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Physical and Mechanical Properties of Cellulose Nanofibril Films from Bleached Eucalyptus Pulp by Endoglucanase Treatment and Microfluidization

Wangxia Wang[1,2] · Ronald C. Sabo[2] · Michael D. Mozuch[2] · Phil Kersten[2] · J. Y. Zhu[2] · Yongcan Jin[1]

Abstract A GH5 hyperthermostable endoglucanase (Ph-GH5) from the archaeon *Pyrococcus horikoshii* and a commercial endoglucanase (FR) were used to treat bleached eucalyptus pulp (BEP) fibers to produce cellulose nanofibrils (CNF) and subsequently to CNF films. TEM imaging indicated that Ph-GH5 produced longer and more entangled CNF than FR with the same number of microfluidization passes. Physical and mechanical properties of CNF films were characterized. Optical opacity of CNF films from FR (10 mg/g) at 40 passes through the microfluidizer can be as low as 3.7 %, compared with 18.2 % from untreated BEP at the same number of passes. CNF films exhibited similar thermal stability with untreated BEP. Highest specific modulus of CNF films was also obtained from FR (10 mg/g), reaching 56 MNm/kg, approximately 271 % of the CNF films from untreated BEP at 40 passes through the microfluidizer. CNF film from Ph-GH5 (1 mg/g) at 40 passes provided the highest specific maximum tensile strength at 120 kNm/kg.

Keywords Endoglucanase treatment · Microfluidization · Cellulose nanofibrils (CNF) · CNF films · Eucalyptus pulp

✉ Phil Kersten
pkersten@fs.fed.us

✉ J. Y. Zhu
jzhu@fs.fed.us

[1] Jiangsu Provincial Key Lab of Pulp and Paper Science and Technology, Nanjing Forestry University, Nanjing 210037, China

[2] USDA Forest Service, Forest Products Laboratory, Madison, WI 53726, USA

Introduction

Cellulose, a linear polysaccharide of 1, 4 linked β-D-glucose, is the main reinforcing constituent in plant cell walls [1, 2]. Cellulose aggregates regularly along the chain, resulting in inter and intra-molecular hydrogen bonds and hydrophobic interactions, and forms fibrous structures called microfibrils or elemental fibrils [3]. The elemental fibrils or microfibrils have been reported to have remarkable mechanical properties with an elastic modulus measured to be about 150 GPa [4]. Such impressive mechanical properties provide a wide range of potential applications, which attract many researches to seek an economical and environmental-friendly approach to prepare it.

Cellulose nanofibrils (CNF), an obtainable form of elemental fibrils or microfibrils isolated from cell walls, can be used in nanocomposites, coating additives, food packaging and gas barriers because of its low thermal expansion, good mechanical and optical properties [5, 6]. Enzymatic pretreatments enable the production of CNF with significantly reduced energy consumption and facilitate disintegration of cellulosic wood fibers into CNF [7, 8]. Moreover, the CNF produced from enzymatically pretreated cellulosic wood fibers showed a more favorable structure than those produced by acid hydrolysis. Fibers subjected to a very low enzyme concentration (0.02 %) were successfully disintegrated while molecular weight and fiber length were well preserved [8]. Our previous study [9] reported CNF production from bleached eucalyptus fibers by endoglucanase pretreatment and subsequent microfluidization based on Henriksson's concept [8]. The results show that enzymatic pretreatment can facilitate nanofibrillation and reduce energy consumption. Energy cost is the major concern for commercial utilization of

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mechanical CNF [10, 11]. The GH5 hyperthermostable endoglucanase (Ph-GH5), a laboratory pure endoglcanase, can produce longer and entangled CNF, while the commercial endoglucanase (FR) that contains non-protein compounds produced shorter and more uniform CNF. According to the reports [12, 13], the mechanical property of CNF products was highly related to the nanofibrillar network. However, the physical and mechanical properties of CNF from different cellulases and loadings are barely compared.

In the present study, the produced CNF by endoglucanase pretreatment and microfluidization [9] were used for making cellulose nanofibril films. Physical and mechanical properties were studied for better understanding the nanofibrillar network from different pretreated CNF.

