Cellulose Nanocomposites by Melt Compounding of TEMPO-Treated Wood Fibers in Thermoplastic Starch Matrix

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To facilitate melt compounding of cellulose nanofibrils (CNF) based composites, wood pulp fibers were subjected to a chemical treatment whereby the fibers were oxidized using 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO). This treatment introduced negatively charged carboxylate groups to the fibers. TEMPO-treated fibers (TempoF) were added to a mixture of amylopectin starch, glycerol, and water. Granules were prepared from this mixture and processed into CNF composites by extrusion. TempoF were easier to process into composites as compared with non-treated pulp fibers (PF). SEM revealed partial disintegration of TempoF during melt processing. Consequently, TempoF gave composites with much better mechanical properties than those of conventional composites prepared from pulp fibers and TPS. Particularly, at 20 wt% TempoF content in the composite, the modulus and strength were much improved. Such a continuous melt processing route, as an alternative to laboratory solvent casting techniques, may promote large-scale production of CNF-based composites as an environmentally friendly alternative to synthetic plastics/composites.

Keywords: Cellulose nanofibrils; Thermoplastic starch; Extrusion; Mechanical properties; Nanocomposites

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INTRODUCTION

The transformation of biomass and agricultural residues into green materials is gaining interest out of environmental concerns. Improved performance of biobased materials is interesting, as it could lead to applications that are currently possible only with synthetic materials. Cellulose nanofibrils (CNF) are nanoscale constituents disintegrated from biomass using mechanical processes (Turbak *et al.* 1983), and they can form biobased materials with enhanced performance compared to current analogues based on microfibers. CNF have fibrous structure with a high aspect ratio exceeding 100, high modulus (Iwamoto *et al.* 2009), and can form tough networks (Sehaqui 2011). CNF have good potential for applications in films (Henriksson *et al.* 2008; Sehaqui *et al.* 2010a), foams (Sehaqui *et al.* 2010b; Svagan *et al.* 2008), aerogels (Paakko *et al.* 2008; Saito *et al.* 2011; Sehaqui *et al.* 2011a,c) and polymer matrix composites. CNF have been combined with matrices such as plasticized starch (Angles and Dufresne 2001; Svagan *et al.* 2007), polyvinyl alcohol (PVA) (Bruce *et al.* 2005; Gea *et al.* 2010; Zimmermann *et al.* 2004), epoxy (Bruce *et al.* 2005), hemicellulose (Bruce *et al.* 2005), and cellulose derivatives (Sehaqui *et al.*

2011b,2012; Zhou *et al.* 2009; Zimmermann *et al.* 2004), polyurethane (Seydibeyoglu and Oksman 2008), a styrene copolymer (Favier *et al.* 1995; Malainine *et al.* 2005; Samir *et al.* 2004), polylactic acid (PLA) (Iwatake *et al.* 2008; Wang and Drzal 2012), and thermoset resins (Yano *et al.* 2005).

CNF addition to polymers can result in strong reinforcement effects (Bruce *et al.* 2005; Sehaqui *et al.* 2011b; Seydibeyoglu and Oksman 2008; Svagan *et al.* 2007; Zimmermann *et al.* 2004). With only a small amount of CNF used in soft polymers (*e.g.*, elastomers), significant improvements in mechanical properties can be obtained. For instance, 6 wt% of CNF in a styrene copolymer matrix can increase its strength and stiffness from 0.18 MPa and 0.2 MPa to 6.3 MPa and 114 MPa, respectively (Samir *et al.* 2004). The styrene copolymer matrix had a lower glass transition temperature than the composite, and mechanical properties were measured in the transition region. With stiffer polymers, high content of CNF leads to remarkable mechanical performance. Hence, 54 vol% of CNF in a hydroxyethylcellulose (HEC) matrix results in modulus and strength of 8 GPa and 200 MPa (Sehaqui *et al.* 2011b). Additionally, CNF may provide good thermomechanical properties (Iwatake *et al.* 2008; Malainine *et al.* 2005; Samir *et al.* 2004; Sehaqui *et al.* 2011b; Svagan *et al.* 2007), limited creep (Johnson *et al.* 2009; Sehaqui *et al.* 2011b; Suryanegara *et al.* 2010), and thermal expansion (Nogi and Yano 2008), optical transparency (Iwamoto *et al.* 2007; Nogi and Yano 2008; Okahisa *et al.* 2009), high oxygen barrier performance (Aulin *et al.* 2012; Liu *et al.* 2011; Wu *et al.* 2012), and additional functionalities (Boujemaoui *et al.* 2012; Olsson *et al.* 2010). Diverse applications of CNF-based materials could therefore be envisioned in food packaging, transportation, or in electronic displays.

