



Synthesis and characterization of cellulose/silica hybrid materials with chemical crosslinking

Kongliang Xie ^{*}, Yanhong Yu, Yaqi Shi

Modern Textile Institute, Donghua University, Shanghai 200051, PR China

ARTICLE INFO

Article history:

Received 19 June 2009

Accepted 22 June 2009

Available online 28 June 2009

Keywords:

Nanocellulose
Organic/inorganic
Hybrid
Crosslinking
Sol–gel process

ABSTRACT

The cellulose/silica hybrid biomaterials are prepared by sol–gel covalent crosslinking process. The tetraethoxysilane (TEOS) as precursor, γ -aminopropyltriethoxysilane (APTES) as couple agent, and 2,4,6-tri[(2-epihydrin-3-bimethyl-ammonium)propyl]-1,3,5-triazine chloride (Tri-EBAC) as crosslinking agent, are used in the sol–gel crosslinking process. The chemical and morphological structures of cellulose/silica covalent crosslinking hybrids are investigated with micro-FT-IR spectra, nitrogen element analysis, X-ray diffraction, SEM, AFM, and DSC. The results show that the cellulose/silica hybrids form new macromolecular structures. In sol–gel process, inorganic particles are dispersed at the nanometer scale in the cellulose host matrix, bounding to the cellulose through covalent bonds. The cellulose/silica covalent crosslinking hybrid can form good and smooth film on the cellulose. The thermal properties of organic/inorganic hybrids are improved.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

Nanofibers and nanoporous microspheres have remarkable large surface-to-volume ratio, unusual strength, high surface energy, high surface reactivity and excellent thermal and electric properties. Nanofibers and nanocomposite materials have gained much interest due to the remarkable change in properties (Guo et al., 2008; He, Wan, & Xu, 2007; Ramirez et al., 2008). Typical advantages of organic polymers are flexibility, low density, toughness, and formability, whereas nano-silica has excellent mechanical and optical properties, such as surface hardness, modulus, strength, transparency, and high refractive index (Duo, Li, Zhu, & Zhou, 2008; Hou, Yu, & Shi, 2008; Hou, Zhou, & Wang, 2009; Xie & Hou, 2008; Xie, Hou, & Wang, 2008). These materials can be combined effectively, a new class of high performance or highly functional organic–inorganic hybrid materials have been achieved (Chen, Wang, & Chiu, 2008; Sun & Deng, 2008; Xie, Liu, & Li, 2007; Zeng, Liu, & Zhang, 2008). A lot of attempts have been carried out to make nanocomposites or nanofibers. Electrospinning has the unique ability to produce nanofibers and nanoporous microspheres of different materials in various fibrous assemblies (He, Xu, Wu, & Liu, 2007; Hou, Wang, & Yu, 2009). However, cellulose-based nanocomposites are very difficult to produce by the use of electrospinning 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 (Dharmaraj et al., 2006; Musyanovych, Wienke, Mailander, Walther, & Landfester, 2008; Ohno, Tagawa, Itoh, Suzuki, & Matsuda, 2009; Samuneva et al., 2008).

The sol–gel reaction involves the hydrolysis of silica precursors and condensation of the resulting hydroxyl groups to form a nanostructure. The sol–gel process has been widely used in the fields of mesoporous materials, membrane materials and intelligent hybrid hydrogel (Addamo et al., 2008; Pappas, Liatsi, Kartsonakis, Danilidis, & Kordas, 2008; Seckin, Koytepe, & Ibrahim, 2008; Xie, Zhang, & Yu, 2009). One simple method is mixing organic compounds with a metal alkoxide, such as tetraethoxysilane (TEOS). During the sol–gel process the inorganic mineral is deposited in the organic compound matrix forming hydrogen bonding between organic phase and inorganic phase. Another method is to introduce triethoxy silyl groups into the organic compounds prior to the sol–gel reactions with TEOS. Some organic/inorganic hybrid on the basis of different inorganic precursors and organic compounds, such as chitosan, alginate, PEG, PVA, AA, PAAG, have been reported. Several applications have been already developed for this kind of hybrid materials particularly in the biomedical field. The dispersed inorganic particles impart the properties of hardness, brittleness, and transparency, whereas density, free volume and thermal stability depend on the organic host polymer (Kataoka et al., 2005; Li et al., 2008; Zhou, Cui, Zhang, & Yin, 2008).

