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Preparation of polysilsesquioxane-urethaneacrylate copolymer film reinforced with chitin nanofibers

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ABSTRACT

Chitin nanofibers (CNFs) reinforced silsesquioxane-urethaneacrylate (SSQ-UA) copolymer films were prepared. CNFs-SSQ-UA nanocomposite films were highly transparent due to the filling of nanometer sized (10–20 nm) CNFs inside the hybrid organic–inorganic SSQ-UA copolymer. CNFs due to their crystalline structure drastically increased Young's moduli and the tensile strengths of the composite and decreased the thermal expansion. High thermal stability of polysilsesquioxane improved heat resistance of CNFs.

1. Introduction

Silsesquioxane is the compound with the chemical formula $(RSiO_{3/2})_n$, where R is either hydrogen or organic group such as any alkyl, alkylene, aryl, arylene, and has various structural orders including cage, ladder, and irregular structures (Baney, Itoh, Sakakibara, & Suzuki, 1995). Its characteristic structure with intermediate between organic compounds and ceramics offers great potential to prepare multifunctional materials. Since multifunctional properties resulting from organic/inorganic hybrid groups of silsesquioxane increases its flexibility, optical transparency, and better thermal stability (Zhang, Shi, Li, & Lin, 1988), it is recognized as a strong candidate for high performance substrate for future electrooptical devices, such as a substrate for flexible display, electronic paper, solar cell, and optical waveguide (Li, Wang, Ni, & Pittman, 2001). High temperature dimensional stability is strongly required for these applications. This is because thermal expansion causes damage for several substances deposited on an electronic substrate during the thermal assembly process. However, silsesquioxane polymer film has generally high thermal expansion, due to the organic part of the hybrid polymer (Fu, Huang, Huang, & Chang, 2008).

Chitin is the second most abundant biopolymer with a (1,4)-α-*N*-acetyl glycosaminoglycan-repeating structure. It is biosynthesized at a rate of 10^{10}–10^{11} tons per year (Nair & Dufresne, 2003). Although chitin is a semicrystalline biopolymer with nano-sized fibrillar morphology and excellent material properties, most chitin is thrown away as industrial waste. Recently, we have prepared chitin nanofibers from crab and prawn shells and mushroom cell-wall (Ifuku, Nomura, Morimoto & Saimoto, 2011). The chitin nanofibers have a highly uniform structure with a 10–20 nm width and a high aspect ratio (Fig. 1). Since the nanofiber has excellent mechanical properties such as a high Young's modulus, high fracture strength and low thermal expansion owing to the extended crystalline structure, it is useful for a reinforcement filler to create high-performance nanocomposites (Nishino, Matsui, & Nakamae, 1999; Vincent & Wegst, 2004; Wada & Saito, 2001). We have previously reported chitin nanofiber reinforced plastic (Ifuku, Morooka, Nakagaito, Morimoto, & Saimoto, 2011). Due to the nano-size effect, the nanocomposite was highly transparent. We consider that the previous study is applicable for polysilsesquioxane to obtain a transparent nanocomposite film. And we expect that the nanofiber filler reduce the thermal expansion and improve the mechanical properties of polysilsesquioxane due to the reinforcement effect. In this study, we prepared chitin nanofiber reinforced