Water-based processing methods are of particular interest since CNF are mostly obtained as aqueous suspensions. CNF and water-based polymers or emulsions can be mixed and subjected to papermaking-like processing involving filtration and drying (Larsson *et al.* 2012; Sehaqui *et al.* 2011b; Wang and Drzal 2012; Zimmermann *et al.* 2004). Porous composite foams and aerogels can be prepared by freeze drying (Sehaqui *et al.* 2010b) or supercritical drying (Sehaqui *et al.* 2012) of water-based CNF composite mixtures. There are also other processing methods. Nanostructured composites can be prepared by *in-situ* polymerization of monomers in presence of well dispersed high surface area nanofiber network (Boujemaoui *et al.* 2012) leading to covalent bonding at the polymer/CNF interface. Nanofiber networks can be impregnated with a thermoset resin and subjected to curing (Yano *et al.* 2005). Since these methods are relatively recent, they require development of novel techniques for large-scale production or require adaptation in current technologies (*e.g.* vacuum filtration may be adapted in current paper making processes). In contrast, melt processes of thermoplastics are well established techniques. The possibility to incorporate CNF in composites using continuous melt processes would therefore be important for large-scale industrial application of bionanocomposites.

One challenge for CNF composites emanates from the initially high amount of water in the CNF suspension. Drying of CNF may lead to a considerable lowering of its surface area, agglomeration, and reduced reinforcement potential. Nevertheless, 0 to 20 wt% CNF suspension was successfully incorporated into a thermoplastic starch matrix by twin screw extrusion, leading to a 2- to 3-fold increase of its strength and stiffness (Hietala *et al.* 2013). In another recent study, the efficiency of the twin-screw extrusion process to fibrillate cellulose fibers and TEMPO-treated fibers into micro/nanosize in the same step as the compounding of thermoplastic starch (TPS) was examined (Hietala *et al.* 2014). Recently, powdered polypropylene and fibrillated pulp were melt-compounded in the presence of a compatibilizer (maleic anhydride grafted polypropylene), resulting in composites with up to 60 % cellulose content and strongly improved strength and stiffness relative to the neat polypropylene (Suzuki *et al.* 2013). In the early pioneering work, Boldizar *et al*. (1987) attempted disintegration of cellulose into submicroscopic microfibrils by processing prehydrolyzed cellulose and thermoplastic matrices. In the present work, a somewhat similar approach was pursued for the preparation of CNF-based composites in a process whereby chemically treated wood fibers (TempoF) were partially disintegrated in a thermoplastic starch (TPS) matrix using shear forces of a Brabender mixer and a single-screw extruder. The goal is to show the advantage of the fiber treatment with respect to the mechanical properties in tension of the processed biocomposites. Furthermore, pursuing disintegration of treated wood fibers to a nanoparticulate form simultaneously during melt processing of the biocomposites may result in lower demands in terms of energy consumption, and in terms of handling of water contained in the CNF suspension. Further optimization of the process using a twin-screw extruder may be attempted in future studies. Mechanical properties of the TPS/TempoF composites were characterized in tension and compared to properties of a neat TPS and to conventional composites prepared from TPS and untreated wood pulp fibers.

EXPERIMENTAL

Materials

Pure potato amylopectin starch (PAP) was kindly supplied by Lyckeby AB (Kristianstad, Sweden). Never-dried bleached softwood sulphite pulp was kindly supplied by Nordic Paper Seffle AB (Sweden). All other reagents (glycerol at 87% and stearic acid) were purchased from Sigma Aldrich.

Pretreatment of Wood Fibers

TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy, free radical)-mediated oxidation method was used for the pretreatment of wood pulp fibers (Saito *et al.* 2007). The pulp was first dispersed in water in which sodium bromide and TEMPO were dissolved (1 and 0.1 mmol per gram of cellulose, respectively). The concentration of the pulp in water was 2 wt %. The reaction was started by addition of sodium hypochlorite (5 mmol per gram of cellulose) dropwise into the dispersion. During the addition of NaOCl, carboxylate groups were forming on the surface of the fibrils, and the pH decreased. The pH of the reaction was then maintained at 10 by sodium hydroxide addition. After all of the NaOCl was consumed, the pulp fibers were filtered and washed several times with deionized water until the filtrate solution was neutral.