Materials and Methods

Materials

Two types of CNF were prepared from a bleached kraft eucalyptus pulp (BEP, Fibria, Aracruz, Brazil) according to the method previously reported [9]. The pulp was first subjected to endoglucanase pretreatment with enzyme loadings of 10, 1, 0.1, 0.01 mg protein/g fiber (abbreviated as mg/g in the following discussion). Pretreatment was conducted at a solid loading of 5 % (w/v) and buffered at pH 5.0 and 70 °C using a lab endoglucanase Ph-GH5 and 50 °C using a commercial endoglucanase FR. The pretreated fibers were mechanically disintegrated using a microfluidizer (M-110EH, Microfludics Corp., Westwood, MA). A CNF water suspension with concentration of 0.3 wt% was obtained. The procedure of CNF production was shown in Fig. 1.

Preparation of CNF Films

CNF films were prepared by pressure filtration of 2 g CNF from 0.3 wt% suspension. Prior to filtration, the suspension was stirred for 12 h to ensure well dispersed nanofibrils. All films were filtrated at room temperature under air pressure of 50 psi in a Hazardous Waste Filtration (YT30142HW, Millipore Corporation, USA) with a stainless steel cylinder of 142 mm in diameter. The filtration Membrane (JVWP14225, Millipore Corporation, USA) had a reported pore size of 0.1 μm supported by filter paper (P2, Fisher Scientific, USA). After filtration, the wet film was stacked between wax-coated papers. The assembly was then sandwiched between two steel plates, and a 23 kg weight was place on the plates to minimize deformation (changed wax-coated paper frequently) at room temperature for 24 h [14]. When the film reached about 80–90 % solids content, it was then put into an oven at 60 °C for 24 h pressed by 23 kg weight. The labels of CNF films were listed in Table 1.

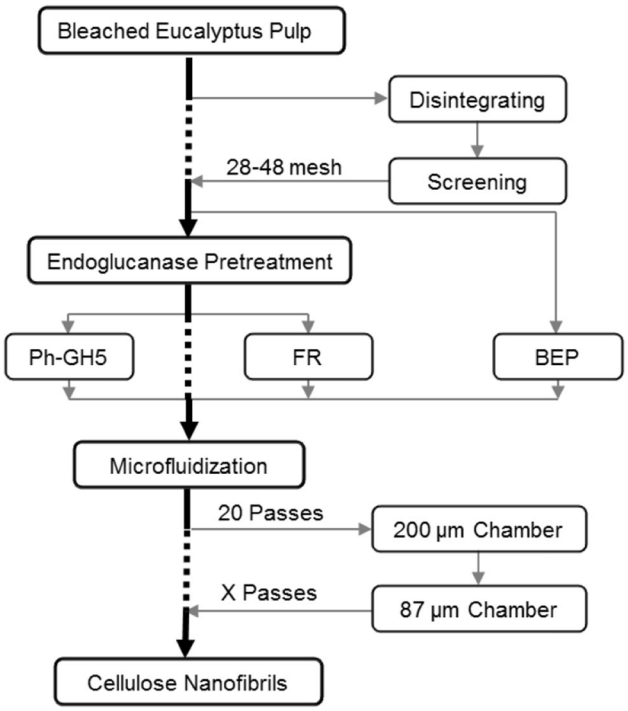

Fig. 1 Production of cellulose nanofibrils (CNF). (Ph-GH5: GH5 hyperthermostable endoglucanase from *Pyrococcus horikoshii*; FR: commercial endoglucanase)

Determination of Degree of Polymerization

The degree of polymerization (DP) of the CNF was measured according to TAPPI Standard Test Method T230 om-08 [15]. Vacuum dried cellulosic solids of 0.1 g was first dispersed with 10 mL distilled water, and then added 10 mL of 1 M cupriethylenediamine solution. The viscosity of the resultant solution was determined with a capillary viscometer. The DP of the cellulose was calculated using the following expression [16]: $DP^{0.905} = 0.75$ [954 log$X$ − 325], where X is the measured viscosity.

