biodegradability, cotton is one of the most favorable fabric materials [6]. However, vast external hydroxyl groups cause them water-absorbent and easily stained by liquids. For this reason waterproof and water-repellent finishes are required in particular for cotton fabrics.

It is known that linear polysiloxane is mechanically weak and easily tears. Besides, there are plentiful voids and gaps on the cotton surface due to its typical structure of twisted and woven fibers. Consequently, those two factors are not helpful to form the compact hydrophobic coating and then adversely influence hydrophobicity of the finished fabrics especially after they were washed a lot of times. To overcome this dilemma, different cross-linkers [7,8] or cross-linking methods [6,9] were designed to improve the density of the hydrophobic polysiloxane coating on cotton surface, which should profit hydrophobicity of the treated fabric.

As the roughness of the cotton is usually on a relatively large-scale, many efforts have been made to generate small-scaled structures to further increase hydrophobicity of the treated

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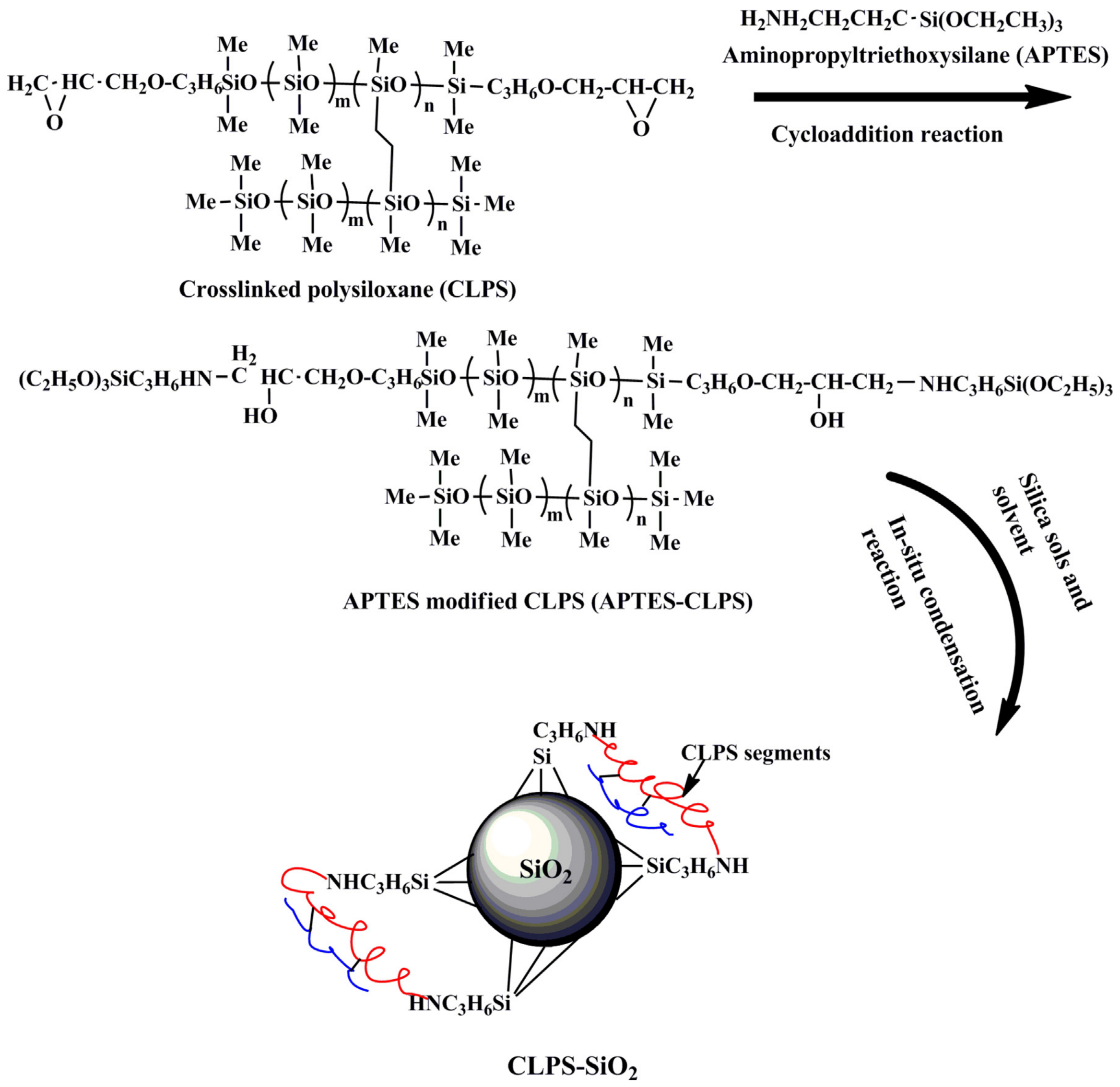

Scheme 1. Preparation procedure for the crosslinked polysiloxane/SiO_2 nanocomposite (CLPS-SiO_2).

cotton fabrics, i.e., superhydrophobicity. Inorganic nanoparticles, such as SiO_2 [10,11], TiO_2 [12,13] and ZnO [14,15], are often chosen to be anchored onto the cotton surface through sol–gel and layer-by-layer (LBL) methods. However, these works have used lots of toxic material, organic solvents in several stages to achieve these properties. Polymer nanocomposites (PNs) offer the possibility of developing a new class of nanofinishing materials which can endow cottons with multi-functionality, such as desired wettability, UV protection, antimicrobial and conductivity properties by simple methods [16]. To date, PNs have been fabricated by sol–gel methods, in-situ condensation routes and using compounding methods. But the last one has unfavorable aggregation of nanoparticles and weak bond of nanoparticles onto the cotton substrates. Two former methods rely on the chemical modification of the nanoparticle surface and then promote adhesion of it to the polymer matrix, eventually; it can solve the above disadvantages and often be chosen to prepare the PNs. Herein, introducing the alkoxysilane groups into the polymer either as end groups or pendant groups to co-hydrolysis and co-condensation in the sol–gel system is a popular method. However, the trialkoxysilyl groups incorporated on the polymer in advance are not stable. The more practical method is to exploit a coupling agent with trialkoxysilyl groups by using an in-situ sol–gel process [17].

In our previous work [18], crosslinked polysiloxane with reactive epoxy groups (CLPS) was prepared to form the denser hydrophobic coating on cotton surface, and also to generate new joints between coatings and fibers matrix aiming at the preferable washing durability of the finished fabric. Finally, the expected result was obtained. To further enhance the hydrophobicity of the treated fabric and construct the superhydrophobic cotton fabric conveniently via polymer nanocomposite on basis of our as-prepared CLPS, introducing the alkoxysilane groups into the CLPS polymer to co-hydrolysis and co-condensation in the sol–gel system is indispensable. So the present work firstly prepared the crosslinked polysiloxane with end-capped triethoxysilanes (APTES-CLPS) through the reaction of aminopropyltriethoxysilane (APTES) and our previously developed CLPS, and then synthesized crosslinked polysiloxane/SiO_2 nanocomposite (CLPS-SiO_2) via the in-situ condensation reaction of silica sols and APTES-CLPS in solvent. The whole preparation route is illustrated in Scheme 1. At last, CLPS-SiO_2 was applied as surface modification agent to treat cotton fabrics. Chemical structure and thermal property of the as-prepared products were characterized by Fourier transform