Processing of the Composites

PAP starch, glycerol, water with a starch:glycerol:water ratio of 100:30:30, stearic acid (less than 1 wt% of total weight), and the pretreated/untreated fibers (0 to 20 wt% related to PAP weight) were assembled in a container and gently mixed manually to form a consistent mixture. Note that water refers to the total water, *i.e*., water present in cellulose fibers and additional water. The ratio starch:glycerol:water was selected according to work by VanSoest and Knooren 1997. For the preparation of composites with more than 3 wt% of fibers (treated or untreated), the addition of fibers led to an excess of water, and the samples were therefore stored at ambient conditions or in the oven at 50 °C when too much water remained until the desired amount of water in the samples remained. Thereafter, all components were premixed in a Brabender Plasticorder (Duisburg, Germany) for homogenization of the components. The premixing was done at a temperature of 110 °C for 10 min. At this stage, the presence of water and heat disrupt the crystalline structure of starch, a process known as gelatinization of starch. Furthermore, some disintegration of TEMPO-treated fibers by the Brabender Plasticorder may have occurred, but this has not been investigated. The mixture was allowed to cool down before introducing it in a rotating blades machine for the preparation of ready to use granulates. The granulates were then fed into a single screw extruder (BX18, Axon, Sweden) equipped with a flat sheet die (45 * 0.7 mm^2) and a screw with a compression zone (root diameter from 12 to 15 mm), a 12 mm flight distance and a L/D ratio of 36 : 1. Further information on the extruder and screw are available at www.axonmachinery.se/ccol1.htm. The temperature of the 5 heating zones of the extruder from the feed zone to the die were set at 140 °C, 140 °C, 150 °C, 130 °C, and 95 °C, respectively, according to a method reported by VanSoest and Knooren (1997). The slit die melt temperature was kept below 100°C to prevent the melt from boiling and to give a bubble-free extrudate (VanSoest and Knooren 1997). The neat TPS sample was prepared as the composites but without adding fibers. After samples production, they were conditioned at a temperature of 23 °C and a relative humidity of 50% for at least 10 days prior to their characterization.

FTIR

Infrared spectra of untreated and TEMPO-treated pulp fibers were recorded using a FTS 6000 spectrometer (Portmann Instruments AG, Biel-Benken, Switzerland). For each sample, the diamond crystal of an Attenuated Total Reflectance (ATR) accessory was brought into contact with the area to be analyzed. All spectra were recorded between 4000 and 600 cm^{-1} with a resolution of 4 cm^{-1} and 32 scans.

Titration of Carboxyl Group Content

Carboxylate group content of TEMPO treated pulp fibers was determined by an electric conductivity titration method (Saito and Isogai 2004). Fibers in suspension at pH ~ 2.5 were titrated with successive 200 µL of a 0.05 M sodium hydroxide solution until the pH reaches 11. The COOH content could be then determined from the plateau obtained in the curve representing electrical conductivity *vs.* volume of NaOH added.

Digital Microscopy

Untreated and TEMPO-treated pulp fibers were dyed with Astra Blue before observing them in a digital microscope (Leica DVM2500 model VZ700 C).

Equilibrium Moisture Content

Conditioned samples at 50% RH and 23 °C were weighed and then dried in an oven at 105 °C for several hours until a constant weight was achieved. The equilibrium moisture content was calculated with respect to the dry weight of the sample.

Tensile Mechanical Properties

Tests of tensile mechanical properties of the samples were performed using a MiniMat Tester 2000 equipment having a 200 N load cell. The shape of the samples was a standard dog-bone shape with a narrow part having a length and width of 16 mm and 4 mm, respectively. The samples were cut according to the machine direction, and they were tested at a cross-head speed of 5 mm.min^{-1}. Five to eight specimens were tested per sample at a controlled humidity of 50% and a temperature of 23 °C. The strain was measured in the Minimat from the cross-head displacement.

Field-emission Scanning Electron Microscopy (FE-SEM)

A Hitachi S-4800 scanning electron microscope, operated at 0.5 to 0.7 kV, was used to capture secondary electron images of fractured surfaces. The samples were mounted in a metal holder and coated with a 3 to 4 nm layer of gold prior to their observation.

RESULTS AND DISCUSSION

In earlier work, cellulose/starch nanocomposites have been processed from water-based mixtures by solvent casting (Svagan *et al.* 2007) or by first disintegrating CNF from biomass using mechanical processes, then incorporating CNF water suspensions during melt processing of thermoplastic starch (TPS) (Hietala *et al.* 2013). The present strategy is different since it was attempted to disintegrate pretreated biomass into CNF during melt processing. This could lead to lower energy consumption for composites processing. In a first step, wood fibers were subjected to a TEMPO-mediated oxidation pretreatment in order to introduce negatively charged carboxyl groups to the fibrils. The success of the TEMPO pretreatment reaction was confirmed by FTIR in which a new peak corresponding to carboxylate groups located at 1600 cm^{-1} was observed (Fig. 1).

