Transparent Cellulose/Polyhedral Oligomeric Silsesquioxane Nanocomposites with Enhanced UV-Shielding Properties

Ye Feng, Jinming Zhang*, Jiasong He, Jun Zhang*

Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Engineering Plastics, Institute of Chemistry, Chinese Academy of Sciences (CAS), Beijing, 100190, China

Abstract

The solubility of eight types of polyhedral oligomeric silsesquioxane (POSS) derivatives in an ionic liquid 1-allyl-3-methylimidazolium chloride (AmimCl) and the dispersion of POSS in cellulose matrix were examined. Only a special POSS containing both aminophenyl and nitrophenyl groups (POSS-AN, $\text{NH}_2:\text{NO}_2 = 2:6$) was selected to prepare nanocomposites, because of its good solubility in AmimCl and high stability during the preparation process. POSS-AN nanoparticles were uniformly dispersed in a cellulose matrix with a size of 30-40 nm, and so the resultant cellulose/POSS-AN nanocomposite films were transparent. The mechanical properties of the films achieved a maximum tensile strength of 190 MPa after addition of 2 wt% POSS-AN. Interestingly, all of the cellulose/POSS-AN films exhibited high UV-absorbing capability. For the 15 wt% cellulose/POSS-AN film, the transmittance of UVA (315-400 nm) and UVB (280-315 nm) was only 9.1% and nearly 0, respectively. The UV aging

*Corresponding author.

Address: Institute of Chemistry, Chinese Academy of Sciences
Zhongguancun North First Street 2, 100190 Beijing, China
Tel: +86 10 62613251, Fax: +86 10 62613251.

E-mail address: zhjm@iccas.ac.cn (JM Zhang), jzhang@iccas.ac.cn (J Zhang)

and shielding experiments showed that the transparent cellulose/POSS-AN nanocomposite films possessed anti-UV aging and UV shielding properties.

Key words: cellulose nanocomposite; POSS; UV-shielding; anti-UV aging

1. Introduction

Biopolymers are non-toxic, environmentally friendly and biodegradable materials (Rinaudo, 2006; Nair & Laurencin, 2007). Currently, there is a fast growing tendency to use biopolymers for replacing nondegradable materials, thereby reducing the environmental pollution. However, some properties of biopolymers are not good enough to meet the requirments in the real world. Incorporation of nanoparticles into biopolymers to fabricate biopolymer-based nanocomposites is an effective and simple method to markedly improve mechanical, electrical, thermal, optical, and other particular properties of materials. Therefore, biopolymer nanocomposites, which contain the advantages of biopolymers and the functionalities of nanoparticles, have attracted much attention (Kueseng & Jacob, 2006; Darder, Aranda & Ruiz-Hitzky, 2007).

Cellulose, 1,4- β -glucan, is the most abundant biopolymer on the earth. (Klemm, Heublein, Fink & Bohn, 2005; Khalil, Bhat & Yusra, 2012). Compared to synthetic polymers, cellulose based materials have advantageous such as being degradable, available and environment friendly. However, because cellulose is neither meltable nor soluble in common solvents, it is not easy to employ it as the matrix of the polymer composites. To develop non-derivatizing solvents of cellulose is essential to utilize the natural cellulose (Liu, Zhang, Zhou & Wu, 2008; Zhang, Feng, Liu & Zhu, 2012; Zhang,

Liu, Zheng & Zhu, 2012; Hameed, Xiong, Salim & Guo, 2013). Recently, as new kinds of aprotic polar solvents, ionic liquids (ILs), which can dissolve efficiently cellulose, present a new and versatile platform for cellulose chemists (Cao et al., 2009; Zhang et al., 2010; Hameed, Guo, Tay & Kazarian, 2011). Via using ILs as solvents, many works have been done to fabricate cellulose-based composites with different kind of fillers, such as carbon nanotubes (Zhang et al., 2007), halloysite (Soheilmoghaddam & Wahit, 2013; Soheilmoghaddam, Wahit, Mahmoudian & Hanid, 2013; Hanid, Wahit, Guo, Mahmoudian & Soheilmoghaddam, 2014), ZnO nanoparticles (Bagheri & Rabieh, 2013).

