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Preparation and characterization of cellulose hybrids grafted with the polyhedral oligomeric silsesquioxanes (POSS)

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ABSTRACT

The cellulose hybrids with polyhedral oligomeric silsesquioxane (POSS) are synthesized by cross-linking graft reaction. Dimethylol dihydroxy ethylene urea (DDEU) as cross-linking agent is used in the graft reaction. The chemical and surface morphological structures of the am-POSS grafted cellulose hybrids are characterized with micro-FT-IR spectra, silicon element analysis, X-ray diffraction, SEM, AFM, and DSC. The results show that the am-POSS grafted cellulose hybrids form new macromolecular structures containing POSS nano-silica particles. POSS particles are evenly dispersed at the nanometer scale in the cellulose host matrix, bonding to the cellulose through covalent bonds. The thermal properties of the am-POSS grafted cellulose hybrids are improved.

1. Introduction

Nanofibers and nanocomposite materials have gained much interest due to the remarkable change in properties (Guo et al., 2008; He, Wan, & Xu, 2007; Kulpinski, 2005). Hybrid organic–inorganic molecules like polyhedral oligomeric silsesquioxanes (POSS) can serve as model nanofillers. POSS can be effectively incorporated into polymers by copolymerization, grafting, or even blending through traditional processing methods (Ramirez et al., 2008; Seckin, Koytepe, & Ibrahim, 2008). POSS has a nanometer-sized confine structure with a cubic silica core and can be functionalized with a variety of organic compounds. Organic/inorganic hybrids containing POSS have attracted considerable attention for dielectric, heat-resistant and radiation-resistant paint and coatings due to the fact that thermal degradation of POSS leaves behind a “self-healing” SiO_2 layer. POSS and its derivatives have been reported as candidates in modifying a wide range of thermoplastics such as polyolefin (Fina, Tabuani, Frache, & Camino, 2005; Zhou, Cui, Zhang, & Yin, 2008), pocarbonate (Zhao & Schiraldi, 2005), polyamide, polycaprolactone and polylactide (Choi, Harcup, Yee, Zhu, & Laine, 2001; Ricco, Russo, Monticelli, Bordo, & Bellucci, 2005).

The cellulose fiber is one of the excellent natural biomaterials. Cellulose has been explored as a substrate for composite materials because of the presence of functional groups that may be employed in various activation processes (Hou, Zhou, & Wang, 2009; Xie, Hou, & Wang, 2008b). Chemical modification of cellulose can change itself chemical and morphological structures for different purpose (Hou, Wang, & Wu 2008; Xie, Hou, & Sun, 2008a). The incorporation of nanoscale particles into cellulose matrix leads to a strong interfacial interaction. Typical advantages of cellulose-based hybrids are flexibility, low density, toughness, and formability, whereas nano-sized POSS has excellent mechanical, optical and thermal properties, such as surface hardness, modulus, strength, transparency, and high refractive index. These materials can be combined effectively, and a new class of high performance or highly functional organic–inorganic hybrid materials have been achieved (Chen, Wang, & Chiu, 2008; Duo, Li, Zhu, & Zhou, 2008; Musyanovych, Wienke, Mailander, Walther, & Landfester, 2008). A lot of attempts have been carried out to make cellulose-based nanocomposites (Jeon, Mather, & Haddad, 2000; Kulpinski, 2005; Samuneva et al., 2008). These composite materials are biocompatible, biodegradable and possess low toxicity in biomedical field. However, high even dispersion system at the nanometer scale in the cellulose host matrix is very difficult to be produced by traditional techniques. Recently, the sol–gel method has definitely proved its exceptional potential by providing a possibility of synthesizing a significant number of new nanomaterials with high degree of homogeneity and purity at a molecular level and with extraordinary physical and chemical properties. POSS and its derivatives as candidates to modify cellulose are scarcely reported.

