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Thermal degradation of nano-cellulose hybrid materials containing reactive polyhedral oligomeric silsesquioxane

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ABSTRACT

Nano-cellulose hybrids containing reactive polyhedral oligomeric silsesquioxane (R-POSS) were synthesized by staring crosslinking reaction using reactive polyhedral oligomeric silsesquioxane containing multi-*N*-methylol groups. Thermal degradation properties of nano-cellulose hybrid materials containing R-POSS were investigated by TGA and DSC. Surface chemical ingredients of the nano-cellulose hybrids were analyzed by X-ray photoelectron spectroscopy (XPS). Chemical structure and morphology of charred residue were analyzed by SEM, FT-IR, and ^{13}CNMR. The results show that nano-cellulose hybrids obtained obviously improved their elastic properties. The atom percent of silicone in the nano-cellulose hybrids were obvious higher than that of control sample. The incorporation of R-POSS in the cellulose slightly decreased the thermal degradation temperature. Chemical structure of charred residue was mainly inorganic SiO_xC_y network structure. SiO_xC_y net frameworks formed maintain fiber shape after mass loss of 91%.

1. Introduction

In the last years, nanofibers and nanocomposite materials have gained much interest due to the remarkable change in properties (Bordes, Hablot, Pollet, & Averous, 2009; Hall, Jayaraman, & Schweizer, 2009; He, Wan, & Xu, 2007; Song, He, Hu, Chen, & Liu, 2008). Polyhedral oligomeric silsesquioxanes (POSS) have a nanometer-sized confine structure with a cubic silica core and can be functionalized with a variety of organic compounds. The nanoscopic size of POSS enables POSS segments to effectively reinforce polymer chain segments and control chain motion at the molecular level through maximizing the surface area and chemical interactions of the nano-reinforcement with the polymer. Organic/inorganic hybrids containing POSS have attracted much interest from academic and industrial researchers for dielectric, heat-resistant and radiation-resistant materials (Fina, Tabuani, Frache, & Camino, 2005; Guo et al., 2008; Hou, Wang, & Yu, 2009; Phillips, Haddad, & Tomczak, 2004; Seckin, Koytepe, & Ibrahim, 2008; Xie, Zhang, & Yu, 2009). POSS can be prepared through the hydrolytic condensation of a organic siloxane (Feher & Wyndham, 1998; Janowski & Pielichowski, 2008). However, POSSs with multi-reactive groups as candidate regents, which can be crosslinked with polymer, are scarce. Reactive polyhedral oligomeric silsesquioxane containing multi-*N*-methylol (R-POSS) is a functional and attractive staring monomer for new reinforcement materials (Xie, Wang, & Xu, 2010; Xie, Zhang, & Chen, 2010). R-POSS has highly reactive multi-*N*-methylol groups and has excellent potential application as nano-sized cores for starburst dendrimers. Chemical structure of R-POSS containing multi-*N*-methylol groups is shown in Scheme 1.

Cellulose fiber is an excellent, natural biomaterial (Hou, Zhou, & Wang, 2009). 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. A lot of attempts have been carried out to make cellulose-based nanocomposites (Jeon, Mather, & Haddad, 2000; Kulpinski, 2005; Xie, Hou, & Zhang, 2009, Xie, Yu, & Shi, 2009). These composite materials are biocompatible, biodegradable and possess low toxicity in biomaterials field. However, a highly dispersed system at the nanometer scale in the cellulose host matrix is very difficult to be produced by traditional techniques. R-POSS can be used to prepare nano-cellulose hybrids. POSS can be effectively incorporated into a cellulose matrix by crosslinking reaction. The incorporation of nanoscale POSS particles into cellulose matrix leads to a strong interfacial interaction (Duo, Li, Zhu, & Zhou, 2008; Jeon et al., 2000; Xie, Zhang, et al., 2009). Typical advantages of cellulose-based hybrids are flexibility, low density, toughness, and formability, whereas nano-sized POSS has excellent mechanical, optical, thermal properties, and high refractive index.

