Self-reinforced poly(lactic acid) nanocomposites with integrated bacterial cellulose and its surface modification

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ABSTRACT

Bacterial cellulose (BC) nanofibers, with and without silane surface modification, were incorporated into self-reinforced poly(lactic acid) (SR-PLA) nanocomposites at 1 and 10 wt%. Disintegrated BC was combined with electrospun PLA fiber mats by film stacking and compression molding at 165°C for 40 sec to obtain SR-PLA/BC hybrid films. The effect of nanocellulose addition and its surface modification on the structure, morphology, and properties of the resulting composites were investigated. It was found that BC was a highly effective reinforcement for SR-PLA nanocomposites, providing a noticeable increase in the film's strength and modulus. Moreover, surface modification of BC was shown to further enhance the film performances due to an improved PLA/BC interfacial interaction. At an optimum BC content, these hybrid films also exhibited outstanding ductility and toughness. Water vapor barrier properties were also enhanced, especially when modified BC was integrated in the SR-PLA films.

1. Introduction

Poly(lactic acid) (PLA), derived from biomass such as corn, starch, and sugar beet, is one of the most recognized bio-based and biodegradable polymers for commercial applications these days due to its good optical and mechanical properties, biocompatibility, and relative ease of processing [1–3]. Nonetheless, the inherent brittleness, low thermal resistance, and poor barrier properties to oxygen and water of PLA have been a major obstacle to expand its further commercial use [4–7].

Self-reinforcement is a promising way to enhance mechanical, thermal, and other properties of thermoplastic polymers as well as provides several additional benefits, including ease of recycling, low density, good compatibility between reinforcement and matrix phases and it is potential to improve the impact resistance and toughness of a brittle polymer like PLA [8–10]. The concept of ‘self-reinforced’ (SR) polymer, ‘all-polymer’, or ‘single polymer’ composites was initiated in the 1970’s for polyethylene (PE) and has later been successfully extended to a range of other polymers, including PLA, PET, polypropylene (PP), poly(methyl methacrylate) (PMMA), liquid crystalline polymer (LCP), and cellulose [11]. Various technologies have been developed to create the self-reinforced polymer composites (SR-PC), starting from hot compaction to partial dissolution and chemical modification.
Many methods have also been used to improve the fabrication and properties of such composites, including cold drawing [8], film-stacking [8,9], filament winding [9,10], co-extrusion [11], and melt-drawing [12]. Currently, SR-PCs have already found a variety of markets and are used in automotive, construction, biomedical, consumer, and packaging applications.

Using the most abundant polymer on earth, Nishino and coworkers introduced a fascinating fully bio-based and biodegradable all-cellulose composite with remarkable mechanical performances and high transparency in 2004 [13]. Following on from this work, a number of all-cellulose nanocomposites have been created which combined the advantages of nanofiber reinforcement and self-reinforcement [14–18]. In these works, either microcrystalline cellulose, bacterial cellulose, or cellulose nanofibers were used as starting materials, while lithium chloride/N,N-dimethylacetamide or 1-butyl-3-methylimidazolium chloride (BMIMCl) liquid ionic has been used as solvent systems for the surface swelling process, followed by fusing the nanocellulose fibers together under pressure and finally followed by removing the solvent to obtain the all- or SR-cellulose nanocomposites.

More recently, a newly developed SR-PLA nanocomposite prepared via hot compaction of stacked electrospun PLA fiber mats was reported by our group [19]. Under the right processing condition, this SR-PLA nanocomposite showed a substantial improvement in all mechanical properties, notably the film’s toughness, when compared to isotropic PLA film. Property improvements were made thanks to a unique multilayer microstructure and unusually high crystallinity that was created in these SR-PLA nanocomposite structures after hot compaction.

Nanoscale reinforcement in polymer composites has received great attention over the last two decades. Lately, also nanocelluloses (i.e. cellulose nanocrystals and nanofibers) have attracted a great deal of interest as reinforcements for polymer composites because they offer many benefits including their bio-based and biodegradable character, wide availability, low density, high mechanical strength, and low thermal expansion [6,20]. Bacterial cellulose (BC), in the form of nanofiber networks, as synthesized by some bacterial species such as *Gluconacetobacter xylinus* and *Acetobactoer hansenii*, has also shown to be an interesting choice as nanoreinforcement due to its high degree of polymerization, crystallinity, and purity. However, the introduction of nanocelluloses into nanocomposites based on hydrophobic polymers like PLA is found to be challenging mainly due to its hydrophilic nature, strong self-association, and tendency to form agglomerates [7,21]. To avoid poor dispersion of nanocelluloses in such polymer matrices, many strategies have been attempted, for instance the use of papermaking processes [4], solvent-based processes [5,20], chemical grafting reactions [7,21], commercial surfactants [22], compatibilizers [23], and other surface modification techniques [2,6]. A good dispersion of nanocelluloses in polymer matrices, strong interfacial adhesion between these two phases, and some improvements in mechanical properties of the subsequent nanocomposites have been demonstrated in some of these works.

