

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 structures and properties of cellulose-based functional films prepared using aqueous alkali/urea systems
(水系アルカリ-尿素系を用いて調製した機能性セルロース系フィルム_の構造と特性)

High-performance films with high optical transparency, flexibility, thermal stability, mechanical strength, biodegradability, and gas barrier properties are in great demand for a wide range of applications, especially in the fields of high performance packaging materials for food and medicine, encapsulation of electronic devices, and flexible organic light-emitting diode (OLED) displays. The gas barrier properties are particularly important because ingress of even very small amounts of oxygen causes most products to deteriorate. Actually, the lack of a practical barrier layer is the primary hurdle faced by the flexible electronics industry. Petroleum-based synthetic polymers such as poly(vinylidene chloride), ethylene vinyl alcohol copolymers, nylon, and polymers with vapor-deposited coatings have been used as gas barrier films for these purposes. However, polymers with vapor-deposited coatings are prone to cracking when they are folded, and additional fabrication processes are therefore needed for such materials. Moreover, most plastic packaging films are discarded as burnable waste or used as landfill after use. This causes environmental problems because such synthetic polymers

are not biodegradable or carbon neutral. Therefore, there is a growing demand to develop new bio-based but high-performance film materials.

Cellulose is the most abundant natural polymer, and has potential as a renewable resource for applications in versatile commodity and high-tech materials. Commercial films of regenerated cellulose (i.e. cellophane) are transparent, flexible, and impervious to air, grease, bacteria, and dirt. However, cellophane is prepared through the viscose route that inevitably generates hazardous by-products such as CS_2 and H_2S during manufacture and in post-treatment processes, resulting in serious pollution.

In recent years, a simple route using safe and low-cost alkali/urea solvents has been developed for producing regenerated cellulose materials without producing any hazardous by-products. It involves dissolution of cellulose in aqueous NaOH /urea or LiOH /urea solutions at low temperatures, followed by regeneration of cellulose. Compared to other newly developed cellulose solvents like ionic liquids and N-methylmorpholine-N-oxide hydrate (NMMO), aqueous alkali/urea systems are thought to have great economic and environmental advantages. New cellulose multifilament fibers, films, spheres, porous hydrogels and aerogels have been prepared from the cellulose dopes. These cellulose materials possess a wide range of mechanical properties, excellent thermal stabilities, and high biodegradabilities due to the nature of cellulose.

My doctoral researches are fundamental and applied studies to develop new high-performance cellulose functional films (cellulose and cellulose-based nano-composites) with good gas barrier properties, hydrophobicity, thermal stability, mechanical strength, flexibility, and optical transparency using alkali/urea solutions.

High gas barrier cellulose films

Transparent and bendable regenerated cellulose films prepared from aqueous alkali/urea solutions (Fig. 1) exhibited high oxygen barrier properties at 0% RH, which are superior to those of conventional cellophane, poly(vinylidene chloride), and poly(vinyl alcohol). The oxygen permeabilities of these cellulose films varied widely depending on the conditions used to prepare them. The oxygen permeabilities of the



Fig. 1. Appearance of a cellulose film prepared from the NaOH /urea solution.

cellulose films were negatively correlated with their densities, and cellulose films prepared from solutions with high cellulose concentrations by regeneration in a solvent at low temperatures generally had low oxygen permeabilities.

Moreover, mechanical, thermal and oxygen barrier properties of regenerated cellulose films prepared from aqueous cellulose/alkali/urea solutions can be markedly improved by controlling the drying conditions of the films. By pre-pressing followed by vacuum drying under compression, the tensile strength, Young's modulus, coefficient of thermal expansion and oxygen permeability of the dried film reached 263 MPa, 7.3 GPa, 10.3 ppm K⁻¹ and 0.0007 mL μm m⁻² day⁻¹ kPa⁻¹, respectively. It should be noted that the oxygen transmission rate of this cellulose film was lower than the lowest detection limit of the instrument. Thus, films produced in this way show the highest performance of regenerated cellulose films with no orientation of cellulose chains reported to date. These improved properties are accompanied by a clear increase in cellulose II crystallinity from 50 to 62% during pre-pressing/press-vacuum drying process. At the same time, the film density increased from 1.45 to 1.57 g cm⁻³.

