ACETYLATED TEMPO-OXIDIZED CELLULOSE AS REINFORCING AGENT OF POLY(LACTIC) ACID (PLA)

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Abstract

Composites of poly(lactic) acid (PLA) reinforced with TEMPO-oxidized fibrillated cellulose (TOFC) were prepared to 15, 20, 25 and 30 % weight fraction of fibrils. To aid dispersion and to improve stress transfer, the TOFC was acetylated prior to the fabrication of TOFC-PLA composite films. The acetyl content of acetylated TOFC was 3.9 % which translates to a DS of 0.16. Fibrils were imaged using atomic force microscopy (AFM). Dynamic mechanical analysis (DMA) was used to monitor changes in loss and storage moduli with respect to temperature and moisture. The glass transition temperature (Tg) increased upon addition of TOFC by approx. 20 ºC (50 %) with no significant difference with respect to weight fractions of TOFC. The incorporation of cellulose improved the storage modulus (E'). It was the highest at 30 wt% load of TOFC. The study of mechanical properties in varied humidity conditions showed that the addition of TOFC improves the mechanical properties in a humid environments.

1 Introduction

Cellulose reinforced polymer composites have been extensively studied during the last couple decades [1]. The results show many promising advantages of cellulose reinforced composite materials. It is widely agreed that nanocellulose has many advantages over cellulosic fillers which have dimensions in micrometres or more. Properties such as aspect ratio, surface charge and chemical composition can be more easily controlled in nanocellulose. Moreover, the strength of nanofibrils approaches that of the theoretical cellulose crystal [2]. A number of different techniques are available for the isolation of nanocellulose. Oxidation of pulps with 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) radical is known to provide high aspect ratio nanofibrils, which are potentially suitable for the preparation of nanocomposites [3]. However, the effect of TEMPO-oxidized cellulose on the properties of polymers has not been widely studied.

Herein, a modification of poly(lactic) acid with TEMPO-oxidized fibrillated cellulose (TOFC) is studied. The dynamic mechanical properties of these composite materials are reported. The structure and crystallization are investigated using dynamic scanning calorimetry (DSC). Additionally, the mechanical behaviour is investigated in moist environments using a humidity controlled chamber coupled with dynamic mechanical analysis (DMA).

2 Materials and testing methods

2.1 Chemically modified TOFC

Bleached birch Kraft pulp was oxidized according to the method introduced by Saito et al. [4] under alkaline conditions. The oxidized pulp was dispersed in deionised water and homogenised using a commercial blender. A translucent gel, having a solid content of ~ 0.5 wt%, was obtained. Herein it is termed TEMPO-oxidized fibrillated cellulose (TOFC) since no filtration was performed.

TOFC was acetylated in DMF with acetic acid at 125 ± 5 °C for 45 min. A detailed description of the acetylation reaction can be found elsewhere [5].

The degree of substitution of hydroxyl groups was evaluated using a standard Eberstadt method [6]. It is based on a saponification reaction followed by titration with hydrochloric acid (HCl). The consumption of sodium hydroxide (NaOH) during the saponification reaction is correlated with the acetyl content using *eq. 1*.

$$\text{Acetyl Content } (\%) = \left((D-C)N_a + (A-B)N_b \right) \cdot (4.035/W) \tag{1}$$

where A is the volume of NaOH (ml) added to the sample, B is the volume of NaOH (ml) added to the blank, C is the volume of HCl (ml) added to the sample, D is the volume of HCl (ml) added to the blank, W is the weight of sample (g), N_a and N_b are the normality of HCl and NaOH solutions, respectively. The acetyl content is translated to DS using *eq. 2*.

$$DS = \left(3.86 \cdot \text{Acetyl Content } (\%) \right) / \left(102.4 - \text{Acetyl Content } (\%) \right) \tag{2}$$

Unmodified TOFC was used as a blank sample in the determination of the acetyl content.

2.2 Matrix

Commercially available PLA – poly(lactic) acid (NatureWorks 2002D, NatureWorks, Minnetonka, MN, USA) was used as the matrix. The glass transition temperature (T_g) and melting temperature (T_m) were 58 °C and 150 – 160 °C respectively, according to the manufacturer. PLA was dissolved in chloroform to obtain a suspension having a concentration of 2 wt%. Then it was mixed with the acetylated TOFC dispersed in chloroform to prepare composites to weight fractions of 15, 20, 25 and 30 % based on a dry weight. The mixture was cast onto a release agent treated glass plate and left overnight in a well-ventilated room. Films were finally cured in an oven at 60 °C for 30 min.

2.3 Fourier Transform Infrared Spectroscopy (FT-IR)

DS was also evaluated using FT-IR spectroscopy. Dried samples of non-acetylated and acetylated TOFC were placed in a photoacoustic cell and FT-IR spectra were recorded between 400 and 4000 cm^{-1} using a FTS 600 (Bio-Rad Laboratories Inc., Hercules, CA, USA) spectrometer. A laser operating at a wavelength of 632.8 nm was employed.