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 several functional groups that may be employed in various activation processes. Chemical modification

^{*} Corresponding author. Tel.: +86 21 6237 8237; fax: +86 21 6237 8392.
E-mail address: klxie@dhu.edu.cn (K. Xie).

of cellulose can change itself chemical and morphological structures for different propose (Hou, Wang, & Wu, 2008; Xie et al., 2009). The incorporation of nanoscale particles into cellulose matrix leads to a strong interfacial interaction. During the sol–gel process, the inorganic mineral, such as tetraethoxysilane (TEOS), is deposited in the cellulose matrix forming hydrogen bond between organic phase and inorganic phase. Due to avoiding phase separation, some couple agents, such as γ -aminopropylmethyldimethoxysilane, are used as ends of the organic/inorganic hybrid. Hydrolysis and condensation reactions are basically responsible for polymerization of the inorganic precursors. However, high even dispersion system at the nanometer scale in the polymeric host matrix is very difficult to be produced. The cellulose molecular and nano-silicon dioxide particles with organic groups need to be further modified (Kulpinski, 2005; Mithieux, Tu, Korkmaz, Braet, & Weiss, 2009; Xie, Hou, & Sun, 2008).

In this paper, the cellulose/silica organic/inorganic hybrid biomaterials are synthesized by sol–gel crosslinking process. The tetraethoxysilane (TEOS) as precursor and γ -aminopropyltriethoxysilane (APTES) as couple agents are used in the sol–gel process. The compound containing cationic and multi-reactive groups, 2,4,6-tri[(2-epihydrin-3-bimethyl-ammonium)propyl]-1,3,5-triazine chloride (Tri-EBAC), is used as crosslinking agent in the sol–gel process. The chemical and surface morphological structures of the organic/inorganic hybrids are characterized.

2. Experimental

2.1. Materials

The tetraethoxysilane (TEOS) as precursor and γ -aminopropyltriethoxysilane (APTES) as couple agents were obtained from Hangzhou Dadi Chemical Co., Ltd, Hangzhou, China. 2,4,6-Tri[(2-epihydrin-3-bimethyl-ammonium)propyl]-1,3,5-triazine chloride (Tri-EBAC) as crosslinking agent were obtained from Modern Textile Institute, Donghua University, Shanghai, China. Scoured and bleached cellulose fabrics were obtained from Jinqiu Textile Company, Shaoxing, Zhejiang. Other chemicals were obtained from Shanghai Chemical Reagent Plant, Shanghai, China.

2.2. Preparation of cellulose/silica covalent crosslinking hybrids by sol–gel crosslinking process

TEOS 10 g, alcohol 25 g, distilled water 2.5 g, HCl (36.6%) 1 ml were mixed. Then the mixture was stirred for 30 min at 40 °C until a homogeneous solution was obtained. The solution was called Sol-A.

2,4,6-Tri[(2-epihydrin-3-bimethyl-ammonium)propyl]-1,3,5-triazine chloride (Tri-EBAC) as crosslinking agent was added in the certain concentration solution of Sol-A according to the recipe (shown in Table 1). The mixtures were sufficiently mixed by stirring at room temperature.

The cellulose samples were padded with the sol–gel solutions to give 80% wet pick-up. The dry temperature and time were 105 °C and 1.5 min, respectively. The cure temperature was 150 °C, and cure time was 1.5 min. Three cellulose/silica organic/inorganic hy-

brids were obtained. They were named as CS-0 with Sol-0, CS-1 with Sol-1, CS-2 with Sol-2, respectively.

For comparison, the cellulose sample without the hybrid was cured under the same conditions.

2.3. FT-IR spectra and nitrogen 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 nitrogen content was determined by Elementar Vario(III) (Germany). The samples were dried under vacuum at the temperature of 50 °C before measuring.

2.4. XRD

The control cellulose and cellulose/silica organic/inorganic hybrid 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 of 300 mA, $\lambda = 1.542 \text{ \AA}$.

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.

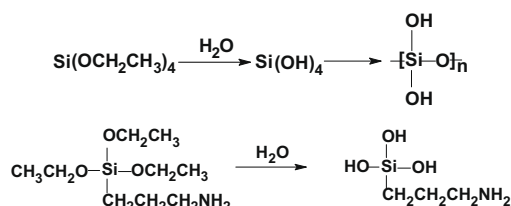
2.7. DSC

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. Preparation and chemical structure of the cellulose/silica covalent crosslinking hybrid by sol–gel crosslinking process

Hydrolysis and condensation reactions of the tetraethoxysilane (TEOS) take place during the sol–gel process. The product of the polycondensation reaction is a typical inorganic glass type material having only –OH groups on the surface. The organically modified silane type of materials can be synthesized from the precursor γ -aminopropyltrimethoxysilane as couple agent. Hydrolysis and condensation reactions of TEOS and γ -aminopropyltrimethoxysilane are shown in Scheme 1. The sol–gel dispersion particles have –OH and



Scheme 1. Hydrolysis of TEOS and APTES.