Polyhedral oligomeric silsesquioxane (POSS) possesses a cage-like molecular structure, as shown in Fig. 1A. The Si-O-Si inorganic cage structure provides high thermal stability and mechanical properties. Meanwhile, the physical and chemical properties of POSS are designable by the change of the substituted groups at one or more of the corner Si atoms (Kuo & Chang, 2011; Paftopoulos & Pielichowski, 2016). POSS molecules can have different inert and active groups, which make POSS molecules compatible with different polymer systems, and form composites with improved thermal and mechanical properties, flame retardant performance, low dielectric properties, improved wettability, etc. (Li, Wang, Ni & Pittman, 2001; Wu & Mather, 2009; Cordes, Lickiss & Rataboul, 2010).

In this work, we combined a flexible and easily-prepared cellulose matrix with functional POSS nanofillers to form cellulose/POSS nanocomposites by using an ionic liquid 1-allyl-3-methylimidazolium chloride (AmimCl) as the dissolution medium. First,

we tested the solubility of different POSS derivatives in the AmimCl. Then, we selected the POSS derivatives with the best solubility to observe their stability during the film preparation process. Finally, the POSS with both aminophenyl and nitrophenyl groups (POSS-AN, $\text{NH}_2:\text{NO}_2 = 2:6$) was used to prepare POSS/cellulose nanocomposites. The resultant cellulose/POSS-AN nanocomposites exhibited high tensile strength of 150-190 MPa. Meanwhile, they were highly transparent in the visible light region, and exhibited strong absorbance in the UV region, resulting in good anti-UV aging and shielding properties.

2. Materials and methods

2.1. Materials

(B)

Samples	Substituted groups (R)	Samples	Substituted groups (R)
POSS- N^+	$[\text{ON}^+(\text{CH}_3)_4]_8 \cdot x\text{H}_2\text{O}$	POSS-H	$[\text{H}]_8$
POSS-A	$[\text{C}_6\text{H}_4\text{NH}_2]_8$	POSS-P	$[\text{C}_6\text{H}_5]_8$
POSS-AN	$[\text{C}_6\text{H}_4\text{NH}_2]_2$ $[\text{C}_6\text{H}_4\text{NO}_2]_6$	POSS-M	$[\text{CH}_3]_8$
POSS-N	$[\text{C}_6\text{H}_4\text{NO}_2]_8$	POSS-S	$[\text{OSi}(\text{CH}_3)_3]_8$

Fig. 1. Structure of POSS (A) and POSS derivatives (B) used in this experiment.

Various modified polyhedral oligomeric silsesquioxane (POSS) with different substituents were purchased from MeiXi Chemical Co., Ltd. (Shenyang, China). The structures of the eight types of POSS are shown in Fig. 1B. Microcrystalline cellulose (MCC) was purchased from FengLiJingQiu Co., Ltd. (Beijing, China, Vivapur 101, purity 99.5%, degree of polymerisation: 220). The ionic liquid AmimCl was prepared in our laboratory according to the method described in our previous work (Zhang, Wu,

Zhang & He, 2005). The water content of AmimCl was below 300 ppm, which was measured by Karl-Fisher titration.

2.2. Experimental methods

The preparation of the cellulose/POSS nanocomposite films includes the following five steps: (a) dissolving certain amount of cellulose and POSS in AmimCl, (b) slowly pouring and spreading the solution on a glass plate, (c) placing the coated glass plate into a coagulation bath (deionised water), then forming the hydrogel, (d) washing the hydrogels with deionised water to remove the remaining AmimCl, and (e) drying the hydrogel to obtain the dry cellulose/POSS nanocomposite films.

