



Manufacturing process centered on dry-pulp direct kneading method opens a door for commercialization of cellulose nanofiber reinforced composites



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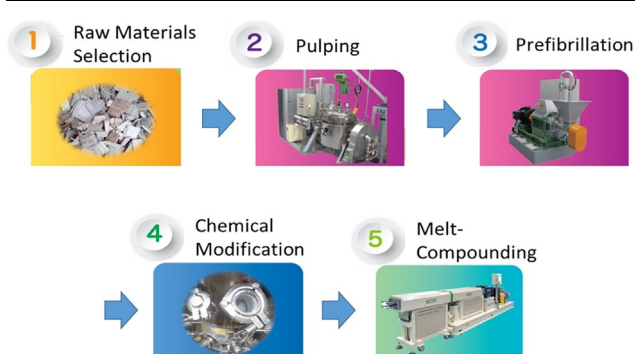
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HIGHLIGHTS

- Nanofibrillation of hydrophobized dry-pulp to cellulose nanofibers (CNFs).
- Dried pulp is nanofibrillated and dispersed in HDPE simultaneously by kneading.
- Addition of 10 wt% CNFs increased the tensile modulus of HDPE by 3.8 times.
- Similar high mechanical reinforcement to polymer: Dry-pulp versus wet-pulp CNFs.
- Upscalable process suitable for existing industrial manufacturing facilities.

GRAPHICAL ABSTRACT



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ABSTRACT

We report an integrated production process that simultaneously nanofibrillates dried pulp and uniformly disperses cellulose nanofibers (CNFs) in resins. Refiner-treated pulp were modified using alkenyl succinic anhydride (ASA) in N-Methyl-2-pyrrolidone (NMP). The ASA treated pulp with DS 0, 0.22, 0.43 and 0.57 was mixed with maleic anhydride-grafted polypropylene (MAPP) powder, CaCO₃ and high density polyethylene (HDPE) powder (pulp content: 10 wt%). The mixture was melt-extruded at 140 °C with HDPE. The dumbbell-shaped specimens were prepared using injection molding. The SEM images of refiner-treated pulp (DS 0.43) and previously nanofibrillated CNFs (DS 0.44) using a bead mill as a comparison, both of which were extracted from the melt compounded composites, showed comparable degrees of nanofibrillation. The highest mechanical reinforcing efficiency was obtained at DS 0.43, which was shown to exhibit the most fibrillated morphology. The tensile modulus increased from 1.08 GPa for neat HDPE, to 3.46 GPa. The tensile strength also increased from 23 MPa (neat HDPE) to 56 MPa. The mechanical properties were very similar to the bead mill-fibrillated CNF-reinforced composite. This is the first report of nanofibrillation of dried pulp with uniform CNF dispersion into hydrophobic HDPE. We have termed the process the Pulp Direct-Kneading Method.

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1. Introduction

Plant cell walls consist of 10–20 nm nanofibers called cellulose nanofibers (CNFs). Owing to favorable mechanical properties such as high strength and low thermal expansion [1–5] and high specific surface area, as well as sustainability and thermal recyclability, CNFs made from plant resources such as wood have significant potential as green reinforcing fillers for plastics. Especially, lightweight nanocomposites reinforced by CNFs have attracted interest from the automotive industries to manufacture lightweight parts contributing to low fuel consumption.

Many studies into the use of CNFs as a reinforcement material have been carried out [6–8]. The majority of this work has focused on improving the interaction between CNFs and polymers; as the polar, strongly hydrophilic nature of CNFs prevents their dispersion in polymers, which are generally hydrophobic and apolar or only weakly polar. In general, there are two approaches to improving the affinity between CNFs and polymers. One is to use compatibilizers that bridge between CNF and polymer molecules [9–17]. The other approach is chemical modification of the surface of the CNFs [6–8,18–21]. These studies contribute to improving the dispersibility of CNFs in hydrophobic polymer, as well as to controlling the interface between CNFs and polymer molecules. However, as Lindström and Aulin observed, scaling-up of nanocellulose production processes and procedures remains the largest challenge for cost-effective nanocomposite manufacturing across the various applications [22]. Similarly, Oksman et al. reviewed the recent developments of the processing cellulose nanocomposites using the melt-processing of thermoplastic, that is the most used production process making polymer composites, and concluded that to produce cellulose nanocomposites for commercial use, the processing of the materials must be developed from laboratory to industrially viable methods [6].

In 2003 we found that refiner-treated wet pulp can be fibrillated to 10–100 nm width nanofibers by kneading [23,24]. This finding was subsequently used in the work of Suzuki et al. [25–28] for the development of CNF-reinforced composites. A mixture of refiner-treated wet pulp and powdered PP or HDPE was fed into a twin-screw extruder so that a mixture of microfibrillated cellulose, consisting of nanometer to submicron diameter fibers, and powdered PP or HDPE was achieved. Melt compounding, along with the evaporation of water in the presence of PP or HDPE powder, prevented aggregation of nanofibrillated pulp and allowed uniform dispersion of nanofibrillated cellulose into the PP or HDPE. These results suggest that as long as hydrogen bonding between CNFs in the dried pulp can be prevented, and the CNF surface shows good affinity with the melted polymers; a simple manufacturing process, which simultaneously nanofibrillates dried pulp and uniformly disperses the CNFs in various resins without using any solvent, is achievable.