Table 1
Ingredients and some properties of the sol–gels.

Samples	Sol-A	H ₂ O	Tri-EBAC	Appearance
Sol-0	10	20	0	Colorless solution
Sol-1	10	20	5	Colorless solution
Sol-2	10	20	10	Colorless solution

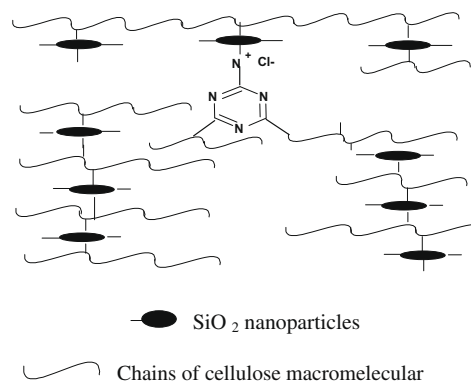
–NH₂ groups. 2,4,6-Tri[(2-epihydrin-3-bimethyl-ammonium)propyl]-1,3,5-triazine chloride has multi-reactive groups. The macromolecular structure of cellulose has a lot of hydroxyl groups. The compound Tri-EBAC as crosslinking agent is able to form covalent bond between cellulose and sol–gel dispersion particles. The crosslinking reactions among hydrolysis products of dispersion particles, cellulose and Tri-EBAC are shown in Scheme 2. The cellulose/silica hybrids form new molecular structures containing not only organic cationic groups but also inorganic nano-silica particles. In sol–gel process, inorganic particles are dispersed in the cellulose host matrix, bounding to the cellulose through covalent bonds, thus forming network organic–inorganic hybrids. The model of cellulose/silica covalent crosslinking hybrid materials in the presence of chemical crosslinking is shown in Scheme 3.

The nitrogen contents of cellulose and cellulose/silica hybrids were determined. The nitrogen contents of control cellulose, CS-1, and CS-2 are 0.346%, 0.416%, and 0.464%, respectively. Compared with the cellulose, the nitrogen contents of cellulose/silica covalent crosslinking hybrids increase. These confirm that the compound Tri-EBAC is able to form covalent bond with cellulose.

Micro-FT-IR spectroscopy was employed to study the chemical structure of the synthesized hybrids. Micro-IR spectra of the cellulose/silica hybrids and cellulose are shown in Fig. 1. The FT-IR spectra of cellulose/silica hybrids (CS-1 and CS-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 cm^{−1} can be related to the presence of –Si–O–C–, –C–O–C–, and Si–C bonds. Moreover, FT-IR spectra assure the presence of –N=C– at 1458 and 1442 cm^{−1} (1,3,5-triazine cycle).

3.2. Surface morphology of the cellulose/silica covalent crosslinking hybrids

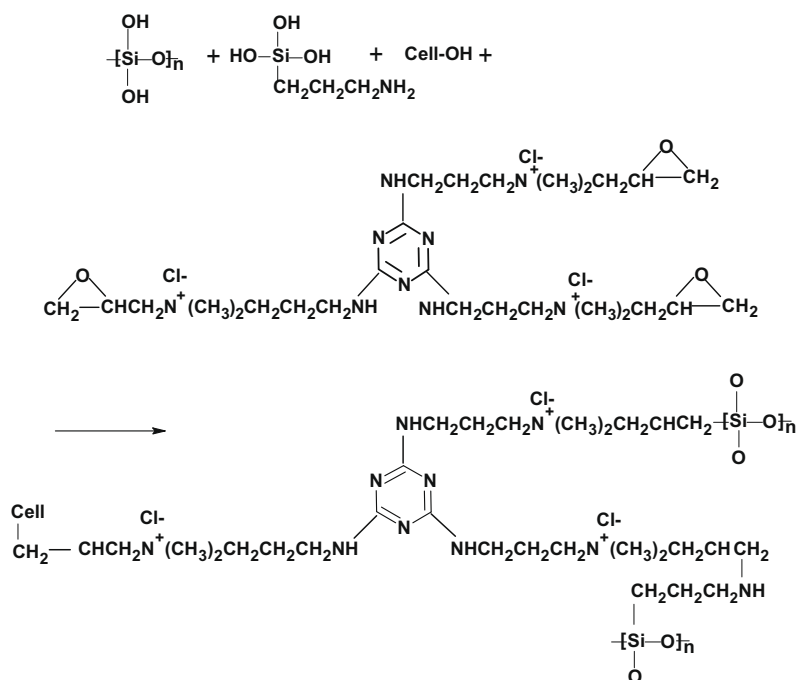
SEM analysis was used to characterize any changes about the surface morphology of the cellulose/silica covalent crosslinking hybrids. Representative SEM micrographs, taken at the magnification



