Carbohydrate Polymers 100 (2014) 179–184

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Cellulose–clay layered nanocomposite films fabricated from aqueous cellulose/LiOH/urea solution

Quanling Yang, Chun-Nan Wu, Tsuguyuki Saito, Akira Isogai*

Graduate School of Agricultural and Life Sciences, The University of Tokyo, 1-1-1 Yayoi, Bunkyo-ku, Tokyo 113-8657, Japan

ARTICLE INFO

Article history:
Received 5 June 2012
Received in revised form 5 October 2012
Accepted 18 October 2012
Available online 26 October 2012

Keywords:
Cellulose
Clay
Montmorillonite
Gas barrier
Nanocomposite

ABSTRACT

Transparent and flexible cellulose–clay (montmorillonite, MTM) nanocomposite films are prepared from cellulose/LiOH/urea solutions. The results show that the composites possess intercalated nanolayered structures. Almost no Na ions are present in MTM, probably because they are substituted by Li ions. The nanocomposite films possess high mechanical strength and gas barrier properties, and lower coefficients of thermal expansion than those of the original cellulose film. In particular, the composite film of 85% cellulose and 15% MTM has the highest tensile strength and Young's modulus 161 and 180% greater than those of the 100% cellulose film, and coefficient of thermal expansion and oxygen permeability at 50–75% RH decrease to 60 and 42–33%, respectively. Moreover, the initial hydrophilic nature of cellulose film changes to somewhat hydrophobic through incorporation of hydrophilic MTM platelets. This is probably because the orientation of cellulose chains on the film surface changes by the formation of numerous hydrogen bonds between cellulose molecules and MTM platelets.

1. Introduction

Recently, understanding and exploiting the unique properties of polymer nanocomposites have received increasing attention (Paul & Robeson, 2008; Svagan et al., 2012; Wang, Cheng, & Tang, 2012). Inorganic films possess higher thermal and chemical resistance as well as a longer lifetime than their polymer counterparts, but they are brittle with poor film-forming ability (Clarizia, Algieri, & Drioli, 2004; Yang & Wang, 2006). In polymer–inorganic nanocomposites, inorganic nanofillers are present in the polymer matrix at almost individual nano-element level and thus nanocomposites behave differently to conventional composites (Braganca, Valadares, Leite, & Galembeck, 2007; Galimberti, Lostritto, Spatola, & Guerra, 2007). Nanocomposites can exhibit a combination of the basic properties of the polymer and inorganic nanofiller, and in some cases offer specific advantages or synergistic properties at particular weight ratios of the two components, such as excellent gas barrier performance, good thermal and chemical resistance and adaptability to harsh environments, while maintaining similar film-forming ability to the original polymer (Lu, Liu, & Duncan, 2003; Tang et al., 2005; Taniguchi & Cakmak, 2004; Zhu, Morgan, Lamelas, & Wilkie, 2001).

Composites of polymers with nanolayered silicates or clays show improved gas barrier, modulus, tensile strength, and thermal stability properties than the polymer alone. The nanolayered platelets of clay form a "tortuous path" for gas molecules in polymer matrices, resembling biomimetic brick and mortar structures (Alexandre & Dubois, 2000; Grunlan, Grigorian, Hamilton, & Mehrabi, 2004; Paul & Robeson, 2008; Ren, Zhu, & Haraguchi, 2011). The addition of nanoclays into polymers has been shown to enhance gas barrier properties relative to the original polymers, and the enhancement is related to the aspect ratio of the nanoclay (Herrera-Alonso, Marand, Little, & Cox, 2009; Paul & Robeson, 2008). Individual clay nanoparticles that can act as gas-impermeable nanoflakes are approximately 1 nm thick, disk-shaped, and possess aspect ratios ranging from 20 to several thousand (Ploehn & Liu, 2006; Priolo, Gamboa, Holder, & Grunlan, 2010; Thompson & Butterworth, 1992; Vali, Hesse, & Kodama, 1992). Polymer–clay nanocomposite materials have been extensively studied since the 1970s (Ebina & Mizukami, 2007; Haraguchi, Ebato, & Takehisa, 2006; Sun, Chu, & Sue, 2010). Sufficient dispersibility of individual nanoclay particles in the polymer matrix is the most significant factor influencing the properties of the composite. However, it is generally difficult to maintain sufficient dispersion of nanoclay particles in composites with high clay loadings. Such clay aggregates cause increased opacity and random platelet alignment that ultimately reduce the gas barrier properties (Kumar et al., 2008; Triantafyllidis, LeBaron, Park, & Pinnavaia, 2006). Thus, incorporation of nanoclay particles into polymeric matrices with high