To prepare a uniformly dispersed nanocomposite in this system, there are two important factors that must be considered: First, in step (a), the nanoparticles must be soluble or dispersed uniformly in the AmimCl, so that no agglomeration occurs during the precipitation. Second, during steps (c) and (d), the POSS nanoparticles must not migrate into the coagulation bath during the exchange of AmimCl and water. Therefore, the experiment was carried out as follows.

2.2.1. Solubility of POSS in AmimCl

In this step, 5 mg of POSS was added to 10 g of AmimCl. The mixture was stirred for 24 h at room temperature, then sonicated for 10 min. Finally, the soluble POSS derivatives were selected to test the stability during the preparation process of films.

2.2.2. Preparation of cellulose/POSS-AN nanocomposite films

Initially, 1 g of cellulose was added to 24 g AmimCl in a three-necked flask and stirred at 80 °C for 2 h to completely dissolve cellulose. Then, different amount of

POSS-AN powders were added to the cellulose/AmimCl solution. After stirring for another 4 h at 60 °C, a vacuum was applied to remove any bubbles trapped in the solution. The solution was then coated onto a glass plate with the help of a spreader, and subsequently regenerated in a water coagulation bath. The water was periodically changed until no chloride ions could be detected by using the AgNO₃ aqueous solution. After the removal of AmimCl, a hydrogel was obtained. We dried the hydrogel to yield a series of cellulose/POSS-AN nanocomposite films containing 0, 1, 2, 5, 10, 15, and 20 wt% POSS-AN for further characterisation. The films were stored in a vacuum desiccator before tests.

2.3. Characterisation methods

2.3.1. Morphology studies

A scanning electron microscope (SEM) (JSM-6700) and a transmission electron microscope (TEM) (JEM-2200) were used to assess the morphology and dispersion of the POSS nanoparticles in the cellulose/POSS-AN nanocomposite films. For SEM observation, these films were quenched in the liquid nitrogen. Then, the cross-sections were sputter-coated with a thin layer of platinum before observation. For TEM analysis, the samples were prepared by using an ultramicrotome (UC6&FC6, Leica) at -60 °C. The 50-100 nm thickness slice was placed onto a carbon-coated TEM grid for TEM observation in the bright field imaging mode.

2.3.2. Tensile properties

The tensile properties of the cellulose/POSS-AN nanocomposite films were tested by using an Instron 3365 universal testing machine with the pneumatic and serrated grip.

Specimens with dimensions of 10 mm × 50 mm were tested using a 5 kN load cell at a strain rate of 2 mm/min. In each case, five specimens were used and the average value was reported.

2.3.3. UV-vis spectra

The films were clipped on a mold with a slit, then observed directly on the UV-vis spectrophotometer (PERSEE TU-1901). A wavelength scan mode over the range of 190 to 700 nm using a 1 nm step size was selected for this purpose.

2.3.4. UV aging and shielding properties

Fig. 2. UV aging and shielding testing.

As shown in Fig. 2, the UV aging and shielding test for the various cellulose/POSS-AN nanocomposite films were carried out by using UVB radiation at air atmosphere in a CL-1000 Ultraviolet Crosslinker (UVP LLC) for different periods (0-14 days). A polypropylene (PP) film was covered by a cellulose/POSS-AN nanocomposite film or a neat cellulose film. The UVB radiation source was G8T5E bulbs (Ushio) with the peak emission at 302 nm. The composite samples were placed at a distance of 12 cm from the light source, corresponding to an exposure of 80,000

$\mu\text{J}\cdot\text{cm}^{-2}$.

2.3.5 Chemical analysis

The surface change in the films was characterized by using attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR). The spectra were recorded with a Nicolet 6700 FTIR spectrometer (Thermo Fisher, USA) from 650 to 3750 cm^{-1} at a resolution of 4 cm^{-1} .

