Defining of the microfibrillation of one-step twin-screw-extruded cellulose fibers by its rheological properties

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ABSTRACT

In this study, the pulp cellulose fibers (CF) and deep eutectic solvent treated cellulose fibers (DES-CF) were extruded by using one-step twin-screw extrusion (TSE) process. The DES-CF (with solid content of 40 wt% before extrusion) was successfully microfibrillated only by one-step extrusion. Unlike, the CF showed partial fibrillation with the same operating process. The width of fibers was measured with different methods such as FE-SEM and fractional test and the width reduction were observed from 25 µm ≤ (before extrusion) to 300 nm ≥ (after extrusion) for the DES-CF.

The main goal of this work was to investigate the microfibrillation of fibers with use of rheometry. The rheological properties of the extruded DES-CF confirmed better fibrillation in comparison with extruded CF and the rheological data are also in agreement with FE-SEM and fractional test.

INTRODUCTION

Microfibrillated cellulose as a bio-based material is into the spotlight due to their great features such as physical, chemical Foster et al.[1], mechanical Bledzki and Gassan[2] and optical properties Simão et al.[3] and also due to the availability of raw sources such as wood, wood pulps and rejected or side-products of industry Siqueira et al.[4] In this regard, there is a high propensity to increase the proportion of the renewable resources in fiber-polymer matrix biocomposites and ultimately to study the rheological and morphological features of these materials for further processing.

Microfibrillated cellulose or cellulose nanofibers (CNF) are produced by different methods such as super grinding Iwamoto et al.[5] microfluidization Taheri and Samyn[6] and recently with use of twin-screw extrusion (TSE) process Hietala et al.[7] The TSE process is on the spotlight in comparison with other methods because of the lower energy consumption and the higher solid content of feeding material. The one-step microfibrillation of cellulose fiber within TSE can be feasible only with the proper extrusion profile; otherwise the cellulose fiber might be fibrillated with increasing of the number of the passes, which is being caused of the fiber degradation Ho et al.[8]

As some of the characterization method such as FE-SEM and fractional test are done in small scale and dilute concentration, the related observation should be confirmed with another method like rheometry in a bulk scale.

This work was examined to understand if the rheological properties of extruded CF and DES-CF show any fingerprint of fibrillation in a steady state flow measurement. As the fibrillation fingerprint (shear versus viscosity plateau) for other processing methods e.g., microfluidization has been reported Taheri and Samyn[6], this work can provide useful information next to other methods such as FE-SEM and fractional test to define the fibrillation of extruded cellulose fibers.

MATERIALS AND METHOD

Materials and preparation

The never dried soft wood dissolving pulp (Domsjö Fabriker, Örnsköldsvik, Sweden) with chemical composition of 3.5 wt% hemicellulose, 0.4 wt% lignin and 0.5 wt% inorganics (TAPPI-T 222 standard) was used as CF in this work. The CF smoothly dried till the solid content of the CF reaching around 40 wt% before extrusion process.

The CF was also treated with use of Potassium carbonate (Honeywell, Seelze, Germany) with MW: 138.21 g/mol as a hydrogen bond donor and Glycerol (VWR chemicals, Leuven, Belgium) with MW: 92.09 as a hydrogen bond acceptor. The treatment was done with molar ratio of 1:5 and consistency of 3%. The treatment was done within 18 hours at 100 ºC and the treated fibers washed and vacuum-filtered several times. The solid content of the DES-CF was controlled to be around 40 wt% before extrusion process.

Twin-screw extrusion

The CF and DES-CF samples with solid content around 40 wt% were extruded using a twin-screw extruder (ZSK-18 MEGALab, Coperion W&P, Germany) with screw speed 200 rpm. The processing temperature set to 90 °C for all zones and set 110 °C at the die. Different extrusion elements such as short conveying, regular conveying, Kneading and tooth mixing were used for processing Hietala and Oksman[9] of CF and DES-CF within extrusion. After extrusion, the solid content of the CF and DES-CF increased >95 wt%. The extruded materials were collected for further FE-SEM, fractional test and rheological characterizations.