In this study, the aim was to further enhance the performances of the novel SR-PLA nanocomposites via the integration of BC. For this purpose, a modified procedure consisting of three main steps was developed; (i) PLA electrospinning and BC disintegration, (ii) integration of disintegrated BC in electrospun PLA mats using a film-stacking method, and (iii) hot compaction of these laminates to create SR-PLA/BC nanocomposite films (see the illustrative scheme in Figure 1). To improve the adhesion between both phases, we also surface functionalized the BC via a one-step silylation method and then incorporated this modified bacterial cellulose (MBC) into the PLA phase to create SR-PLA/MBC nanocomposites. The structure, morphology, and properties of these novel nanocomposite films were studied in comparison with neat SR-PLA and hot-pressed isotropic PLA films. Characterization of all films was carried out using scanning electron microscopy (SEM), differential scanning calorimetry (DSC), thermogravimetric
analysis (TGA), tensile tests, and water vapor transmission (WVTR) measurement.

2. Experimental

2.1. Chemicals and materials

PLA fiber mats were prepared by an electrospinning technique using an in-house build setup. The PLA pellets (intrinsic viscosity of 1.28 dL g⁻¹ and specific gravity of 1.24 g cm⁻³) from NatureWorks (USA) were used as-received and converted into electrospun fiber mats using an 8% w/v PLA solution in 7:3 v/v dichloromethane and dimethylformamide as a solvent system. Ethanol (absolute for analysis grade) was supplied by Merck KGaA (Germany). The surface modifying agent, 3-(trimethoxysilyl) propyl methacrylate (98%), was purchased from Sigma-Aldrich Pte. Ltd. (Singapore).

2.2. Preparation of bacterial cellulose suspension

BC pellicles were produced by cultivation of *Gluconacetobacter xylinus* strain TISTR 975 in the static condition for 10 days. Then, they were harvested and purified by immersing in running water, 2% w/v NaOH, then 0.5% w/v NaOCl, and finally running water, each step for 24 hours, respectively. After purifying, BC pellicles were in white color and have a thickness of around 1 cm. To prepare the BC suspension, a BC pellicle was cut into small cubes (~1 cm³) and then disintegrated into a fiber suspension by a kitchen blender (Philips HR 2094) at a maximum speed until a homogeneous suspension was obtained (approximately 10 min). BC suspensions were then kept in water media for further use.

2.3. Surface modification of bacterial cellulose

First, a BC suspension of 0.2% w/v in water:ethanol (40:60 w/w) was prepared. Then, pH of the suspension was adjusted to 4 with acetic acid and stirred continuously for 1 hour. Next, 0.3 g of 3-(trimethoxysilyl) propyl methacrylate was added into this suspension, followed by heating to 70°C and stirring for another 1 hour. After that, the suspension was left to cool down and was then filtered to collect the modified BC (MBC). Finally, the product was washed with ethanol and kept in ethanol media.

