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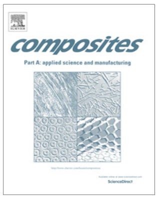

Surface modification of cellulose nanofibers with alkenyl succinic anhydride for high-density polyethylene reinforcement

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Hydrophobic cellulose nanofibers (CNFs) were prepared by surface modification using alkenyl succinic anhydride (ASA). The hydrophobicity of CNFs was varied by changing the degree of substitution (DS) from 0 to 0.83. Modified CNFs were mixed with high-density polyethylene (HDPE) using a twin-screw extruder and the resulting composites were injection molded. The tensile properties initially improved with increasing DS up to ~0.3–0.5, and then decreased with further substitution. The tensile strength and modulus of 10 wt.% HDPE/CNF composites containing 8.8 wt.% ASA (DS: 0.44) were 43.4 MPa and 1.97 GPa, respectively. These values were both almost 70% higher than those of composites containing unmodified CNF, and 100% and 86% higher, respectively, than those for pure HDPE. X-ray computed tomography measurements showed that CNFs modified with a DS of 0.44 were dispersed uniformly within the resin matrix, whilst unmodified CNFs and those modified with a DS of 0.77 agglomerated within the composites.

1. Introduction

Cellulose is a renewable and environmentally friendly bio-based polymer, which is available from non-edible biomass sources such as wood, grass, and agricultural residue. In plant cell walls, cellulose exists as microfibrillar bundles of crystalline nanofibers. It is well known that cellulose microfibrils have several attractive properties, including a low density, high specific surface area, high elastic modulus (138 GPa) [1,2], high strength (estimated to be around 3 GPa) [3], and a low coefficient of thermal expansion (10^{-7} K^{-1}) [4].

Cellulose nanofibers (CNFs), including cellulose microfibrils and their bundles, have received much industry attention for use in film, rheology control such as in paints and coatings, paper and packaging, cosmetic and medical materials and composites. In particular, reinforcement of polymers to improve their mechanical properties is one of the most promising applications of CNFs, and extensive research has been carried out over the past decade on the use of CNFs in thermosetting resins such as phenolic and epoxy resins and in thermoplastic resins such as poly(vinyl alcohol), poly(lactic acid) (PLA) and polypropylene (PP) [5–7].

Among these materials, reinforcement of the polyolefins, polyethylene (PE) and PP, is an important application of CNFs because polyolefins have been widely used in automotive parts, housing, films and packaging. In 1987, a pioneering study was reported by Boldizar et al. [8] in which freeze-dried or spray-dried cellulose nanocrystals (CNCs) prepared from various softwood pulps were compounded with PP followed by injection molding. The fillers did not effectively enhance the tensile properties because of agglomeration. CNFs and CNCs are hydrophilic, which makes it difficult to achieve uniform mixing within hydrophobic resins, and results in insufficient reinforcement efficiency. Although surfactants [9,10], compatibilizing agents [11–14] or surface modification of cellulose, including silane coupling agents [15], organic acid chlorides [16] or diisocyanate [17] have been studied, effective methods for improving the reinforcing efficiency of CNFs and CNCs in PP and PE have not yet been reported.

In the present work, surface modification of CNFs with alkenyl succinic anhydride (ASA) was studied to improve the mechanical properties of CNF-reinforced HDPE. ASA-modified polysaccharides such as waxy maize starch nanocrystals [18], chitin whiskers [19], cellulose whiskers [20], or CNC [21] have been studied during the past few decades. Yuan *et al.* [20] studied chemical modification of cellulose whiskers with iso-octadecenyl succinic anhydride (C18ASA) or n-tetradecenyl succinic anhydride. C18ASA-modified

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cellulose whiskers were well dispersed in 1,4-dioxane and in polystyrene. Khoshkava and Kamal [21] measured surface energies of PP, PLA and CNC, modified with 2-dodecen-1-yl succinic anhydride. The modification improved compatibility between PP and CNC, whereas it had a negative effect on the compatibility between PLA and CNC. However, no attempts to modify CNFs by ASA for composites have been reported.

Here, we studied the effect of CNF modification by ASA with varying DS on CNF compatibility with and reinforcing efficiency for HDPE. The ASA-modified CNFs (ACNFs) were mixed with HDPE using a twin-screw extruder and the resulting composites were injection molded. The reinforcing efficiency of the ACNFs was studied and their dispersibility in HDPE was characterized using X-ray computed tomography (CT).

