Pre-fibrillation of pulps to manufacture cellulose nanofiber-reinforced high-density polyethylene using the dry pulp direct kneading method

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Abstract The dry pulp direct kneading method is an industrially viable, low-energy process for manufacturing cellulose nanofiber (CNF)-reinforced polymer composites, where the chemically modified pulps are nanofibrillated and uniformly dispersed in the polymer matrix during melt compounding. In the present study, cellulose fibers of various sizes ranging from surface-fibrillated pulps (20 μm in width) to fine CNFs (20 nm in width) were prepared from softwood bleached kraft pulps using a refiner and a high-pressure homogenizer. These cellulose fibers were modified with alkenyl succinic anhydride and dried. The dried fibers were used as a feed material for melt compounding in the dry pulp direct kneading method to fabricate CNF-reinforced high-density polyethylene (HDPE). When surface-fibrillated pulps were employed as a feed material, the pulps were nanofibrillated and dispersed uniformly in the HDPE matrix during melt compounding. The resulting composites had much better properties—i.e., much higher tensile modulus and strength values, and much lower coefficient of thermal expansion values—than the composites produced using pulps without pre-fibrillation. However, when CNFs were used as a feed material, they were shortened and agglomerated during melt compounding, and the properties of the composites consequently deteriorated. The study concludes that surface-fibrillated pulp, which can be produced cost-effectively using a refiner on an industrial scale, is more suitable as a feed material than CNFs for melt compounding in the dry pulp direct kneading method. This finding enables the elimination of a preliminary step in the preparation of CNFs from pulps, which is a time-consuming and energy-intensive process.

Keywords Cellulose nanofiber · Pulp · Pre-fibrillation · Polyethylene · Mechanical property · Coefficient of thermal expansion

Introduction

Cellulose nanofibers (CNFs) are fundamental components of the plant cell wall, in which cellulose molecules are extended to form semi-crystalline structures. The extended and aligned cellulose molecules confer excellent mechanical properties and a favorable coefficient of thermal expansion, which makes CNFs attractive for reinforcing polymers. Consequently, there is high demand for CNF/polymer
composites for use in automotive parts, electric appliances, and building materials (Yano 2005; Moon et al. 2011; Abdul Khalil et al. 2012; Dufresne 2013; Miao and Hamad 2013; Oksman et al. 2016; Ramu et al. 2019). However, despite these attractive properties, CNF/polymer composites are not widely used in industrial applications. One of the main reasons for this is the low affinity between hydrophilic CNFs and hydrophobic polymers. Owing to hydrogen bonding between their OH groups, CNFs aggregate in hydrophobic polymers during melt compounding. Therefore, many researchers have attempted to overcome this low affinity by chemically modifying the surfaces of CNFs (Hassan et al. 2014; Sato et al. 2016; Yano et al. 2018), adding compatibilizers (Qiu et al. 2005; Volk et al. 2015; Sakakibara et al. 2016; Suzuki et al. 2016), and/or modifying the process used to mix CNFs and polymers (Hietala et al. 2013; Suzuki et al. 2013; Oksman et al. 2016).

Generally, CNF-reinforced thermoplastic polymer composites are produced by first producing CNFs from pulps, and then melt compounding the CNFs with thermoplastic polymers (Wang and Sain 2007; Hietala et al. 2013; Abdul Khalil et al. 2014; Hassan et al. 2014). However, we have recently developed a dry pulp direct kneading method (Igarashi et al. 2018) to manufacture CNF-reinforced thermoplastic polymer composites. In this method, pulps are modified with alkenyl succinic anhydride (ASA) and dried. The dried ASA-treated pulps are used as a feed material for melt compounding with thermoplastic polymers. The pulps are nanofibrillated and uniformly dispersed in the polymer matrix during melt compounding. This approach combines the two processes—i.e., producing the CNFs and melt compounding them with thermoplastic polymers—thereby significantly reducing the duration, energy, and cost of manufacturing. This process also increases the aspect ratio of the fibers (length/width) by changing their width from the micro-scale (pulp) to the nano-scale (CNF) during melt compounding, thereby enhancing the mechanical properties of the composites. Therefore, if CNFs rather than pulps are used as the feed material for melt compounding with thermoplastic polymers in the dry pulp direct kneading method, the CNFs may be further fibrillated to finer CNFs, thereby further improving the mechanical properties of the CNF-reinforced thermoplastic polymer composites. However, the effects of pulp pre-fibrillation on the morphology and mechanical properties of the composites have not been reported before.