CHARACTERIZATION

Morphology

The morphology of the CF and DES-CF was observed with use of Metso fractionator Laitinen and Niinimäki[10] (Valmet Automation Oy, Kajaani, Finland) equipped with IMG image analyzer software (Valmet Automation Oy, Kajaani, Finland) and Field emission scanning electron microscope (FE-SEM) (ZEISS ULTRA plus FE-SEM, Carl Zeiss AG, Oberkochen, Germany). For both fractional and FE-SEM observation the diluted samples with solid content of 0.3 and 0.01 wt% were prepared, respectively. For FE-SEM a dilute samples were vacuum filtered with use of membrane with particle retention of 0.2 µm (Whatman, UK).

Rheology

The rheological measurement of CF and DES-CF suspensions was done via Discovery HR-1 Hybride TA Instrument (New Castle, DE, USA) in the gap of 1.5 mm by bob and cup accessories and with the diameter of 27.97 mm and 30.35 mm, respectively. The steady state shear versus viscosity tests were done to investigate rheological properties of bulk CF and DES-CF suspensions with total concentration of 2.5 wt% at 25 °C. The rotational measurements were done under ascending and descending controlled shear rate of 30 minutes (15 minutes for ramping-up and 15 minutes for ramping-down) to show the suspension stability at shear rates interval of 0.1 to 1000 s^{-1}.

RESULTS AND DISCUSSION

Fractionation of the fibers

The fractional test was done for original CF (before extrusion), CF (after extrusion) and DES-CF (after extrusion) to compare the width changes of the samples.

The fractional test was reported in 5 different fractions, which the largest fibers classified in the first fraction and the smallest fibers classified in the fifth fraction. Table 1 shows the largest fibers (21-27 µm) were existed for non-extruded CF and the width of fibers smoothly reduced for extruded CF and vividly decreased for DES-CF. The second fraction (13-21 µm) confirmed that with only one-step extrusion process the amount of large fibers decreased for DES-CF and the fibrillation are showed up in the third (13-8 µm) and the fourth (5-8 µm) fractions. The fractional data indicated that the one-step TSE resulted in more fibrillation for DES-CF sample and ultimately increment of smallest fibers in the fifth (4-5 µm) fraction.

Table 1. Fractional test of CF (before extrusion), CF and DES-CF (after extrusion). "F" represents fraction and the "digit" represents 1-5 different fractions.

Samples	F1 (%) 21-27 µm	F2 (%) 13-21µm	F3 (%) 8-13 µm	F4 (%) 5-8 µm	F5 (%) 4-5 µm
Non-extruded CF	70.33	12.72	11.27	3.86	1.81
Extruded CF	33.60	26.94	25.11	11.97	2.3
Extruded DES-CF	2.11	7.77	48.97	35.00	6.13

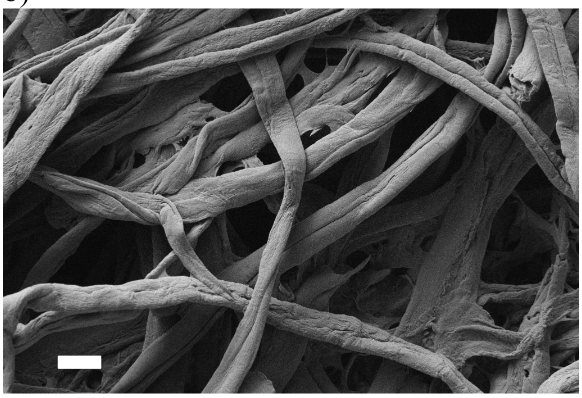
<u>Microstructure of the fibers</u>

As the microstructures of the fibers cannot be tracked with use of fractional test, the FE-SEM was done to observe the fibrillation and the width changes of the CF (before extrusion), CF and DES-CF (after extrusion).