2. Materials and methods

2.1. Materials

Needle-leaf bleached kraft pulp (NBKP) was supplied by Oji Holdings Corporation (Tokyo, Japan) with a 20–25 wt.% solid content. The Canadian Standard Freeness (CSF) of the NBKP was less than 100 ml. The lignin content was 0 wt.% according to Klason's method, TAPPI standard T230om-02. N-Methyl-2-pyrrolidon (NMP) was purchased from Mitsubishi Chemical Corporation (Tokyo, Japan). 4-Dimethylaminopyridine (DMAP) was purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). ASA (hexadecenylsuccinic anhydride, T-NS135) was supplied by SEIKO PMC Corporation (Tokyo, Japan). Maleic anhydride grafted polypropylene (Toyotac, PMA-H1000P) was purchased from Toyobo Co., Ltd. (Osaka, Japan). The MW and the amount of maleic anhydride grafted were 7.2×10^4 and 5.7 wt.%, respectively, according to the supplier. HDPE (Flo-Beads, HE3040, mp: 130 °C) was purchased from Sumitomo Seika Co., Ltd. (Tokyo, Japan). The average particle size was 11 μm according to the supplier. All chemicals were used as received.

2.2. Preparation of cellulose nanofibers

NBKP was mechanically disintegrated using a bead mill (NVM-2; AIMEX Co., Ltd., Tokyo, Japan). The beads mill is effective to prepare a large amount of CNF required for melt compounding. NBKP was diluted with distilled water to 0.75 wt.%, followed by bead mill treatment twice at 20 °C, at a feed speed of 600 ml/min, with 1-mm ZrO_2 beads at a packing ratio of 80%. Fig. 1 shows scanning electron microscope (SEM) images of the CNFs.

2.3. Surface modification of cellulose nanofibers

CNFs were treated with ASA in an NMP solvent, as shown in Fig. 2. The typical procedure for preparing ACNFs is described as follows for a DS of 0.77. A CNF slurry was filtered under reduced pressure until it reached 20–25 wt.% solids content. Then, 1 kg of wet CNF (solid content 22.5 wt.%) and 900 g of NMP were mixed in a mixer (Tri-mix TX-5; Inoue Mfg., Inc. Kanagawa, Japan), followed by evaporation of water under reduced pressure at 20–60 °C. Then, 360 g of ASA, 8.6 g of DMAP in 100 g of NMP and 76.7 g of K_2CO_3 were added to the mixture and stirred for 1 h at 70–80 °C. The treated CNF was washed with a series of acetone, ethanol, aqueous acetic acid, and distilled water to prepare wet ACNFs.

2.4. Preparation of cellulose nanofiber composites

The process to prepare composites in this study consists of 4 steps those are mixing, kneading and drying, melt extruding and injection molding, as shown in Fig. 3. CNF that is disintegrated in water must be dried before melt compounding with hydrophobic polymers. However, CNFs aggregate as they dry. To overcome this difficulty, freeze-drying or the solvent exchange method were applied, although both methods require large amounts of organic solvent to adequately remove water. Recently, one study succeeded in continuous drying and compounding of CNF and PP

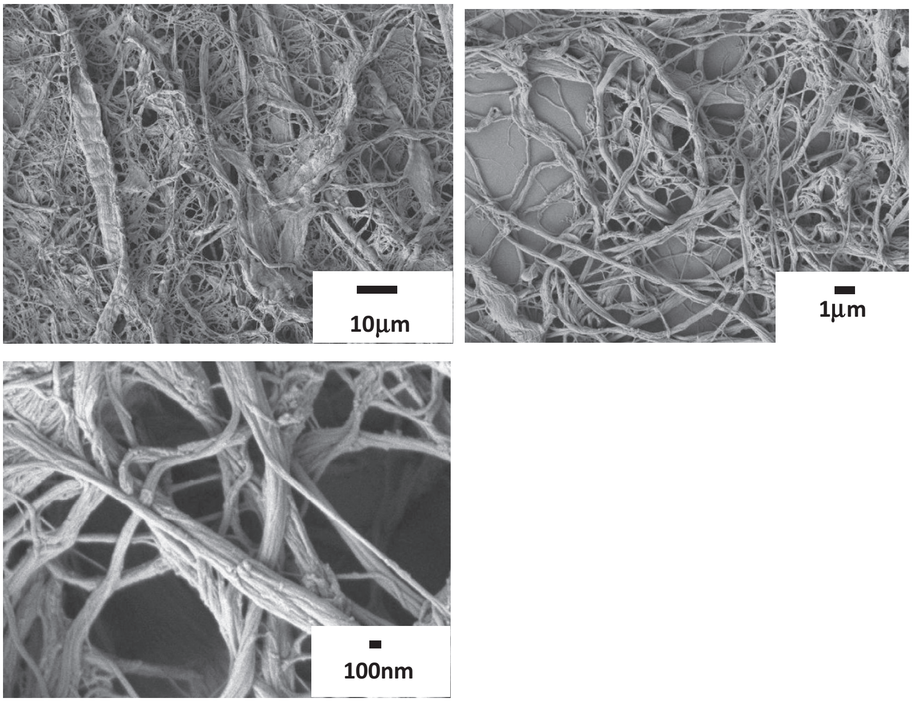

Fig. 1. Scanning electron microscope images of CNFs disintegrated by bead mill.

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