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Drying Cellulose Nanofibrils: Morphology Characterization

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Abstract

Increasing research activity on cellulose nanofibril-based materials provides great opportunities for novel, scalable manufacturing approaches. Cellulose nanofibrils (CNFs) are typically processed as aqueous suspensions because of their hydrophilic nature. One of the major manufacturing challenges is to obtain dry CNFs while maintaining their nano-scale dimensions. Five methods were examined to dry cellulose nanocrystal (CNC) and nanofibrillated cellulose (NFC) suspensions: (1) oven drying, (2) air drying, (3) freeze drying (FD), (4) critical-point drying (CPD), and (5) spray-drying (SD). Morphologies of the dried CNFs were studied using scanning electron microscopy (SEM). Oven drying and air drying were deemed to be not suitable for obtaining nano-scale cellulose fibrils. Critical-point drying was found to preserve the nano-scale of the CNFs. Freeze drying formed ribbon-like structures of the CNFs. Spray-drying was found to provide a potentially scalable manufacturing process to preserve the nano-scale size of the cellulose fibrils. From the point view of obtaining a dry form of CNFs for manufacturing nanocomposites, spray-drying is proposed as a method to dry aqueous CNF suspensions.
Keywords: cellulose nanofibril, drying, freeze drying, critical-point drying, spray-drying

Introduction

The application of cellulosic nanofibrils (CNFs) as a reinforcing phase in composites has gained increasing attention (Siro and Plackett 2010, Siqueira et al. 2010, Klemm et al. 2011, Moon et al. 2011). With the size decrease from bulk wood cells to nanofibrils, the elastic modulus of cellulose is reported to increase from about 10 GPa to 70 GPa (Jeronimidis 1980), which would result in significant mechanical property improvement for cellulose nanofibril-reinforced polymer composites. Besides, biodegradability, low density, worldwide availability, low price and modifiable surface properties provide potential opportunities to develop a new generation of composites based on natural fibers. However, compared with conventional reinforcements of glass fibers or inorganic fillers, CNFs are not currently used in industrial practice, especially in the field of extrusion or similar thermal melting processes. During thermal melting processes, water is not tolerated. CNFs are typically produced as aqueous suspensions because of their hydrophilic nature. Therefore, drying of aqueous suspensions of CNFs and understanding the drying process are necessary to use them in developing polymer composites.

The objective of the present study is to investigate the effect of different drying methods on the material properties of dried CNF and to find a suitable method to obtain a scalable manufacturing method to produce commercially viable amounts of CNFs. Different CNF suspensions were studied including nanofibrillated cellulose (NFC) suspensions and cellulose nanocrystal (CNC) suspensions. Each suspension was dried using five methods: (1) air drying, (2) oven drying, (3) freeze drying, (4) critical-point drying, and (5) a novel spray-drying method. The morphologies and size of the dried products were examined using scanning electron microscopy (SEM).

Experimental

Suspension preparations: Two CNF suspensions were involved: (1) 6.49 wt. % of cellulose nanocrystal suspension (CNC) from the Forest Product Laboratory in Madison, Wisconsin, and (2) a commercial product of nanofibrillated cellulose (NFC) suspension ARBOCEL MF 40-10 in 10 wt. % from J. RETTENMAIER & SOHNE GMBH+CO.KG, Germany. Before drying, distilled water was added into the original suspensions and mixed using a Speed Mixer® for 4 minutes at 2000 rpm to obtain final weight concentrations of CNC and NFC at 2 %. The stability of diluted suspensions was examined for a period of several weeks.

Suspension drying: Air drying (AD) of the suspensions was conducted at room temperature with 65±5 % RH for 48 hours by settling the suspensions in plastic containers. Oven drying (OD) was performed at 105 °C for 24 hours in glass beakers. Prior to freeze drying (FD), CNF suspensions (about 20 ml) were frozen in vials at a temperature of -80 °C for 24 hours. Frozen suspensions were then transferred to a Virtis Freezemobile 25 SL freeze dryer, which has a condenser temperature of -80 °C and a vacuum of 11 mTorr. Lyophilization was allowed to continue for 72 hours. Critical-point drying of the prepared suspension was conducted on the

Tousimis Samdri PVT-3 Critical-Point dryer. A graded series of ethanol concentrations (50%, 75%, 95%, and 100%) was used to chemically dehydrate the samples before drying. A novel spray-drying method was conducted using Mini Spray Dryer B-290 (Buchi, Switzerland) Details of the spray drying process are the subject of a provisional patent application.