2.4. Fabrication of SR-PLA nanocomposite films integrated with nanocelluloses

Four pieces of PLA fiber mats were cut from the electrospun mats to a size of 70 mm × 70 mm and weighed. Disintegrated BC suspensions of 100 mL with BC contents of 1% and 10% w/w (based on PLA weight) were then prepared. After that, the first PLA fiber mat was placed onto a porcelain filter funnel connected to a vacuum system and one-third of the BC suspension was filtered and deposited onto this PLA fiber mat. After that, the second PLA fiber mat was placed on top and the BC deposition step was repeated. These steps were repeated for the third PLA fiber mat. Finally, a fourth PLA fiber mat was placed on top and 30 mL of ethanol was thoroughly poured onto these stacked PLA/BC mats to wash out and replace the remaining water in the system. It should be noted that if this ethanol rinsing step is not performed, PLA hydrolysis or degradation will occur in the subsequent hot pressing step, resulting in discoloration of the PLA-based film. After rinsing, the PLA/BC multilayer structure was removed from the funnel and left at an ambient temperature for 30 min and then further dried in a hot air oven at 50°C for another 15 min to ensure complete removal of the ethanol. Next, this dried PLA/BC multilayer film was cut into 16 rectangular pieces and stacked into a square mold (3 cm × 3 cm × 150 μm). From our previous report on the fabrication of SR-PLA nanocomposites [19], an optimal hot compaction temperature of 165°C was selected based on the end-set melting temperature of the electrospun PLA fiber mats as revealed by DSC analysis. In this work, the optimum hot compaction time was fixed to 40 sec to achieve optimum selective surface melting and bonding of the PLA nanofibers to create an SR-PLA film with optimal mechanical properties as reported in our previous work [19]. The final layup was placed in a hot pressing machine (Scientific LP-S-80, Labtech Engineering) and the hot compaction process was programmed as follows: (1) preheating, 1 min 45 s, (2) venting, 2 s, (3) pressing at a pressure of 6 MPa, 40 s, and (4) cooling, 10 min. After this processing cycle, the sample was removed from the mold and a SR-PLA/BC hybrid nanocomposite film was obtained. For the SR-PLA nanocomposite films integrated with MBC, all preparation steps were the same but here MBC was used instead of the unmodified BC. Neat SR-PLA film and isotropic PLA film (prepared by hot pressing PLA pellets) were used for comparison.

2.5. Fourier transform infrared spectroscopy

Fourier transform infrared (FTIR) spectra of the films were carried out using a Perkin Elmer model Spectrum GX in transmission mode. Spectra were recorded in the range of 4,000 cm⁻¹–400 cm⁻¹ with 4 cm⁻¹ resolutions and an accumulation of 4 scans.
2.6. Thermal analysis

Thermal behavior of the film samples was studied using a thermogravimetric analyzer (TGA) (Mettler Toledo 851e). A sample of approximately 6 mg–8 mg was used, and all experiments were conducted with a constant heating rate of 10°C/min, from 40 to 500°C, under a nitrogen atmosphere (flow rate of 50 mL/min).

DSC (Mettler Toledo 822e) was performed on a sample of 5 mg–7 mg and heating from 40°C to 250°C at a rate of 10°C/min. The corresponding glass transition temperature (Tg) and melting temperature (Tm) of the film samples were determined. Also, crystallinity (\(\chi_c\)) of each sample was calculated using the following equation:

\[
\chi_c(\%) = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m} \times 100
\]

where \(\Delta H_m\) is the melting enthalpy and \(\Delta H_{cc}\) is the cold crystallization enthalpy. The melting enthalpy of 100% crystalline PLA (\(\Delta H_m^0\)) is considered to be 93.0 J/g [5].

2.7. Mechanical testing

Tensile tests were carried out using a universal testing machine (Instron 5560), operating with an extension rate of 1 mm/min at room temperature and 50% relative humidity. The rectangle specimens (15 mm in gauge length and 3 mm in width) were cut from the molded films. Ultimate tensile strength (\(\sigma\)), Young’s modulus (\(E\)), and tensile toughness (\(U_t\)), calculated from the area under the stress–strain curve were evaluated from five repeats for each sample.

2.8. Morphological observation

Morphology of electrospun PLA fiber mats and fracture surfaces of the film specimens was observed by SEM (LEO 1450 VP) at an accelerating voltage of 10 kV. The specimens were mounted vertically on aluminum stubs using aluminum adhesive tape and then sputter coated with a thin layer of gold prior to the examination.

2.9. Water vapor transmission

WVTR was determined by a modified method according to ASTM E96. A film specimen with diameter of 2 cm was set horizontally on an aluminum cup which was filled with silica gel. Then, the test cup was placed in an environmental chamber at a controlled temperature of 38°C and relative humidity of 90% (accelerated condition). After that, the cup was weighted every hour for 5 hours. WVTR (g.m⁻².day⁻¹) was determined by the following equation:

\[
WVTR = \frac{G/t}{A}
\]

where \(G/t\) is slope of the curve of weight gain (g) as a function of time (h) and \(A\) is test area (m²).