In this paper, the cellulose-based hybrid containing POSS are synthesized by cross-linking graft reaction. Octa-aminopropylsisesquioxane (POSS–NH_2) as candidate and dimethylol dihydroxy ethylene urea (DDEU) as cross-linking agent are used

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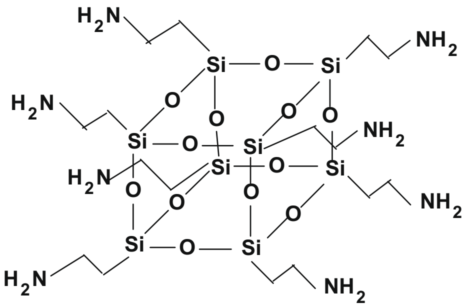


Scheme 1. Chemical structure of POSS–NH_2.

Table 1
Ingredients in the chemical cross-linking process (g).

Samples	Sol-POSS	H_2O	Sol-DDEU	$MgCl_2$
1	10	80	10	0.1
2	30	60	10	0.1

in the graft process. The chemical and surface morphological structures of the organic/inorganic hybrids are characterized.

2. Experimental

2.1. Materials

The alcohol solution containing POSS–NH_2, (20% w/w) (Sol-POSS) and the solution of dimethylol dihydroxy ethylene urea (40% w/w) (Sol-DDEU) were obtained from National Research Center of Dying and Finishing, Shanghai, China. Chemical structure of octa-aminopropylsisesquioxane (POSS–NH_2) is shown in Scheme 1.

Scoured and bleached cellulose fabrics (cotton fibers) were obtained from Jinqiu Textile Company, Shaoxing, China. Other chemicals were obtained from Shanghai Chemical Reagent Plant, Shanghai, China.

2.2. Preparation of am-POSS grafted cellulose

Dimethylol dihydroxy ethylene urea as cross-linking agent was added in the certain concentration solution of Sol-POSS according to the recipe (shown in Table 1). $MgCl_2$ as catalyst was used in the cross-linking reaction. The mixtures were sufficiently mixed by stirring at room temperature.

The cellulose samples were padded with the POSS–NH_2 mixtures to give 80% wet pick-up. The dry temperature and time were 105 °C and 3 min, respectively. The cure temperature was 150 °C, and cure time was 1.5 min, respectively. The samples were then washed in warm water 60 °C until neutral to remove unfixed POSS and dimethylol dihydroxy ethylene urea. The samples were air-dried at room temperature. The am-POSS grafted cellulose materials with chemical cross-linking were obtained. They were named as CP-1 and CP-2, respectively.

2.3. FT-IR spectra and silicon content

FT-IR spectra of the samples were measure by a OMNI Sampler of the Nexus-670 FT-IR-Raman spectrometer (Nicolet Analytical Instruments, Madison, WI) using a single ART reflecting method.

The percentage silicon content was determined by Leeman Prodigy (USA). The samples were dried under vacuum at the temperature of 50 °C before measuring.

2.4. XRD

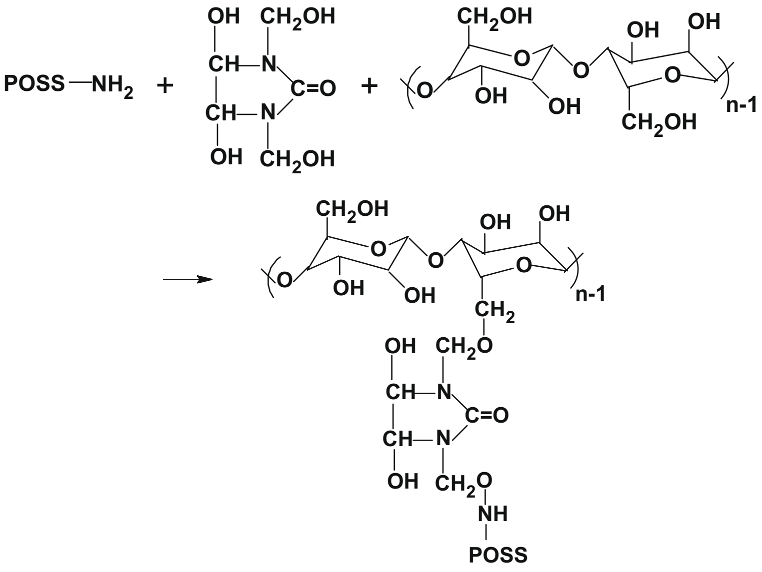
The control cellulose and am-POSS grafted cellulose samples were cut into powder, respectively. The X-ray diffraction patterns of the fabrics (XRD) were measured with a D/max-2550 PC X-ray Diffractometer (Rigaku Corporation, Japan), which used Cu-K target at 40 kV 300 mA, λ = 1.542 Å.