Morphology examination: Scanning electron microscopy (SEM) studies on the morphologies of dried samples were carried out using an AMR 1000 (AMRay Co.) scanning electron microscope. All samples were sputter-coated with gold before the microscopic observations were obtained. SEM images were taken at an accelerating voltage of 10 kV at various magnifications.

Results and Discussions

The morphologies of air-dried CNC and NFC are shown in Figure 1. Air drying of the two suspensions formed bulk materials with different surface roughness and fracture surfaces. In removing water from the suspensions, the distance between the cellulose nanofibrils or nanocrystals becomes smaller and the molecular contact is finally reached because of the capillary forces and diffusion forces. Under this situation, strong intermolecular hydrogen bonds were developed to form solid bulk materials. Air-dried NFC exhibits a smoother top surface (Figure 1A) than the bottom surface (Figure 1B). Settling of the prepared NFC suspensions at room temperature precipitated the large particles on the bottom, indicating that the NFC suspension is not thermally stable. Parts of the fibers in the original suspension are short in length and large in diameter (Figure 1A and B). At the same time, deposition of small scale cellulose nanofibrils was observed on the top surface while not on the bottom. The surfaces of dried CNC are much smoother than those of NFC, indicating a denser packing for CNC. This might be caused by the much smaller size of cellulose nanocrystals in the suspensions (Figure 1C and F). The morphologies of oven-dried samples are similar to the air-dried samples and are not shown in this paper.

The morphologies of freeze-dried NFC and CNC are shown in Figure 2. The dried samples from the two suspensions formed similar plate materials with different sizes (Figures 3A and D), differing from AD or OD samples. Large size in length and width is caused by the lateral agglomeration of cellulose nanofibrils or nanocrystals. This lateral fibril aggregation has been demonstrated by Hult et al. (2001). The thickness of these plate materials can reach to the sub-micrometer size range. The close-up evaluation on the surface morphologies shows that the FD samples are similar to those dried in air or the oven. For the CNC, much smoother surfaces were obtained for freeze-dried samples compared with those air or oven-dried (Figure 2F versus 1F). During the freeze drying process, the capillary forces are minimized (Lyne and Gallay 1954) and no bulk material was formed. However, the lateral agglomeration still occurred which may indicate that capillary forces are mainly responsible for the formation of bulk material in air or oven drying processes. The lateral aggregation may be driven by diffusion forces or perhaps

hydrogen bonding. This may further indicate that the cellulose nanofibrils or nanocrystals in the suspension just align laterally with many layers and each layer has different amounts of nanofibrils or nanocrystals laterally bonded together. Elazzouzi-Hafraoui et al. (2008) demonstrated that CNC consisting of several laterally parallel crystallites has the dimensions of a nanofibril. Considering the sheet structure of cellulose, the proposed weak hydrogen bonds (Nishiyama et al. 2003) or hydrophobic bonds (Jarvis 2003) between different sheets of cellulose fibrils are more easily broken than the lateral hydrogen bonds (Klemm et al. 1998).

The morphologies of critical-point dried samples from NFC suspensions are shown in Figure 3. During the dehydration CNC suspensions, water in the suspension cannot be replaced by ethanol. CPD cannot be applied to CNC suspensions and no dry form of CNC was obtained from the CPD method. The reason for the observation may be the strong three-dimensional hydrogen bonding formed between water molecules and cellulose nanocrystals. From the micrographs in Figure 3, nano-scale cellulose nanofibrils were observed. CPD is the best drying method from the point view of obtaining nano-scale CNFs. However, even using the CPD method, nanofibril aggregates were also observed during dehydration using ethanol (Thimm et al. 2000). The nanofibril size in the original suspensions may be smaller than these shown in the micrographs. In addition, these micrographs have also demonstrated that large diameter and short fibrils existed in the NFC suspension.

The morphologies of the spray-dried samples are shown in Figure 4. These micrographs show that SD of cellulose suspensions formed particles with different morphologies. The common dimensions are in micrometers. Many particles with nano-scale dimensions were also observed. Drying of the CNC suspension formed spherical particles with different sizes while drying of NFC formed irregular shaped particles. Spherical CNC material may be related to the agglomeration of small nanofibrils while the NFC particles may be partially related to the original configuration of CNFs in the suspensions.