Transmission Electron Microscopy

Specimens for transmission electron microscopy (TEM) were diluted and sonicated to disperse the particles. TEM grids (ultrathin carbon films supported by fenestrated carbon films) were floated on drops of approximately 5 μL sample for 1–2 min. They were then swished through two consecutive 250 μL drops of 2 % aqueous uranyl acetate. Excess stain was removed by capillary action and gentle blotting resulted in negatively stained particles. The

Table 1 Labels of CNF films

Label	Endoglucanase pretreatment	Microfluidization
BEP-40	Untreated BEP	X = 20 passes*
BEP-50	Untreated BEP	X = 30 passes*
Ph-GH5-10-40	Ph-GH5 pretreated BEP at 10 mg/g enzyme loading	X = 20 passes*
Ph-GH5-1-40	Ph-GH5 pretreated BEP at 1 mg/g enzyme loading	X = 20 passes*
FR-10-40	FR pretreated BEP at 10 mg/g enzyme loading	X = 20 passes*
FR-1-30	FR pretreated BEP at 1 mg/g enzyme loading	X = 10 passes*
FR-1-40	FR pretreated BEP at 1 mg/g enzyme loading	X = 20 passes*
FR-0.1-30	FR pretreated BEP at 0.1 mg/g enzyme loading	X = 10 passes*
FR-0.1-40	FR pretreated BEP at 0.1 mg/g enzyme loading	X = 20 passes*
FR-0.01-30	FR pretreated BEP at 0.01 mg/g enzyme loading	X = 10 passes*
FR-0.01-40	FR pretreated BEP at 0.01 mg/g enzyme loading	X = 20 passes*

* All samples first passed 20 times through 200 μm chamber, and then passed an additional X times through 87 μm chamber

samples were imaged using a Philips CM100 transmission electron microscope (FEI Company, Portland OR) with an accelerating potential of 100 keV. Images were captured on Kodak SO-163 electron image film and later scanned into digital images using 600 dpi resolution.

Light Transmittance and Optical Opacity

The visible light transmittance of CNF (0.1 %, w/v) was measured using a UV–Vis spectrophotometer (Model 8453, Agilent Technologies, Inc., USA). Percent transmittance at 600 nm (T_{600}) was recorded. Optical opacity of the CNF films was measured by TAPPI Standard Test Method T 519 om-06 [17]. The presented optical opacity was normalized to 50 μm thickness.

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) of CNF films was carried out based on Pyris 1 TGA thermogravimetric analyzer (PerkinElmer Inc., Waltham, MA). The sample was first ground into powder and vacuum oven dried overnight at 45 °C. About 5 mg sample was evenly and loosely distributed in an open sample pan for TGA. The temperature was controlled from 50 to 700 °C with a heating rate of 10 °C/min. A high purity nitrogen stream with a rate of 20 mL/min was continuously passed into the furnace before thermal decomposition was carried out to prevent any unwanted oxidative decomposition. The TGA thermal curve was displayed as weight percent (%) versus temperature.

Tensile Test

The tensile properties of the CNF films were tested according to ASTM D638-10 [18]. The specimens were cut to conform to ASTM D638-10 type V dog bone shape using a special die (Qualitest, FL, USA) and were subsequently conditioned at 50 % RH and 23 °C for at least 1 week prior to testing in a room, which was also conditioned at 50 % RH and 23 °C. The tests were performed on an Instron Model 5566 equipped with a 440 N load cell at a crosshead speed of 10 mm/min. Each condition has twelve specimens prepared for the test. An LX 500 laser extensometer (MTS Systems Corporation, MN, USA) was used to determine the displacement with sampling frequency of 10 Hz. The laser recorded the displacement between two strips of reflective tape initially placed approximately 8 mm apart on the necked-down region of the dog-bone specimens. Strain was calculated from the determined displacement and initial gage length. The data were fit to a hyperbolic tangent in order to extract the modulus as the initial slope of the stress–strain curve. The results for each condition are based on at least six specimens.

Results and Discussion

CNF Morphology

TEM images show endoglucanase pretreatment can facilitate disintegration efficiently [9]; CNF had more uniform nanosized diameters after pretreatment even with less passes through the microfluidizer compared with untreated samples (Fig. 2). Ph-GH5 produced longer and more entangled CNF than FR with the same number of microfluidization passes, mainly due to FR reduced DP dramatically and resulted in much shorter fibers than with Ph-GH5, even at very low loading (0.01 mg/g), as shown in Table 2. Mechanical integrity of CNF films strongly depends on CNF network [12]. The mechanical properties of CNF films were further investigated.