3. Results and discussions

3.1. Solubility of POSS in AmimCl

It is well known that the good dispersion of nanofillers in the solvent and the matrix is essential to prepare nanocomposites with excellent properties (Fina, Tabuani & Camino, 2010). The POSS nanoparticles with different substituted groups have different properties (Cordes, Lickiss & Rataboul, 2010). So do the ionic liquids (ILs), which are composed of various cations and anions (Sun, Rodríguez, Rahmana & Rogers, 2011). Moreover, there are many kinds of intermolecular interactions in ILs, for example, electrostatic interaction, hydrogen-bonding interaction, π - π interaction, Van der Waals interaction, and so on. It is not enough to judge the dispersion of POSS in ILs by using only the polarity of POSS derivatives and ILs. Thus, the dispersion and selection of POSS derivatives had to be investigated at first.

The eight types of POSS fillers with different substituents were added into AmimCl to clarify the solubility of POSS in AmimCl. The containers of the mixtures were labelled on the basis of the substituents in the POSS fillers. As shown in Fig. 3A, it is evident that only three mixtures of AmimCl and POSS fillers marked POSS- N^+ , POSS-A and POSS-AN are optically clear. Other five mixtures are opaque. This phenomenon is correlated to the polarity of the substituted POSS. Because AmimCl is a

polar solvent, it prefers to give strong interactions with the POSS derivatives with a high polarity. Furthermore, the hydrogen bonds interaction may exist between the amino groups and AmimCl, which facilitates the dissolution of POSS. Finally, only the soluble POSS fillers (POSS-N⁺, POSS-A and POSS-AN) were selected to test the stability during the film preparation process.

Fig. 3. Photographs of (A) POSS with different substituted groups in AmimCl, (B) cellulose/POSS-AN/AmimCl solutions (4 wt% cellulose in the solutions; 0-20 wt% POSS-AN referred to the total mass of cellulose and POSS), and (C) cellulose/POSS-AN nanocomposite films (1-15 wt% POSS-AN referred to the total mass of cellulose and POSS).

3.2. Selection of POSS derivatives for preparing nanocomposite film

Three different types of POSS derivatives (POSS-N⁺, POSS-A and POSS-AN) were soluble in AmimCl. Among them, we selected the POSS derivatives, which not only had a high solubility in AmimCl, but also did not migrate during the coagulation and washing processes. Because deionised water was used as the coagulation bath, the solubility of the POSS in water and AmimCl/water mixture is particularly important. POSS-N⁺ was soluble in water, and POSS-A was soluble in the AmimCl/water mixture. Thus, they were washed out during the exchange process of AmimCl and water (steps c and d). Interestingly, POSS-AN with partial aminophenyl and partial nitrophenyl groups, was insoluble in both water and AmimCl/water. Though optical observation, UV-vis spectra of the coagulation bath and TGA results of cellulose/POSS films, it was found that POSS-AN did not migrate during the coagulation and washing processes, and as a result was selected as the source of the nanoparticles.

3.3. Cellulose/POSS-AN nanocomposite films

3.3.1. Morphology and dispersion

By adding 1-20 wt% POSS-AN (with respect to the total mass of cellulose and POSS) into the cellulose/AmimCl solution (4 wt%), we obtained a group of transparent solutions (Fig. 3B). After solution casting, coagulation, water washing and drying, we obtained a series of transparent cellulose/POSS-AN nanocomposite films (Fig. 3C).

The POSS-AN powders are tan coloured powders, so the colour of the POSS/cellulose/AmimCl solutions gradually deepened as the POSS-AN content increased. All of the solutions were clear and transparent, even when the POSS-AN content was as high as 20 wt%. Optical photographs (Fig. 3C) are presented to show the

cellulose/POSS-AN nanocomposite films containing 1-15 wt% POSS-AN. They exhibited a similar colour change to that of the POSS/cellulose/AmimCl solutions. The increase of the POSS-AN content made the cellulose/POSS-AN films darken, but all of the films remained transparent and homogeneous.