In the present study, ASA-treated cellulose fibers of various sizes—i.e., from pulps (20 μm in width) to fine CNFs (20 nm in width)—were used as feed materials for melt compounding with high-density polyethylene (HDPE) using the dry pulp direct kneading method. Their effects on the morphology, mechanical properties, and coefficient of thermal expansion values of the composites were investigated. There was an optimum degree of pre-fibrillation to ensure the production of composites with ideal morphologies and mechanical properties.

Materials and methods

Materials

Softwood bleached kraft pulps (NBKPs) were supplied by Oji Holdings Corporation (Tokyo, Japan) as never-dried kraft pulps with pulp contents of 20–25 wt% in water. The Canadian Standard Freeness (CSF) of the NBKPs was 720 mL (as per TAPPI standard T227om-09), and the NBKPs were 2.02 mm long (as per JAPAN-TAPPI standard T8226-2). N-Methyl-2-pyrrolidone (NMP) was purchased from Mitsubishi Chemical Corporation (Tokyo, Japan). ASA (T-NS135) was supplied by SEIKO PMC Corporation (Tokyo, Japan). Maleic anhydride-grafted polypropylene (MAPP) (TOYO-TAC, PMA-H1000P) was purchased from TOYOBO Co., Ltd (Osaka, Japan); its weight-average molecular weight was 7.2 × 10^4 g/mol and the amount of grafted maleic anhydride was 5.74 wt%, as stated by the supplier. HDPE powders (FLO-BEADS, HE3040, mpt: 130 °C) were purchased from SUMITOMO SEIKA Co., Ltd (Tokyo, Japan). The average particle size was 11 μm as stated by the supplier. HDPE pellets (J320, mpt: 130 °C) were purchased from Asahi Kasei Chemicals Co., Ltd (Tokyo, Japan). Calcium carbonate (CaCO3) was purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). All the materials were used as received.

Pre-fibrillation of pulps

Cellulose fibers of various sizes ranging from surface-fibrillated pulps to fine CNFs (20 nm in width)
were prepared from NBKPs using a refiner and a high-pressure homogenizer (HPH). The NBKPs were treated using a refiner until the CSF was less than 100 mL. The degree of polymerization—calculated from the relative viscosity—was 940, as per TAPPI standard T230om-99. The lignin content was 0 wt% according to the Klason lignin method (TAPPI standard T230om-02). The refiner-treated pulps were 0.66 mm in length, as per JAPAN-TAPPI standard T8226-2. The refiner-treated pulps in water (0.5 wt%, 2 L) were disintegrated mechanically using a HPH (Star Burst 10, HJP-25,008 K; Sugino Machine Co., Ltd., Japan) at 15 °C. The nozzle size was 0.17 mm and the pressure was approximately 200 MPa. The HPH treatment was repeated up to ten times.

In the present study, five types of cellulose fibers were prepared: pulps that had not been pre-fibrillated, pulps that had been treated with the refiner, and CNFs treated with the refiner and the HPH (one pass, three passes, or ten passes).

Field-emission scanning electron microscopy

The cellulose fibers were investigated by field-emission scanning electron microscopy (FE-SEM; JSM-6700 F; JEOL, Ltd., Tokyo, Japan) at an acceleration voltage of 1.5 kV. Before observation, the cellulose fibers were coated with platinum using an ion sputter coater (Auto-Fine Coater JFC-1600; JEOL, Ltd., Tokyo, Japan).

X-ray diffraction

X-ray diffraction patterns of the cellulose fibers were obtained using an X-ray diffractometer (UltraX 18HF; Rigaku Corp., Tokyo, Japan) at 30 kV and 200 mA. The degree of crystallinity of each type of cellulose fiber was calculated using the method described by Segal et al. (1959).

Dewatering time of the cellulose fiber suspensions

A specially designed vacuum filter was used to characterize the ease with which water could be removed from suspensions of the cellulose fibers of various sizes. The filtration system comprised filter papers and a large-aperture stainless steel mesh sieve. Three sheets of quantitative ashless filter paper (each with a diameter of 185 mm; 5 A; Advantec Toyo Kaisha Ltd., Japan) were wetted with distilled water prior to the test. The filter papers were sandwiched between O-rings and placed on the sieve. The filtration system was placed between two hollow cylinders. The cellulose fiber suspension (600 g; 0.1 wt%) was poured into the upper cylinder at 20 °C. The suspension was then gently stirred before applying a vacuum of -30.3 kPa (± 0.4) to the lower cylinder. The time taken to filter the cellulose fibers through the system was recorded.