Scheme 3. Model of cellulose/silica covalent crosslinking hybrid materials.

of 5000 and 10,000 of cellulose/silica hybrids are shown in Fig. 2, respectively. Fig. 2a is the SEM micrograph of cellulose/silica hybrid fiber without Tri-EBAC (CS-0). Fig. 2b is the SEM micrograph of cellulose/silica crosslinking hybrid with Tri-EBAC (CS-1). From Fig. 2a and b, it can be seen that the surface of the cellulose/silica hybrid fiber without Tri-EBAC (CS-0) is rough. Nanoparticles can not form good film on the cellulose because of phase separation. The surface of cellulose/silica hybrid fiber with Tri-EBAC (CS-1) is smooth. The cellulose/silica covalent crosslinking hybrid also has heterogeneous structure with well-defined nanounits. Nanoparticles can form good film on the cellulose because of covalent crosslinking.

SEM and AFM data for the cellulose/silica covalent hybrid are in very good agreement. AFM data for the cellulose/silica covalent hybrid and the cellulose are shown in Figs. 3 and 4, respectively. AFM images show that surface morphology of the cellulose/silica covalent hybrid have obvious different from surface morphology of the cellulose. The AFM (shown in Figs. 3 and 4) graphs show the topography of the cellulose/silica covalent hybrid with the height distribution profiles of surface roughness. It can be seen that the



Scheme 2. Chemical structure of organic/inorganic network hybrids.

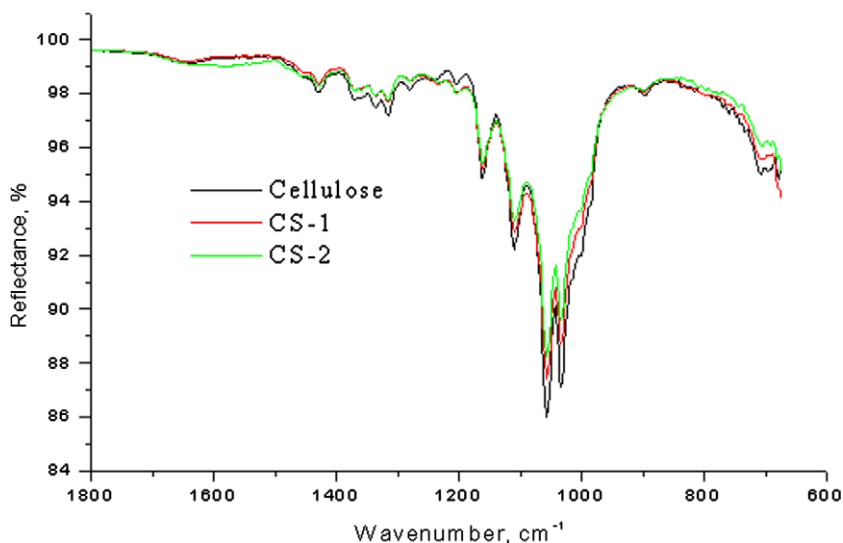


Fig. 1. Micro-FT-IR spectra of the cellulose/silica hybrids and the cellulose.

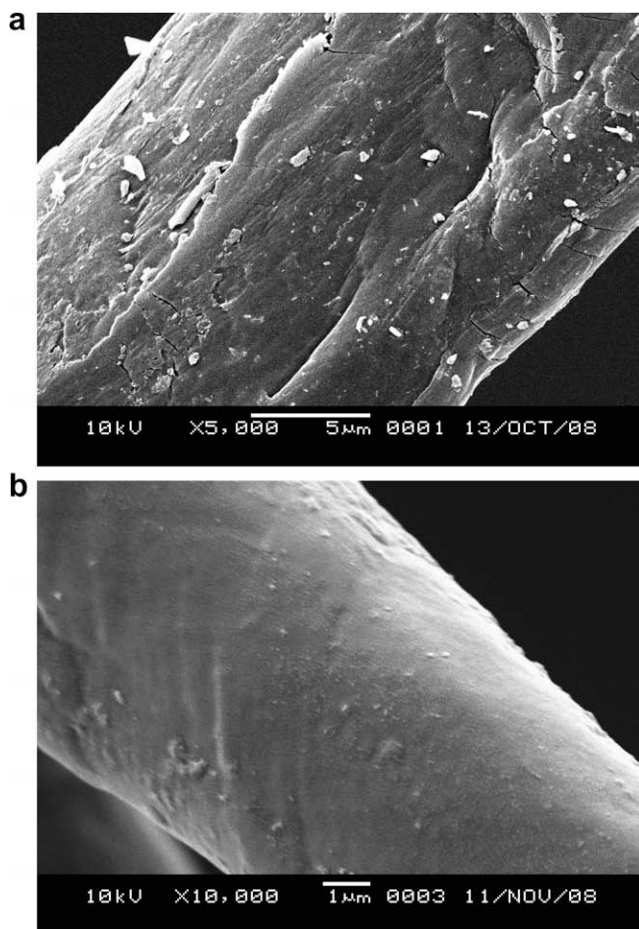


Fig. 2. SEM micrograph of the cellulose/silica hybrid fibers: (a) cellulose/silica hybrid fiber without Tri-EBAC and (b) cellulose/silica crosslinking hybrid fiber (CS-1).

