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Mechanical properties of polypropylene composites reinforced by surface-coated microfibrillated cellulose

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ABSTRACT

Polypropylene (PP)/microfibrillated cellulose (MFC) composites were prepared by coating nano to sub-micrometer width and several micrometer length MFC with a surfactant, polyoxyethylene (10) nonylphenyl ether. The composites were produced by melt compounding using a twin screw extruder and subsequent hot compression or injection moldings. Although the coating provided good dispersion of the MFC in the PP matrix, reinforcing effects on the Young's modulus and yield strength were negligible because of weak adhesive interactions between PP and MFC mediated by the surfactant. Addition of maleic anhydride grafted PP (MAPP) to the PP/surface-coated MFC composites improved the interfacial adhesive interaction, leading to a high Young's modulus and strength at yield while maintaining the large plastic deformation. Injection molded PP (80 wt%)/surface-coated MFC (10 wt%) composites containing 10 wt% MAPP showed 45% higher Young's modulus and 50% higher yield strength than the neat PP.

1. Introduction

Plant fibers, which are abundant renewable resources, exhibit high specific strength and stiffness, and industrial use of plant fibers as fillers in plastic composites have attracted much interest. Plant fibers are micron-size thick and are composed of bundles of cellulose microfibrils, which are semi-crystalline cellulose fibers with nano-size thickness. Therefore, plant fibers are turned into nanofibrous forms by chemical and mechanical treatments. One type of such nanofibers is called microfibrillated cellulose (MFC), which can be obtained by a high pressure homogenizing treatment [1,2].

The cellulose crystals exhibited high Young's modulus, such as about 137 GPa [3]. Since the wood cellulose microfibrils included amorphous region, their Young's modulus and strength were estimated as 29–36 GPa [4] and 1.6–3 GPa [5,6], respectively. They do not melt and their thermal degradation begins at 250 °C [7]. These features allow the use of MFC for fillers in polymer matrix composites.

Nakagaito and Yano [8] reported that MFC/phenolic composites showed higher Young's modulus, strength, and strain at break than untreated wood pulp/phenol composites. Fibrillation provided dense bonding of the fillers in the composites, contributing to their high stiffness. Furthermore, the fibrillation eliminated the weak parts of the original fibers, which act as crack initiators, and simultaneously increased bond densities, which play a role in effective crack stopping, resulting in increases in the strength and strain at break. These advantages are expected to lead to wide application of MFC reinforced composites in industry, such as for packaging, furniture and components for automobile.

Polypropylene (PP) is one of the most important and widely used polyolefin. Its low density, low production cost, design flexibility, and recyclability make it a popular choice as a matrix material in composites. PP is hydrophobic, leading to compatibility issues when fillers with polar surfaces, such as cellulose, are used. The lack of compatibility causes inhomogeneous dispersion of the cellulose fibers in the matrix and poor interfacial adhesion between fillers and matrix. To solve this problem, maleic anhydride grafted PP (MAPP) has commonly been used as a compatibilizer for PP/plant microfiber composites [9].

Ljungberg et al. [10] investigated two approaches: MAPP addition and filler surface-coating using a surfactant to achieve homogenous filler dispersion in PP/cellulose nano-rod cast films. The cellulose nano-rods were obtained from tunicate and had smaller aspect ratios than typical MFC. The MAPP showed an insufficient compatibilizing effect for filler dispersion in the PP matrix, probably because of the large specific surface area of the cellulose nano-rods. In contrast, surface coating with a phosphate ester of polyoxyethylene (10) nonylphenyl ether [11] gave a homogeneous dispersion in the PP matrix, resulting in the cast films exhibiting a high Young's modulus, strength, and strain at break [10,12]. Based

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on this encouraging finding, surface coating could be promising for improving of MFC dispersion in PP matrix, resulting in enhancing the mechanical properties of the composites. However, such an attempt in the use of MFC with high aspect ratio and melt extrusion process has not yet been studied.

This study aimed to investigate the reinforcing effects of surface-coated MFC on the mechanical properties of PP composites. Surface coating of MFC with surfactant is expected to provide good dispersion in the PP matrix. The composites were prepared by melt compounding using a twin screw extruder and subsequent hot compression or injection moldings to afford practicality from an industrial point of view. The addition of MAPP to the composites was studied for interfacial adhesion between the PP and MFC.

2. Materials and methods

2.1. Materials

Commercial PP (Novatec FG3Q, ethylene–propylene random copolymer, ethylene content = 4.5 mol%, melt flow rate = 9 g/10 min determined according to JIS K7210:1999) and MAPP (Umex1010, M_w = 30,000, maleic anhydride content = 10 wt% [13]) were purchased from Japan Polypropylene Corporation and Sanyo Chemical Industries, Ltd., respectively. Polyoxyethylene (10) nonylphenyl ether (PNE) was purchased from Wako Pure Chemical Industries, Ltd., Japan and used as the surfactant. MFC (trade name BiNFi-s, Fig. 1) was purchased from Sugino Machine Ltd., Japan [14]. Other chemicals and solvents were from commercial sources and used without any further purification.