2.5. SEM

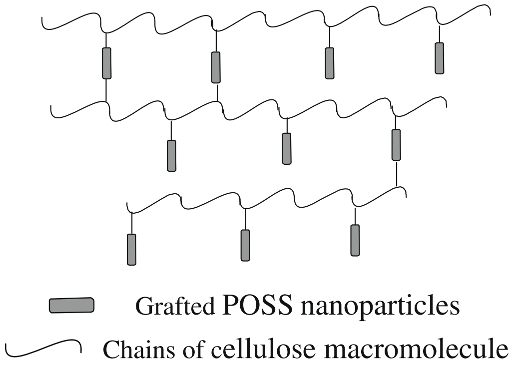
For SEM analysis, the samples were sputtered with gold and then examined with a JSM 5600LV scanning electron microscope (JEOL, Tokyo, Japan), operated at 15 kV.

2.6. AFM

Atomic force microscope (AFM) image was obtained with SPM Multimode-Nanoscope IIIa (Digital Instruments, USA) at room temperature, in tapping mode.



Scheme 2. Graft cross-linking reaction of cellulose and POSS–NH_2.



Scheme 3. Model of am-POSS grafted cellulose hybrid materials.

2.7. DSC

A DSC 822e differential scanning calorimeter (Mettler/Toledo, Greifensee, Switzerland) was used. Samples of about 5 mg, placed in a DSC pan, were heated from 25 to 400 °C at a scanning rate of 10 °C/min, under a constant flow of dry nitrogen.

3. Results and discussion

3.1. Cellulose graft with am-POSS by chemical cross-linking

The molecule of dimethylol dihydroxy ethylene urea has two reactive groups (—CH_2OH). The macromolecular structure of cellulose has a lot of hydroxyl groups (—OH). Octa-aminopropylsisesquioxane ($POSS–NH_2$) can be grafted into cellulose macromolecular by dimethylol dihydroxy ethylene urea. The compound DDEU as cross-linking agent is able to form covalent bonds between cellulose and $POSS–NH_2$ particles. The graft cross-linking reaction of cellulose and $POSS–NH_2$ are shown in Scheme 2. In graft reaction, POSS particles are dispersed in the cellulose host matrix, bonding to the cellulose through covalent bonds, thus forming cellulose-based hybrids. The model of am-POSS grafted cellulose hybrid materials is shown in Scheme 3.

Micro-FT-IR spectroscopy was employed to study the chemical structure of the am-POSS grafted cellulose hybrids. The FT-IR spectra of cellulose hybrids (CP-1, CP-2) exhibit that the bands at 1079 and 710 cm^{-1} are assigned to ν_{as}, ν_s of —Si—O—Si— vibrations. But at the same time, the band at 1079 and 1180 cm^{-1} can be related to the presence of —Si—O—C—, —C—O—C—, and Si—C bonds. In order to reconfirm silicon element in the cellulose matrix, the silicon contents of cellulose hybrids were determined. The results show that the silicon contents of the control cellulose, CP-1 and CP-2 are 54.66, 314.19 and 672.19 $\mu g/g$, respectively. It can be seen that am-POSS has been grafted to cellulose macromolecular. These confirm that the compound DDEU is able to form covalent bond with cellulose and $POSS–NH_2$. The am-POSS grafted cellulose hybrids form new molecular structures containing nano-POSS particles.