Conclusions

The effect of various drying methods on the morphologies of CNFs was investigated for CNC and NFC by direct comparison using SEM. Different drying techniques and different sources of CNF suspensions provide different morphologies after drying. Air drying and oven drying were deemed to be not suitable for obtaining nano-scale cellulose fibrils. Critical-point drying was found to preserve the nano-scale of the CNFs. Freeze drying formed ribbon-like structures of the CNF. Spray-drying was found to provide a potentially scalable manufacturing process to obtain cellulose fibrils on the nano-scale. For obtaining nano-scale cellulose fibrils, CPD is the best technique to preserve the nano-dimensions. However, CPD is appropriate for drying small amounts of nanofibrils and may not be suitable for commercial scale-up. From the point view of obtaining a dry form of CNFs for manufacturing nanocomposites, spray-drying is proposed as a method to dry aqueous cellulose nanofibril suspensions.

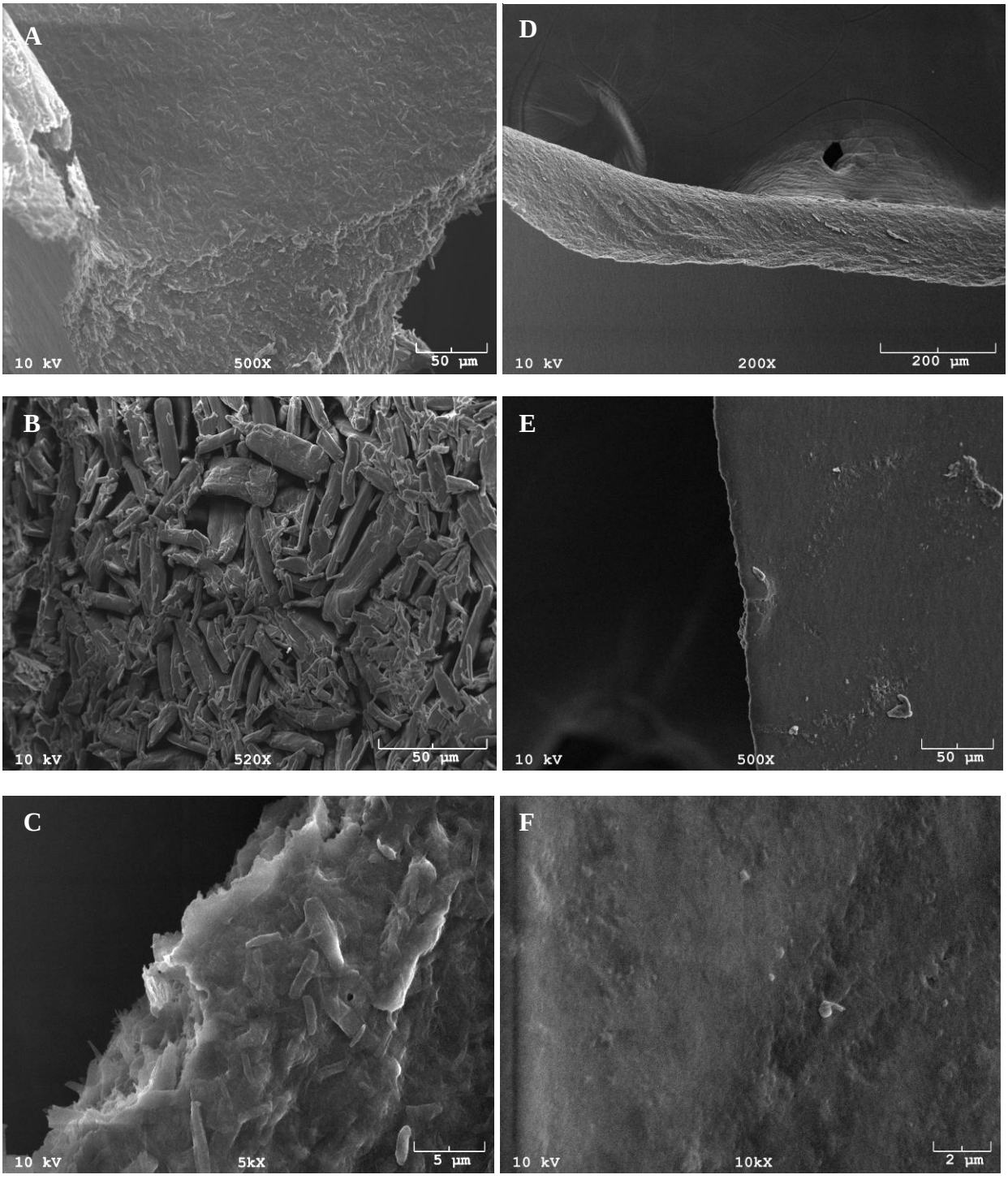

Figure 1. Morphologies of air-dried NFC: (A) (B) (C) and CNC: (D) (E) (F).

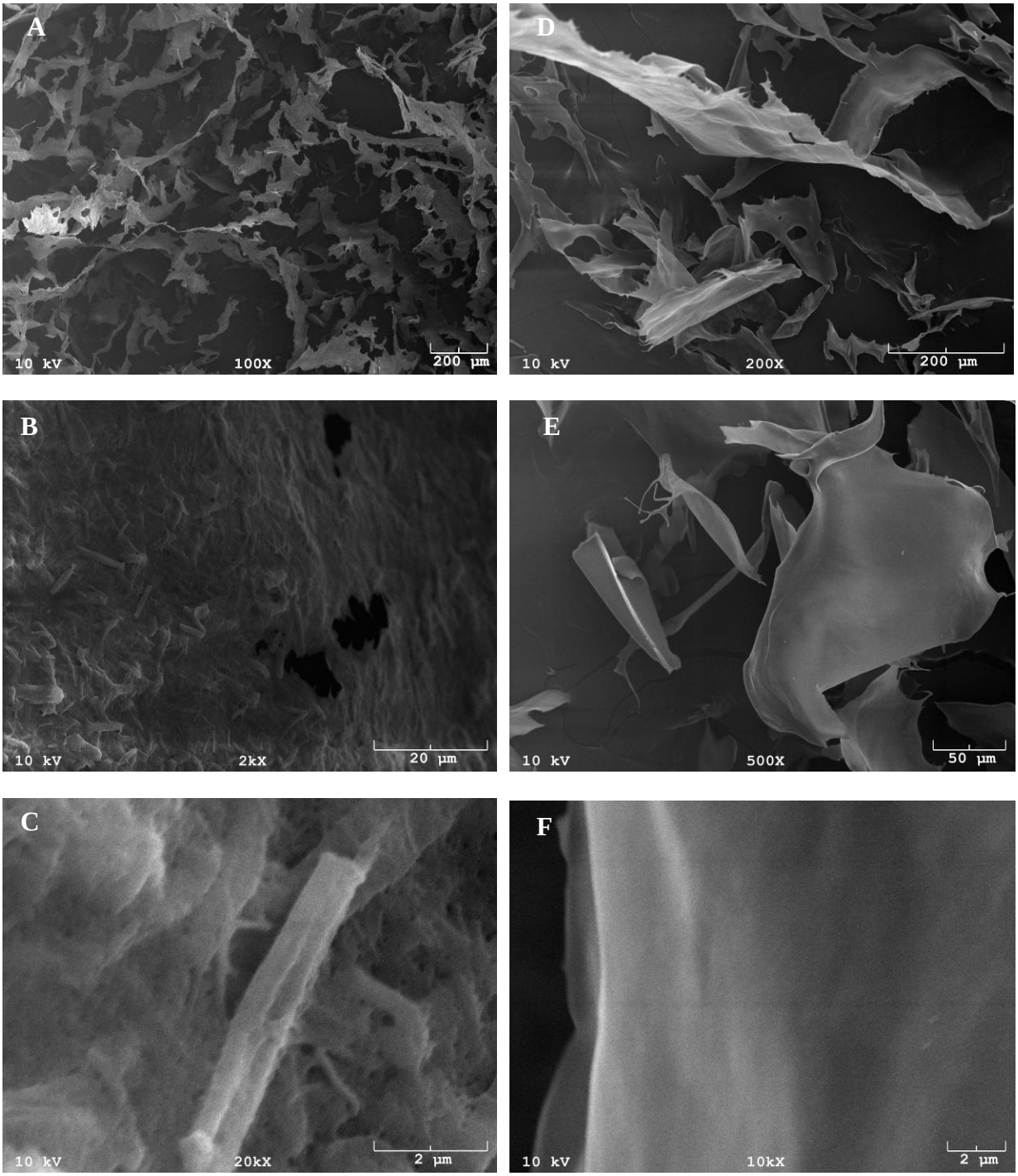

Figure 2. Morphologies of freeze dried NFC: (A)(B)(C) and CNC: (D)(E)(F).

