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Synthesis and characterization of polyurethane/microcrystalline cellulose bionanocomposites

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ABSTRACT

In this study, novel polyurethane/cellulose hybrid bionanocomposite films have successfully been prepared by dispersing microcrystalline cellulose in a polyurethane matrix. Incorporation of microcrystalline cellulose in a polyurethane matrix improved the mechanical properties significantly. The polyurethane/cellulose bionanocomposites were characterized by Fourier transform infrared spectroscopy, X-ray diffraction and transmission electron microscopy (TEM). The TEM results confirm that the nanoparticles were dispersed uniformly in polymer matrix. Additionally, thermogravimetric analysis data showed an improvement of thermal stability of novel nanocomposite films as compared to the neat polymer.

1. Introduction

Polyurethanes are part of a very versatile group of materials where the elasticity of rubber is combined with the toughness and durability of metals which allows the engineer to replace rubber, plastic and metal with the ultimate in abrasion resistance and physical properties [1–4]. These polymers have a large variety of applications due to their unique properties, such as high strength, high hardness, high modulus and high elongation at break. Therefore, there are so many problems these materials can solve from automotive parts to building and construction, from medicine to electronics, from textiles to furniture [5–8].

Polymer-based nanocomposites reveal considerable improvements in mechanical, dielectric magnetic, thermal optical and acoustic properties compared to the pure organic polymers at very low-volume fractions of the reinforcing phase [9–11]. Cellulose, due to their attractive intrinsic properties such as nanoscale dimensions, high surface area, low density, unique morghology, high specific strength and Young's modulus and very low coefficient of thermal expansion, is a promising reinforcement [12–23].

Cellulose is the world's most abundant natural, renewable, biodegradable polymer, and a classical extracellular high performance skeletal biocomposite consisting of a matrix reinforced by fibrous biopolymer. The whisker like microfibrils, which are near defect free crystals with axial physical properties approaching those of perfect crystals, are biosynthesized and deposited in a continuous fashion by plants or animals. Cellulosic nanomaterials including microfibrillated cellulose, microcrystalline cellulose and cellulose nanocrystals have been applied as the reinforcing filler in a wide range of polymer matrices. In these hybrid composites, polyurethanes are promising candidate as matrix polymers due to their hydrophilic nature [24–26]. The hydroxyl units on the cellulose nanofibril surface may interact favorably with the polyurethane.

In the present article, we report the synthesis and characterization of polyurethane/microcrystalline cellulose (PU/MCC) bionanocomposites. The resulting nanocomposites were investigated using Fourier transform infrared (FT-IR) spectroscopy, thermogravimetric analysis (TGA), X-ray diffraction (XRD), and transmission electron microscopy (TEM). In addition, mechanical properties of nanocomposites are also investigated.

2. Experimental

2.1. Materials

All chemicals were purchased from Fluka Chemical Co. (Buchs, Switzerland), Aldrich Chemical Co. (Milwaukee, WI), Riedel-deHaen AG (Seelze, Germany) and Merck Chemical Co. *N*,*N*-Dimethylacetamide (DMAc, Merck) was purified by distillation under reduced pressure over barium oxide. Microcrystalline cellulose was purchased from Sigma–Aldrich. *N*,*N*-Dimethylformamide

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(DMF, Merck), toluene-2,4-diisocyanate (TDI, Aldrich), phenolphthalein (PHP, Merck), lithium chloride (99%, Sigma), and 1,4-butanediol (1,4-BG, Fluka) were used as received.

2.2. Techniques

FT-IR spectra were recorded with a Jasco-680 spectrometer (Japan) in the range of 400–4000 cm^{-1}. Vibration bands were reported as wavenumber (cm^{-1}). FT-IR spectra of all samples were collected by making their pellets in KBr as a medium. The diffraction pattern of related materials was recorded in the reflection mode using a Bruker, D8 Advance diffractometer. Nickel filtered CuKα radiation (radiation wavelength, $\lambda = 0.154$ nm) was produced at an operating voltage of 45 kV and a current of 100 mA. The morphology and dispersity analysis were performed on transmission electron micrograph (TEM) analyzer on Philips CM 120 operating at 100 kV. Thermogravimetric analysis (TGA) was performed with a STA503 win TA at a heating rate of 10 °C/min from 25 °C to 800 °C under nitrogen atmosphere.

2.3. Polymer synthesis

TDI (0.5 g, 2.87×10^{-3} mol) and PHP (0.5172 g, 1.43×10^{-3} mol) at a molar ratio of 2:1 were dissolved in DMF solvent and then heated to 90 °C with stirring under nitrogen atmosphere for 5 h to form prepolymer. 1,4-BG (0.1294 g, 1.43×10^{-3} mol) was added to the prepolymer with stirring at room temperature for 5 h to complete the reaction. The PU film was produced by casting from its DMF solution, and the solvent was removed at 80 °C.

PU: FT-IR (KBr, cm^{-1}): $\upsilon = 3384$ (s, NH stretching vibration), 2964 (m, CH stretching vibration), 1747 (s, stretching vibration of both urethane and ester carbonyl), 1596 and 1504 (s, stretching vibrations of C=C), 1205 (m, C–O stretching vibration).

2.4. Preparation of PU/MCC nanocomposites

The nanocomposites of PU/MCC with different weight percentages of MCC (3, 5, 10 and 15) were prepared as follows.