3.2. Surface morphology of the am-POSS grafted cellulose hybrids

SEM analysis was used to characterize any changes about the surface morphology of the am-POSS grafted cellulose hybrids. Representative SEM micrographs, taken at the magnification of 10,000 of CP-1 and CP-2 hybrids are shown in Fig. 1, respectively. Fig. 1a is the SEM micrograph of CP-1. Fig. 1b is the SEM micrograph of CP-2. From Fig. 1(a and b), it can be seen that the surface of the am-POSS grafted cellulose hybrids have a lot of nano-sized particles. POSS nanoparticles disperse in cellulose matrix. The am-POSS grafted cellulose hybrids also have heterogeneous structure with well-defined nanounits. Meantime, the particle side of CP-2 is bigger than that of CP-1. It shows that the size of nanoparticles becomes bigger with increasing the concentration of Sol-POSS.

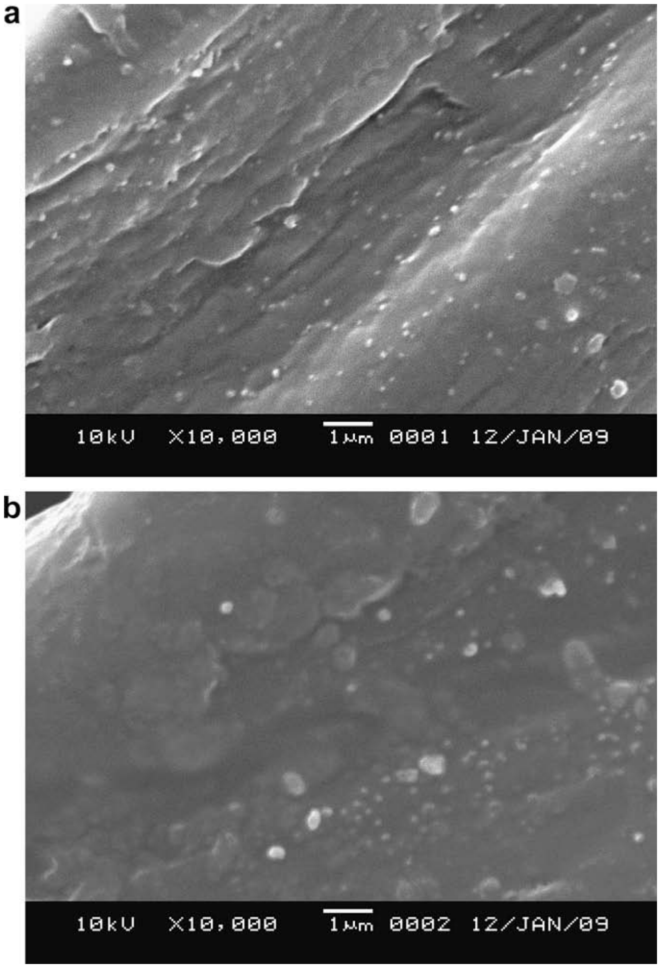


Fig. 1. SEM micrographs of the am-POSS grafted cellulose hybrids. (a) CP-1, (b) CP-2.

AFM was used to further characterize the surface morphology of the am-POSS grafted cellulose hybrids. AFM data for the CP-1 and CP-2 hybrids are shown in Figs. 2 and 3, respectively. The AFM graphs (shown in Figs. 2 and 3) show the topography of the am-POSS grafted cellulose hybrids with the height distribution profiles

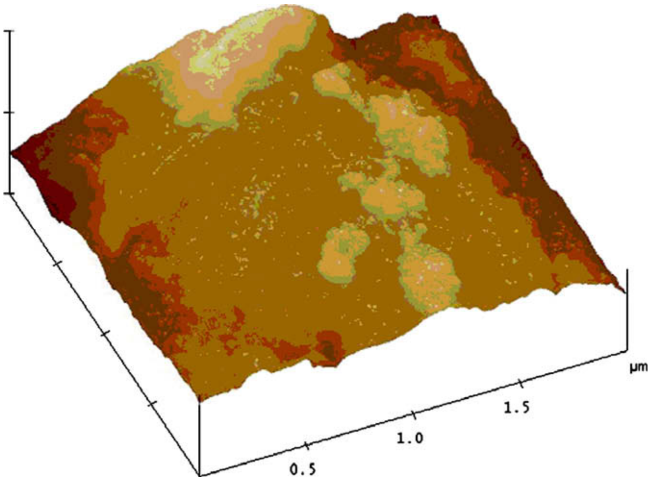


Fig. 2. AFM three dimensional image of CP-1 sample.