In this paper, the nano-cellulose hybrids containing POSS are synthesized by crosslinking reaction using R-POSS containing multi-*N*-methylol groups. Thermal degradation properties of nano-cellulose hybrid materials containing R-POSS are investi-

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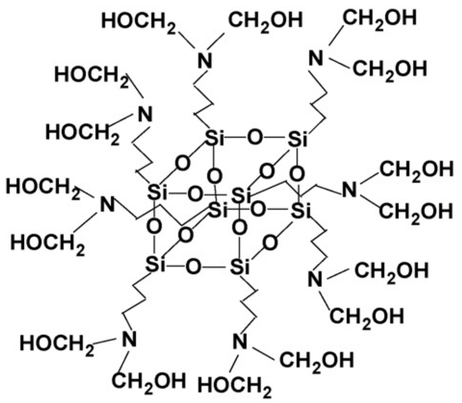


Scheme 1. Chemical structure of R-POSS containing multi-*N*-methylol groups.

gated. Chemical structure and morphology of charred residue are analyzed. The physical properties and surface ingredient of the nano-cellulose hybrids are discussed.

2. Experimental

2.1. Materials

R-POSS containing multi-*N*-methylol groups was obtained from National Research Center of Dying and Finishing, Shanghai, China. A scoured and bleached cellulose fabric (cotton fibers) was obtained from Jinqiu Textile Company, Shaoxing, China. Other chemicals were obtained from Shanghai Chemical Reagent Plant, Shanghai, China.

2.2. Preparation of nano-cellulose hybrids

R-POSS was diluted with distilled water to certain concentration solution or suspensions. Citric acid and $MgCl_2$ as catalysts were used in the crosslinking reaction. Ingredients in the chemical crosslinking process are shown in Table 1 . The mixtures were sufficiently mixed by stirring at room temperature.

Cellulose fabrics were padded with the R-POSS mixtures to give 80% wet pick-up. The drying temperature and time were 95 °C and 3 min, respectively. After drying, the fabrics were cured for 1.5 min at 165 °C. The nano-cellulose hybrids containing R-POSS were obtained. They were named as NCH-1, NCH-2, NCH-3 and NCH-4, respectively.

2.3. Measurements

Dry crease recovery angle (CRA) was determined according to ASTM method D-1296-98. Values of CRA in both warp and weft directions were determined. The samples were conditioned at 20 °C and 65% relative humidity for at least 24 h before testing. CIE whiteness index was tested according to AATCC test method 110-2000.

Thermogravimetric analyses (TGA) were carried out at a heating rate of 10 °C/min in nitrogen using a Setaram TG 92 Thermobalance. 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 °C to 400 °C at a scanning rate of 10 °C/min, under a constant flow of dry nitrogen.

FT-IR spectra of the samples were measured by an OMNI Sampler of the Nexus-670 FT-IR-Raman Spectrometer (Nicolet Analytical Instruments, Madison, WI). ^{13}CNMR spectrum was recorded on a Bruker AV 400 (Bruker Co., Faellanden, Switzerland).

X-ray photoelectron spectroscopy (XPS) was carried out with a Thermo ESCALAB 250 (USA), using Al Kα excitation radiation ($h\nu$ = 1486.6 eV). 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.

Table 1
Ingredients in the chemical crosslinking process (g).

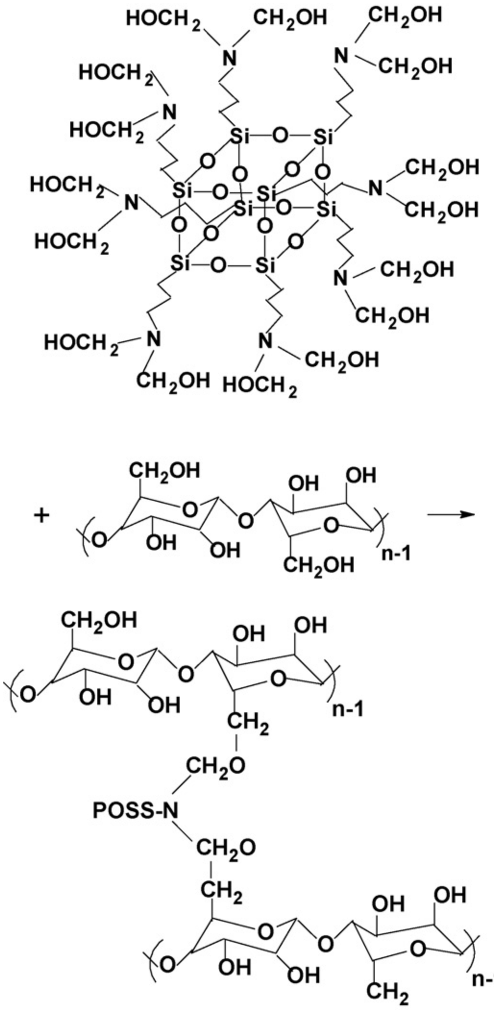
Samples	R-POSS	H_2O	Ethanol	$MgCl_2$	Citric acid
NCH-1	0.8	97.2	2	1.5	0.1
NCH-2	1.2	96.8	2	1.5	0.1
NCH-3	1.6	96.4	2	1.5	0.1
NCH-4	2.4	95.6	2	1.5	0.1