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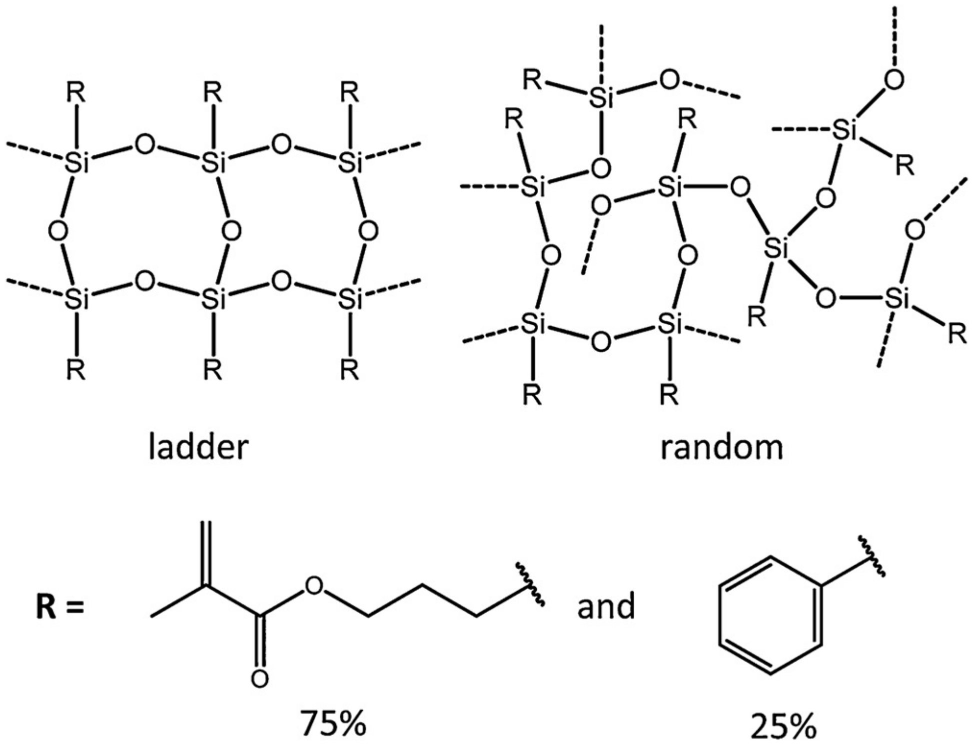

Fig. 1. Chemical structures of silsesquioxane oligomer used in this study.

polysilsesquioxane to make a high and multi performance materials and characterized their optical, thermal, and mechanical properties for the development of substrates for future electrooptical devices.

2. Experimental

2.1. Materials

Chitin powder from crab shells was purchased from Nacalai Tesque, Inc. The degree of substitution of amino groups of the chitin was 3.9%, which was calculated from the C and N content in the elemental analysis data. Silsesquioxane was obtained from Nagase ChemteX Co., Ltd. Bifunctional urethaneacrylate oligomer (EBECRYL 9270, M_w 1000) was obtained from Daicel-Cytec Co., Ltd. 2-Hydroxy-2-methylpropiophenone photo initiator was obtained from Tokyo Kasei Kogyo Co., Ltd.

2.2. Preparation of polysilsesquioxane (PSSQ) nanocomposite reinforced with CNFs

CNFs were prepared from commercially available chitin powder isolated from crab shell according to the previously reported procedure (Ifuku et al., 2010). The CNFs were diluted by 0.1 wt.% in distilled water. The suspension was filtered under reduced pressure using a polytetrafluoroethylene membrane filter (Millipore; pore size, 0.2 μm) to make a CNF sheet. The wet sheet was then dried by pressing at 100 °C for 30 min. The CNFs sheet was cut into 5 cm × 5 cm and had approximately 50 μm thickness and 90 mg weight. The sheet was impregnated by dipping into the matrices of mixtures SSQ and UA under reduced pressure. Five different types of matrices mixtures were prepared by mixing silsesquioxane (SSQ) and bifunctional urethane acrylate (UA) in the ratio of SSQ/UA = 5/0, 4/1, 3/2, 2/3, and 1/4 with 2-hydroxy-2-methylpropiophenone as a photoinitiator. Concentration of photoinitiator was constant in all experiments (3% (w/w)). The SSQ-UA impregnated CNFs sheets of all the above SSQ/UA mixture were cured for free radical polymerization by UV irradiation for 8 min at 40 mW cm^{-1} (SPOT CURE SP-7, Ushio Inc.). The cured nanocomposites reinforced with CNFs thus obtained had approximately 70 μm thick, and the NF content was approximately 50 wt.%. SSQ-UA films without CNFs were also obtained by UV irradiation using same mixtures of SSQ, UA, and photoinitiator. Densities of thus obtained CNF sheet, neat, SSQ/UA copolymer and their nanocomposite films were 0.63, approximately 1.2, and approximately 1.2 (g/cm^3), respectively.