cellulose/silica covalent hybrid has the surface with irregularities of a quite small height.

The XRD data illustrate the influence of inorganic nanoparticles on the intensity and shade of the patterns. XRD patterns of the cellulose/silica network hybrids are shown in Fig. 5. The main peaks of

CS-1 at 15.1° , 16.49° , and 22.86° associate with cellulose structure. The main peaks of CS-2 at 14.72° , 16.50° , and 22.68° also associate with cellulose structure. But the peaks at about 23.50° associated with nano-SiO₂ structure may be overlapped.

3.3. Thermal properties of cellulose/silica hybrid materials

The thermal properties of cellulose/silica covalent crosslinking hybrids are different from pure cellulose polymer. Differential scanning calorimetry (DSC) is one of important methods for observing the thermal characteristics of materials. DSC plots of the pure cellulose fiber and organic/inorganic hybrids (CS-1 and CS-2) were measured and shown in Fig. 6.

The DSC plots for cellulose, CS-1 and CS-2 contain first endothermic peaks at temperatures of 74.11°C , 74.24°C , and 71.02°C , respectively. These endothermic peaks are probably associated with the removal of water from the cellulose and cellulose/silica hybrid chains. Comparison with CS-2, the lower peak area obtained in the DSC plot of CS-1 probably is due to the decrease of the amount of cationic groups in the cellulose chains because of lower concentration of Tri-EBAC.

For cellulose, the second endothermic peak initiates at 336.02°C , finishes at 369.81°C . The endothermic change obtained in the DSC plot for cellulose is associated with decomposition processes, which may occur within the fabric during heating. For the CS-1, CS-2, the second endothermic peaks initiate at 236.04°C and 218.58°C , finish at 284.79°C and 271.78°C , respectively. The endothermic peaks are estimated that there are the interaction between organic components and inorganic components. DSC plots of cellulose/silica 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).

For the CS-1, CS-2, the third endothermic peaks initiate at 324.17°C and 315.77°C , finish at 380.97°C and 369.59°C , respectively. The endothermic changes obtained in the DSC plots may be associated with the decomposition of a part of inorganic/organic hybrids. Moreover, the endothermic peaks are also small. This indicates that the decomposition of cellulose/silica hybrids may take place in the organic phase. This phenomenon shows that thermal properties of organic/inorganic hybrids are improved. The organic/inorganic hybrid nanomaterials not only exhibit the thermal properties of inorganic compounds, but also exhibit the thermal properties of organic polymer.

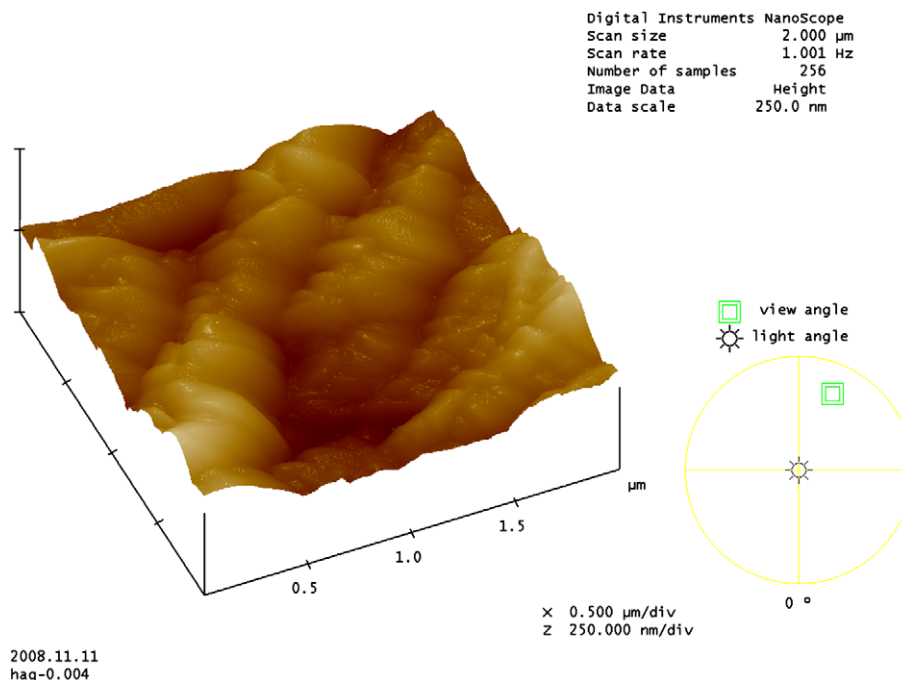


Fig. 3. AFM three-dimensional image of the control sample (cellulose fiber).