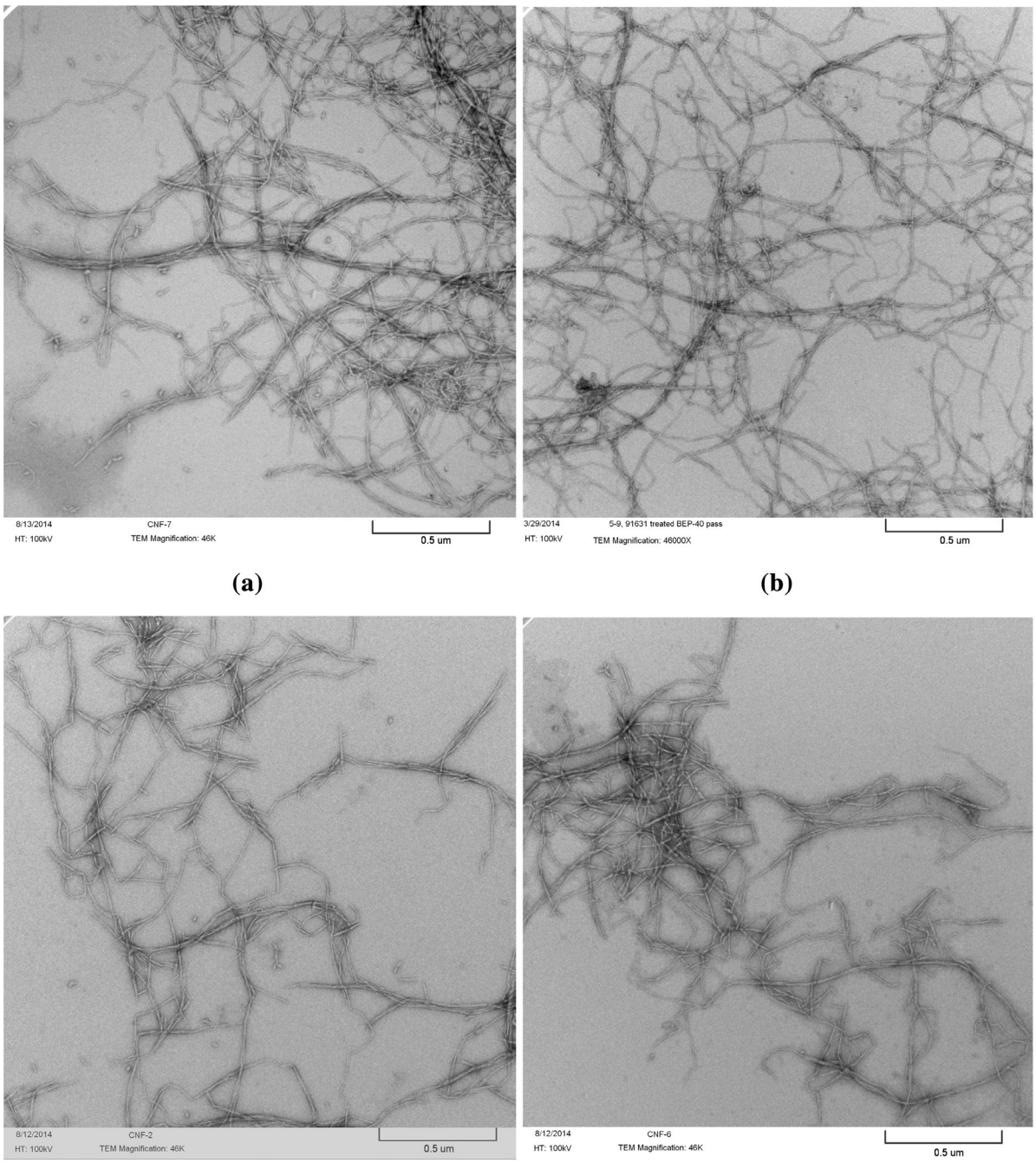

Fig. 2 TEM of cellulose nanofibrils (CNF). **a** BEP-50 pass, scale = 0.5 μm, **b** Ph-GH5 (1 mg/g)-40 pass, scale = 0.5 μm, **c** FR (0.1 mg/g)-40 pass, scale = 0.5 μm, **d** FR (0.01 mg/g)-40 pass, scale = 0.5 μm