2.3. Measurements

The regular light transmittances of optically transparent nanocomposite films were measured by a UV-vis spectrophotometer (JASCO-V550). Refractive indices were measured at 25 °C with an Atago Abbe refractometer (DR-A1) with accuracy less than 0.0001 units. Tensile strengths and Young's moduli were measured by a universal testing instrument (AG-X, Shimadzu), for samples 50 mm long and 10 mm wide at a cross head speed of 1 mm min^{-1} with a gage length of 30 mm. At least three specimens were used for testing. The coefficients of thermal expansion (CTE) were evaluated with a thermomechanical analyzer (Q400, TA instruments). Specimens for CTE measurement were 30 mm long and 3 mm wide with a 20 mm span. The specimens were postcured for the measurements in advance to complete polymerization. The measurements were carried out from 30 to 165 °C by raising temperature at a rate of 5 °C min^{-1} in a N_2 atmosphere in tensile mode under a load of 0.05 N. The CTE values were determined in the second run. Thermogravimetric analyses were carried out with TG8120 (Rigaku) apparatus. Measurements were conducted in the range 100–500 °C at a heating rate of 10 °C min^{-1} under N_2 condition.

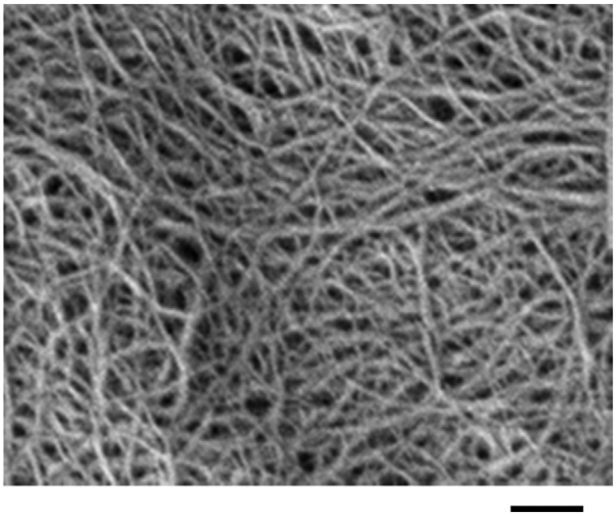

Fig. 2. Chitin nanofibers prepared from crab shell. Scale bar shows 200 nm.

3. Results and discussion

3.1. Transparency of CNFs composite films

CNFs were prepared from commercially available dry chitin powder as described in the article (Ifuku et al., 2010). The structure was highly uniform with a width of 10–20 nm and a high aspect ratio (Fig. 2). We prepared SSQ based nanocomposite films reinforced with CNFs by impregnation of SSQ oligomer into CNF sheet followed by photo polymerization. The SSQ oligomer used in this study has mixed structure of irregular and ladder shape (Fig. 1). The organic moieties of the hybrid oligomer consist of 75% 3-methacryloyloxypropyl group and 25% phenyl group. Due to the high crosslink density, polymerized SSQ was too brittle. Therefore, bifunctional UA oligomer with molecular weight of approximately 1000 was mixed as reactive diluent in the ratio of SSQ/UA = 5/0, 4/1, 3/2, 2/3, and 1/4, and copolymerized. Neat CNF sheet was not transparent as % transmittance is nil as can be seen in Fig. 3 measured in visible region. While neat poly-SSQ film had approximately 90% transmittance. After SSQ-UA matrix impregnation and subsequent polymerization, the obtained CNFs nanocomposites in different ratios of SSQ/UA became highly transparent for visible light. CNFs sheets blended with SSQ-UA had good transparency (85% at 600 nm) in case of SSQ/UA ratio 5/0. Blending with 1/4 ratio of SSQ/UA, CNFs sheet transparency decreased slightly to 80% compared with 85% for 5/0 blending ratio of SSQ/UA. The composite films became transparent due to nano-sized composition of CNF sheet (Yano et al., 2005). Since the width (10–20 nm) of CNFs was much shorter than the wavelength of visible light (380–760 nm), the nanocomposites cause less light scattering than a microfiber reinforced composite at the interface between nanofiber and SSQ-UA matrix.

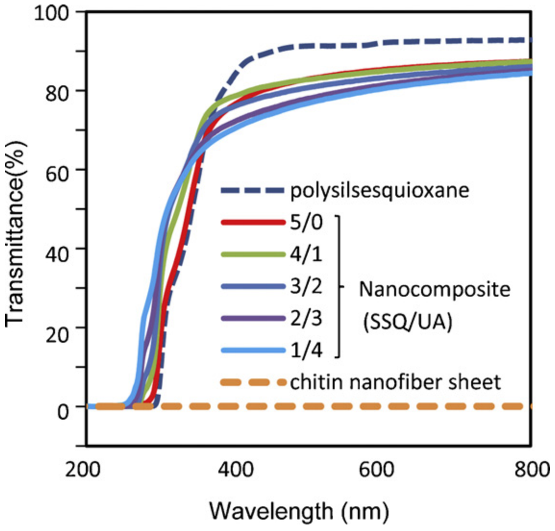

Fig. 3. Regular light transmittance spectra of chitin nanofiber composite films (solid line), polysilsesquioxane film and chitin nanofiber sheet (dashed line).