Fig. 4. (A) SEM photographs of the cross sections and (B) TEM photographs of two cellulose/POSS-AN nanocomposite films with 5 wt% and 10 wt% POSS-AN.

To investigate the dispersion state of POSS-AN in cellulose, SEM was used to observe the cross sections of the cellulose/POSS-AN nanocomposite films. Fig. 4A shows that the cross sections of the cellulose/POSS-AN nanocomposite films are homogeneous. There are not obvious POSS-AN aggregation. Thus, the POSS-AN was well dispersed in the cellulose matrix.

TEM was used to further characterise the dispersion and size of the POSS-AN

particles in the cellulose/POSS-AN nanocomposites. Fig. 4B shows that the POSS-AN particles with a size of 30-40 nm are uniformly dispersed in the matrix. As the POSS-AN content increases, the number of the nanoparticles increases. Most of nanoparticles maintain a homogeneous dispersion in the matrix. Only a small quantity of particle-aggregation appears. These results are consistent with the literature (Althues, Henle & Kaskel, 2007), which states that the diameter of nanoparticles (less than 40 nm) is essential to obtain transparent nanocomposites.

3.3.2. Mechanical properties

Fig. 5. The mechanical properties of cellulose/POSS-AN nanocomposite films with 0-20 wt% POSS-AN.

Good mechanical strength is the basis for a material, which is widely adopted. The mechanical properties of the cellulose/POSS-AN nanocomposite films, including the tensile strength and Young's modulus, are summarized in Fig. 5. As seen from the results of the tensile test, the nanocomposite films possessed good Young's modulus of

6-9 GPa and high tensile strengths of 150-190 MPa, which were far above those of conventional commercial polyolefin films, such as polyethylene (PE) and polypropylene (PP) (the tensile strength = 20-40 MPa). The tensile properties of the cellulose/POSS-AN nanocomposites increased with the content of POSS-AN up to 2 wt%, and then fluctuated. The cellulose/POSS-AN nanocomposites film with 2 wt% POSS-AN achieved a maximum tensile strength of 190 MPa. This phenomenon is probably correlated to the dispersion-aggregation state of POSS-AN nanoparticles and the interfacial interaction between POSS-AN and cellulose.

3.3.3. UV-vis spectra

Fig. 6. (A) UV-vis spectra and (B) transmittance of UVA and UVB of cellulose/POSS-AN nanocomposite films (thickness = 25 μ m).

Fig. 6A shows the UV-vis spectra of the cellulose matrix and cellulose/POSS-AN nanocomposite films. The cellulose film had a high transmittance in the visible region. After the addition of the POSS-AN, the transparency was still very good, and the change of the visible light transmittance was insignificant, because the POSS-AN was

dispersed in the matrix at the nanometer scale. In the UV region, absorption of neat cellulose was negligible. Most of the UV was not absorbed. After adding POSS-AN, the cellulose/POSS-AN nanocomposite films showed significant absorption in the UV region, due to the existence of the chromophores (aminophenyl and nitrophenyl groups) in POSS-AN.

Fig. 6B shows the transmittance of the UVA (T (UVA)) and UVB (T (UVB)). The T (UVA) and T (UVB) can be calculated using Eqs. (1) and (2), respectively.

$$T(\text{UVA}) = \frac{\int_{315}^{400} T_{\lambda} \times d\lambda}{\int_{315}^{400} d\lambda}, (1)$$

$$T(\text{UVB}) = \frac{\int_{280}^{315} T_{\lambda} \times d\lambda}{\int_{280}^{315} d\lambda}, (2)$$

where T_{λ} is the transmittance of the light at the wavelength λ .