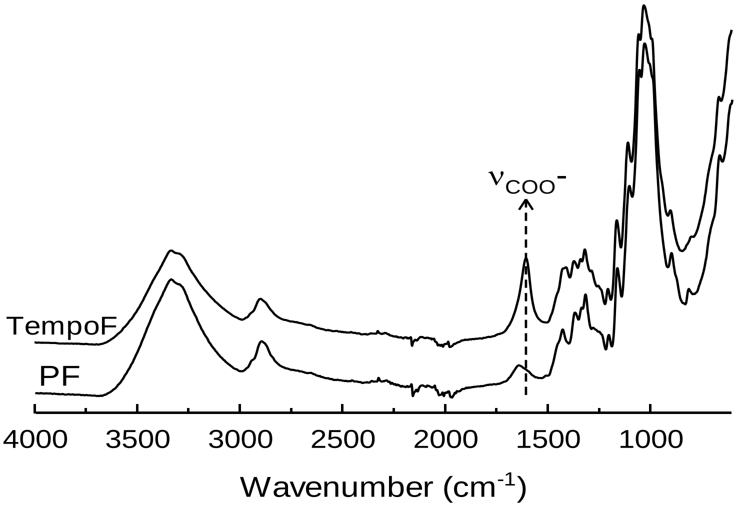


Fig. 1. FTIR spectra of PF and TempoF showing the absorbance peak of carboxylates (ν_{COO^-}) for TempoF

The carboxyl group content of treated fibers was as high as 0.98 mmol.g^{-1} corresponding to a degree of substitution (DS) of 0.15. This DS was relatively high since the modification occurred at the surface of the fibrils leaving the inner crystalline structure of native cellulose unchanged. Consequently, the repulsive action of the negative carboxylate charges at the surface of the TEMPO-treated wood fibers (TempoF) increased swelling in water as compared with non-treated wood pulp fibers (PF) (swelling from *ca.* 25 µm for PF to *ca.* 70 µm for TempoF; see digital microscopy images in Fig. 2). This may facilitate their subsequent disintegration. TempoF were premixed with starch powder, glycerol, and water to form granules. These were subjected to the shear action of a single-screw extruder to produce composites with a cellulose content of up to 20 wt%. For comparison, two reference materials were chosen, namely a neat thermoplastic starch (TPS) and a composite of wood fibers (PF) and starch prepared in the same way as the TPS/TempoF composite but without subjecting wood fibers to any pretreatment.

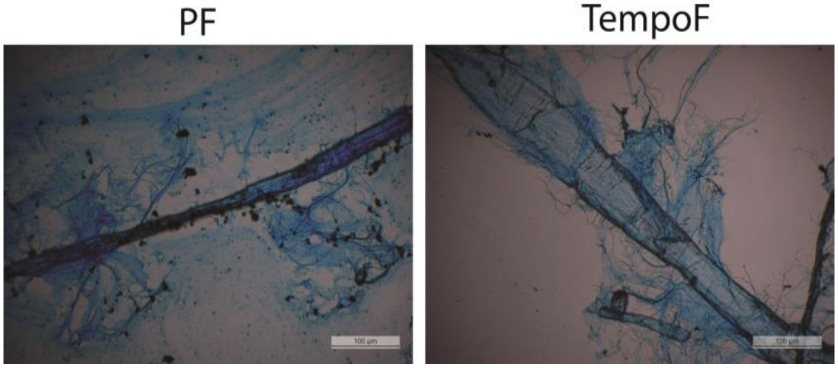


Fig. 2. Digital micrographs of PF and TempoF showing the swollen state of TempoF. Scale bar is 100 microns.

After processing and conditioning at 50% RH and 23 °C, the moisture content of different materials was determined. Results are shown in Fig. 3. Data were in the range 11.8 to 14.7 wt%. Some water evaporation after processing and conditioning occurred, since initial water content prior to melt processing was in the range 14.3 to 15.8 wt% (based on the total weight). Lower moisture content may be due to some evaporation during processing. The water content of all samples after processing and conditioning (corresponding to water content during mechanical testing) was fairly constant, such that further comparison of their properties could be made.