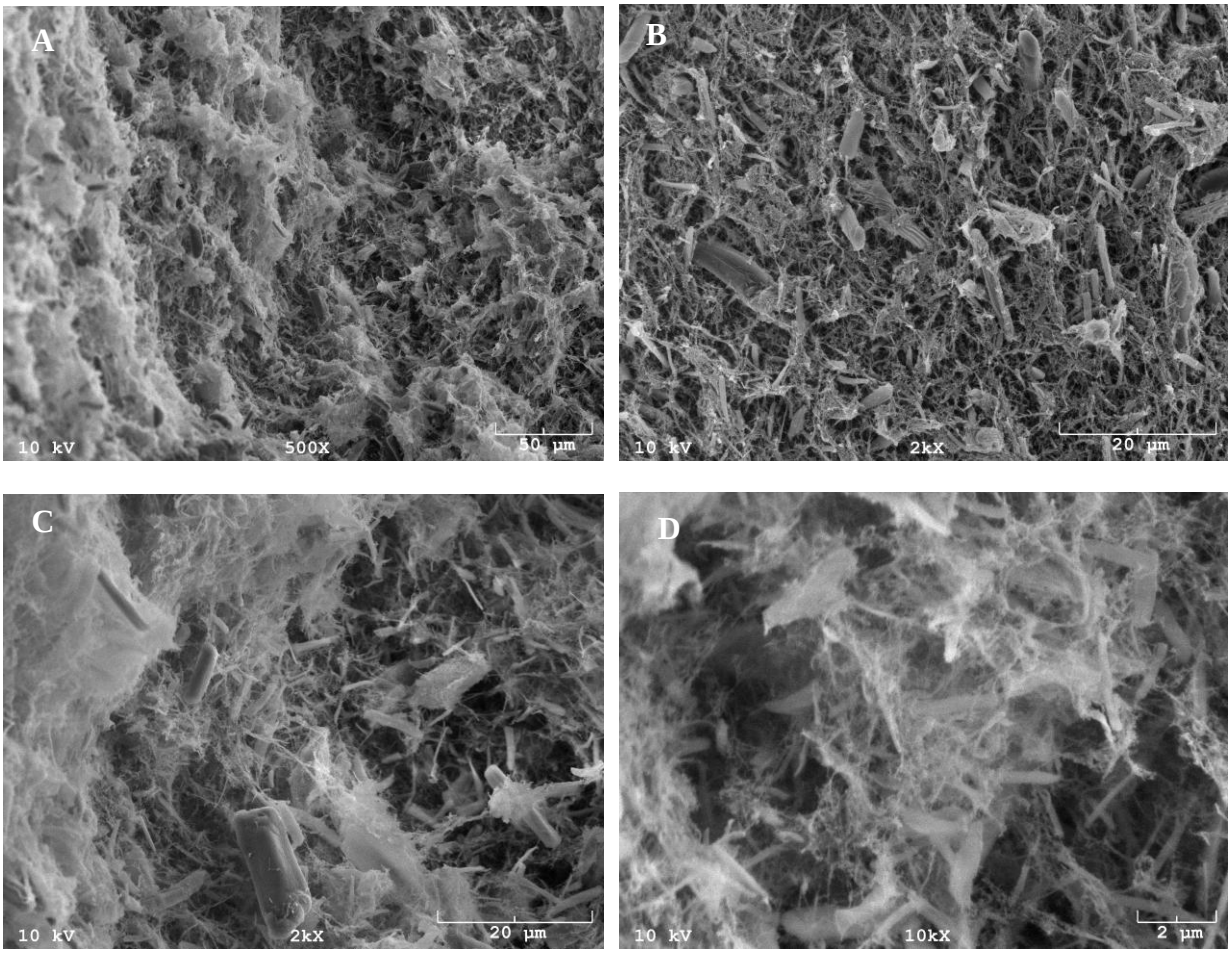

Figure 3. Morphologies of critical-point dried NFC at various magnifications: (A) (B) (C) (D).