2.3 Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) was employed to study the morphology of TOFC before and after acetylation. TOFC suspensions of ~ 0.1 wt% in DMF prior acetylation and in acetone after acetylation were centrifuged at 8000 rpm for 45 min at 20 °C. The supernatant was spin coated (3000 rpm for 1 min) onto a poly(ethylene) imine (PEI) treated silica substrate. TOFC films were imaged in tapping mode using a Nanoscope IIIa multimode scanning probe AFM (Digital Instruments Inc., Santa Barbara, CA, USA). Silicon cantilevers (NSC15/AIBS, MicroMasch, Tallin, Estonia) having a radius of ~ 10 nm, according to the manufacturer, were used in imaging.

2.4 Dynamic mechanical thermal analysis (DMTA) and differential scanning calorimetry (DSC)

Composite films were cut into parallel sided strips having dimensions of approx. 5.3 by 12 mm (width by length). Specimens were loaded in a DMTA Q800 (TA Instruments, New Castle, DE, USA) and tested at a frequency of 1 Hz. The temperature varied between 0 and + 250 ℃ at a heating rate of 3 ℃/min.
Isothermal DMA was carried out on the same instrument equipped with a humidity controlled chamber. The relative humidity (RH) was cycled between 0 and 90 %. The stabilization time was 240 min at both RH levels at 23 °C.

3 Results

3.1 DS and morphology of TOFC

The acetyl content of acetylated TOFC was 3.9 % calculated using Eq. 1 and it can be translated to a DS of 0.16 by applying Eq. 2. The FT-IR spectra (Fig. 2) show vibrational bands at ~1735 cm^{-1} and at ~1365 cm^{-1} corresponding to carbonyl (C=O) [7, 8] and C-H symmetric bending in the methyl (CH$_3$) [9, 10]. All-in-all this indicates the presence of acetyl group, thus successful acetylation. The band appearing at ~1608 cm^{-1} is evidence of effective TEMPO oxidation, since it can be assigned to the carbonyl group in sodium carboxylate (COONa) [11].
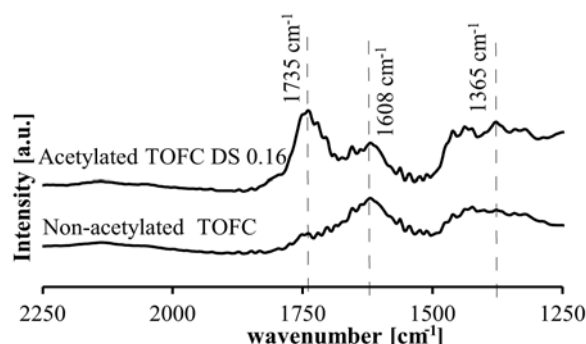

Figure 1. FT-IR spectra of non-acetylated and acetylated TOFC.

Fig. 2 illustrates TOFC suspended in water (a) and acetylated TOFC suspended in acetone (b). Although the solvent exchange procedure led to a somewhat aggregated system of the acetylated TOFC, nano-sized fibrils can be distinguished from the phase image (Fig. 2b). It is

worth noting that phase images (Fig. 2) are of the dried films, thus in media fibrils are probably better isolated.
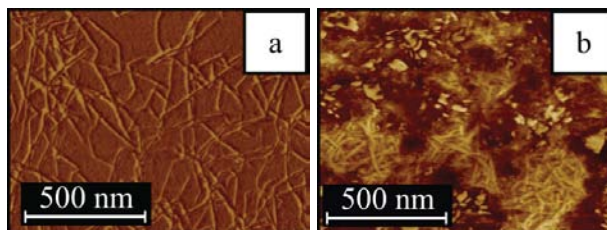

Figure 2. AFM phase images of TOFC in DMF prior to acetylation (a) and after acetylation in acetone (b).

The aspect ratio of fibrils slightly decreased when dispersed in low polarity media, most probably due to partial surface acetylation.

3.2 Structure and thermomechanical properties of composites

DMTA tests showed that composites were stronger compared to the pure PLA film (Fig. 3). The storage modulus increased by ~ 50% at 30 wt% load at 20 °C. The increment was more evident at temperatures exceeding the T_g. For instance, at 50 °C the storage modulus was approx. 10-fold higher at 30 wt% load of TOFC compared to pure PLA.
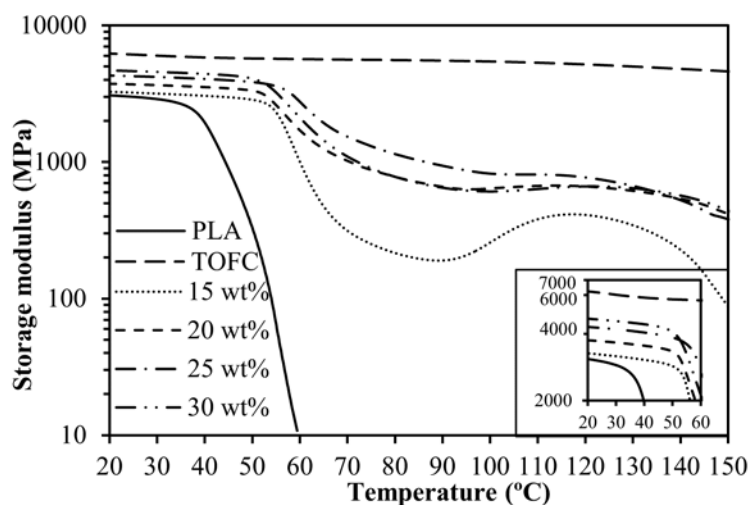

Figure 3. Storage modulus vs. temperature at TOFC contents of 0, 15, 20, 25 and 30 wt %. The inset shows the storage modulus between 20 and 60 °C.

