論　文　の　内　容　の　要　旨

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論文題目　Studies on structures and properties of nanocellulose/layered silicate composites
（ナノセルロース／層状ケイ酸塩複合体の構造と特性に関する研究）

Nacre is a natural organic/inorganic composite with excellent mechanical properties and has recently been attracting much attention in the field of materials science. Nacre has a unique layered hierarchical structure that is composed of plate-like calcium carbonate and adhesive organic biopolymers. A man-made material inspired by the nacre structure is polymer/layered silicate (PLS) nanocomposites. The PLS nanocomposites have been used in a range of practical materials from automobile parts to packaging materials.

Silicate is the most abundant mineral on Earth. Layered silicate is a material consisting of plate-like particles with thickness a few nanometer, and is found in natural clay minerals. When these silicate nanoplatelets are incorporated into polymer matrices as a filler, mechanical, thermal, and gas-barrier properties of the host polymeric materials are effectively improved as compared with other fillers. Representative layered silicates are montmorillonite (MTM) and saponite (SPN). The MTM nanoplatelet is about 1 nm thick, and has a sandwiched structure comprising an inner octahedral metal layer and two outer silicate tetrahedral layers. The surfaces and edges of the MTM nanoplatelets are negatively and positively charged, respectively. The MTM nanoplatelets are very similar in structure to the SPN ones. The differences between MTM and SPN are that, 1) the silicon ions are substituted mainly with Al^{3+} and Mg^{2+}, respectively, and 2) the platelet size of SPN (~50 nm) is much smaller than that of MTM (~300 nm).

Cellulose is the most abundant polymer on Earth and a major component of wood biomass, which is thus a key source of sustainable materials on an industrial scale. In recent years, cellulose microfibrils have been attracting much attention as a new biobased nanomaterial with excellent properties, so-called “nanocellulose”. Wood cellulose can be dispersed as completely individualized microfibrils through 2,2,6,6-tetramethyl-piperidinyl-1-oxyl (TEMPO)-mediated oxidation and subsequent mild mechanical treatment in water. The TEMPO-oxidized cellulose nanofibrils (TOCNs) thus obtained have the narrowest fibril width of ~3 nm and highest aspect ratios of over 100 in the nanocellulose family.

In the present study, a new type of PLS nanocomposites is prepared from TOCNs and layered silicates through a simple process of cast-drying their water dispersions. The resulting TOCN/layered silicate composites have closely-packed layered nanostructures, in which the silicate nanoplatelets are homogeneously distributed in the TOCN matrices.

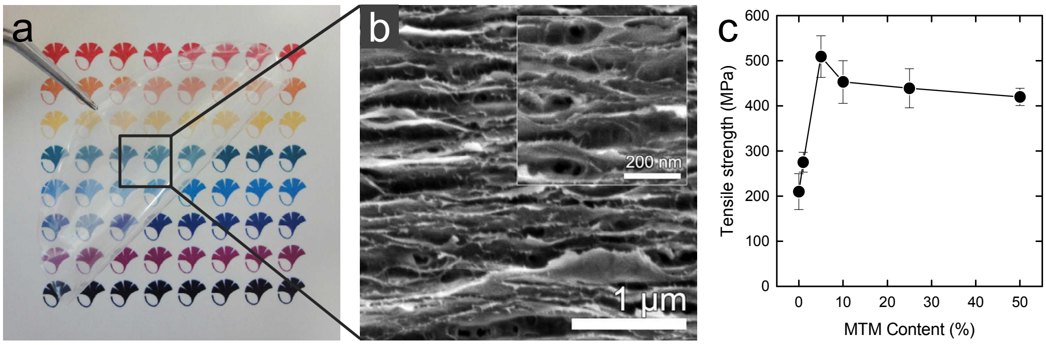

Figure 1. (a) Appearance, (b) cross-sectional SEM image, and (c) tensile strengths of the TOCN/MTM composites.

These composites have low densities yet exhibit excellent performances in mechanical and oxygen-barrier properties. The material properties of the composites, however, strongly depend on the aspect ratios of the silicate nanoplatelets. In the preset study, natural MTM and synthetic SPN nanoplatelets were used as the layered silicates. MTM nanoplatelets have higher aspect ratios than SPN ones, while SPN nanoplatelets have higher dispersibility in water than MTM ones. These characteristics of MTM and SPN nanoplatelets govern the material properties of the TOCN/layered silicate composites as follows,

Optical transparency: Neat TOCN films are optically transparent. However, light transmittance of the TOCN/MTM composites linearly decreases with increasing MTM content. In contrast, the TOCN/SPN composites are transparent regardless of SPN content, which can be explained by the higher dispersibility of SPN nanoplatelets in the TOCN matrices.