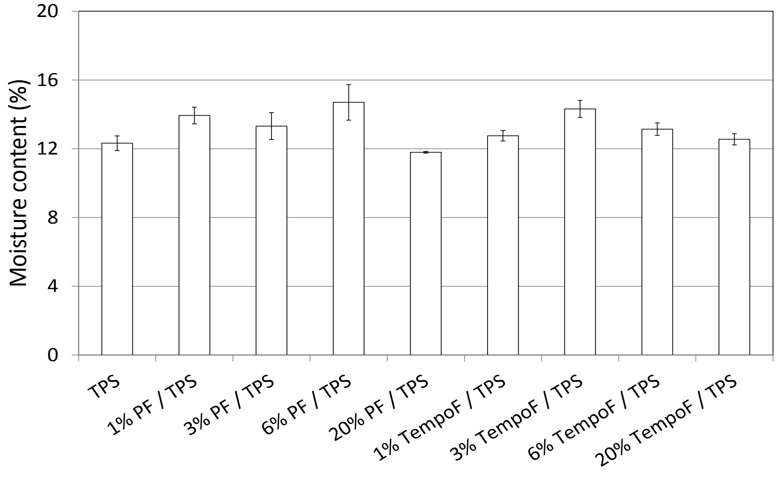


Fig. 3. Moisture content of TPS, PF / TPS, and TempoF / TPS composites

Tensile mechanical properties of the neat TPS, TPS/PF, and TPS/TempoF composites at 6 wt% and 20 wt% fiber contents are shown in Figs. 4A and 4B, respectively. Tensile modulus and strength data are compiled in Table 1. At 6 wt% reinforcement, the modulus of TPS/PF composites was not changed compared to neat TPS modulus, while it was lowered at 20 wt% content of untreated PF fibers (Table 1). Heterogeneous fiber structure and poor PF distribution in the composite contributed to these effects. The low shear forces encountered in the single screw extruder, and the relatively low screw speed used (40 rpm) were apparently not enough for good dispersion of PF in the starch matrix. Indeed, the extrusion of the TPS/20 wt%PF composite was difficult. The strength data show an increase of the TPS/PF properties compared to neat TPS by 14% and 31% at 6 wt% and 20 wt% PF content, respectively.

Interestingly, a much stronger reinforcing effect was observed for the TPS/TempoF composites compared to both pure TPS and TPS/PF composites. At 20 wt% TempoF content, the strength and modulus increased by *ca*. 2 and 5 fold, respectively, compared to data for neat TPS (see Table 1). The TEMPO-treatment of wood fibers prior to melt processing had thus been effective in enhancing mechanical performance of the corresponding composite. It will be shown that this is due to partial disintegration of TempoF in the starch matrix. Better load carrying performance of the composite is realized due to high aspect ratio and improved dispersion of reinforcement. This is in contrast to TPS/PF composites. The difference in mechanical properties between PF and TempoF composites may arise from differences in aspect ratio and degree of dispersion. The components of the PF composite may not be as well mixed as the TempoF composites.

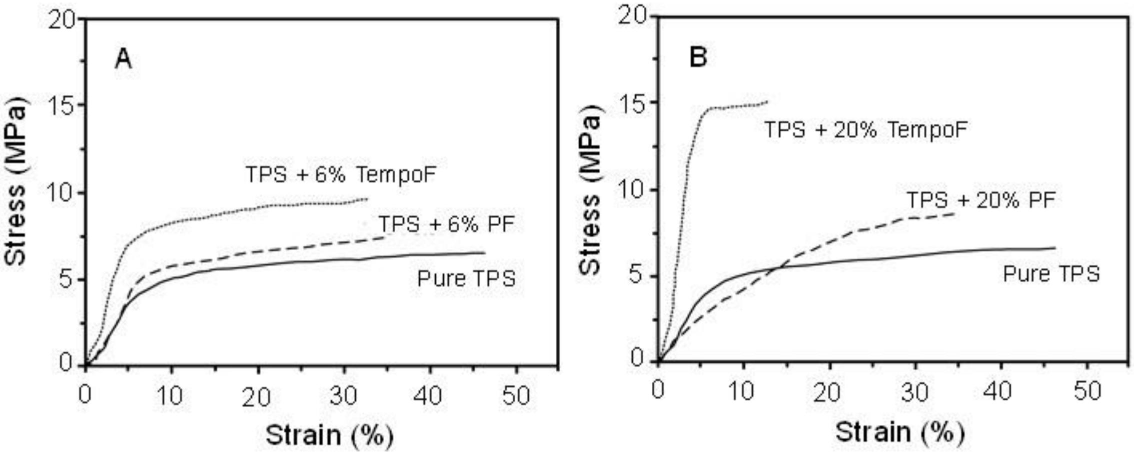


Fig. 4. Tensile stress-strain curves of TPS and composites with (A) 6 wt% fiber content and (B) 20 wt% fiber content

Table 1. Tensile Mechanical Properties of Pure TPS matrix, and Composites of PF and TempoF