Optical Property of CNF Films

Optical opacity of CNF films was shown in Fig. 3. All samples produced by the microfluidizer exhibited excellent optical transparency with opacity less than 20 %. Endoglucanase pretreatment and increasing the number of passes through microfluidizer can lower the optical opacity of CNF films for all conditions. The opacity data of CNF films were in good accordance with the light transmittance data of CNF. The opacity of CNF films from FR (10 mg/g) at 40 passes through the microfluidizer (represented as FR-10-40, similar sample representation convention will be used throughout the text) can be as low as 3.7 %, compared with 18.2 % from untreated BEP at the same number of

Table 2 Degrees of polymerization of BEP fibrils after different passes of microfluidization

Passes	BEP	Ph-GH5-10	Ph-GH5-1	FR-10	FR-1	FR-0.1	FR-0.01
0	1148 ± 23	857 ± 21	941 ± 4	424 ± 9	542 ± 10	639 ± 21	784 ± 19
10	1076 ± 17	627 ± 24	847 ± 22	224 ± 23	289 ± 18	464 ± 20	576 ± 13
20	1028 ± 24	475 ± 12	727 ± 29	79 ± 26	151 ± 16	319 ± 15	420 ± 11
30	644 ± 24	283 ± 25	454 ± 12	ND	ND	85 ± 24	198 ± 25
40	599 ± 17	247 ± 25	412 ± 25	ND	ND	39 ± 15	139 ± 25
50	570 ± 12						

ND not detectable

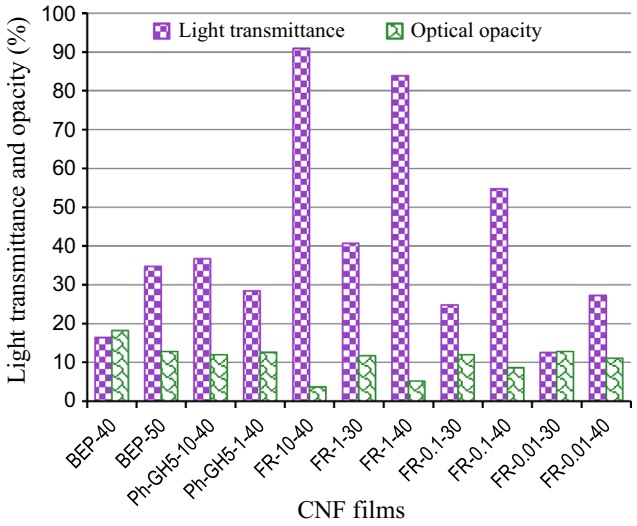

Fig. 3 Light transmittance of CNF and optical opacity of CNF films

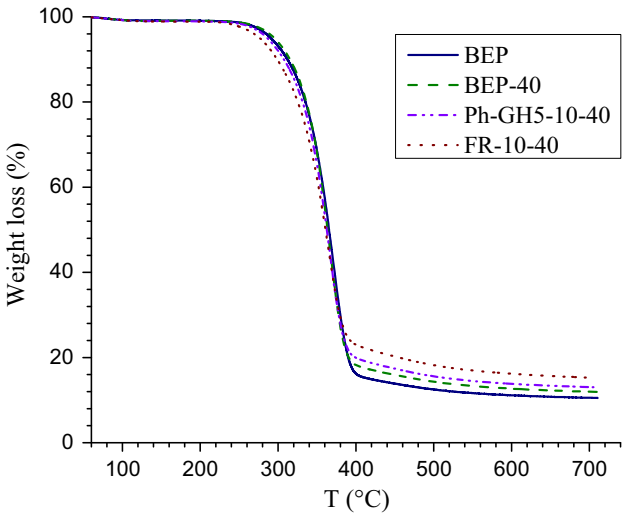

Fig. 4 TGA curves of CNF films

passes. Corresponded light transmittance of CNF was 91 versus 16.5 %. The low opacities or high transmittances of FR-10-40 and FR-1-40 were due to the relatively shorter fibrils at relatively higher commercial endoglucanase loadings [9].