2.2. Surface coating of MFC

The MFC was coated with PNE according to a previously reported method [10–12]. The MFC and PNE (1:4 in weight ratio) were mixed in water at a concentration of 5 wt%. The resulting aqueous suspension was freeze dried and redispersed in toluene using sonication for 1 min. The excess PNE was removed by centrifugation (3 times) at 15000 rpm and 25 °C for 5 min. Finally, a toluene dispersion of PNE-coated MFC was obtained. The weight ratio of MFC to coated PNE was 1:0.5.

2.3. Preparation of composites

PP and MAPP were dissolved in toluene at 100 °C, and the toluene dispersion of PNE-coated MFC was mixed with the resulting hot solution. After evaporation of the toluene on a hot plate at 120 °C and following complete drying in a vacuum oven at 110 °C for 6 h, a dry mixture of PP, MAPP, and PNE-coated MFC was obtained. The dry mixture was melt compounded using a twin screw extruder (2D15W, Laboplastomill 4C150, Toyo Seiki Seisaku-sho, Ltd., Japan) at 30 rpm and 170 °C, and cut into pellets.

The composites were prepared by hot compression or injection molding. In compression molding, the pellets were compressed at 180 °C and 10 MPa for 5 min and immediately cooled to 20 °C using another press machine. The thickness of the obtained films was about 0.4 mm. In injection molding, the pellets were melted at 190 °C and injected into a dumbbell mold at 1.5 MPa. The mold temperature was 28 °C. The dimension of the central rectangular part of the dumbbell specimens was 2 (thickness) × 4 (width) × 20 (length) mm^3.

2.4. Characterization

The mechanical properties of the compression and injection molded samples were determined by tensile tests using an Autograph (Shimadzu Corporation, Japan). The compression molded films were punched into dumbbell shapes having a central rectangular part of 0.4 (thickness) × 5 (width) × 30 (length) mm^3. The tensile tests were conducted with a cross head speed of 10 mm/min. Three measurements were carried out for each sample and mean values were calculated.

Differential scanning calorimetric (DSC) measurements were performed using a Pyris 1 DSC (Perkin-Elmer, U.S.). The samples (about 7 mg) were heated to 200 °C at a rate of 10 °C/min and held at temperature for 10 min. The samples were then cooled to 50 °C at a rate of 10 °C/min. The exothermic and endothermic peaks were denoted as the melting temperature (T_m) in the heating step and the crystallization temperature (T_c) in the cooling step, respectively. The heat of fusion (ΔH_m) and the crystallization enthalpy (ΔH_c) were determined from the area of the melting and crystallization peaks, respectively.

3. Results and discussion

3.1. Dispersion of MFC in toluene

The MFC with nano to sub-micrometer width and several micrometer length (Fig. 1) could not be dispersed in toluene because of its hydrophilic nature. Fig. 2 shows the quality of uncoated and PNE-coated MFC dispersions in water and toluene.

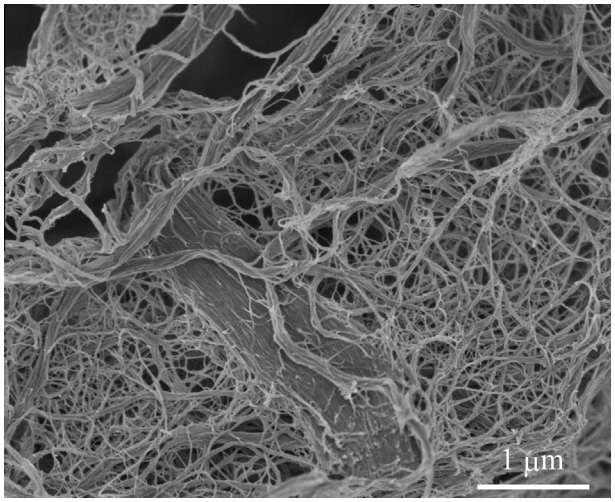

Fig. 1. Scanning electron microscopy image of MFC.

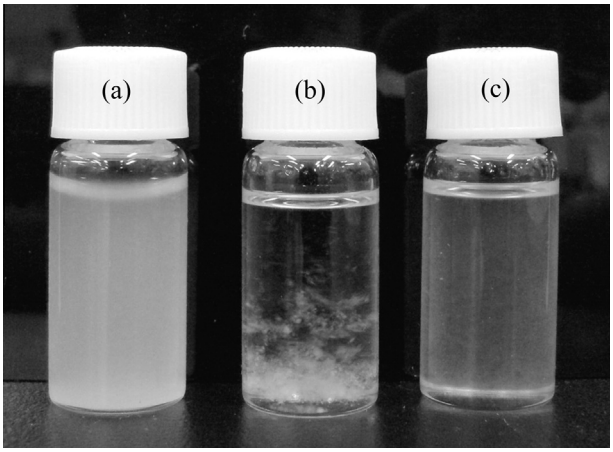

Fig. 2. Photographs of uncoated MFC suspended in (a) water and (b) toluene, and (c) PNE-coated MFC suspended in toluene. All MFC contents were 0.1 wt%.