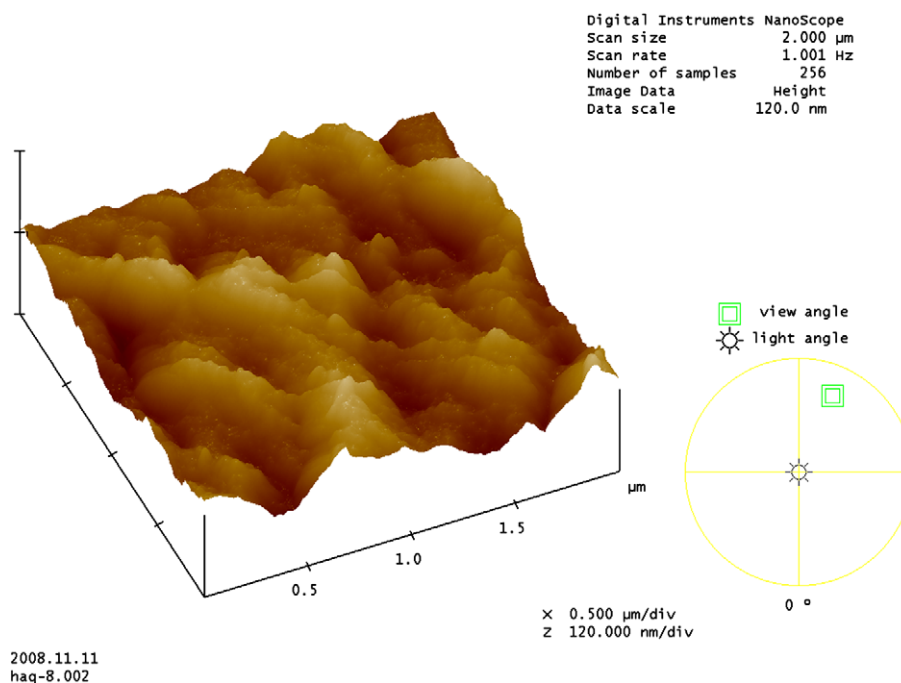


Fig. 4. AFM three-dimensional image of the CS-1 hybrid.

4. Conclusions

The cellulose/silica covalent hybrid materials are prepared by sol–gel process. 2,4,6-Tri[(2-epihydrin-3-bimethyl-ammonium)propyl]-1,3,5-triazine chloride (Tri-EBAC), is used as cross-linking agent in the sol–gel process. The nitrogen contents and micro-FT-IR spectroscopy of cellulose/silica hybrids indicate that the cellulose/silica hybrid form new molecular structures contain-

ing not only organic cationic groups but also inorganic nano-silica particles. In sol–gel process, inorganic particles are dispersed at the nanometer scale in the cellulose host matrix, bounding to the cellulose through covalent bonds. The surface of cellulose/silica hybrid without Tri-EBAC can not form good film on the cellulose. The surface of cellulose/silica hybrid with Tri-EBAC can form good and smooth film on the cellulose because of covalent crosslinking. The thermal properties of organic/inorganic hybrids are improved.

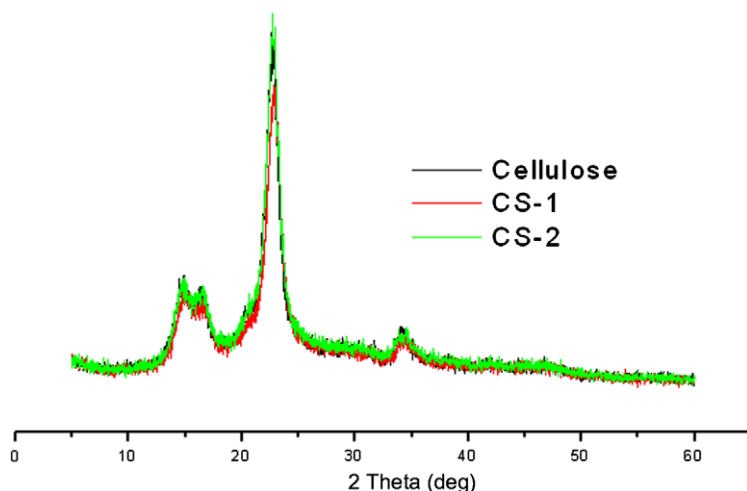


Fig. 5. XRD patterns for the cellulose/silica covalent crosslinking hybrids.