Thermal Properties of CNF Films

TGA was undertaken to investigate the thermal performance of CNF films. Representative TGA curves of CNF films at a heating rate of 10 °C/min from 50 to 700 °C are shown in Fig. 4. The region I is defined as the initial mass stage portion found from 50 °C to about 240 °C. In region I, a slight mass loss below 3 % is mainly caused by the evaporation of water from CNF films. Region II is defined as the major mass loss stage starting at the temperature where the mass loss deviated from the plateau region (240–400 °C). The weight loss in this region ranges from 75 % (FR-10-40) to 82 % (BEP). This major mass loss is due to structural degradation of nanocellulose with the formation of CO_2, H_2O, CO and solid char [19, 20]. The weight loss in Region III (400–700 °C) is about 7 % by the further degradation of products from Region II.

The thermal properties of CNF films after endoglucanase pretreatment and mechanical fibrillation are barely changed compared with raw material (BEP), except small differences in total weight loss. However, chemical (TEMPO/acid) process produced nanofilms exhibited rather different thermal properties with higher thermal degradation and weight loss than untreated CNF films [20–22].

Mechanical Property of CNF Films

Tensile strength (σ) of CNF films is presented in Fig. 5a. Although there are little differences in the densities of CNF films (1400–1500 kg/m^3), specific tensile strength (σ/ρ) have also been reported to take the density (ρ) variation into account. The density of a CNF film was measured by measuring the film weight, area and thickness using a digital caliper [13]. The σ/ρ values range from 89 to 120 kNm/kg in this study, which were 2–3 times that of handsheets made of BEP with Canadian Standard Freeness (CSF) of 300 mL [23]. Mechanical properties of CNF films