Different amounts of MCC and a trace amount (<0.3 wt%) of LiCl were mixed with DMF, kept stirring at 80 °C for 8 h under nitrogen atmosphere. Then TDI (0.5 g, 2.87×10^{-3} mol) and PHP (0.5172 g, 1.43×10^{-3} mol) at 2:1 molar ratio were added. Prepolymer was produced after stirring at 90 °C for 5 h. Then 0.1278, 0.1233, 0.1232, and 0.1232 g of 1,4-BG were added into the prepolymers with 3, 5, 10, and 15 wt% MCC, respectively. The addition amount of 1,4-BG was determined by the measured amount of residual NCO groups in the prepolymer in order to have a 1:1 molar ratio between NCO groups and accessible OH groups. After stirring at room temperature for 5 h and removal of solvent at 80 °C, elastic films were obtained.

PU/C5 wt%: FT-IR (KBr, cm^{-1}): $\upsilon = 3293$ (s, NH stretching vibration), 2969 (m, CH stretching vibration), 1737 (s, stretching vibration of both urethane and ester carbonyl), 1610 and 1504 (s, stretching vibrations of C=C), 1542 (s, stretching vibration combined with out-of-the plane bending of C–N of urethane groups), 1228 (s, C–O stretching vibration).

3. Result and discussions

3.1. Preparation of PU/MCC bionanocomposites

PU/MCC bionanocomposite films were prepared from dispersed MCC and PHP and TDI monomers by a polymerization method followed by solvent casting. First, MCC was swelled. Partial polymerization of the monomers was carried out in the swollen state. A chain extender was added to the system for increasing molar mass. Polymerization continued, and molar mass increased further. The solvent evaporated, and a smooth, solid nanocomposite film was formed. In the first swelling step, hydrogen bonding between the cellulose nanofibrils in the MCC particulate fillers was weakened by DMF and Li^{+}. As the monomers were added, they were able to enter into the swollen gel-like nanofibrils. With increasing temperature to 80 °C, polymerization started.

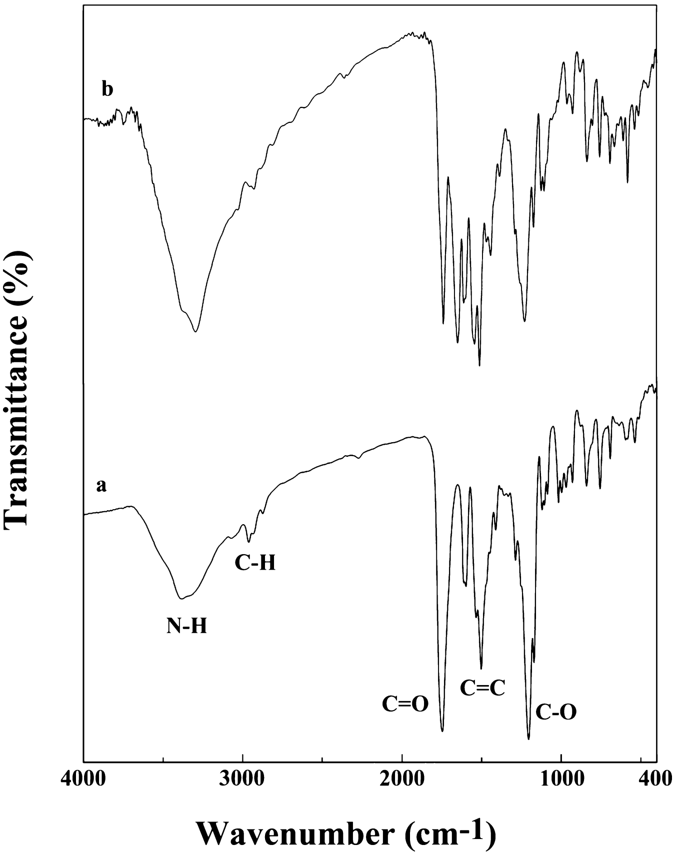

Fig. 1. FT-IR spectra of (a) Pure PU; (b) PU/C5 wt%.

3.2. FT-IR spectra

FT-IR spectra were used to study the chemical structure of the matrix polymer. FTIR spectra of the pure PU and PU/MCC5 wt% are shown in Fig. 1. For pure PU, the NH stretching vibration exhibits a strong absorption peak centered at around 3384 cm^{-1}. Simultaneously, only a single prominent peak band centered at 1747 cm^{-1} assigned to the stretching vibration of both urethane and ester carbonyl was observed. The FT-IR spectrum of prepolymer showed a lowered NCO peak in the nanocomposites as compared with in the pure PU. The NCO peak is associated with end groups in the prepolymer. The reaction of some surface hydroxyls in MCC with TDI was confirmed by the appearance of new absorption bands at 1646 and 1510 cm^{-1}, which was assigned to the absorption of carbonyl groups, NH bending deformation associated with asymmetric stretching, respectively. With increasing MCC contents, the intensity of these absorbance bands is increased. While these absorbance bands were observed at 1747–1711 and 1550 cm^{-1} in the pure PU.

3.3. XRD patterns

XRD patterns for the pure PU and the hybrid film 5 wt% are shown in Fig. 2. The diffraction peaks at $2\theta = 14.62, 16.29, 22.48, 20.1$