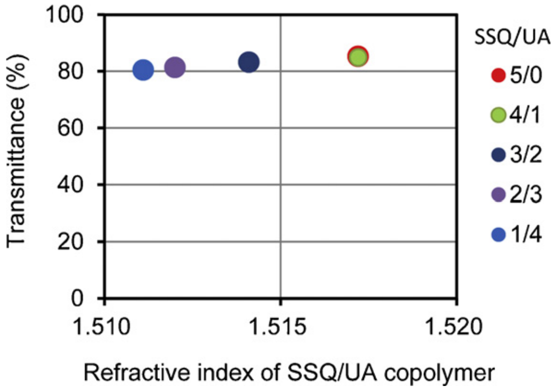

Fig. 4. Regular light transmittance of chitin nanofiber composite films at 600 nm versus the refractive index of SSQ/UA copolymer.

At 600 nm since transmittance of nanocomposites were 85–80%, the optical loss caused by nanofiber reinforcement were only in the range 5–10% despite the high fiber content of 50 wt.%. The transmittance of nanocomposites increased as ratio of SSQ increased. The change in the transmittance is linearly associated with refractive index (RI) of matrix as shown in Fig. 4. RI of the matrix increased from 1.511 to 1.517 with increasing ratio of SSQ from 1/4 to 5/0 ratio of SSQ/UA which resulted in the increase in transparency of the nanocomposite. Authors have reported similar relationship between % transmittance versus RI of the bacterial cellulose NFs blended with a number of acrylic resins (Nogi, Handa, Nakagaito, & Yano, 2005).

The chitin nanofiber sheet obtained in this study can be available like a paper, though the novel paper is composed of nano-meter thick fibers. Several patterns can be printed on the nanofiber paper that we have prepared using a domestic inkjet printer (Fig. 5a). The printed NF paper became transparent (Fig. 5b) after matrix impregnation. This newly established technique of transparent printing on such a thin (70 μm) composite sheet can have application in printing of wiring used in electronic devices or electronic papers.

3.2. Thermal characterization of CNF composite films

Thermal expansion is related to the depth of the atomic bond energy function and has an inverse relationship with Young's modulus (Nakagaito, Nogi, & Yano, 2010). Since CNFs show an efficient Young's modulus due to the extended crystal structure (Nishino et al., 1999; Vincent & Wegst, 2004), the coefficient of thermal expansion (CTE) of crystalline chitin compound is $1.4 \times 10^{-6}\,K^{-1}$ (Wada & Saito, 2001). Therefore CNFs are better material as reinforcing element to reduce the high thermal expansion of poly-SSQ.

Fig. 6 shows the CTE of neat CNFs and its composites. Although neat poly-SSQ (SSQ/UA = 5/0) was too fragile to measure the thermal expansion, the CNF reinforced nanocomposite was tough for CTE measurement. CTE of CNF sheet without SSQ matrix was only $8.0 \times 10^{-6}\,K^{-1}$. While CTE of SSQ-UA copolymer films without CNFs was high in the range $96.2–164.0 \times 10^{-6}\,K^{-1}$ depending on the ratio of SSQ/UA as shown by bars in Fig. 6. CTEs of all