T_g was taken from the DMTA curve as an inflection point of the storage modulus. The addition of TOFC effectively altered the thermal stability of composites (Fig. 3, Table 1). The T_g increased by ~ 50% at 30 wt % load of TOFC compared to pure PLA. In addition the thermal behavior of the composites was different with respect to the TOFC load. Composites with 15 wt % load of TOFC exhibited a slight increase in storage modulus within temperature range 100 to 120 °C. This could be indicative of cold crystallization taking place within the matrix. At higher filler contents, cold crystallization was not observed implying changes in crystallization behavior of the composites due to formation of a percolated network as has been shown previously [5].

TOFC load	DMTA
(wt%)	T_g (ºC)
0	39.2
15	57.8
20	56.8
25	61.5
30	57.3

Table 1. Thermal properties of TOFC reinforced composites compared to pure PLA

3.3 Effect of moisture on mechanical behavior

The dynamic mechanical behavior of composites was investigated in humid environments and compared to a pure PLA film. The results (Fig. 4) revealed that TOFC improved the mechanical properties of composite films compared to the pure PLA even at 90 % RH.
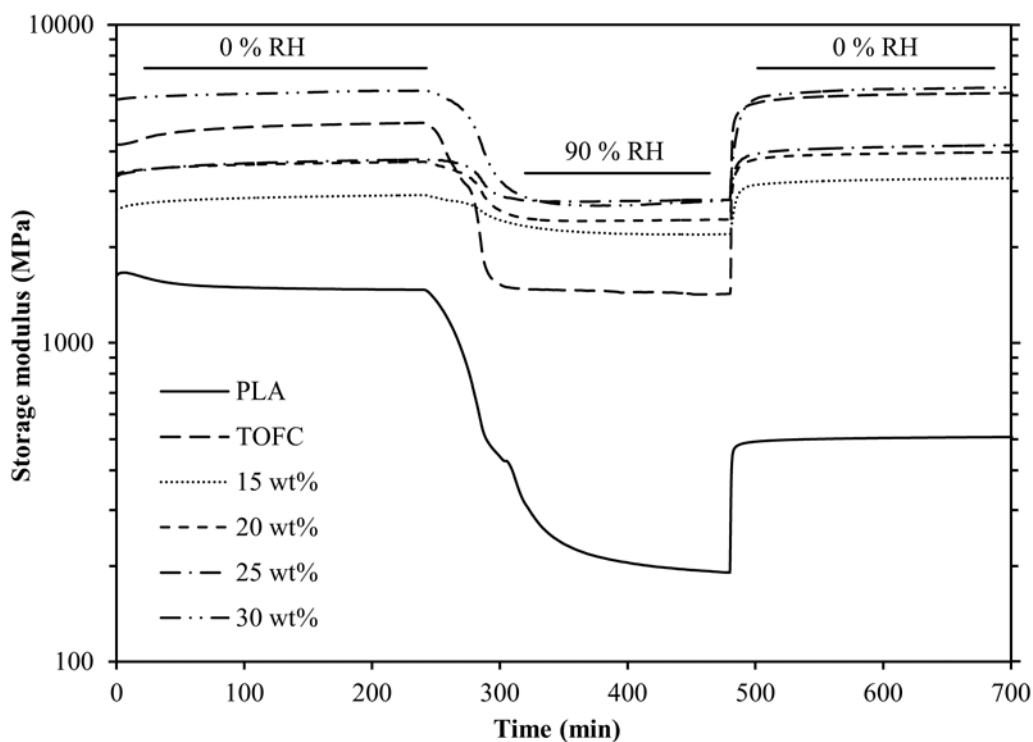

Figure 4. The influence of environmental RH on the storage modulus of PLA films with 0, 15, 20, 25 wt % of TOFC and pure TOFC film.

Although a significant drop in the storage modulus is observed at 90 % RH the overall trend remains, i.e. the higher the TOFC content the greater the storage modulus. As it could have been envisaged the highest drop in the storage modulus was observed in pure TOFC film due to its hydrophilic nature. Nevertheless, the strength properties were recovered after a single humidity cycle and exhibited even higher values compared to the initial ones, probably due to alignment of the nanofibrils [12].

4. Conclusions

TOFC was successfully acetylated in DMF leading to a better dispersion within the non-polar matrix. Although some slight aggregation of the fibrils took place the storage modulus and T_g of PLA was improved upon the incorporation of TOFC. Additionally, the composite films having higher loads of TOFC showed better mechanical properties in humid environments. All-in-all this implies that cellulose can be used as environmentally friendly non-toxic filler of polymers.

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