3. Results and discussion

3.1. Preparation and elastic properties of nano-cellulose hybrid materials containing R-POSS

The molecule of R-POSS has eight corners with sixteen reactive groups (–CH_2OH). The *N*-methylol groups impart high-reactivity. The macromolecular structure of cellulose has numerous hydroxyl groups (–OH). R-POSS can crosslink with cellulose macromolecules. The crosslinking reaction of cellulose and R-POSS is shown in Scheme 2.

In the crosslinking process, POSS particles are dispersed in the cellulose host matrix, and bonded to the cellulose through covalent bonds. Physical properties of nano-cellulose hybrids containing R-



Scheme 2. Crosslinking reaction mechanism of cellulose and R-POSS.

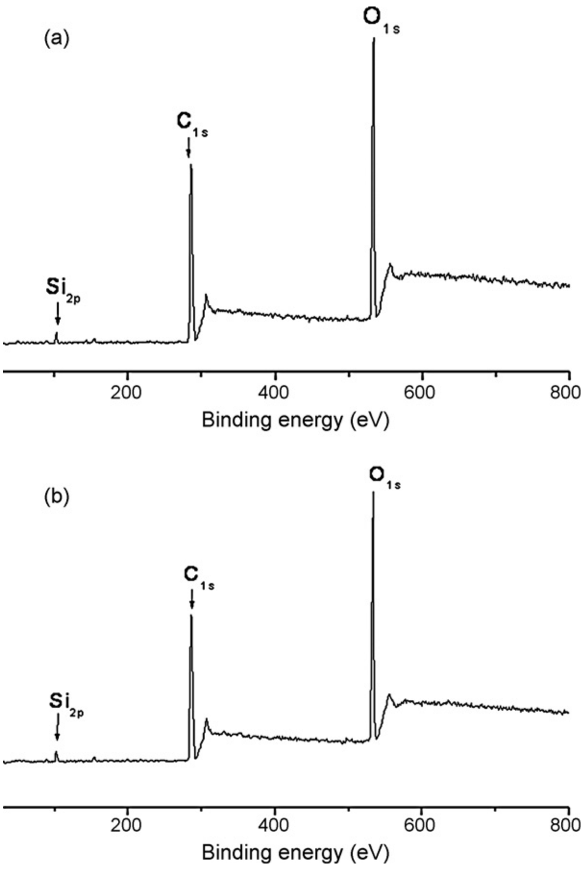


Fig. 1. XPS survey spectra of the nano-cellulose hybrids.

POSS can be changed. Crease recovery angles and whiteness index of synthesized nano-cellulose hybrids were measured. The results are listed in Table 2. It can be seen that the crease recovery angles of nano-cellulose hybrids significantly increased from 104.71 (control sample) to 184.53 (NCH-4). Cellulose hybrids obtained through R-POSS crosslinking reaction increased elastic properties of nano-cellulose. With increase of R-POSS concentration, the whiteness indexes of nano-cellulose slightly decreased.

3.2. *Surface analysis of nano-cellulose hybrid materials containing R-POSS*

After POSS particles are bonded to cellulose through covalent bonds, surface chemical ingredient of nano-cellulose hybrids containing R-POSS must be changed. In order to investigate the surface ingredient and structure of nano-cellulose hybrids, X-ray photoelectron spectroscopy is applied. Fig. 1 shows XPS survey spectra obtained using Al Kα excitation radiation ($h\nu = 1486.6$ eV). In Fig. 1a and b are survey spectra of nano-cellulose NCH-3, and nano-cellulose NCH-4, respectively. The peaks at around 284 eV and 533 eV are attributed to C1s and O1s, respectively. The peak at around 102 eV is assigned to Si2p. In Fig. 1a and b, it can be seen from the survey spectra, the C1s, O1s, and Si2p peaks are predominant. The corresponding high-resolution XPS spectra of C1s are recorded. The peak intensity of binding energy 284.8 in nano-cellulose NCH-3 and NCH-4 are higher than that of control sample. It can be seen that C–C and C–Si bonds in the nano-cellulose surfaces significantly increase.