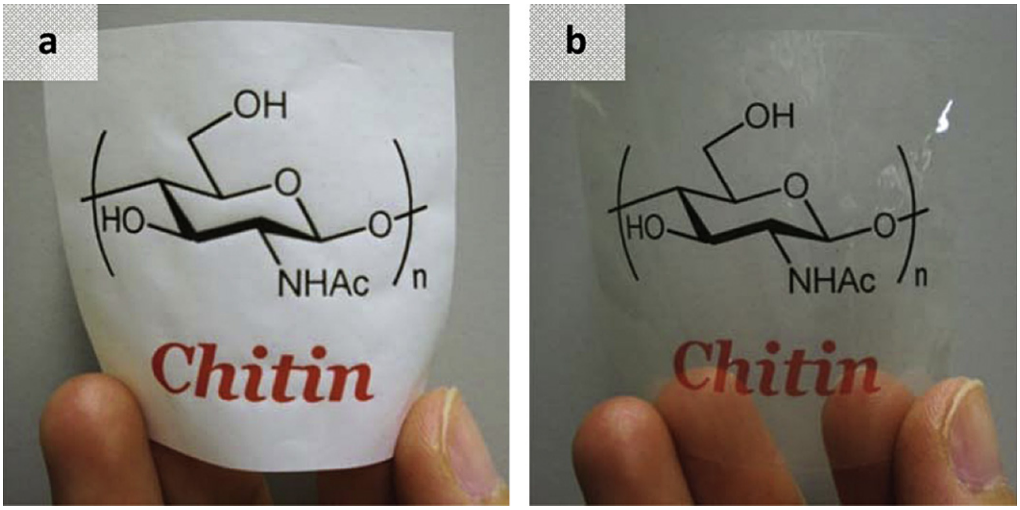

Fig. 5. The appearance of (a) chitin nanofiber sheet and (b) nanocomposite. "Chitin" and its molecular structure were printed on the sheet using inkjet printer.

nanocomposites decreased significantly to a constant value of approximately $30 \times 10^{-6}\,K^{-1}$. These values corresponded to 66–81% decreased compared to the corresponding to the SSQ-UA matrices used. Thus, CNFs with low CTE worked effectively to decrease the thermal expansion of SSQ-UA copolymer film as a result of reinforcement.

Owing to the inorganic component, SSQ has high thermal stability and have been used to improve heat resistance property of polymers (Fina et al., 2006). Therefore, we investigated heat resistant property of nanocomposites to study effect of complexation of CNFs with SSQ-UA copolymers. Fig. 7 shows the differential thermogravimetric (DTG) analysis of CNF composite films and its composites. Though, decomposition temperature of CNFs was at 318 °C, the decomposition bands shifted to higher temperatures when CNF blended with SSQ-UA copolymer. Decomposition of composites occurred at higher temperature was due to the blending of CNF with SSQ of high thermal stability of 420 °C. TGA curves of nanocomposites had two peaks at approximately 350 °C and 376 °C. With increasing ratio of SSQ and decreasing ratio of UA, the lower temperature band gradually decreased and higher temperature peak became more prominent. Two TGA bands of nanocomposites noticed at 350 °C and 376 °C came from thermal decomposition of poly-UA and poly-SSQ, respectively. Thus, the thermal stability of the chitin nanofiber was significantly improved by compounding with thermally stable SSQ. This improvement indicates that CNF and SSQ-UA copolymer had high affinity and strong interaction with each other at their interface. In general, since carbohydrate polymer has low decomposition temperature, this finding is advantageous for expanding the application of the chitin nanofibers as filler for nanocomposite materials.

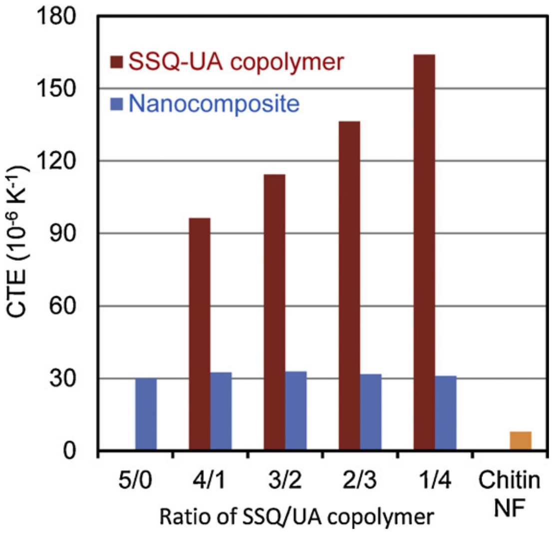

Fig. 6. Coefficient of thermal expansion of SSQ-UA copolymer films and their chitin nanofiber composites.