As shown in Fig. 6B, T (UVA) and T (UVB) decreased sharply with the increase of the POSS-AN content. After adding 5 wt% POSS-AN, the T (UVA) decreased from 87.3% to 29.4%, and the T (UVB) decreased from 83.2% to 1.3%. When the POSS-AN content reached 15 wt%, the T (UVA) and T (UVB) decreased to 9.1% and nearly 0, respectively. Therefore, the cellulose/POSS-AN nanocomposite films exhibit full absorption of UVB and above 90% absorption of UVA, implying that the incorporation of POSS into cellulose can effectively block UV transmission.

3.3.4. Anti-UV aging properties

Fig. 7. FTIR spectra of neat cellulose and cellulose/POSS-AN nanocomposite (10 wt% POSS-AN) films for different UV radiation exposure time.

We used neat cellulose and cellulose/POSS-AN nanocomposite films containing 10 wt% POSS-AN for comparison. They were exposed to UV radiation for studying their anti-UV aging properties as a function of UV radiation exposure time. The FTIR spectra of the cellulose and cellulose/POSS-AN nanocomposite films are shown in Fig. 7. The peak at 1724 cm^{-1} was assigned to the carbonyl group, whose intensity increased as the extension of the UV radiation exposure time. The carbonyl group was absent in the neat cellulose (Kumer, Negi, Bhardwaj & Choudhary, 2012), so its presence in exposed cellulose indicated that some groups in cellulose was oxidized at the UV-lights irradiation, which perhaps was via a free-radical route (Seldén, Nyström & Långström, 2004; Chen, Yang & Zhang, 2011).

On the front side of cellulose film, a generated carbonyl peak appeared at 1724

cm⁻¹ as the UV radiation time increased. When the UV radiation time was set to 7 days, the peak was noticeable. After 14 days, the intensity of the peak increased further. However, for the cellulose/POSS-AN nanocomposite film with 10 wt% POSS-AN, the 1724 cm⁻¹ peak was negligible after a UV radiation exposure for 7 days. After a UV radiation exposure for 14 days, there was a clear carbonyl absorption peak. Compared to the front side of films, the peak intensity of the carbonyl group on the back side was weaker. Especially, on the back side of cellulose/POSS-AN nanocomposite films, no obvious carbonyl absorption peak appeared even after a UV radiation exposure for 14 days. Thus, the cellulose/POSS-AN nanocomposite films exhibit good anti-UV aging property, and are expected to be used as the UV protection film.

3.3.5. UV shielding properties

Fig. 8. FTIR spectra of PP film covered by: (A) cellulose and (B) cellulose/POSS-AN nanocomposite (5 wt% POSS-AN) films for different UV radiation time.

In addition, we designed an experiment to compare the UV shielding properties of the cellulose and cellulose/POSS-AN nanocomposite films. We overlaid the cellulose

film and cellulose/POSS-AN nanocomposite film (5 wt% POSS-AN) separately on PP films, then exposed them to UV radiation for 3 and 6 days. After UV radiation, the PP films were separated, and their FTIR spectra (Fig. 8) were recorded. As shown in Fig. 8A, the PP covered by the neat cellulose film exhibited obvious carbonyl peaks after a UV radiation for 3 days. However, the PP sample did not exhibit a significant carbonyl peak even after a UV radiation for 6 days (Fig. 8B). This phenomenon indicates that the PP films were better shielded by the cellulose/POSS-AN nanocomposite film.

These above UV aging and shielding experiments clearly indicate that the addition of POSS-AN to cellulose enhanced the UV resistance and shielding properties of the films.

4. Conclusions

In this work, cellulose/POSS nanocomposite films were prepared by using AmimCl as the dissolution medium. The flexible renewable cellulose was used as the matrix, and the organic-inorganic POSS derivatives were used as the nanofillers. Compared with other POSS derivatives, the POSS-AN provided better compatibility in both the AmimCl and cellulose/POSS nanocomposite films. The POSS-AN gave a nanoscale dispersion in the matrix over a size range of 30-40 nm. The addition of POSS-AN yielded a maximum tensile strength of 190 MPa at 2 wt% POSS-AN. In addition, the cellulose/POSS-AN nanocomposite films exhibited good UV aging resistance and UV shielding performance as the POSS content increased, thus they are expected to be used as efficient UV-shielding coatings for packaging applications. These cellulose/POSS-AN nanocomposite films may therefore be considered a novel type of

green material and expand the application field of cellulose-based materials.