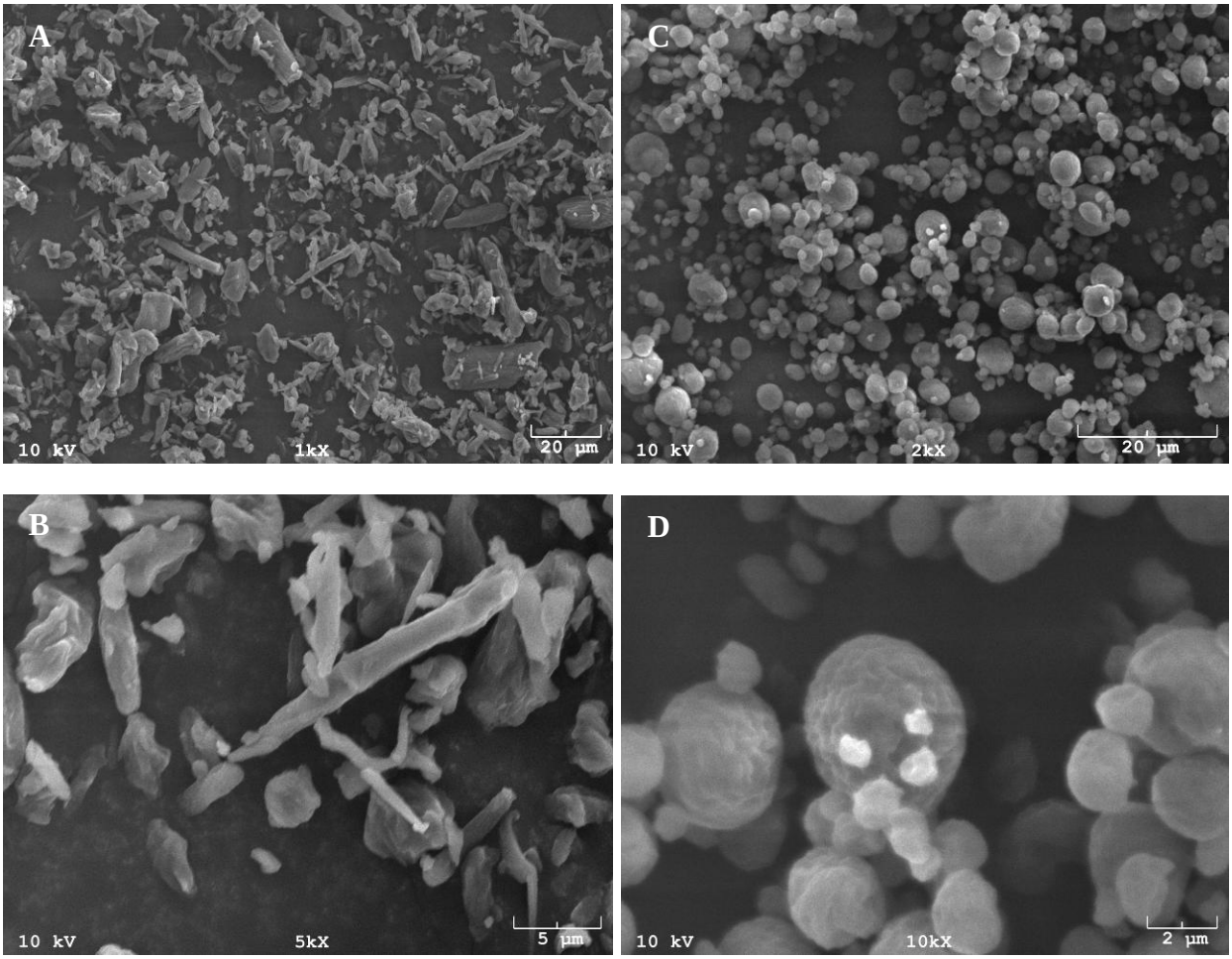

Figure 4. Morphologies of a novel spray dried NFC: (A) (B) and CNC: (C) (D).

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