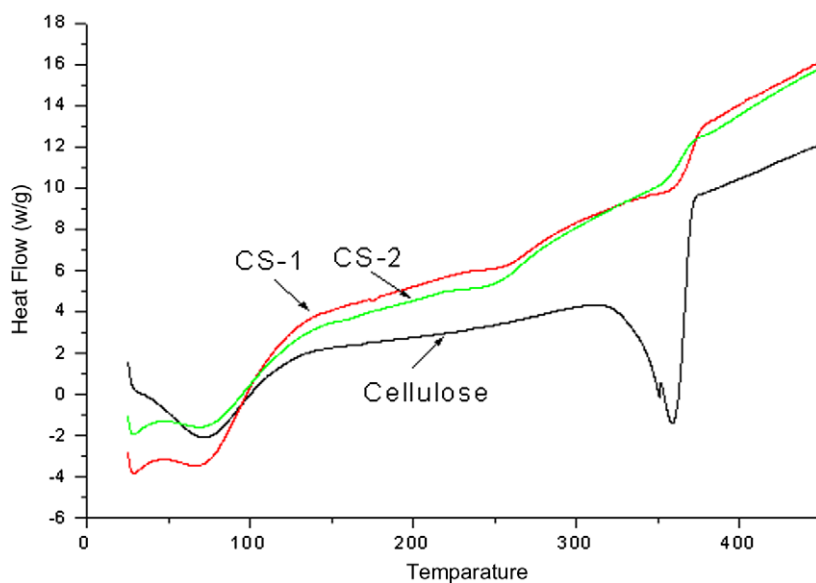


Fig. 6. DSC plots of cellulose/silica hybrids.

The organic/inorganic hybrid nanomaterials not only exhibit the thermal properties of inorganic compounds, but also exhibit the thermal properties of organic polymer.

References

- Addamo, M., Augugliaro, V., Paola, A. D., Garcia-Lopez, E., Loddo, V., Marci, G., et al. (2008). Photocatalytic thin films of TiO_2 formed by a sol-gel process using titanium tetraisopropoxide as the precursor. *Thin Solid Films*, 516, 3802–3807.
- Chen, H., Wang, L., & Chiu, W. (2008). Synthesis and characterization of MEH-PPV/nanosized titania hybrids prepared via in situ sol-gel reaction. *Materials Chemistry and Physics*, 112, 551–556.
- Dharmaraj, N., Prabu, P., Nagarajan, S., Kim, C. H., Park, J. H., & Kim, H. Y. (2006). Synthesis of nickel oxide nanoparticles using nickel acetate and poly(vinyl acetate) precursor. *Materials Science and Engineering B*, 128, 111–114.
- Duo, S., Li, M., Zhu, M., & Zhou, Y. (2008). Polydimethylsiloxane/silica hybrid coatings protecting kapton. *Materials Chemistry and Physics*, 112, 1093–1098.
- Guo, X., Guo, H., Fu, L., Zhang, H., Carlos, L. D., Deng, R., et al. (2008). Synthesis and photophysical properties of novel organic-inorganic hybrid materials covalently linked to a europium complex. *Journal of Photochemistry and Photobiology A: Chemistry*, 200, 318–324.
- He, J., Wan, Y., & Xu, L. (2007). Nano-effects, quantum-like properties in electrospun nanofibers. *Chaos, Solitons and Fractals*, 33, 26–37.
- He, J., Xu, L., Wu, Y., & Liu, Y. (2007). Mathematical models for continuous electrospun nanofibers and electrospun nanoporous microspheres. *Polymer International*, 56, 1323–1329.
- Hou, A., Wang, X., & Wu, L. (2008). Effect of microwave irradiation on the physical properties and morphological structures of cellulose. *Carbohydrate Polymer*, 74, 934–937.
- Hou, A., Wang, X., & Yu, Y. (2009). Preparation of the cellulose/silica hybrid containing cationic groups by sol-gel crosslinking process and its dyeing properties. *Carbohydrate Polymers*, 77, 201–205.
- Hou, A., Yu, J., & Shi, Y. (2008). Preparation and surface properties of the polysiloxane material modified with fluorocarbon side chains. *European Polymer Journal*, 44, 1696–1700.
- Hou, A., Zhou, M., & Wang, X. (2009). Preparation and characterization of durable antibacterial cellulose biomaterials modified with triazine derivatives. *Carbohydrate Polymers*, 75, 328–332.
- Kataoka, K., Nagao, Y., Nukui, T., Akiyama, I., Tsuru, K., Hayakawa, S., et al. (2005). An organic-inorganic hybrid scaffold for the culture of HepG2 cells in a bioreactor. *Biomaterials*, 26, 2509–2516.
- Kulpinski, P. (2005). Cellulose fibers modified by silicon dioxide nanoparticles. *Journal of Applied Polymer Science*, 98, 1793–1798.
- Li, J., Srinivasan, S., He, G. N., Kang, J. Y., Wu, S. T., & Ponce, F. A. (2008). Synthesis and luminescence properties of ZnO nanostructures produced by the sol-gel method. *Journal of Crystal Growth*, 310, 599–603.
- Mithieux, S. M., Tu, Y., Korkmaz, E., Braet, F., & Weiss, A. S. (2009). In situ polymerization of tropoelastin in the absence of chemical cross-linking. *Biomaterials*, 30, 431–435.
- Musyanovych, A., Wienke, J. S., Mailander, V., Walther, P., & Landfester, K. (2008). Preparation of biodegradable polymer nanoparticles by miniemulsion technique and their cell interactions. *Macromolecular Bioscience*, 8, 127–139.
- Ohno, T., Tagawa, S., Itoh, H., Suzuki, H., & Matsuda, T. (2009). Size effect of TiO_2 - SiO_2 nano-hybrid particle. *Materials Chemistry and Physics*, 113, 119–123.