3.3. Mechanical characterization of CNF composite films

CNFs have excellent mechanical properties and they are good materials to use as reinforcing element to improve mechanical properties of composite materials (Nishino et al., 1999; Vincent & Wegst, 2004). Young's moduli and tensile strengths of SSQ-UA copolymer films and their CNFs composites are shown in Fig. 8. Young's moduli of SSQ-UA with the ratio of 3/2, 2/3, and 1/4 without CNFs decreased from 1571 to 128 MPa with increasing the ratio of reactive diluent UA oligomer. This is due to decrease in crosslinking density with decreasing the amount of strengthening hybrid component SSQ. The SSQ-UA films with the ratio of 5/0 and 4/1 were too fragile to measure the mechanical properties so their bars are not shown in Young's moduli plot. Nanocomposites were tough enough for the testing due to CNF support. Young's moduli of these nanocomposites significantly increased and reached in the range

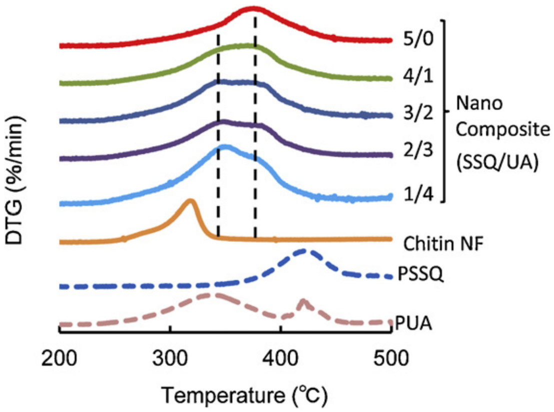

Fig. 7. Thermogravimetric analysis of chitin nanofiber composite films.

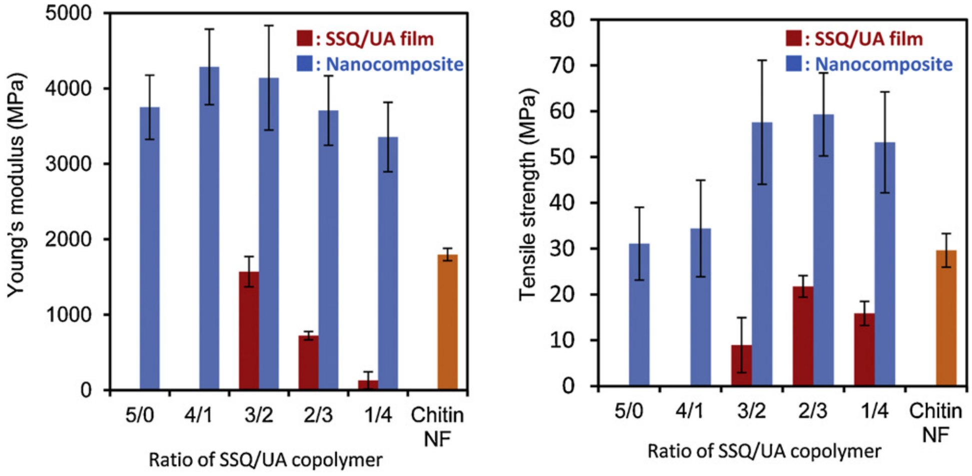

Fig. 8. Young's modulus and tensile strength of silsesquioxane films and their nanocomposites. Error bars show standard deviations.

3.36–4.29 GPa. The tensile strengths also significantly increased in the range 31–59 MPa. It is important to notice that each Young's moduli and tensile strength of the chitin nanofiber composites were higher than that of CNF sheet or SSQ-UA copolymer. The higher Young's moduli and tensile strength of composite is due to SSQ-UA matrix embedded in every space of CNF sheet and strongly interacts with NF at the interface thus resulted in the increase of the reinforcement effect. The enhancements of mechanical properties of composite strongly support that a CNF sheet with a high Young's modulus (1.80 GPa) and a high tensile strength (30 MPa) worked effectively as a reinforcement filler for SSQ-UA copolymer.