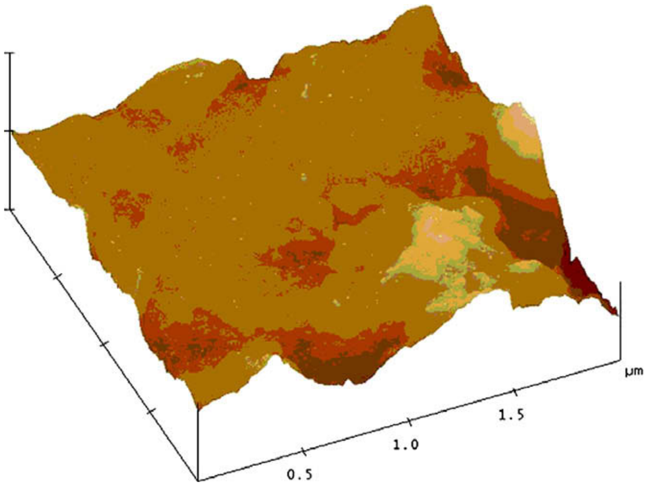


Fig. 3. AFM three dimensional image of CP-2 sample.

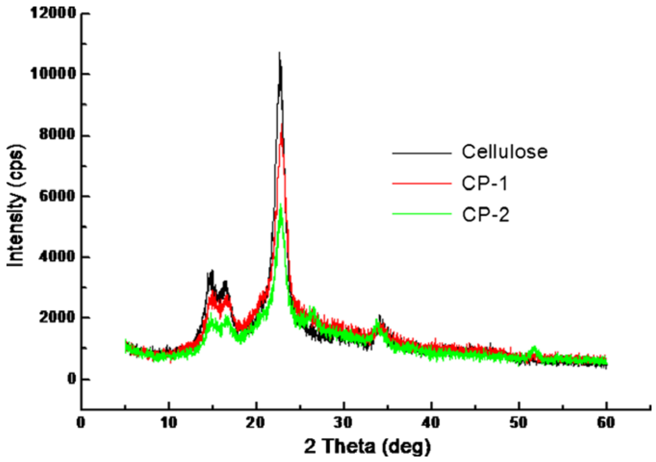


Fig. 4. XRD patterns for the am-POSS grafted cellulose hybrids.

of surface roughness. It can be seen that the am-POSS grafted cellulose hybrids have the surface with irregularities of a quite small height. There are many POSS particles (50–500 nm) uniformly dispersed in cellulose matrix. No discernable phase separation is observed. SEM and AFM data for the am-POSS grafted cellulose hybrids are in very good agreement. AFM images show that surface morphology of the am-POSS grafted cellulose hybrids has obvious difference from surface morphology of cellulose.

3.3. Crystal morphology of the am-POSS grafted cellulose hybrids

The XRD data illustrate the influence of POSS nanoparticles on the intensity and shape of the patterns. The octa-aminopropylsisesquioxane (POSS–NH_2) has typical nano-SiO_2 crystals. X-ray patterns feature main peaks of POSS–NH_2 at 7.82°, and 23.50° associated with nano-SiO_2 crystals structure. XRD patterns of the am-POSS grafted cellulose hybrids are shown in Fig. 4. The main peaks of CP-1 at 15.2°, 16.38°, and 22.86° associate with cellulose structure. The main peaks of CP-2 at 14.61°, 16.52°, and 22.67° also associate with cellulose structure. Many researchers reported POSS could crystallize when they were copolymerized with polymers (Fina et al., 2005; Kataoka et al., 2005; Ohno, Tagawa, Itoh, Suzuki, & Matsuda, 2009). However, in Fig. 4, no observed POSS crystal in cellulose matrix is probable due to the lower concentration of POSS–NH_2 or the peaks at about 23.50° associated with nano-SiO_2 structure may be overlapped.