Sample	Tensile modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
TPS	99 ± 14	6.4 ± 4.5	47.5 ± 4.1
TPS+6 wt%PF	100 ± 17	7.3 ± 1.8	34.0 ± 2.9
TPS+20 wt%PF	55 ± 7	8.4 ± 2.6	33.8 ± 5.4
TPS+6 wt%TempoF	*200 ± 35*	*9.3 ± 0.5*	34.3 ± 3.7
TPS+20 wt%TempoF	*490 ± 38*	*14.9 ± 0.6*	13.6 ± 3.1

The plot of modulus and strength versus fiber content is shown in Fig. 5, including lower fiber contents. In the whole range of fiber content studied (0 to 20 wt%), an increase in modulus and strength was observed for TPS/TempoF composites. The PF on the other hand led to composites showing small reinforcement effects on modulus. Strength increased somewhat with PF content. Interpretation is not straightforward, but the PF distribution was poor. Note that the TPS had low modulus and strength in the unreinforced reference state, due to the high glycerol content (30 wt%). This means that the load transfer function of the matrix was poor for discrete PF fibers.

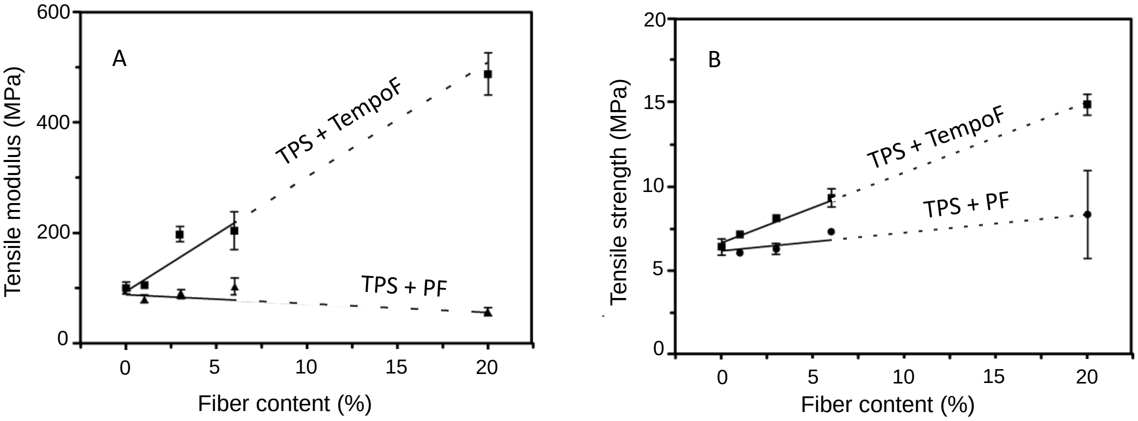


Fig. 5. (A) Tensile modulus and (B) tensile strength as a function of fiber content in the composites. Fiber concentrations in the range 6-20 wt% are not available, and therefore a dotted line has been plotted in this range.

Comparison of current data with literature is difficult, since mechanical properties of the TPS composites depend on many parameters such as the nature of the starch matrix, the amount and types of plasticizers, the processing method, and the coupling between the fiber and matrix. Starch composites having 50% glycerol and 20% CNF prepared by solvent casting displayed a modulus and strength of 780 MPa and 15 MPa versus a modulus and strength of only 1.6 MPa and 0.36 MPa for the pure starch matrix (Svagan *et al.* 2007). TPS composites having 30% sorbitol and 20% CNF prepared by twin-screw extrusion displayed a modulus and strength of 1317 MPa and 17.5 MPa versus a modulus and strength of 455 MPa and 8.8 MPa for the pure TPS matrix (Hietala *et al.* 2013). All these results confirm the good reinforcing potential of CNF in starch.

Tensile-fractured samples were observed in SEM to verify the state of the fibers in the composites. The micrographs (Fig. 6) show that the composite with 6 wt% PF had a relatively smooth surface characterized by fiber pull-out. At 20 wt% PF content, the extent of fiber pull-out was obviously higher, resulting in a much rougher fracture surface. Wood fibers with a diameter of 20 to 30 microns could be easily distinguished in the micrographs, thus giving evidence of the absence of PF disintegration during melt processing. On the other hand, TPS/TempoF did not show much sign of "macro" fiber pull-out, giving a much smoother surface at 20 wt% reinforcement. Some porosity was apparent for both materials (TPS/PF and TPS/TempoF). At high magnification, a fairly good distribution of ~30 nm wide nanofibers in the matrix was observed. Nanofiber pull-out could be detected (upper right in 20 wt% TempoF / TPS high magnification). Effects observed for TempoF/starch composites could be due to better fiber-matrix adhesion, since the surface of TempoF was modified. In recent work on melt processing of PVA and microcrystalline cellulose, the addition of microcrystalline cellulose resulted in strong interfacial interaction with PVA through hydrogen bonding. As a result, the crystallization of PVA was confined and its melting temperature was decreased, which was beneficial (Sun *et al.* 2014).