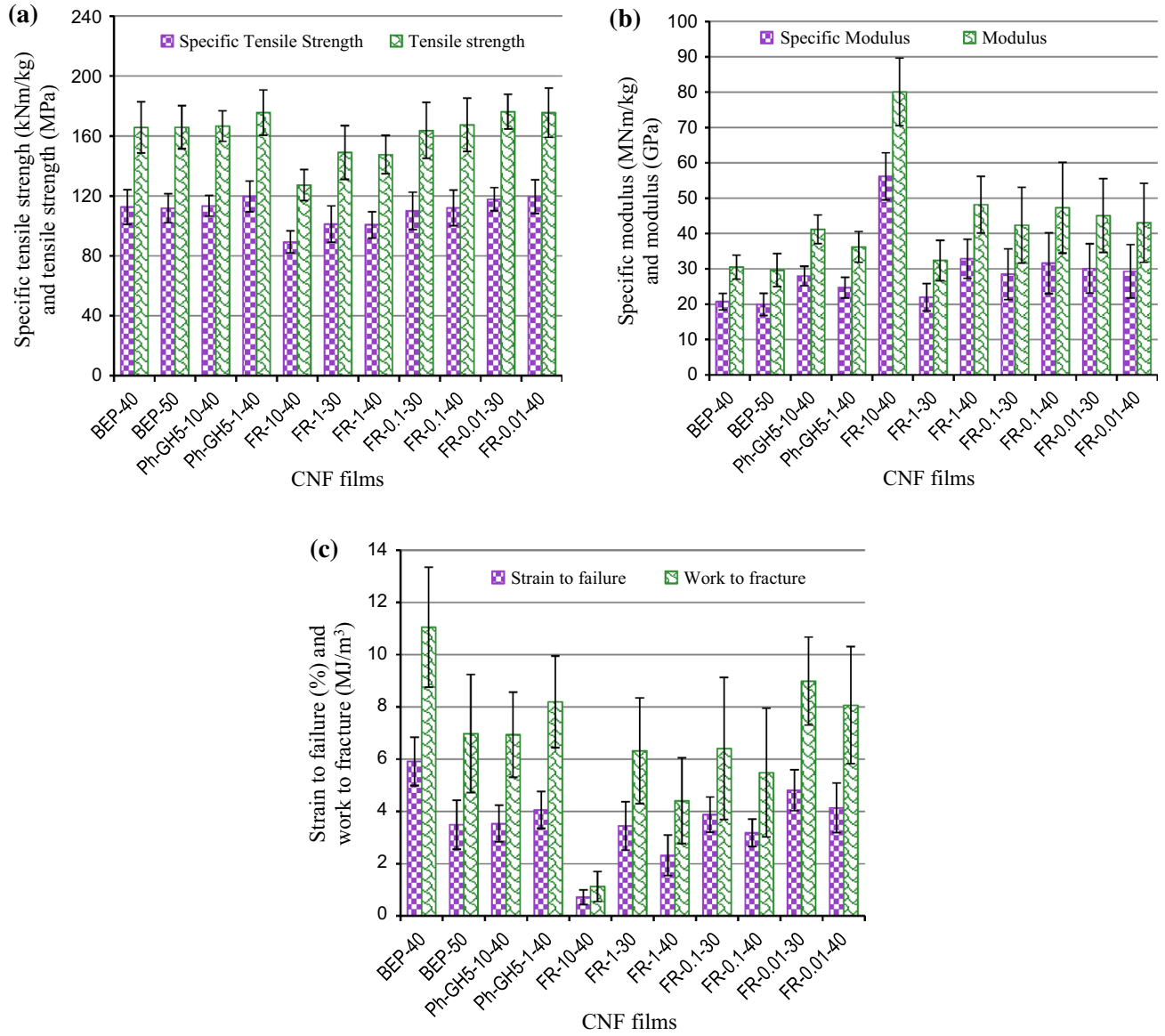

Fig. 5 Mechanical properties of CNF films: **a** specific tensile strength and tensile strength, **b** specific modulus and modulus, **c** strain to failure and work to fracture

mainly depend on single fiber mechanical property and interfiber bonding [23], which can be affected by fiber aspect ratio [24]. Ph-GH5 pretreatment produced longer and more entangled nanofibrils at 1 mg/g cellulase loading, resulting in the highest specific tensile strength (120 kNm/kg). FR dramatically reduced the DP resulting in short fiber especially at a high cellulase loading. σ/ρ values of FR pretreated CNF film was only 89 kNm/kg. With the decreasing of FR loading, σ/ρ values slightly increased due to reduced fiber cutting (Fig. 6a). A specific tensile strength of 119 kNm/kg was achieved at 0.01 mg/g FR loading. There were no obvious differences in tensile strength with or without 10 more pass through 87 μm chamber of microfluidizer after 30 passes for FR treated samples or 40 passes for untreated sample.

Relatively high modulus (E) of CNF films was achieved as reported in Fig. 5b. Endoglucanase pretreatment can increase the modulus of CNF films in various degrees. FR-10-40 has the largest specific modulus (E/ρ) at 56 MNm/kg compared with 21 MNm/kg for BEP-40. Increasing cellulase loading is helpful for improving E/ρ value, especially for cellulase loading from 1 to 10 mg/g (Fig. 6a). Ph-GH5-10-40 had a 14 % greater E/ρ value than Ph-GH5-1-40, while FR-10-40 had a 71 % greater E/ρ value than FR-1-40. Specific modulus showed slight increase for FR-1 and FR-0.1 when the pass through microfludizer was increase

