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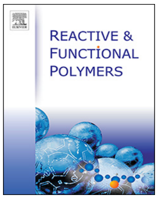

Influence of the morphology of zinc oxide nanoparticles on the properties of zinc oxide/nanocellulose composite films

Ruizhi Ning[a], Miyuki Takeuchi[a], Jin-Ming Lin[b], Tsuguyuki Saito[a], Akira Isogai[a,*]

[a] *Department of Biomaterial Sciences, The University of Tokyo, Bunkyo-ku, Tokyo 113-8657, Japan*
[b] *Department of Chemistry, Beijing Key Laboratory of Microanalytical Methods and Instrumentation, Tsinghua University, Beijing 100084, People's Republic of China*

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ABSTRACT

Zinc oxide (ZnO) nanoparticles with different morphologies, including spheres, rods, and needles, and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-oxidized cellulose nanofibrils (TOCNs) were mixed in water and then cast and dried to give ZnO/TOCN (1:9 *w*/w) composite films to investigate the influence of ZnO nanoparticle morphology on composite film properties. TOCNs were used as the matrix of ZnO-containing composite films because TOCN films have high transparencies. The film densities varied from 1.25 to 1.63 g/cm^3 and porosities ranged from 5.4 to 22 vol% depending on the ZnO nanoparticle morphology. The (100) plane of the rod- and needle-like wurtzite ZnO particles were preferentially oriented to the composite film surfaces. The Young's modulus and tensile strength of the composite films were similar regardless of nanoparticle morphology, whereas the ZnO/TOCN films with higher porosities had greater elongations at break and works of fracture. The composite films with rod- and needle-like ZnO particles had low oxygen permeability at 50% relative humidity. All the ZnO/TOCN composite films screened ultraviolet (UV) light, and the film with spherical ZnO nanoparticles had the highest visible-light transmittance. The ZnO/TOCN composite films and their components showed photoluminescence when exited by UV light with the highest intensity at 370-nm UV light. The composite films in aqueous methylene blue (MB) solution under UV irradiation restricted the UV-induced ZnO-catalyzed degradation of MB.

1. Introduction

Cellulosic materials are attracting increasing attention because they are the most abundant and renewable biomass materials on Earth. Various nano-sized celluloses (nanocelluloses) have recently been developed, and the fundamental properties and applications of these new bio-based nanomaterials have been studied intensively. In particular, 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-oxidized cellulose nanofibrils (TOCNs) and nanocrystals have surface structures and charges, morphologies, and properties that differ from those of other nanocelluloses [1–3]. TOCNs with homogeneous widths of ~3 nm and high aspect ratios > 100 prepared from wood cellulose can be individually dispersed in water. These TOCNs originate from the crystalline wood cellulose microfibrils biosynthesized in trees. Transparent, flexible, strong TOCN films with extremely low coefficients of thermal expansion (CTEs) and high oxygen barrier properties under dry conditions can be prepared by casting and drying aqueous TOCN dispersions [1–4]. Moreover, when TOCNs are combined with inorganic nanofillers such as nanoclays [5,6], carbon nanotubes [7], or zinc oxide (ZnO) nanoparticles [8], the resulting nanofiller/TOCN composite films can display unique mechanical, optical, thermal, electrical, and oxygen barrier properties. However, because TOCNs have abundant sodium carboxylate groups, TOCN films and nanofiller/TOCN composite films are hydrophilic and their oxygen barrier properties decrease markedly at high relative humidity (RH) conditions.

In our previous paper, ZnO/TOCN composite films with various ZnO/TOCN weight ratios were prepared using spherical ZnO nanoparticles by mixing ZnO and TOCNs in water and subsequent casting and drying the ZnO/TOCN aqueous dispersions [8]. The optical, thermal, hydrophilic/hydrophobic, and mechanical properties of these composite films were investigated in terms of their ZnO content. The porosity of the composite films increased with ZnO content. The aggregation of cationic ZnO particles and anionic TOCN may have caused the formation of porous structures in the ZnO/TOCN composite films. The ZnO/TOCN composite film with a ZnO/TOCN weight ratio of 1:9 displayed high visible light transparency as well as ultraviolet (UV) screening properties. The ZnO/TOCN composite films had low CTEs, although their CTE values did increase with ZnO content.