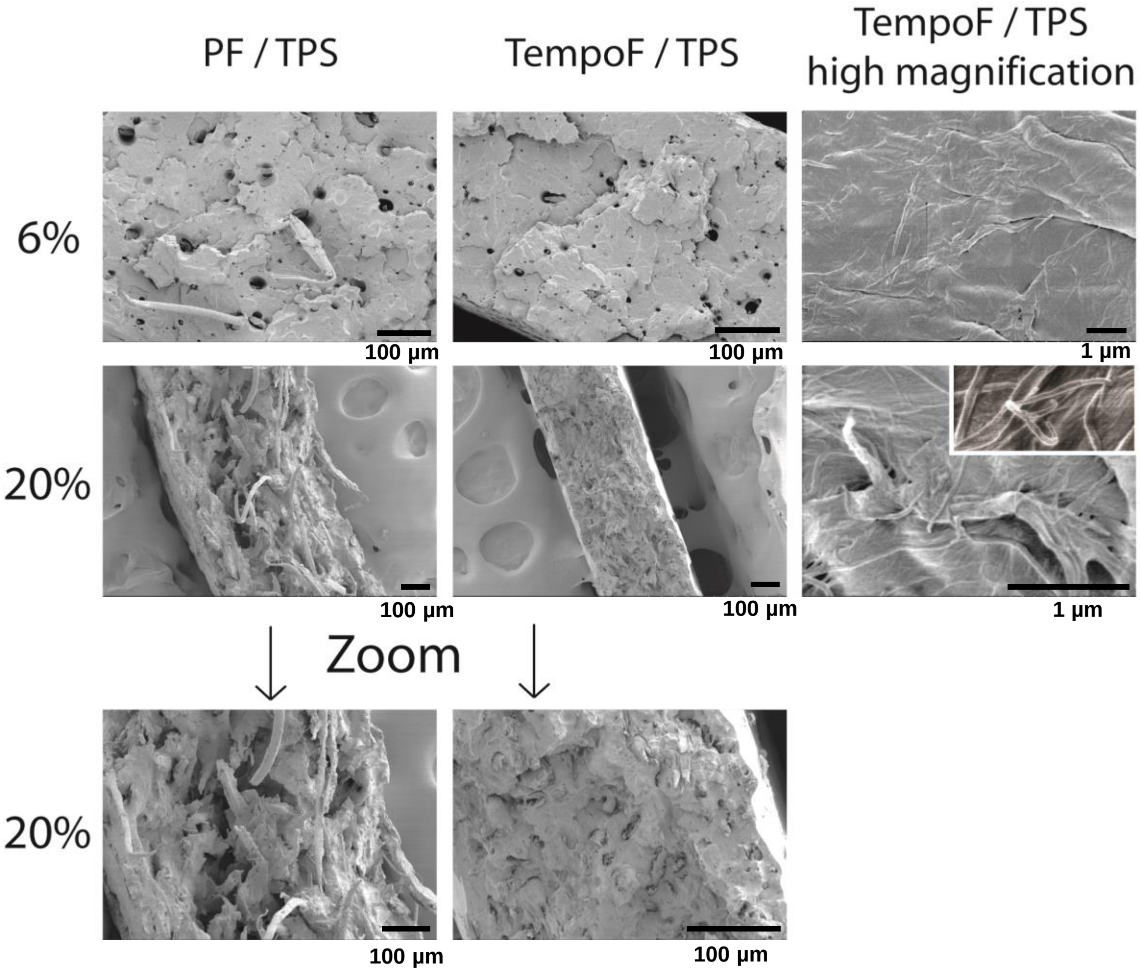
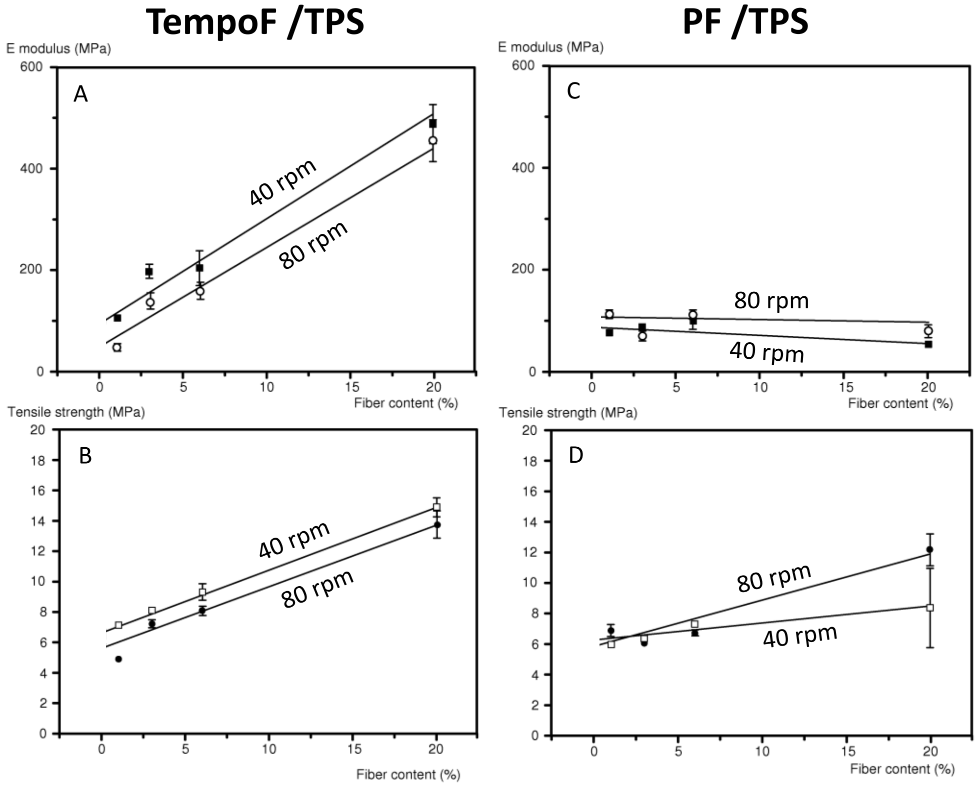