High-performance cellulose biocomposite materials

The hydrophilicity of cellulose materials results in greater amounts of moisture sorption and a significant increase in the oxygen permeability under higher humid conditions, thus restricting their potential applications. Hence, the cellulose films were composited with nanoclay or surface modified by alkyl ketene dimers (AKDs) which are both from natural resources to improve their oxygen barrier properties at high humid conditions.

Cellulose based nanocomposites reinforced with nanoclay: Transparent flexible regenerated cellulose–nanoclay (saponite or montmorillonite) nanocomposite films (Fig. 2) were prepared from cellulose/LiOH/urea solutions. The composites possessed intercalated nanolayered structures of clay platelets. They exhibited high mechanical strength, Young's modulus, and gas barrier properties, and lower coefficients of thermal expansion than

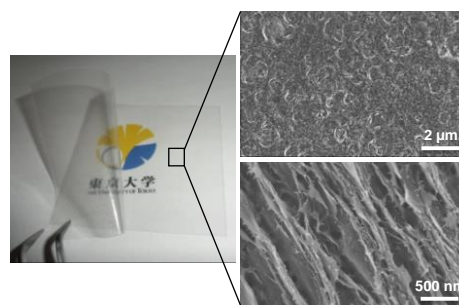


Fig. 2. Appearance (left), SEM images of surface (upper right) and cross-section (lower right) of a cellulose-montmorillonite (MTM) film.

those of the original LiOH/urea regenerated cellulose film. In particular, the composite film containing 85% cellulose and 15% natural montmorillonite clay exhibited tensile strength and Young's modulus that were 161 and 180% greater than those of the cellulose film, respectively, and its coefficient of thermal expansion and oxygen permeability at 50–75% RH were 60 and 42–33% lower than those of the cellulose film, respectively. Moreover, the initial hydrophilic nature of the cellulose film changes to somewhat hydrophobic through incorporation of hydrophilic clay platelets.

Hydrophobization of cellulose films by surface modification with AKD: Transparent and water repellent gas barrier cellulose films were fabricated by surface modification of LiOH/urea regenerated cellulose films by soaking in cationic AKD dispersion, drying, and heating. AKD-treated cellulose films still exhibited very low oxygen transmission rates which were lower than the lowest detection limit of the instrument at 0% RH. Water contact angles on the cellulose film increased from 50 to 110° after AKD treatment (Fig. 3), and water uptake (immersion in water for 6 days) decreased from 92 to 20 %. Moreover, oxygen permeability decreased from 0.56 and 5.8 to 0.13 and 2.1 mL $\mu\text{m m}^{-2} \text{day}^{-1} \text{kPa}^{-1}$ at 50 and 75 % RH, respectively, when the AKD content of the film was increased from 0 to 0.2%. The present AKD-treated cellulose film also had high light transparency and mechanical properties. AKD components were stable on the AKD-treated film surfaces without hydrolysis at 2 months. The chemical structures of the AKD components at the AKD/cellulose interfaces were also studied by extraction treatments of AKD from AKD-treated cellulose films using chloroform, hot water, and dioxane/water mixture. The results of extraction treatments indicated original AKD was the main AKD component of the AKD/regenerated cellulose films; however, quite a small amount of β -ketoesters are likely to form at the AKD/AUC interfaces.

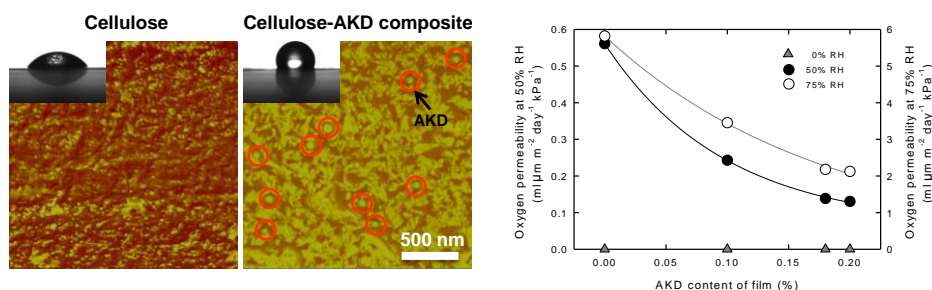


Fig. 3. AFM images (left) and oxygen permeability at 0, 50 or 75% RH (right) of cellulose and cellulose-AKD composite; the inserts are relevant water droplets on the film surface.