---

* Corresponding author. Tel.: +81 3 5841 5538; fax: +81 3 5841 5269.
E-mail address: aisogai@mail.ecc.u-tokyo.ac.jp (A. Isogai).

0144-8617/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2012.10.044

degrees of exfoliation and orientation is currently the most important challenge to fabricate polymer–clay nanocomposites with enhanced properties (Osman, Mittal, Morbidelli, & Suter, 2004; Wu et al., 2012).

Petroleum-based polymers are generally used as matrices in most polymer–clay nanocomposites, and thus are non-biodegradable and not environmentally friendly. New biopolymer materials that are renewable, biocompatible, and biodegradable are in great demand. Cellulose is the most abundant biopolymer on earth, and is attracting renewed interest for materials and energy applications (Cerruti et al., 2008; Klemm, Heubletin, Fink, & Bohn, 2005; Mahmoudian, Wahit, Ismail, & Yussuf, 2012). Regenerated cellulose films prepared from aqueous alkali/urea solutions were found to exhibit good mechanical properties, optical transparency, biocompatibility, biodegradability, and oxygen barrier properties under dry conditions (Cai & Zhang, 2005; Qi, Chang, & Zhang, 2009; Yang, Fujisawa, Saito, & Isogai, 2012; Yang, Fukuzumi, Saito, Isogai, & Zhang, 2011; Yang et al., 2009; Yang, Lue, & Zhang, 2010; Yang, Qin, & Zhang, 2011). However, the oxygen permeability of the cellulose films significantly increased at high humidity (Yang, Fukuzumi, et al., 2011; Yang, Saito, & Isogai, 2012).

In this work, cellulose-based nanocomposite films fabricated from LiOH/urea/cellulose (LUC) solutions were reinforced with natural montmorillonite (MTM) clay particles to improve their mechanical strength, thermal stability and gas barrier properties under humid conditions. The relationships between the nanostructure of clay particles in the cellulose matrix and mechanical, optical, gas-barrier and hydrophilic properties are studied for cellulose–clay nanocomposites with various weight ratios. These cellulose–clay nanocomposites are expected to have superior properties as well as being new eco-friendly materials.

2. Materials and methods

2.1. Materials

A filter paper pulp (highly purified cotton linters, Advantec Co., Ltd., Japan) was used as the cellulose sample with a viscosity-average molecular weight of $8.6 \times 10^4\ \mathrm{g\,mol^{-1}}$ (Yang, Fukuzumi, et al., 2011). Natural MTM with an aspect ratio of 300–600 (Kunipia F, Kunimine Industries Co., Ltd., Japan) was used as the nanoclay sample. The chemical formulae of MTM clay is $Na_{2/3}Si_8(Al_{10/3}Mg_{2/3})O_{20}(OH)_4$, respectively. All reagents and solvents were of laboratory grade and used as received from Wako Pure Chemicals, Tokyo, Japan.

2.2. Preparation of cellulose/MTM composite films

A solution of LiOH/urea/H_2O with a weight ratio of 4.6:15:80.4 was prepared. A desired amount of MTM was dispersed in the above solution, which was then stirred for 2 h at room temperature. The MTM dispersion was further agitated at 7500 rpm for 2 min using a double-cylinder-type homogenizer (Excel Auto ED-4, Nissei, Japan) and then with an ultrasonic homogenizer with a 26 mm probe tip diameter at an output power of 300 W for 6 min (US-300T, Nissei, Japan) at room temperature. The MTM dispersion thus obtained was then cooled to −12 °C in a refrigerator. A desired amount of cellulose was dispersed in the cooled MTM dispersion, which was stirred immediately at 1200 rpm for 10 min to obtain a transparent solution with cellulose content of 4 wt.% (Yang, Fukuzumi, et al., 2011). The blend solution was degassed by centrifugation at 5600 × g for 10 min, spread on a glass plate as a 0.5 mm thick layer, and then immersed in acetone at room temperature for 30 min to allow regeneration (Yang, Fukuzumi, et al., 2011). The resulting sheet-like hydrogel was thoroughly washed by soaking in water, fixed on a poly(methyl methacrylate) plate with adhesive tape to prevent shrinkage, and air-dried at ambient temperature.