Fig. 1 depicts the FE-SEM micrographs of non-extruded CF, extruded CF and extruded DES-CF. The FE-SEM of non-extruded CF (Fig. 1a) was in agreement with fractional data and confirmed the existence of the large fibers. However, the FE-SEM of extruded CF (Fig. 2b) showed some width reduction. According to the Fig. 1c, the vivid fibrillation was observed for the extruded DES-CF and the FE-SEM micrographs are in agreement with fractional test.

a)

b)



c)

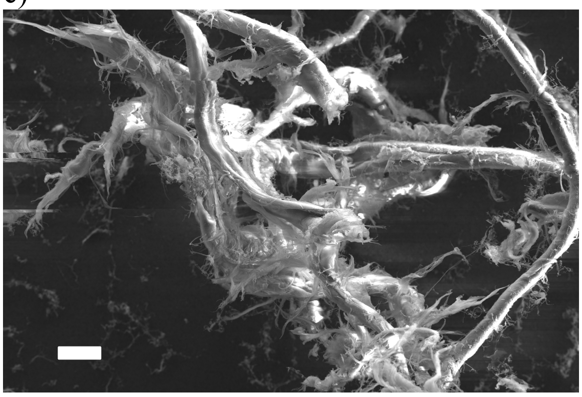


Figure 1. The FE-SEM images of a) non-extruded CF, b) extruded CF and c) extruded DES-CF. All scale-bars are 20 µm.

Flow behaviour of the fibers

The rheological properties of the fiber suspension can reveal the fibrillation fingerprints of the disintegrated cellulose fibers and can be used as a suitable complementary data (next to other methods e.g., FE-SEM and fractional test). The FE-SEM and fractional test are used either with small amount of the materials or with low concentration. Unlike, the rheological measurements are provided with the large amount of the materials and the flow properties and morphological changes can be firmly reflected the behaviour of the bulk sample and resulting in more reliable interpretation.

The rheological behaviour of the extruded CF and DES-CF in form of water suspension (2.5 wt%) were done to elucidate how the flow properties of the extruded material changed within the shear interval. Fig. 2 represents the shear rate versus viscosity of extruded CF and DES-CF. The extruded DES-CF showed greater ramp up/down viscosity in comparison with extruded CF at very low shear rate. The linear region of extruded DES-CF between 0.1 to 10 s^{-1} also showed the greater yield stress in comparison with extruded CF.

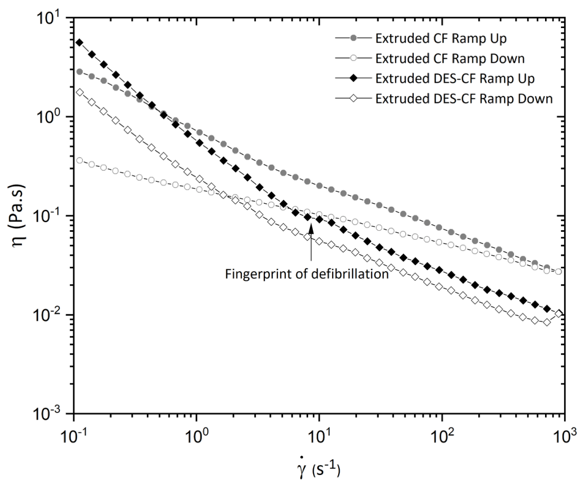


Figure 2. Shear rate versus viscosity plots of extruded CF and DES-CF. The solid symbols are from ascending shear rate and the open symbols are from descending shear rate.

The hysteresis between ramp up and ramp down shear versus viscosity test can be interpreted for two-phase materials. The treated sample (DES-CF) showed smaller hysteresis, which can be related to better uniformity in comparison with untreated sample.

In general, the plateau of steady state rheometry test at intermediate shear rate is related to the defibrillation of cellulose materials Karppinen et al.[11] The flow property of DES-CF showed strong shear thinning behaviour and the clear fingerprint of fibrillation of bulk material. The plateau might be related to the fiber networks and packing of small and large fibers.

CONCLUSIONS

The fibrillation of one-step extruded CF and DES-CF was studied by using the fractional test, FE-SEM and rheometry. The fractional data confirmed the fibrillation was greater for DES-CF sample. The FE-SEM observation was also in agreement of fractional data. The rheological properties of DES-CF confirmed that the fibrillation, which was observed via FE-SEM are not local and can be valid for the bulk medium. The DES-CF showed the less hysteresis in comparison with CF sample; confirming more uniformity of treated sample (DES-CF).

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