Acknowledgements

This work was supported by the National Science Foundation of China (No. 21174151, and No. 51425307).

References

- Althues, H., Henle, J., & Kaskel, S. (2007). Functional inorganic nanofillers for transparent polymers. *Chemical Society Reviews*, 36, 1454-1465.
- Bagheri, M., & Rabieh, S. (2013). Preparation and characterization of cellulose-ZnO nanocomposite based on ionic liquid ([C₄mim] Cl). *Cellulose*, 20, 699-705.
- Cao, Y., Wu, J., Zhang, J., Li, H. Q., Zhang, Y., & He, J. S. (2009). Room temperature ionic liquids (RTILs): A new and versatile platform for cellulose processing and derivatization. *Chemical Engineering Journal*, 147, 13-21.
- Chen, J., Yang, M. S., & Zhang, S. M. (2011). Immobilization of antioxidant on nanosilica and the aging resistance behavior in polypropylene. *Composites: Part A* 42, 471-477.
- Cordes, D. B., Lickiss, P. D., & Rataboul, F. (2010). Recent Developments in the Chemistry of Cubic Polyhedral Oligosilsesquioxanes. *Chemical Reviews*, 110, 2081-2173.
- Darder, M., Aranda, P., & Ruiz-Hitzky, E. (2007). Bionanocomposites: A new concept of ecological, bioinspired, and functional hybrid materials. *Advanced Materials*, 19, 1309-1319.
- Fina, A., Tabuani, D., & Camino, G. (2010). Polypropylene-polysilsesquioxane blends.

347 *European Polymer Journal*, 46, 14-23.

348 Hameed, N., Guo, Q., Tay, F. H., & Kazarian, S. G. (2011). Blends of cellulose and
 349 poly(3-hydroxybutyrate-co-3-hydroxyvalerate) prepared from the ionic liquid
 350 1-butyl-3-methylimidazolium chloride. *Carbohydrate Polymers*, 86, 94-104.

351 Hameed, N., Xiong, R., Salim, N. V., & Guo, Q. (2013). Fabrication and
 352 characterization of transparent and biodegradable cellulose/poly (vinyl alcohol) blend
 353 films using an ionic liquid. *Cellulose*, 20, 2517-2527.

354 Hanid, N. A., Wahit, M. U., Guo, Q. P., Mahmoodian, S., & Soheilmoghaddam, M.
 355 (2014). Development of regenerated cellulose/halloysites nanocomposites via ionic
 356 liquids. *Carbohydrate Polymers*, 99, 91-97.

357 Khalil, H. P. S. A., Bhat, A. H., & Yusra, A. F. I. (2012). Green composites from
 358 sustainable cellulose nanofibrils: A review. *Carbohydrate Polymers*, 87, 963-979.

359 Klemm, D., Heublein, B., Fink, H. P., & Bohn, A. (2005). Cellulose: Fascinating
 360 biopolymer and sustainable raw material. *Angewandte Chemie-International Edition*,
 361 44, 3358-3393.

362 Kueseng, K., & Jacob, K. I. (2006). Natural rubber nanocomposites with SiC
 363 nanoparticles and carbon nanotubes. *European Polymer Journal*, 42, 220-227.

364 Kumar, A., Negi, Y. S., Bhardwaj, N. K., & Choudhary, V. (2012). Synthesis and
 365 characterization of methylcellulose/PVA based porous composite. *Carbohydrate*
 366 *Polymers*, 88(4), 1364-1372.

367 Kuo, S. W., & Chang, F. C. (2011). POSS related polymer nanocomposites. *Progress in*
 368 *Polymer Science*, 36, 1649-1696.