Surface modification of the cellulose fibers

Each type of cellulose fiber was modified with ASA in NMP (an alternative eco-friendly method is currently under investigation). Because ASA reacts with water before reacting with the OH groups of the cellulose fibers, water was replaced with an aprotic organic solvent—i.e., NMP—before the ASA treatment. Furthermore, cellulose fibers swell in NMP, thereby facilitating the reaction—i.e., esterification—on the surfaces of the cellulose fibers. The wet cellulose fibers (500 g; solid content 20–25 wt%) were mixed with 450 g of NMP using a mixer (Tri-mix TX-5; INOUE MFG., Inc. Kanagawa, Japan). The water was then evaporated under reduced pressure at 20–60 °C. ASA (80 g) in 50 g of NMP and 25 g of K₂CO₃ were added to the cellulose fibers/NMP, and the mixture was stirred for 1 h at 70–80 °C. The cellulose fibers were then washed with a series of acetone, ethanol, aqueous acetic acid, distilled water, and isopropanol to produce ASA-treated cellulose fibers in isopropanol. Acetone and ethanol were used to produce a hydrophilic solvent by gradually changing its polarity. Acetic acid was used to replace the ASA functional end structure COOK with COOH (Sato et al. 2016, 2019). Isopropanol was used to disperse the ASA-treated CNFs in the HDPE, and improve the mechanical properties of the composites (Sato et al. 2021).

The degree of substitution (DS) of the cellulose fibers was calculated from the area under the 1740 cm⁻¹ absorbance peak in the Fourier-transform infrared (FT-IR) spectrum. Attenuated total reflection infrared (ATR-IR) spectra were recorded using an FT-IR spectrometer (Spectrum One, Perkin Elmer) in the range 600 to 4000 cm⁻¹ at a resolution of 2 cm⁻¹. A spectrum was obtained by accumulating 16 scans and normalized using the 1315 cm⁻¹ peak attributable
to the cellulose CH$_2$ vibration. The band attributable to the C=O stretching vibration mode of the acyl group (1735–1750 cm$^{-1}$) increased significantly in the modified cellulose fibers, indicating esterification. The DS and the area under the 1740 cm$^{-1}$ peak were correlated in advance by titration of the cellulose fibers. Each of the ASA-treated cellulose fibers prepared in the present study had a DS of 0.4 ± 0.03. In a previous study (Sato et al. 2016), ASA-treated CNFs with DS values from 0 to 0.83 were prepared. The results showed that ASA-treated CNFs with a DS of 0.44 were most uniformly dispersed in the HDPE, and the resulting composites had the best tensile properties.

Preparation of composites

Composites comprising each of the five types of ASA-treated cellulose fibers were prepared. The ASA-treated cellulose fibers were mixed with MAPP, CaCO$_3$, and HDPE powders in isopropanol for 10 min using a propeller type mixer. The weight ratio of the ASA-treated fibers (cellulose fiber:ASA):MAPP:CaCO$_3$:HDPE powders was 54(30:24):12.9:3:30. In our preliminary experiments using bead mill-disintegrated CNFs, we verified that MAPP acts as a compatibilizer and improves the mechanical properties of ASA-treated CNF/HDPE composites (the tensile modulus increased from 2.19 to 2.52 GPa at a DS of 0.15). Our previous study (Sato et al. 2019) also showed that CaCO$_3$ improves the tensile modulus of ASA-treated CNF/MAPP/HDPE composites.

The isopropanol was filtered from the mixture under reduced pressure until the solid content reached approximately 50 wt%, and the mixture was then crushed in a mixer (Waring blender). The crushed mixture was dried during mixing (Tri-mix TX-5; INOUE MFG., Inc. Kanagawa, Japan), and isopropanol was finally evaporated under reduced pressure at 20–60 °C. The powders of the mixture and HDPE pellets were melt-compounded using a twin-screw extruder (KZW15-TW; Technovel Corp., Osaka, Japan) at a screw speed of 200 rpm and a feed rate of 50 g/h. The ratio of the length of the screw to its diameter (L/D) was 45 and the diameter of the extruder was 15 mm. The extruder included six heating zones and the barrel temperatures were set from the zone next to the hopper at 110, 130, 130, 140, 140, and 140 °C, as shown in Fig. 1. The extrudate was cut into pellets using a pelletizer. The weight ratio of ASA-treated fibers (cellulose fiber:ASA):MAPP:CaCO$_3$:HDPE powders: HDPE pellets in the composite pellets was 18(10:8):4.3:1:10:66.7.