Table 2
Elastic properties of nano-cellulose hybrids containing R-POSS.

Samples	Crease recovery angle (W + F,°)	Whiteness index
Control	104.71	73.34
NCH-1	142.67	71.12
NCH-2	159.38	69.24
NCH-3	172.24	68.84
NCH-4	184.53	68.17

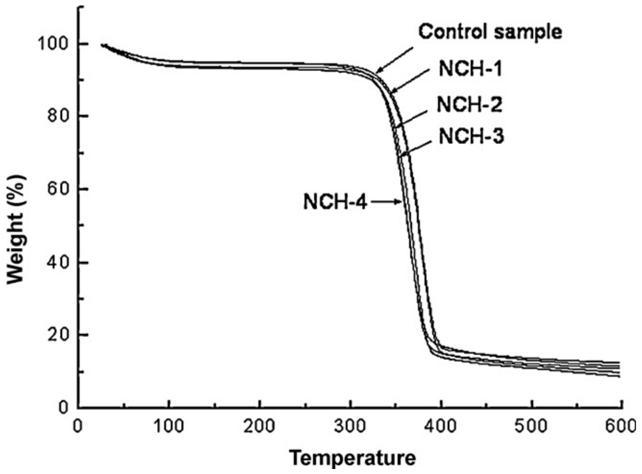


Fig. 2. TG curves of control sample and nano-cellulose hybrids.

3.3. *Thermal degradation of nano-cellulose hybrids containing R-POSS*

In order to investigate thermal degradation properties of nano-cellulose hybrids containing R-POSS, thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) of nano-cellulose hybrids are measured. The TGA plots of the nano-cellulose hybrids are shown in Fig. 2. Pyrolytic degradation of nano-celluloses occurs in one apparent main step. Onset of degradation for NCH-1, NCH-2, NCH-3, NCH-4 are at around 352.6 °C, 344.8 °C, 339.0 °C, and 337.8 °C, respectively. Mass loss yielding of residues for NCH-1, NCH-2, NCH-3, NCH-4 are 10.97%, 9.93%, 8.79%, and 11.56% at 600 °C in nitrogen, respectively. Pyrolytic degradations of nano-celluloses are similar with control cellulose sample. Onset of degradation for control sample is at around 353.1 °C. Yielding of residue for control sample is 12.56% at 600 °C. It is assigned to the typical thermal degradation of cellulose. The corporation of R-POSS in the cellulose slightly decreases thermal degradation temperature. However, the nano-cellulose hybrids do not obviously modify the apparent degradation pathway in nitrogen.

Differential scanning calorimetry (DSC) is one of important methods for observing the thermal characteristics of materials. DSC plots of the cellulose fiber and the nano-cellulose hybrids were measured and shown in Fig. 3. For cellulose, the endothermic peak is at 379.5 °C. The endothermic change obtained in the DSC plot for cellulose is associated with decomposition processes. For the nano-cellulose hybrids NCH-1, NCH-2, NCH-3, NCH-4, the endothermic peaks are at 375.9 °C, 371.8 °C, 362.8 °C and 359.5 °C, respectively. Fig. 3 shows that the degradation temperatures of nano-cellulose hybrids are slight lower than that of control sample. Spectrum data of DSC are consistent to that of TG. The results show that nano-cellulose hybrids containing R-POSS does not improve their thermal degradation properties. The reason may be that crosslinked cellulose macromolecule with R-POSS inhibit the intermolecular slippage. Cellulose is readily charred due to the inhibition of slippage the molecules chain motion. The results are different from some reported references about composites containing POSS (Bourbigot, Turf, Bellayer, & Duquesne, 2009; Liu, Huang, & Liu, 2007; Mantz et al., 1996; Song et al., 2008). This phenomenon

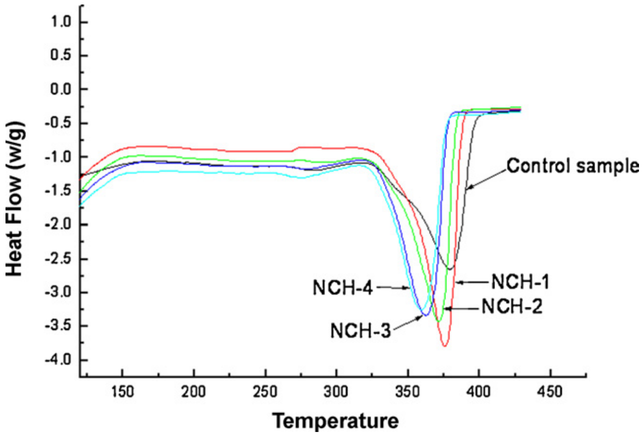


Fig. 3. DSC curves of nano-cellulose hybrids.

is probable due to the lower concentration of POSS in the nano-cellulose hybrids.