- zPappas, G. S., Liatsi, P., Kartsonakis, I. A., Danilidis, I., & Kordas, G. (2008). Synthesis and characterization of new SiO₂–CaO hollow nanospheres by sol–gel method: Bioactivity of the new system. *Journal of Non-Crystalline Solids*, 354, 755–760.
- Ramirez, C., Rico, M., Torres, A., Barral, L., Lopez, J., & Montero, B. (2008). Epoxy/POSS organic–inorganic hybrids: ATR-FTIR and DSC studies. *European Polymer Journal*, 44, 3035–3045.
- Samuneva, B., Djambaski, P., Kashchieva, E., Chernev, G., Kabaivanova, L., Emanuilova, E., et al. (2008). Sol–gel synthesis and structure of silica hybrid biomaterials. *Journal of Non-Crystalline Solids*, 354, 733–740.
- Seckin, T., Koytepe, S., & Ibrahim, A. H. (2008). Molecular design of POSS core star polyimides as a route to low-k dielectric materials. *Materials Chemistry and Physics*, 112, 1040–1046.
- Sun, Q., & Deng, Y. (2008). Morphology studies of polyaniline lengthy nanofibers formed via dimmers copolymerization approach. *European Polymer Journal*, 44, 3402–3408.
- Wu, W., Jia, M., Chen, J., Shao, L., & Chu, G. (2004). ACTA. *Materials Composite*, 21, 70–75.
- Xie, K., Liu, H., & Wang, X. (2009). Surface modification of cellulose with triazine derivative to improve printability with reactive dyes. *Carbohydrate Polymers*. doi:10.1016/j.carbpol.2009.05.013.
- Xie, K., & Hou, A. (2008). Synthesis, properties and application of cationic reactive disperse dyes containing quaternary group. *Journal of Dispersion Science and Technology*, 29, 436–439.
- Xie, K., Hou, A., & Sun, Y. (2008). Chemical graft of cellulose with the ion-pair emulsion containing the reactive groups and its dyeing properties. *Journal of Dispersion Science and Technology*, 29, 1385–1390.
- Xie, K., Hou, A., & Wang, X. (2008). Dyeing and diffusion kinetics of modified cellulose with triazine derivatives containing cationic and anionic groups. *Carbohydrate Polymers*, 72, 646–651.
- Xie, K., Liu, Y., & Li, X. (2007). Synthesis and properties of the novel surface-active dyes containing fluorocarbon groups: Part 1. Synthesis and dyeing properties of the novel surface-active dyes on silk fabric. *Materials Chemistry and Physics*, 105, 199–203.
- Xie, K., Zhang, Y., & Yu, Y. (2009). Preparation and characterization of cellulose hybrids grafted with the polyhedral oligomeric silsesquioxanes (POSS). *Carbohydrate Polymers*, 77, 858–862.
- Zeng, K., Liu, Y., & Zhang, S. (2008). Poly(ethylene imine) hybrids containing polyhedral oligomeric silsesquioxanes: Preparation, structure and properties. *European Polymer Journal*, 44, 3946–3956.
- Zhou, Z., Cui, L., Zhang, Y., & Yin, N. (2008). Preparation and properties of POSS grafted polypropylene. *European Polymer Journal*, 44, 3057–3066.