Dumbbell-shaped specimens were prepared from the pellets using an injection molding machine (NPX7-1 F; Nissei-Plastic Industrial Co., Ltd., Nagano, Japan, Fig. 2). The injection molding machine included six heating sections where the barrel temperature could be set. The barrel temperature was increased from the feed Sect. (155 °C) to the nozzle Sect. (170 °C). The injection pressure and speed were 100 MPa and 80 mm/s, respectively. The mold temperature was set at 40 °C and the cooling time was 10 s. Figure 3 summarizes the procedure for fabricating the composites described above.

Tensile test

The tensile properties of the composites were determined using a universal testing machine (Model 3655; Instron Corp., Canton, MA, USA) with a crosshead speed of 10 mm/min at 23 °C. The shape of the test sample—i.e., a width of 5 mm (narrow portion) and a thickness of 1 mm—is shown in Fig. 3. The load cell of the machine was 5 kN. The strain at failure was measured using a video camera. The tensile modulus was calculated from the stress–strain curve. Five specimens were tested and the average values are reported.

Thermomechanical test

The coefficient of thermal expansion (CTE) values of the composites were determined using a thermomechanical analyzer (TMA/SS6100; SII Nanotechnology Inc., Japan). Each specimen was 30 mm long, 1 mm thick, and 5 mm wide. Before analysis, each specimen was heated at 110 °C for 48 h to remove
moisture, and allowed to cool in a desiccator. The original grip distance was 20 mm and the specimen was tested under a tensile load of 29.4 mN. The measurements were acquired in the range -5 to 130 °C at a heating rate of 5 °C/min under a nitrogen atmosphere (60 mL/min). The CTE was evaluated as the fractional change in length per degree of temperature change in the range 0 to 60 °C.

X-ray computed tomography

The dispersibility and degree of fibrillation of the cellulose fibers in the composites was determined by X-ray computed tomography (CT) (SKY Scan 1172 instrument; Bruker-Micro CT, Kontich, Belgium). Observations were made at the center of each dumbbell-shaped specimen.

Extraction of cellulose fibers from composites

To remove the HDPE matrix, each composite sample was placed in a stainless steel mesh container, which was immersed and stirred in boiling p-xylene (160 °C). The sheet-like cellulose fibers left in the stainless steel mesh were used to determine the degree of fibrillation of the cellulose fibers in the composites by FE-SEM. To determine the lengths of the cellulose fibers in the composites, the fibers left in the stainless steel mesh were dispersed in ethanol (0.001 wt%). The resulting dilute dispersion was dried on a glass plate for FE-SEM investigation. The lengths of 100 cellulose fibers were determined from the FE-SEM images.

Results and discussion

Pre-fibrillation of the pulps

Figures 4 and 5 show, respectively, optical micrographs and FE-SEM micrographs of the cellulose fibers treated using the refiner and the HPH. It should be noted that in the FE-SEM micrographs (Fig. 5), the scale bars for the pulps that had not been pre-fibrillated are 100 μm (Fig. 5a), whereas those for the HPH-treated pulps are 500 nm (Fig. 5d and f). Two FE-SEM micrographs with those scale bars are presented for the refiner-treated pulps (Fig. 5b and c). Both figures indicate that the degree of fibrillation increased during the refiner and subsequent HPH treatments. Most of the refiner-treated pulps were not fibrillated to CNFs (20 μm width), but their surfaces were fibrillated, which suggests that external fibrillation occurred. External fibrillation involves cutting or removing the primary wall and the outer layer of the
Fig. 4 Optical micrographs of cellulose fibers: a pulps that had not been pre-fibrillated, b refiner-treated pulps, c high-pressure homogenizer (HPH)-treated (one pass) cellulose nanofibers (CNFs), d HPH-treated (three passes) CNFs, and e HPH-treated (ten passes) CNFs.

