

論文の内容の要旨

生物材料科学専攻

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論文題目 Studies on preparation and characterization of zinc oxide/TEMPO-oxidized cellulose
nanofiber composite films
(酸化亜鉛／TEMPO 酸化セルロースナノファイバー複合化フィルムの調製と特性解析
に関する研究)

Chapter 1. Introduction

I prepared composite films consisting of ZnO nanoparticles and TEMPO-oxidized cellulose nanofibers (TOCNs) using simple mixing procedures of the two components followed by casting and drying, in which different amounts or morphologies of ZnO nanoparticles were used. The relationships between the preparation conditions and properties of the composite films were investigated. Multiple functions of the as-prepared nanocomposite films such as optical, mechanical, thermal, hydrophilic, anti-microbial properties as well as photocatalytic activities and oxygen permeabilities were investigated based on the preparation conditions and nanostructures of the composite films. Moreover, UV-induced degradation and cellular compatibility of TOCNs in aqueous dispersions were investigated in terms of contents and counter-ions of surface carboxylate groups of TOCNs, respectively.

Chapter 2. Preparation of ZnO/TOCN nanocomposite films and property investigation of the films with different ZnO contents

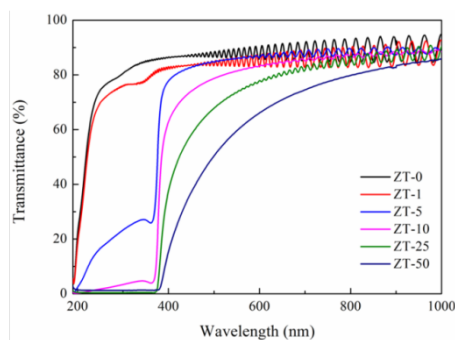


Fig. 1 UV-vis spectra of ZnO/TOCN composite films

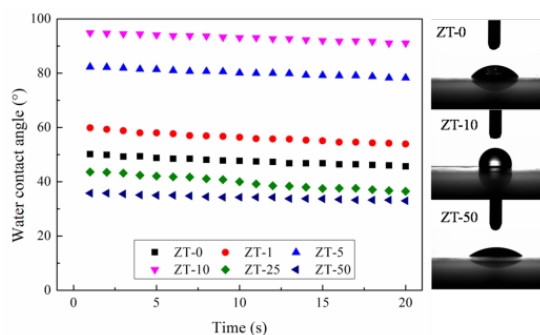


Fig. 2 Water contact angles on ZnO/TOCN composite films

(The ZnO/TOCN composite films with ZnO:TOCN weight ratios of 0:100, 1:99, 5:95, 10:90, 25:75, and 50:50 are denoted by ZT-0, ZT-1, ZT-5, ZT-10, ZT-25, and ZT-50, respectively.)

ZnO/TOCN composite films with 0–50% ZnO contents were prepared by mixing ZnO/water and TOCN/ water dispersions at various weight ratios under the same stirring, sonicating, and subsequent casting and drying conditions. Fundamental, optical, thermal, surface wetting, mechanical, and antimicrobial properties were investigated in terms of ZnO contents. The ZnO/TOCN composite films showed characteristic UV-shielding properties with high light transparencies, depending on ZnO contents (Fig. 1). The composite films had low CTEs (<10 ppm/K), although the CTE value increased with increasing ZnO content probably because film porosities increased with ZnO content. In the case of composite films with high porosities, the films consisted of stiff TOCNs and ZnO particles and soft air components, the tensile strength and strain-to-failure decreased slightly with increasing ZnO content from 0 to 10%. The 50% ZnO-containing film had explicitly ductile properties because of its high porosity. Even though both TOCNs and ZnO particles are hydrophilic, the composite films exhibited various surface wettabilities, depending on the ZnO content (Fig. 2). This behavior is explainable in terms of the surface roughness of the composite film or the presence of small air fractions on the film surface, according to Cassie's law. The ZnO/TOCN composite films displayed effective antibacterial activity, especially towards Gram-negative bacterium *Escherichia coli*. Any distinct improvement of thermal degradation point (T_d) was not observed for the composite films; their weight decreases started at ~ 200 °C in N_2 atmosphere irrespective of the ZnO content.

Chapter 3. Influence of the morphology of ZnO nanoparticles on films properties of ZnO/TOCN composites

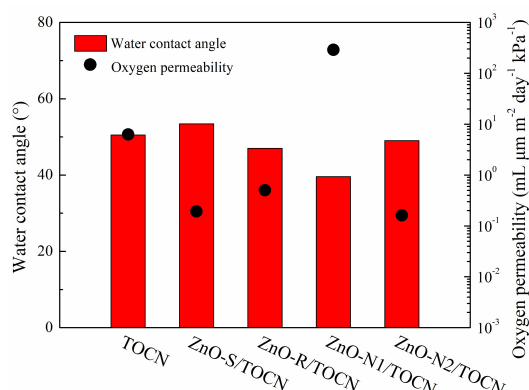


Fig. 3 Water contact angle and oxygen permeability of neat TOCN and ZnO/TOCN composite films

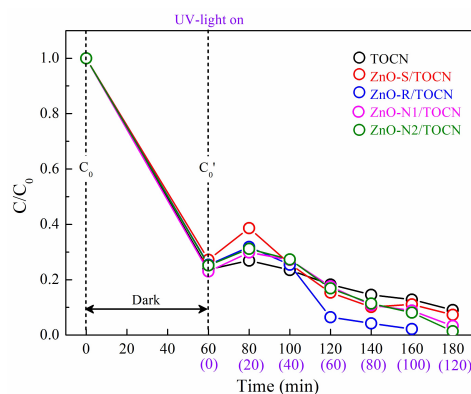


Fig. 4 Photocatalytic degradation of methylene blue by neat TOCN or ZnO/TOCN composite films

(The ZnO/TOCN composite films prepared with spherical ZnO-S, rod-like ZnO-R, needle-like ZnO-N1 and ZnO-N2 ZnO particles, which gradually increase in diameter and aspect ratio in turn, are denoted as ZnO-S/TOCN, ZnO-R/TOCN, ZnO-N1/TOCN, and ZnO-N2/TOCN, respectively.)