3.4. *Chemical analysis of degraded residue of cellulose hybrids*

Nano-cellulose hybrids were charred in nitrogen using thermogravimetric analysis method. Mass loss yielding of residue for NCH-3 is 8.79% at 600 °C. Chemical structure and morphology of degraded residue of cellulose hybrids are analyzed by SEM and FT-IR and ^{13}CNMR. Representative SEM micrograph, taken at the magnification of 200 of charred cellulose fibers is shown in Fig. 4. Fig. 4 shows that charred nano-cellulose fibers at 600 °C does not become powders and maintain excellent fiber shape. Mantz et al. (1996) investigated the thermolysis of some POSS and they assigned the pyrolytic decomposition to the partial loss of the organic substituents of POSS followed by formation of SiO_xC_y networks. After nano-cellulose hybrids containing POSS are charred in nitrogen, they also may be formed SiO_xC_y networks. SiO_xC_y net frameworks formed keep fiber shade after mass loss at 91%. Some silica particles are formed on the surface of charred nano-cellulose hybrids.

In order to further investigate chemical structure of degraded residue of nano-cellulose hybrid, micro-fourier transform infrared (FT-IR) and ^{13}C nuclear magnetic resonance (^{13}CNMR) were measured. In micro-IR spectrum, the main peaks are simple because of charred degradation. The main band at 1629 cm^{-1} is assigned to C-C stretching vibration. The bands at 1384 cm^{-1} and 1117 cm^{-1} are assigned to C–O and Si–O–Si stretching vibration, respectively. ^{13}CNMR spectrum of charred nano-cellulose residue is shown in Fig. 5. ^{13}CNMR spectrum of residue shows that the peaks at 128.56 ppm and 79.68 ppm are attributed to C–C bonds and C–Si, respectively. The peaks at 28.11–38.92 ppm are attributed to C–Si bonds. They demonstrate that chemical structure of charred residue is SiO_xC_y network.

Fig. 4. SEM photograph of degraded residue of nano-cellulose hybrids in nitrogen.

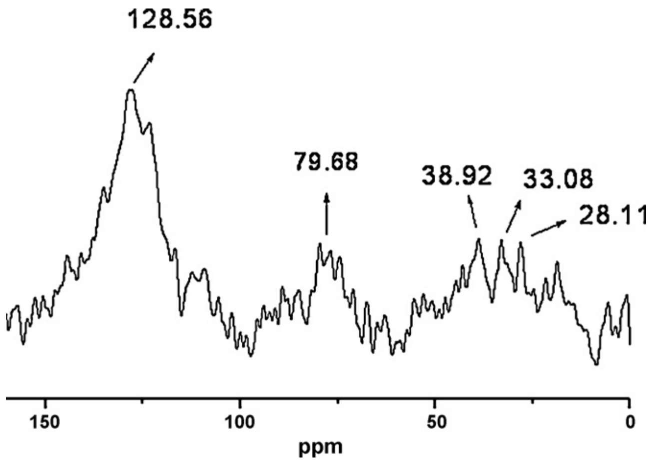


Fig. 5. ^{13}CNMR spectrum of charred nano-cellulose residue.

4. Conclusions

Nano-cellulose hybrids containing POSS are synthesized by crosslinking reaction using R-POSS containing multi-*N*-methylol groups. The cellulose hybrids obtained through R-POSS crosslinking reaction obviously increase elastic properties of nano-cellulose. With increase of R-POSS concentration, the crease recovery angles of nano-cellulose significantly increase. Because of R-POSS crosslinking reaction, C–C and C–Si bonds in the nano-cellulose surfaces significantly increase. The atom percent of silicone in the nano-cellulose hybrids are obvious higher than that of control sample. However, the corporation of R-POSS in the cellulose slightly decreases thermal degradation temperature. Chemical structure of charred residue is inorganic SiO_xC_y network.

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