Fig. 5 Field-emission scanning electron microscopy (FE-SEM) images of the cellulose fibers: a pulps that had not been pre-fibrillated, b, c refiner-treated pulps, d high-pressure homogenizer (HPH)-treated (one pass) cellulose nanofibers (CNFs), e HPH-treated (three passes) CNFs, and f HPH-treated (ten passes) CNFs.
secondary wall (the \(S_1\) layer) of a pulp, which allows fluffing of the pulp surface and accelerates fibrillation of the inner walls (the \(S_2\) and \(S_3\) layers) of the pulp (Uetani and Yano 2011).

A HPH is often used to manufacture CNFs from pulps (Baati et al. 2018; Phanthong et al. 2018). Unlike a bead mill, a HPH does not cause contamination during the fibrillation process. In the present study, a HPH was used to fibrillate the refiner-treated pulps. Fibers with a wide range of widths were produced by passing the refiner-treated pulps through the HPH (one passage). Some surface-fibrillated pulps were fibrillated to CNFs of 20–100 nm width, suggesting that internal fibrillation—i.e., delamination and fibrillation of the inner \(S_2\) and \(S_3\) layers—occurred, whereas some surface-fibrillated pulps of approximately 20 \(\mu\)m width remained. After three passages of the fibers through the HPH, most of the fibers were CNFs of 20–100 nm width, but some micro-sized fibers of several \(\mu\)m width (named CMFs hereafter) were observed. After ten passages through the HPH, the fibers became fine CNFs of approximately 20 nm width, and neither pulps nor CMFs remained.

It is not easy to quantify the degree of fibrillation of cellulose fibers with a wide range of sizes (from pulps to fine CNFs) using a single experimental method. In our preliminary study, the CSF test was conducted on the pulps and CNFs produced in the present study. However, it was not possible to determine the freeness of the HPH-treated CNFs because they were too small. Therefore, the viscosities of water dispersions of the cellulose fibers and the specific surface areas of the fibers were measured. These two test methods reflected differences in the degree of fibrillation between the CNFs and the fine CNFs, but could not detect differences between the pulps that had not been pre-fibrillated and the surface-fibrillated pulps. Consequently, in the present study the dewatering time test was used to characterize the degree of fibrillation of the cellulose fibers. The dewatering time test successfully determined the time required to filter the cellulose fiber–water slurries of all the cellulose fibers, ranging from the pulps that had not been pre-fibrillated to the fine CNFs. As shown in Table 1, the dewatering time increased as the degree of fibrillation increased. In particular, the dewatering time of the HPH-treated (one pass) CNFs was approximately eight times that of the refiner-treated pulps, which mirrored the significant difference in the degree of fibrillation between those two pulps (see Figs. 4 and 5). It should also be noted that long dewatering times greatly increase the cost of producing dried HPH-treated (one pass) CNFs, which is a disadvantage in an industrial setting.

Fibrillation of pulps under high shear stress can decrease the crystallinity of cellulose fibers, which may affect their reinforcing efficiency (Iwamoto et al. 2007; Ho et al. 2015). The X-ray diffraction patterns and crystallinities of the refiner-treated pulps and HPH-treated (one pass, three passes, and ten passes) CNFs are shown in Fig. 6; Table 1, respectively. All the cellulose fibers had similar diffraction patterns and crystallinities, which indicates that the HPH treatments had little effect on the crystal structures and crystallinities of the cellulose fibers prepared in the present study.

Mechanical properties and CTEs of the composites

Typical stress–strain curves of the composites from the tensile tests are shown in Fig. 7, and their mechanical properties (tensile modulus, tensile strength, and strain at failure) are summarized in Table 2. Elongation–temperature curves of the composites from the thermomechanical tests are shown in Fig. 8, and the CTE values are summarized in Table 2. Because the HPH treatments facilitated nanofibrillation of the refiner-treated pulps, it may be expected that the HPH-treated CNFs would have higher reinforcing efficiency than the refiner-treated pulps. However, the composites produced using the refiner-treated pulps and the HPH-treated (one pass) CNFs had similar tensile modulus, tensile strength, and CTE values, as shown in Table 2. Interestingly, further increases in the number of passages through the HPH caused deterioration of the properties—i.e., a decrease in the tensile modulus and strength, and an increase in the CTE. As shown in Fig. 6; Table 1, the HPH treatments had little effect on the crystal structures and crystallinities of the cellulose fibers prepared in the present study. Therefore, the crystal structures and crystallinities of the cellulose fibers were not the factors to deteriorate the properties. It should be noted that the properties of the composites produced using the HPH-treated (ten passes) CNFs were similar to those of the composites produced using the pulps that had not been pre-fibrillated.
Morphology of the composites