TOCNs and ZnO nanoparticles with different morphologies, i.e., spheres, rods, and needles, were mixed in water. The ZnO/TOCN mixtures were then cast and dried to prepare ZnO/TOCN (1:9 w/w) composite films to investigate the influence of ZnO nanoparticle morphology on composite film properties. The film densities varied from 1.25 to 1.63 g/cm³ and porosities ranged from 5.4 vol% to 22 vol% depending on the morphology of ZnO nanoparticles. The (100) plane of the rod- and needle-like wurtzite ZnO particles were preferentially oriented to the composite film surface. 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 consisting of rod- and needle-like ZnO particles had low oxygen permeability at 50% relative humidity (Fig. 3). All the ZnO/TOCN composite films screened UV light, and the film containing spherical ZnO nanoparticle had the highest visible-light transmittance. The ZnO/TOCN composite films and their components showed photoluminescence when excited by UV light with the highest intensity at 370-nm UV light. The UV-induced ZnO-catalyzed degradation of methylene blue (MB) in water was restricted in the presence of TOCN (Fig. 4), which may be caused by electrostatic interactions (or aggregation) between anionic TOCN elements and cationic MB molecules.

Chapter 4. UV irradiation-induced degradation of TOCNs

In the previous section, it was found that TOCN is degraded by UV irradiation. In this section, therefore, UV-degradation behavior of TOCN was investigated in detail. A softwood bleached kraft pulp was oxidized by the TEMPO/NaBr/NaClO system under different oxidation conditions to prepare TOCNs with various carboxylate contents. Water dispersions of these TOCNs were homogeneously subjected to UV irradiation experiment using a photochemical reactor equipped with a high pressure mercury lamp at the main wavelength of 365 nm. Changes in light transmittance and viscosity of the TOCN/dispersion and

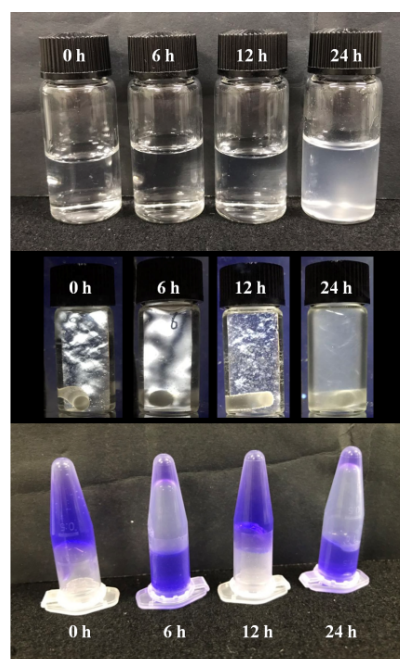


Fig. 5 Changes in transparency, birefringence, and viscosity of TOCN/water dispersions after UV irradiation for 0-24 h.

those in nanofiber morphology, functional groups, crystal structure, and molecular weight of the TOCNs were investigated in terms of UV-irradiation time and carboxylate content of TOCNs. Aqueous TOCN dispersions showed interesting changes in light transmittance and viscosity under different UV-irradiation time (Fig. 5). As the UV-irradiation time was increased, the pH values of the dispersion decreased, showing some acid groups are formed from TOCN during UV irradiation.

The weight recovery ratios of UV-treated TOCNs decreased with the UV-irradiation time, when the TOCNs were recovered as gels after addition of methanol to the UV-treated aqueous TOCN dispersion. Moreover, the average lengths and carboxylate contents of UV-treated TOCNs decreased with UV-irradiation time. Because the pH values decreased for the UV-treated TOCN dispersions, some carboxylate groups were detached from TOCNs and simultaneously some new acid groups were formed as water/methanol-soluble low-molecular-weight compounds. The length of TOCN decreased to ~150 nm, which corresponds to the lengths of cellulose nanocrystals prepared by acid hydrolysis of plant celluloses. Molecular weights and molecular weight distributions of UV-treated TOCNs were analyzed by size-exclusion chromatography attached with multi-angle laser-light scattering (SEC-MALLS). The results showed that molecular weight of the original TOCN significantly decreased with UV-irradiation time; UV-induced depolymerization of TOCN molecules as well as shortening of TOCN length was achieved in this study. X-ray diffraction analysis of the UV-treated TOCNs showed that no significant decreases in crystallinity index or crystal width of celluloses I was observed.

Chapter 5. Cellular biocompatibility of TOCNs with different counter-ions

Cellular biocompatibility of TOCNs with different counter-ions was investigated in terms of overall cell viability, all/dead cell population analysis, and intracellular changes of reactive oxygen species and mitochondrial mass and potential. TOCNs showed good cellular biocompatibility. When TOCNs with low carboxylate contents were used, the number of dead cells slightly increased. However, TOCNs with high carboxylate contents exhibited dead cell proportion at normal level. Counter-ions of TOCNs had some influences on biocompatibility. In particular, potassium counter-ion resulted in lower cellular biocompatibility than others.