Recently, we developed hydrophobic CNFs through surface modification with alkenyl succinic anhydride (ASA) [29]. The dried modified CNFs were mixed with HDPE using twin-screw extrusion and X-ray CT observation revealed that the modified CNFs were dispersed homogeneously in the HDPE. Based on these previous results, in this study we developed the “Pulp Direct-Kneading Method”, which simultaneously nanofibrillates dried pulp and uniformly disperses cellulose nanofibers into hydrophobic resin such as HDPE. The mechanical properties of the HDPE composites, as well as their degrees of nanofibrillation and fiber dispersibility, were compared with a composite that used previously nanofibrillated CNFs using a bead mill before melt compounding.

2. Materials and methods

2.1. Materials

Softwood bleached kraft pulp (NBKP) was supplied by Oji Holdings

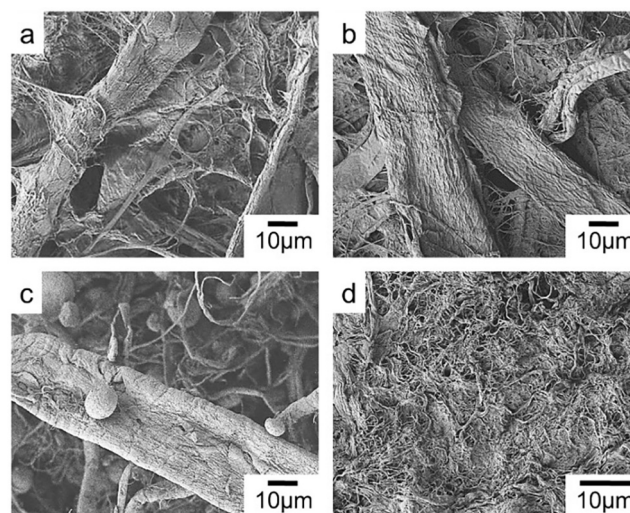


Fig. 1. FE-SEM images of NBKP morphologies during composite processing: a) Refiner-treated NBKP, b) Chemically modified refiner-treated NBKP, c) Mixture of Pulp and resin powders, d) Bead mill fibrillated CNFs.

Corporation (Tokyo, Japan) as never-dried kraft pulp with a solids content of 20–25 wt% pulp. The pulp was refiner-treated until the Canadian Standard Freeness (CSF), as per TAPPI standard T227om-09, was less than 100 mL. The degree of polymerization was 940, calculated as the value of relative viscosities, as per TAPPI standard T230om-99. The lignin content was 0 wt% according to the Klason lignin method, TAPPI standard T230om-02. As a comparison, refiner-treated NBKP (CSF: less than 100 mL, Fig. 1a) was mechanically disintegrated using a bead mill (NVM-2; AIMEX Co., Ltd., Tokyo, Japan) to produce CNFs (Fig. 1d). Refiner-treated 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, and 1 mm ZrO₂ beads at a packing ratio of 70%. The CNF slurry was filtered under reduced pressure until it reached 20–25 wt% solids content.

N-Methyl-2-pyrrolidone (NMP) was purchased from Mitsubishi Chemical Corporation (Tokyo, Japan). ASA (alkenyl succinic anhydride, T-NS135) was supplied by SEIKO PMC Corporation (Tokyo, Japan). Maleic anhydride-grafted polypropylene (TOYO-TAC, PMA-H1000P) was purchased from TOYOBO Co., Ltd (Osaka, Japan). The MW (molecular weight) and amount of maleic anhydride grafted were 7.2×10^4 and 5.74 wt%, respectively, as stated by 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 as stated by the supplier. HDPE (pellet, J320, mp: 130 °C) was purchased from Asahi Kasei Chemicals Co., Ltd (Tokyo, Japan). All chemicals were used as received.

2.2. Surface modification of cellulose nanofibers

Refiner-treated pulp and CNFs were treated with ASA in NMP. ASA reacts with water before reacting with the OH group of CNFs. Therefore, we replaced water with an aprotic organic solvent, such as NMP, before ASA treatment. 500 g of wet sample (refiner-treated pulp or CNFs, solids content 20–25 wt%) and 450 g of NMP were mixed (Trimix TX-5; INOUE MFG., Inc. Kanagawa, Japan), followed by evaporation of water under reduced pressure at 20–60 °C. ASA (80 g) in 50 g of NMP and 25 g of K₂CO₃ were added and the mixture was stirred for 1 h at 70–80 °C. The treated sample was washed with a series of acetone, ethanol, aqueous acetic acid, distilled water, and isopropanol to give the wet ASA modified sample.

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