The cellulose fibers in the HDPE matrix were investigated by X-ray CT (Fig. 9) and FE-SEM (Fig. 10). The X-ray CT image shows density distribution in three-dimensional space with spatial resolution of 700 nm. In Fig. 9, the HDPE matrix—which was less dense than the cellulose fibers—is shown in blue, and cellulose fibers larger than 700 nm are shown in white. It should be noted that the cellulose fibers observed in the X-ray CT images were pulps and CMFs, whereas the CNFs could not be detected because their width was beyond the spatial resolution of X-ray CT. Both figures indicate that the composites produced using pulps that had not been pre-fibrillated contained many large fibers of approximately 10 μm width, which suggests that nanofibrillation of those pulps did not occur during melt compounding. However, the composites produced using the refiner-treated pulps had many CNFs of 20–100 nm width, and some CMFs of several micrometers width, and these fibers were dispersed uniformly in the HDPE matrix. Because the refiner-treated pulps were 20 μm in width before melt compounding (see Fig. 5b), the surface-fibrillation of the pulps using the refiner promoted the nanofibrillation of the pulps as well as the uniform dispersion of the CNFs during melt compounding.

When the HPH-treated (one pass and three passes) CNFs were used as feed materials, the composites had many CNFs of 20–100 nm width and some CMFs of several micrometers width. Their morphologies were similar to the morphology of the composites produced using the refiner-treated pulps. In contrast, the composites produced using the HPH-treated (ten passes) CNFs contained agglomerated CNFs (see the increase in spherical white regions in the X-ray CT image (Fig. 9)).

Figure 11 shows length frequency distribution of the cellulose fibers. The composites produced using the refiner-treated pulps and the HPH-treated (one pass) CNFs had longer fibers than those

![X-ray diffraction patterns of the cellulose fibers.](image)

Table 1 Dewatering times of cellulose fiber–water slurries and crystallinities of the cellulose fibers

| Cellulose fiber                        | Dewatering time (s) | Crystallinity (%) |
|----------------------------------------|---------------------|-------------------|
| Pulps without pre-fibrillation         | 6                   | 75.1              |
| Refiner-treated pulps                  | 40                  | 76.2              |
| HPH-treated (1 pass) CNFs              | 318                 | 76.9              |
| HPH-treated (3 passes) CNFs            | 636                 | 74.7              |
| HPH-treated (10 passes) CNFs           | 1644                | 78.4              |

Fig. 6 X-ray diffraction patterns of the cellulose fibers. The peak intensity of X-ray diffraction from the (200) planes was used to calculate the degree of crystallinity according to the method described by Segal et al. (1959)
produced using the HPH-treated (three passes and ten passes) CNFs. It should be noted that the composites produced using the pulps that had not been pre-fibrillated had long fibers—i.e., the lengths of all the measured fibers were greater than 0.15 mm—although the results are not shown in the figure.

Table 3 summarizes the relationships between the pre-fibrillated pulps and the morphologies and properties of the composites. When the pulps that had
not been pre-fibrillated were fed into the twin-screw extruder, they were not nanofibrillated during melt compounding, and the resulting composites had a low tensile modulus, a low strength, and a high coefficient of thermal expansion. In contrast, when the pulps were pre-fibrillated using the refiner, only their surfaces were fibrillated without sacrificing their internal structures. The surface-fibrillated pulps were nanofibrillated during melt compounding; the CNFs retained high aspect ratios (i.e., the ratio of length to width) and were uniformly dispersed in the HDPE matrix. The composites had much better properties—i.e., much higher tensile modulus and strength values, and much lower coefficient of thermal expansion values—than the composites produced using pulps that had not been pre-fibrillated. The one-pass HPH treatment of the refiner-treated pulps changed the surface-fibrillated pulps into CNFs. Nevertheless,
when the HPH-treated (one pass) CNFs were used as feed materials for melt compounding, the composites had similar morphologies and properties to the composites produced using the surface-fibrillated pulps (i.e., the refiner-treated pulps). Further HPH treatment (i.e., more passages through the HPH) produced finer CNFs. However, the finer CNFs were shortened and agglomerated during melt compounding, and therefore adversely affected the properties of the composites.