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* Corresponding author.
E-mail address: aisogai@mail.ecc.u-tokyo.ac.jp (A. Isogai).

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Because ZnO particles have unique optical properties and UV-induced catalytic activities, that depend on their morphology [9,10], the properties of ZnO/TOCN composite films may be affected by the morphology of the ZnO nanoparticles [11–13]. However, the influence of the morphology of ZnO nanoparticles on the properties of ZnO/TOCN composite films has not been investigated. In this study, therefore, ZnO/TOCN composite films containing ZnO nanoparticles with different morphologies are prepared by casting and drying aqueous ZnO/TOCN mixtures. The porous, hydrophilic, thermal, mechanical, optical, and oxygen barrier properties of the ZnO/TOCN composite films as well as their X-ray diffraction (XRD) patterns are investigated to determine the effect of ZnO morphology on the composite properties. Moreover, the UV-induced catalytic degradation behavior of methylene blue (MB: $C_{16}H_{18}ClN_3S$, Fig. S1 in the Electronic Supplementary Material file) dissolved in water in the presence of TOCN and ZnO/TOCN films is studied to characterize the effect of the ZnO/TOCN composite films on the degradation behavior of MB.

2. Experimental

2.1. Materials

Never-dried softwood bleached kraft pulp was supplied by Nippon Paper (Tokyo, Japan) and used as wood cellulose. TEMPO, ZnO particles with spherical, rod-like, and two needle-like morphologies (denoted as ZnO-S, ZnO-R, ZnO-N1, and ZnO-N2, respectively) were purchased from Sigma-Aldrich (USA). MB (98.5%, Tianjin Chemical Reagent Co., Ltd. Tianjin, China) was used in UV-induced catalytic degradation measurements. Sodium bromide, 2 M sodium hypochlorite solution, sodium hydroxide, sodium borohydride ($NaBH_4$), and other reagents were of laboratory grade and used as received from Wako Pure Chemicals (Tokyo, Japan). TEMPO-oxidized cellulose (TOC) subjected to post reduction with $NaBH_4$ was prepared from the wood cellulose according to previously reported methods [14,15]. The TOC with a sodium carboxylate content of 1.35 mmol/g was suspended in water to give a 0.4% TOC content and then mechanically disintegrated using a high-pressure homogenizer (Star Burst Labo HJP-25005×; Sugio Machine Limited, Toyama, Japan) at 150 MPa for five passes. The small unfibrillated fraction was removed by centrifugation at 12000 ×*g* for 15 min to obtain transparent TOCN/water dispersions. The TOCN concentration was adjusted to 0.4% (*w/v*) by partial removal of water using a rotary evaporator at 40 °C.

2.2. Preparation of ZnO/TOCN nanocomposite films

Each type of ZnO particle was suspended in water at a concentration of 2% (*w/v*), and then the suspensions were sonicated for 1 h in an ultrasonic bath (M1800-J; Yamato Scientific, Tokyo, Japan). The ZnO/water dispersion (2% *w/v*, 0.22 mL) was added to the TOCN dispersion (0.4% w/v, 10 mL) to give a ZnO:TOCN weight ratio of 1:9. The mixture was agitated using a vortex for 30 s and then sonicated in an ultrasonic homogenizer (US-300E; Nihon Seiki, Tokyo, Japan) for 30 s. The vortex and ultrasonic treatments were repeated twice. The obtained ZnO/TOCN aqueous dispersion was poured into a Petri dish with a diameter of 50 mm and then dried in an oven at 40 °C for 24 h. The resulting ZnO/TOCN composite film was carefully peeled off the dish and then placed in a conditioning room at 23 °C and 50% RH. The ZnO/TOCN composite films prepared with ZnO-S, ZnO-R, ZnO-N1, and ZnO-N2 ZnO particles are referred to as ZnO-S/TOCN, ZnO-R/TOCN, ZnO-N1/TOCN, and ZnO-N2/TOCN, respectively. The water contents of the films at 23 °C and 50% RH were calculated from their weights before and after drying at 105 °C for 3 h. The densities and porosities of the films at 23 °C and 50% RH were calculated from their volumes at 23 °C and 50% RH and dry weights.