3.4. Thermal properties of the am-POSS grafted cellulose hybrids

Differential scanning calorimetry (DSC) is one of important methods for observing the thermal characteristics of materials. DSC plots of the pure cellulose fiber and the am-POSS grafted cellulose hybrids (CP-1, CP-2) were measured and shown in Fig. 5, respectively.

The DSC plots for the am-POSS grafted cellulose hybrids, CP-1 and CP-2 contain first endothermic peaks at temperatures of 80.37, 78.19 °C, respectively. These endothermic peaks are probably associated with the removal of water from the am-POSS grafted cellulose hybrid chains. Compared with CP-2, the lower peak area obtained in the DSC plot of CP-1 is probably due to the decrease of the amount of —NH_2 groups in the cellulose chains because of lower concentration of POSS–NH_2.

For cellulose, the second endothermic peak at 358.92 °C. The endothermic change obtained in the DSC plot for cellulose is asso-

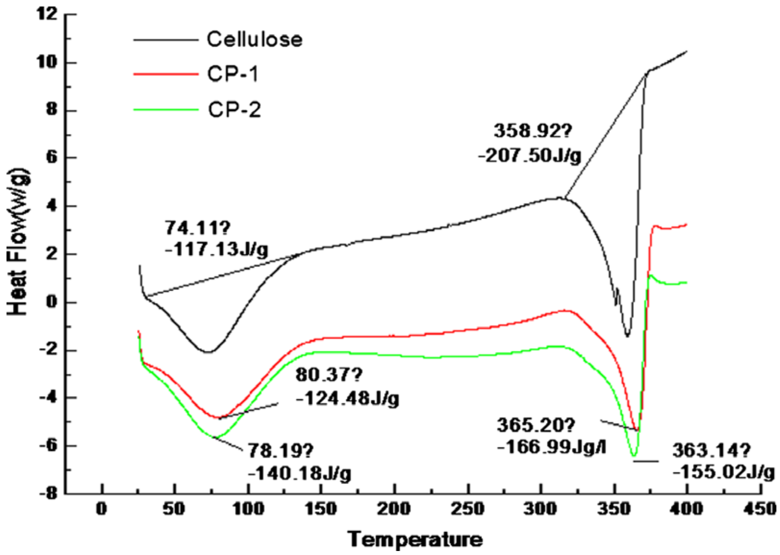


Fig. 5. DSC plot of the am-POSS grafted cellulose hybrids.

ciated with decomposition processes, which may occur within the fabric during heating. For the CP-1, CP-2, the second endothermic peaks are at 365.20 and 363.14 °C, respectively. The thermal properties of the am-POSS grafted cellulose hybrids are different from pure cellulose polymer. The endothermic peaks are estimated that there are the interaction between organic components and inorganic components. DSC plots of the am-POSS grafted cellulose hybrids also indicate that the two endothermic peaks are small. It can be explained that organic component and inorganic component are even (Wu, Jia, Chen, Shao, & Chu, 2004). This phenomenon shows that thermal properties of the am-POSS grafted cellulose hybrids are improved.

4. Conclusions

The cellulose-based hybrid containing POSS are synthesized by cross-linking graft reaction. The silicon contents and micro-FT-IR spectroscopy of the am-POSS grafted cellulose indicate that the am-POSS grafted cellulose hybrids form new molecular structures containing POSS nano-silica particles. POSS particles are dispersed at the nanometer scale in the cellulose host matrix, bonding to the cellulose through covalent bonds. The thermal properties of the am-POSS grafted cellulose hybrids are improved. The am-POSS grafted cellulose hybrid nanomaterials not only exhibit the thermal properties of inorganic compounds, but also exhibit the thermal properties of organic polymer.

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