The results suggest that surface-fibrillated pulps are suitable feed materials for melt compounding, and CNF is not a necessary form. This finding suggests that a preliminary step to prepare CNFs from pulps is not required. It should be noted that the production of CNFs from pulps using a HPH, a grinder, and a bead mill (Iwamoto et al. 2007; Ho et al. 2015) is time-consuming and energy-intensive. Furthermore, the excessive use (i.e., multiple passes) of the HPH adversely affected the properties of the composites owing to the agglomeration of fine CNFs during melt compounding. The excessive use of the HPH also reduced the lengths of the CNFs. It is speculated that the shorter CNFs were more mobile and agglomerated more readily during melt compounding.

The agglomeration of the fine CNFs indicates that when fine CNFs are used as a feed material, the properties of the composites can be improved by mitigating the agglomeration. Melt compounding facilitates the dispersion and distribution of the CNFs in the polymer matrix by mixing them with the molten polymer. However, when the CNFs—including chemically modified CNFs—have low affinity for a polymer matrix such as HDPE, the mixing action facilitates the separation of the CNFs from the polymer matrix (i.e., agglomeration of the CNFs) rather than dispersion and distribution in the matrix. Furthermore, when fine CNFs—such as HPH-treated (three passes and ten passes) CNFs—are mixed with a molten polymer, the mixing action promotes the breakage of the fine CNFs, thereby encouraging their agglomeration. Consequently, when fine CNFs are used as a feed material, their agglomeration during melt compounding may be prevented by (1) further improving the affinity between the fine CNFs and the HDPE and/or by (2) avoiding breakage of the fine CNFs during melt compounding. Further research is needed to solve the problem of the agglomeration of fine CNFs.
Dried, ASA-treated cellulose fibers of various sizes ranging from surface-fibrillated pulps (20 μm in width) to fine CNFs (20 nm in width) were used as feed materials for melt compounding in the dry pulp direct kneading method to fabricate CNF-reinforced HDPE. The study demonstrated that pre-fibrillation of the pulps had a significant impact on the morphologies and properties of the composites. Unexpectedly, the form of cellulose fibers that was most suitable for melt compounding in the dry pulp direct kneading method was the surface-fibrillated pulp, which can be produced cost-effectively on an industrial scale using a refiner, rather than the CNFs. This finding enables the elimination of a preliminary step in the preparation of CNFs from pulps using a time-consuming and energy-intensive process with a HPH, a grinder, and a bead mill. The study also indicates that when fine CNFs are used as a feed material, the properties of

Fig. 11 Length frequency distribution of alkenyl succinic anhydride (ASA)-treated cellulose fibers in composites produced using: a refiner-treated pulps, b high-pressure homogenizer (HPH)-treated (one pass) cellulose nanofibers (CNFs), c HPH-treated (three passes) CNFs, and d HPH-treated (ten passes) CNFs

Conclusions
the resulting composites can be improved by mitigating agglomeration of the fine CNFs. Furthermore, the agglomeration of the fine CNFs during melt compounding may be prevented by (1) further improving the affinity between the fine CNFs and the HDPE and/or by (2) avoiding breakage of the fine CNFs during melt compounding.

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Code availability Not applicable.

Declarations

Conflict of interest The authors have no conflicts of interest to declare.

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Table 3 Summary of pre-fibrillation of the pulps, morphologies of the composites, and properties of the composites

| Process for pre-fibrillation | Form of ASA-treated cellulose fiber before melt-compounding | Form of ASA-treated cellulose fiber after melt-compounding | Length and dispersion of fibers in composites | Ranking of properties of composites* |
|-----------------------------|------------------------------------------------------------|------------------------------------------------------------|---------------------------------------------|-------------------------------------|
| None                        | Pulp                                                      | Pulp                                                      | - Long fibers                              | 5                                   |
| Refiner                     | Surface-fibrillated pulp                                  | CNF (major) and CMF (minor)                                | - Uniform dispersion                       | 1                                   |
| Refiner and HPH (1 pass)    | Surface-fibrillated pulp and CNF                          | CNF (major) and CMF (minor)                                | - Long fibers                              | 1                                   |
| Refiner and HPH (3 passes)  | CNF (major) and CMF (minor)                               | CNF (major) and CMF (minor)                                | - Short fibers                             | 3                                   |
| Refiner and HPH (10 passes) | Fine CNF                                                  | Fine CNF                                                  | - Short fibers                             | 4                                   |

* The properties were tensile modulus, tensile strength, and coefficient of thermal expansion (CTE)
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