Mechanical property: Mechanical properties of the TOCN/MTM composites are characterized by extremely high tensile strength of over 500 MPa, while those of the TOCN/SPN composites are characterized by high toughness of up to 30 MJ m^{-3}. These characteristics in mechanical properties can be interpreted based on models for fracture behavior of PLS composites; high-aspect-ratio MTM nanoplatelets of high surface area can accept sufficient interfacial shear stress to be fractured in the composite, giving the composites with high ultimate strength, while low-aspect-ratio SPN nanoplatelets of low surface area are pulled out from the polymer matrix, giving the composites with high strain-to-failure or high toughness. These excellent mechanical properties of the TOCN/layered silicate composites should arise from strong interactions at the interfaces between the silicate nanoplatelets and TOCNs in the composite.

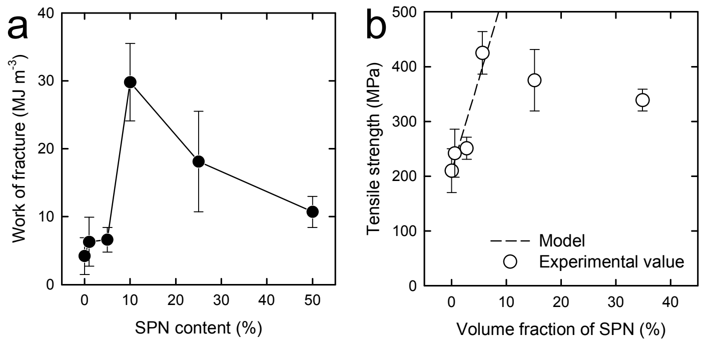

Figure 2. (a) Works of fracture and (b) tensile strengths of the TOCN/SPN composites. The dashed line in b shows the theoretical strength values.

Gas-barrier property: Oxygen- and water vapor-barrier properties of the TOCN/MTM composites are much higher than those of the TOCN/SPN composites. This is because the surface areas of high-aspect-ratio MTM nanoplatelets are much larger than those of low-aspect-ratio SPN ones, which makes the diffusion path of gas molecules longer. The oxygen- and water vapor-barrier properties of TOCN/MTM composites are significantly improved with increasing MTM content. In contrast, SPN nanoplatelets showed no significant contribution to the improvement of gas-barrier properties of the composites.

Hydrophobicity: Water contact angles (CA) of both the TOCN/MTM and TOCN/SPN composites increase with increasing silicate content. However, all the nanoparticles in the composites, or TOCNs, MTM and SPN nanoplatelets, are hydrophilic and have no hydrophobic surfaces. The increase in CA is thus explained by increase in the air area fraction on the microstructured surfaces of the composites; the air area fraction can be calculated from the AFM height profiles of the composite surfaces using the bearing function. The air area fraction on the composite surfaces increases with increasing MTM or SPN content, and the CA values of the composites almost linearly increase with the increase in the air area fraction.

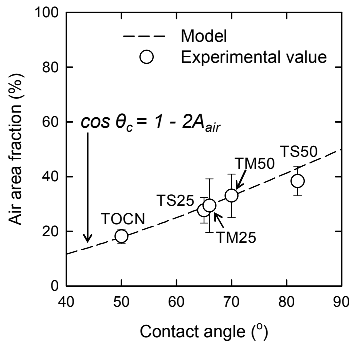

Figure 3. Relationship between the CA and the air area fractions on the surfaces of the TOCN/layered silicate composites.

The thesis is organized as follows:

Chapter 1 is general introduction for PLS nanocomposites, layered silicates, and nanocelluloses.

In *Chapter 2*, the TOCN/MTM composites are shown. The TOCN/MTM composites have distinct and closely-packed layered nanostructures, and exhibit extremely high mechanical strength comparable to those of steels and higher oxygen-barrier performances than commercial oxygen-barrier films.

In *Chapter 3*, the TOCN/SPN composites are shown. The TOCN/SPN composites are highly transparent and show exceptionally high toughness. The high toughness of the TOCN/SPN composites is interpreted based on a model for fracture of polymer composites reinforced with low-aspect-ratio platelets. Differences in mechanical and oxygen-barrier properties between the TOCN/MTM and the TOCN/SPN composites are explained based on those in aspect ratio between MTM and SPN nanoplatelets.

In *Chapter 4*, water vapor permeabilities and CA of the TOCN/layered silicate composites are shown. The water vapor permeabilities of TOCN/layered silicate composites show a similar trend to their oxygen permeabilities. The CA increase with increasing silicate content, even though both TOCNs and silicate nanoplatelets are hydrophilic. This strange increase in CA is interpreted based on the surface microstructures of the composite films.

Chapter 5 is conclusive remarks.