The weight ratios of cellulose and MTM in the composite films investigated were 100:0, 95:5, 90:10, 85:15 and 80:20, which are denoted LUC, LUC–MTM5, LUC–MTM10, LUC–MTM15 and LUC–MTM20, respectively. In addition, a desired amount MTM was dispersed in deionized water, and the dispersion was stirred and agitated as described above to prepare a 2 wt.% MTM dispersion. The obtained MTM dispersions were dried in a ventilated oven at 40 °C for 3 days to obtain films of MTM.

2.3. Analyses

X-ray diffraction (XRD) patterns of the films were acquired in reflection mode using a RINT 2000 diffractometer (Rigaku, Tokyo, Japan) with monochromator-filtered Cu K_α radiation ($\lambda = 0.15418$ nm) at 40 kV and 40 mA. The films were frozen in liquid nitrogen, immediately snapped and then vacuum-dried. The surfaces and cross-sections (fracture surfaces) of the films were coated with osmium using a Meiwafosis Neo osmium coater at 10 mA for 5 s, and observed with a Hitachi S4800 field-emission scanning electron microscope (SEM) at 2 kV. Energy-dispersive X-ray (EDX) analysis of MTM and the composite films was carried out using a Horiba EMAX Energy spectroscope attached to the SEM. In the case of SEM-EDX analysis, the acceleration voltage and accumulation time were set to 10 kV and 500 s, respectively.

The optical transmittance of the films was measured from 400 to 800 nm using a JASCO V-670 UV–Vis spectrophotometer. Tensile tests were performed using a Shimadzu EZ-TEST instrument equipped with a 500 N load cell. Rectangular strips 2 mm × 30 mm in size were cut from the films and tested with a span length of 10 mm at a rate of $1.0\ \mathrm{mm\,min^{-1}}$. At least 10 measurements were carried out for each sample. The thermal expansion of the films following preheating at 120 °C for 10 min was determined under a load of 0.03 N and a nitrogen atmosphere from 28 to 100 °C at $5\ ^\circ\mathrm{C\,min^{-1}}$ using a Shimadzu TMA-60 thermomechanical analyzer.

The rates of oxygen and water vapor transmission of the films were determined at 23 and 37.8 °C, respectively, using a Mocon Ox-Tran Model 2/21MH and Mocon Permatran-W Model 1/50G (Modern Controls Inc., US) under standard conditions (ASTM 3985). Each measurement was continued until the rate of O_2 or water vapor transmission reached a stable value. The gas permeability was calculated from the gas transmission rate and film thickness, and the standard deviations for each film were within ±5%. The film thickness was measured by a micrometer at five points for each sample, and all the films prepared in this study were 30 μm with statistical errors within 3%. The films were conditioned at 23 °C and 50% relative humidity (RH) for 2 days and the moisture contents under these conditions were calculated from the film weights before and after heating at 105 °C for 3 h. The films were immersed in deionized water at room temperature for 6 days to reach swelling equilibrium and water uptakes $W_{(\text{water uptake})}$ were calculated from the film weights before and after heating at 105 °C for 3 h according to the following equation:

$$W_{(\text{water uptake})} = \frac{m_{(\text{wet})} - m_{(\text{dry})}}{m_{(\text{cellulose})}} \times 100\% \qquad (1)$$

where $m_{(\text{wet})}$ is the weight of the LUC–MTM film after being immersed in water, $m_{(\text{dry})}$ is the weight of the film after heating, and $m_{(\text{cellulose})}$ is the dry weight of cellulose component in $m_{(\text{dry})}$. Contact angles of water droplets with a volume of 2 μL on the films were measured at 23 °C and 50% RH using a FAMAS DM500 instrument (Kyowa Interface Science Co. Ltd., Japan).