2.3. Characterization of ZnO particles and ZnO/TOCN composite films

Average sizes and ζ-potentials of ZnO particles were measured in water using a particle size analyzer (Delsa Nano HC, Beckman Coulter, Germany). Scanning electron microscopy (SEM) observation of ZnO particles and ZnO/TOCN composite film surfaces was performed using a field-emission microscopy (Hitachi S4800, Tokyo, Japan) at acceleration voltages of 1.0 kV. The ZnO/TOCN film surfaces were coated using a carbon coater (CC-40-F, Meiwa Shoji, Co., Japan) before SEM observation. XRD patterns of ZnO particles and ZnO/TOCN composite films were obtained using a diffractometer (Rigaku RINT 2000, Tokyo, Japan) with monochromatized Cu Kα radiation ($\lambda = 0.15418$ nm) at 40 mV and 40 mA. Ultraviolet-visible (UV–vis) transmittance spectra and photoluminescence spectra following excitation at 370 nm were obtained for the ZnO/TOCN composite films using a V-670 UV–Vis spectrophotometer (JASCO, Japan) and FP-8500 fluorescence spectrometer (JASCO, Japan), respectively. Water contact angles on the film surfaces were measured using a contact angle apparatus (Kyowa FAMAS DM500; Saitama, Japan) at 23 °C and 50% RH. Tensile tests were performed using a tensile tester (Shimadzu EZ-TEST, Kyoto, Japan) equipped with a 500-N load cell at 23 °C and 50% RH. Rectangular specimens with dimensions of 20 × 2 mm were measured at a crosshead speed of 1.0 mm/min with a 10-mm span length.

2.4. UV-induced catalytic degradation of MB in water

A ZnO/TOCN composite film (30 mg) was added to water (30 mL) containing MB (0.3 mg) in a tube of a photochemical reaction system (TOPT-V; Toption Instrument Co., Ltd., Xi'an, China). A total of eight tubes were set in the reaction system. The mixture in each tube was stirred with a magnetic stirring bar in the dark for 1 h. During stirring, the ZnO/TOCN film was partly disintegrated to ZnO particles and TOCN fragments dispersed in the mixture. UV light was then irradiated onto the continuously stirred mixtures using a high-pressure mercury lamp with the highest intensity at 365 nm (500 W) set in the photochemical reaction system. Every 20 min after starting the UV irradiation, one tube was taken from the system and then the mixture was immediately subjected to centrifugation at 16000 ×*g* for 10 min to remove ZnO particles and TOCN fragments. The absorbance of the supernatant was measured using a UV–vis spectrophotometer (U-3900; Hitachi, Japan). The degree of MB degradation was calculated from change in light absorption of the supernatant at 665 nm.

3. Results and discussion

3.1. Fundamental properties of ZnO/TOCN composite films

SEM images of the ZnO particles are shown in Fig. S2, and their average particle sizes and ζ-potentials are listed in Table 1. The ZnO-S particles had spherical morphology [8], whereas the ZnO-R particles had rod-like morphology. The ZnO-N1 and ZnO-N2 particles had needle-like morphologies with high aspect ratios. All the ZnO particles had positive surface charges ranging from +21 to +29 mV in water, and the average particle sizes increased in the order of ZnO-S < ZnO-R < ZnO-N1 < ZnO-N2, which is consistent with the catalog data provided by the manufacturer (Sigma-Aldrich).

Fig. 1 shows SEM images of the ZnO/TOCN composite film surfaces. The ZnO-S particles could not be observed on the film surface at the magnification level used, indicating that the ZnO-S particles were almost homogeneously dispersed in the film and did not form aggregates. In contrast, the rod-like ZnO-R and needle-like ZnO-N1 and ZnO-N2 particles were clearly observed as bright spots on the surface of the dark TOCN matrix. This indicates that some of the ZnO particles were present as aggregates in the films, showing that complete dispersion of the ZnO particles in water and in the TOCN matrix is difficult to achieve.

All the composite films had similar average thicknesses of