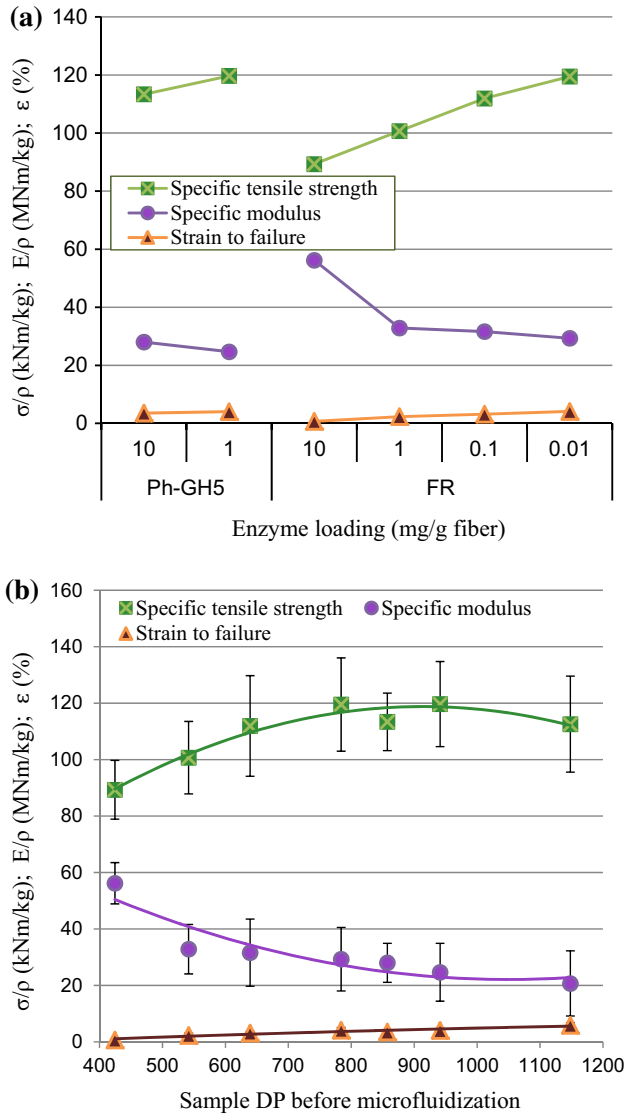

Fig. 6 Mechanical properties of CNF films (after 40 passes through microfluidizer) versus **a** enzyme loading and **b** starting sample DP

from 30 to 40. The modulus of CNF films prepared in this study was much higher than Henriksson's report [12], mainly due to the low density of Henriksson's film (900–1200 kg/m^3). The interfibril bonds may be weakened by reduced hydrogen-bonding density in the more porous network to result in low modulus.

The endoglucanase pretreated CNF films are more brittle than the untreated one. Strain to failure (ε), also called elongation at break, was presented in Fig. 5c. The strain was reduced after endoglucanase pretreatment due to the fact that the short fibers resulted from cutting by endoglucanase reduced the extensibility on tensile deformation. Strain of untreated CNF films with 40 passes (BEP-40) was 5.9 %, which was decreased to 4.1 % when applied 1 mg/g Ph-GH5 pretreatment (Ph-GH5-1-40) or 3.5 % when increased the number of passes through microfluidizer to 50 (BEP-50). Increasing cellulase loading or passes through microfluidizer will decrease the elongation at break at all conditions (Fig. 6a), which implied this parameter was highly dependent on the fibril length. The CNF from very high FR loading has the shortest fibrils resulting in the lowest strain of CNF films at 0.7 %. Toughness, defined as work to fracture (Fig. 5c), is calculated as the area under the stress–strain curve [12]. The toughness of CNF films is highly related to the strain to failure. BEP-40 showed the highest toughness at 11 MJ/m^3, while the toughness of FR-10-40 was only 1 MJ/m^3. According to the TEM results, Ph-GH5-1-40 has longer and more entangled fibrils, while FR-0.01-40 has shorter but more uniform fibrils (Fig. 2). However, these two samples exhibited similar tensile strength, modulus, strain to failure and work to fracture (Fig. 5).

Figure 6b showed the relationship between mechanical properties of CNF films and the DP of the fibers before fibrillation (starting sample DP). The strain (ε) of CNF films has a linear relationship with starting sample DP, which decreased from 5.9 to 0.7 % with DP decreased from 1148 to 424 by various endoglucanase pretreatment. This is in agreement with Henriksson's study [12]. The E/ρ value increased from 21 to 56 MNm/kg gradually with the decrease in DP, whereas σ/ρ value was increased from 113 to 120 kNm/kg at DP of 941 then decreased to 89 kNm/kg with continuing DP decrease. Endoglucanase pretreatment was helpful for improving physical and mechanical properties, but excessive treatment with high enzyme loading will cut the fiber severely and affect the properties of CNF films.

Conclusions

Optical opacity, thermal stability and tensile strength of CNF films produced by endoglucanase pretreatment and subsequent micro-fluidization were investigated in this study. Endoglucanase pretreated CNF films showed better transparency than untreated one but with similar thermal stability. Ph-GH5-1-40 provided the highest maximum tensile strength while FR-10-40 had the greatest modulus with lowest strain. Endoglucanase pretreatment can facilitate producing uniform fibrils. But excessive treatment also can cut fiber severely, which will affect the mechanical properties of CNF films.

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