4. Conclusions

Silsesquioxane-urethaneacrylate (SSQ-UA) films reinforced with chitin nanofibers (CNFs) were prepared and characterized in detail for transparency, thermal and mechanical properties. Neat CNFs sheet was not transparent, but when the cavities of NFs (10–20 nm width) were filled by transparent SSQ hybrid material, the composites of CNFs-SSQ-UA became transparent in a number of ratios of SSQ to UA. For different SSQ to UA ratios, the coefficient of thermal expansion of composites decreased in the range 66–81%. The decrease of thermal expansion is due to the contribution of low thermal expansion of CNFs. Moreover, the thermal stability of the chitin nanofiber was significantly improved owing to the inorganic component of SSQ with high thermal stability. Young's modulus and tensile strength of composites increased compared to neat CNFs or SSQ-UA copolymer due to nano-sized width of CNFs. Thus, SSQ-UA copolymer film reinforced with CNFs with high transparency, high mechanical properties, low thermal expansion, and high thermal stability will be advantageous to use as high performance nanocomposite as substrates for electrooptical devices like electronic paper.

Acknowledgement

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References

Baney, R. H., Itoh, M., Sakakibara, A., & Suzuki, T. (1995). Silsesquioxanes. *Chemical Reviews*, *95*, 1409–1430.

Fina, A., Tabuani, D., Carniato, F., Frache, A., Boccaleri, E., & Camino, G. (2006). Polyhedral oligomeric silsesquioxanes (POSS) thermal degradation. *Thermochimica Acta*, *440*, 36–42.

Fu, H. K., Huang, C. F., Huang, J. M., & Chang, F. C. (2008). Studies on thermal properties of PS nanocomposites for the effect of intercalated agent with side groups. *Polymer*, *49*, 1305–1311.

Ifuku, S., Nogi, M., Abe, K., Yoshioka, M., Morimoto, M., Saimoto, H., et al. (2009). Preparation of chitin nanofibers with a uniform width as α-chitin from crab shells. *Biomacromolecules*, *10*, 1584–1588.

Ifuku, S., Nogi, M., Yoshioka, M., Morimoto, M., Yano, H., & Saimoto, H. (2010). Fibrillation of dried chitin into 10–20 nm nanofibers by a simple method under acidic conditions. *Carbohydrate Polymers*, *81*, 134–139.

Ifuku, S., Nogi, M., Yoshioka, M., Morimoto, M., Yano, H., & Saimoto, H. (2011). Simple preparation method of chitin nanofibers with a uniform width of 10 to 20 nm from prawn shell under the neutral condition. *Carbohydrate Polymers*, *84*, 762–764.

Ifuku, S., Nomura, R., Morimoto, M., & Saimoto, H. (2011). Preparation of chitin nanofibers from mushrooms. *Materials*, *4*, 1417–1425.

Ifuku, S., Morooka, S., Nakagaito, A. N., Morimoto, M., & Saimoto, H. (2011). Preparation and characterization of optically transparent chitin nanofiber/(meth)acrylic resin composites. *Green Chemistry*, *13*, 1708–1711.

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

Nakagaito, A. N., Nogi, M., & Yano, H. (2010). Displays from transparent films of natural nanofibers. *MRS Bulletin*, *35*, 214–218.

Nair, K. G., & Dufresne, A. (2003). Crab shell chitin whisker reinforced natural rubber nanocomposites. 1. Processing and swelling behaviour. *Biomacromolecules*, *4*, 657–665.

Nishino, T., Matsui, R., & Nakamae, K. (1999). Elastic modulus of crystalline regions of chitin and chitosan. *Journal of Polymer Science B: Polymer Physics*, *37*, 1191–1196.

Nogi, M., Handa, K., Nakagaito, A. N., & Yano, H. (2005). Optically transparent bionanofiber composites with low sensitivity to refractive index of the polymer matrix. *Applied Physics Letters*, *87*, 243110.

Vincent, J. F. V., & Wegst, U. G. K. (2004). Design and mechanical properties of insect cuticle. *Arthropod Structure & Development*, *33*, 187–199.

Wada, M., & Saito, Y. (2001). Lateral thermal expansion of chitin crystals. *Journal of Polymer Science B: Polymer Physics*, *39*, 168–174.

Yano, H., Sugiyama, J., Nakagaito, A. N., Nogi, M., Matsuura, T., Hikita, M., et al. (2005). Optically transparent composites reinforced with networks of bacterial nanofibers. *Advanced Materials*, *17*, 153–155.

Zhang, X., Shi, L., Li, S., & Lin, Y. (1988). Thermal stability and kinetics of decomposition of polyphenylsilsesquioxanes and some related polymers. *Polymer Degradation Stability*, *20*, 157–172.