369 Li, G. Z., Wang, L. C., Ni, H. L., & Pittman, C. U. (2001). Polyhedral oligomeric
 370 silsesquioxane (POSS) polymers and copolymers: A review. *Journal of Inorganic and*
 371 *Organometallic Polymers*, 11, 123-154.

372 Liu, S. L., Zhang, L., Zhou, J. P., & Wu, R. X. (2008). Structure and properties of
 373 cellulose/Fe₂O₃ nanocomposite fibers spun via an effective pathway. *Journal of*
 374 *Physical Chemistry C*, 112, 4538-4544.

375 Nair, L. S., & Laurencin, C. T. (2007). Biodegradable polymers as biomaterials.
 376 *Progress in Polymer Science*, 32, 762-798.

377 Raftopoulos, K. N., & Pielichowski, K. (2016). Segmental dynamics in hybrid
 378 polymer/POSS nanomaterials. *Progress in Polymer Science*, 52, 136-187.

379 Rinaudo, M. (2006). Chitin and chitosan: Properties and applications. *Progress in*
 380 *Polymer Science*, 31, 603-632.

381 Seldén, R., Nyström, B., & Långström, R. (2004). UV aging of
 382 poly(propylene)/wood-fiber composites. *Polymer Composite*, 25, 543-553.

383 Soheilmoghaddam, M., & Wahit, M. U. (2013). Development of regenerated
 384 cellulose/halloysite nanotube bionanocomposite films with ionic liquid. *International*
 385 *Journal of Biological Macromolecules*, 58, 133-139.

386 Soheilmoghaddam, M., Wahit, M. U., Mahmoudian, S., & Hanid, N. A. (2013).
 387 Regenerated cellulose/halloysite nanotube nanocomposite films prepared with an ionic
 388 liquid. *Materials Chemistry and Physics*, 141, 936-943.

389 Sun, N., Rodríguez, H., Rahmana, M., & Rogers R. D. (2011). Where are ionic liquid
 390 strategies most suited in the pursuit of chemicals and energy from lignocellulosic

391 biomass? *Chem. Commun.*, *47*, 1405-1421.

392 Wu, J., & Mather, P. T. (2009). POSS Polymers: Physical Properties and Biomaterials
 393 Applications. *Polymer Reviews*, *49*, 25-63.

394 Zhang, H., Wang, Z. G., Zhang, Z. N., Wu, J., Zhang, J., & He, H. S. (2007).
 395 Regenerated-cellulose/multiwalled-carbon-nanotube composite fibers with enhanced
 396 mechanical properties prepared with the ionic liquid 1-allyl-3-methylimidazolium
 397 chloride. *Advanced Materials*, *19*, 698-704.

398 Zhang, H., Wu, J., Zhang, J., & He, J. S. (2005). 1-Allyl-3-methylimidazolium chloride
 399 room temperature ionic liquid: A new and powerful nonderivatizing solvent for
 400 cellulose. *Macromolecules*, *38*, 8272-8277.

401 Zhang, J. M., Zhang, H., Wu, J., Zhang, J., He, J. S., & Xiang, J. F. (2010). NMR
 402 spectroscopic studies of cellobiose solvation in EmimAc aimed to understand the
 403 dissolution mechanism of cellulose in ionic liquids. *Physical Chemistry Chemical*
 404 *Physics*, *12*, 1941-1947.

405 Zhang, X. M., Feng, J. X., Liu, X. Q., & Zhu, J. (2012). Preparation and
 406 characterization of regenerated cellulose/poly (vinylidene fluoride) (PVDF) blend films.
 407 *Carbohydrate Polymers*, *89*, 67-71.

408 Zhang, X. M., Liu, X. Q., Zheng, W. G., & Zhu, J. (2012). Regenerated
 409 cellulose/graphene nanocomposite films prepared in DMAC/LiCl solution.
 410 *Carbohydrate Polymers*, *88*, 26-30.