Fig. 6. SEM micrographs of tensile fractured cross-sections of TPS/PF and TPS/TempoF composites at 6 wt% and 20 wt% fiber contents

Effect of Screw Speed

In an attempt to increase the dispersion of the PF and TempoF in the starch matrix, the screw speed of the extruder was doubled to 80 rpm during manufacturing of the composites. Tensile mechanical properties of corresponding materials are shown in Fig. 7 together with those previously tested at 40 rpm. Results showed a slight decrease of the mechanical properties of the TPS/TempoF composites at the higher screw speed. This is probably related to a degradation of the TPS by hydrolysis or to fiber length reduction at increased screw rotation rate. The dispersion of disintegrated TempoF in the TPS matrix appears to be sufficiently good even at low screw speed without noticeable improvement at higher speed. Indeed, TempoF are known to easily disintegrate even under mild mechanical treatment (*e.g.*, by magnetic stirring) (Saito *et al.* 2007), while non-treated PF requires extensive high-shear homogenization at high pressure for disintegration (Turbak *et al.* 1983). On the other hand, properties of TPS/PF composites are improved at higher speed at 20 wt% fiber content. The poor PF distribution in the starch matrix at 40 rpm is probably improved at higher speed due to higher shear forces encountered by the PF at 80 rpm. TEMPO pretreatment of wood fibers prior to their processing facilitates their disintegration in the matrix at lower power.


TempoF /TPS

PF /TPS

Fig. 7. Tensile modulus (A & C) and tensile strength (B & D) as a function of fiber content (wt%) for TPS/TempoF and TPS/PF composites processed at a screw speed of 40 rpm or 80 rpm

CONCLUSIONS

1. Wood pulp fibers were pretreated by TEMPO-mediated oxidation in order to convert surface hydroxyl groups of cellulose into carboxylates. As much as 0.98 mmol.g^{-1} of negatively charged carboxylates were introduced to the TEMPO-oxidized wood fibers (TempoF) causing them to swell in water. TempoF and thermoplastic starch (TPS) were then melt-processed by Brabender mixing and single-screw extrusion.
2. Mechanical properties of TPS/TempoF displayed a 5 and 2 fold increase in modulus and strength compared to neat TPS and were much better than properties of composites made of TPS and non-treated pulp fibers (PF). This is due to disintegration of TempoF pulp into smaller nanofibers so that the reinforcement efficiency is improved compared with pulp fiber composites.
3. The difference in scale of fiber dimensions between regular wood fibers and TempoF after processing was qualitatively assessed in the biocomposites. Fracture surfaces of TPS/PF was dominated by 20 to 30 µm diameter pulp fiber pull-out, while TPS/TempoF fracture surfaces were smoother and revealed nanofibers *ca.* 30 nm in diameter.
4. These results show property advantages achieved through melt processing of TempoF/TPS biocomposites as compared to the processing of conventional pulp fibers

based biocomposites, and may facilitate development of CNF-based products on large industrial scale.

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