3. Results and discussion

FTIR spectra of the unmodified BC and silane-treated MBC are shown in Figure 2(a). In both spectra, strong peaks at around 3356 and 3284 cm⁻¹, attributed to the hydrogen-bonded hydroxyl group (–OH) stretching vibration in cellulose, are observed. A signal band at ca. 1334 cm⁻¹ is as well due to the in-plane bending vibration of the O–H bonds in the polysaccharides. The absorbency at ca. 2914 and 2897 cm⁻¹ is considered due to C–H asymmetric and symmetric stretching vibration in all hydrocarbon constituents in both BC and MBC [24]. The peak observed at around 1431 cm⁻¹ is related to the C–H bending vibrations of CH₂ [25].

The anticipated chemical reactions during the silane treatment of BC are shown in Figure 2(b). A success in the silylation of BC can be indicated by the occurrence of Si–O–C bonds which has a signal at ca. 1,100 cm⁻¹. From these spectra, it was unclear because of the strong overlapping peaks in the region of 1060 cm⁻¹–1160 cm⁻¹ which are known to be primary due to C–O–C and C–O stretching [26]. However, the presence of a new peak at 802 cm⁻¹ that can be assigned to Si–C stretching vibration in the MBC was observed [27–29].

Photographs of the prepared neat SR-PLA, SR-PLA/BC, and SR-PLA/MBC nanocomposite films placed in front of a multicolored background are compared in Figure 3. It can be seen that the SR-PLA film as well as the SR-PLA hybrid films with 1% BC and 1% MBC is highly transparent. This implied that the presence of BC nanofibers at this low content did not affect the optical properties of PLA and that a good dispersion of BC was achieved in these films. However, in the case of SR-PLA films with 10% BC and 10% MBC, some white spots were apparent, indicating that in this case transparency was somewhat affected. Due to the high content of nanocelluloses, aggregates of BC or MBC in the composite films can be expected [1], which obviously will affect the optical transparency.

Table 1 and Figure 4 summarize the tensile properties and compare the stress–strain curves of all PLA-based films prepared in this work. It is obvious that the neat SR-PLA nanocomposite film prepared by hot compaction of electrospun PLA fiber mats exhibits greatly improved strength, ductility, and toughness as compared to isotropic PLA film and as also reported in our previous work [19]. However, a slight reduction in Young’s modulus of neat SR-PLA films
(prepared by hot pressing for 40 sec) was also noted. After the integration of BC and particularly MBC (1 wt% and 10 wt%), both Young’s modulus and tensile strength of the hybrid nanocomposite films increased. Similar improvements in mechanical properties were reported in several other studies involving the reinforcement of PLA with nanocellulose [1,4,7,22,30]. Clearly, the increment in Young’s modulus and strength of these films can be attributed to a reinforcement effect of the BC itself.

SR-PLA films incorporating modified BC (MBC) showed a significant greater reinforcing effect when compared to unmodified BC (see Table 1). This implied that improved interfacial adhesion from the introduction of organic functionalities on the surface of MBC and stress transfer between the PLA and MBC was established, leading to an effective increase in both the tensile strength and modulus of the films [31]. Interestingly, unlike for unmodified SR-PLA/1%BC films, the elongation at break of these modified SR-PLA/1%MBC films was also substantially increased (see Figure 4), leading to a simultaneous improvement in the nanocomposite film’s strength, stiffness, and toughness. From the series of SEM images (Figure 5), a high degree of plastic deformations and yielding was observed in the fracture surfaces of the SR-PLA/1%MBC films.
(Figure 5(e–f)), leading to a high-tensile toughness. This particular hybrid nanocomposite film exhibited a work to fracture ($U_T$) or tensile toughness of about 4, 10, and 16 times greater than that of neat SR-PLA, SR-PLA/1%BC, and isotropic PLA films, respectively (Table 1). The value of work to fracture of the SR-PLA/1%MBC film (35 MJ/m$^3$) compares also very favorable to the toughness of nanocellulose paper (15 MJ/m$^3$) as reported by Henriksson et al. [32]. However, with the addition of 10% MBC, the stiffening and embrittlement effect as a result of the higher MBC content were shown to prevail, reducing the ductility of the SR-PLA/10%MBC film and restricting the yielding of PLA [1,7,9,22]. On the other hand, a possible reason for the reduction in the hybrid SR-PLA/BC nanocomposite film’s ductility is that the addition of BC may affect the fusing and bonding between the individual layers of PLA nanofibers during hot-compaction. Since, the compatibility between BC and PLA is rather poor, these BC/PLA interfaces may act as defects in the films. Presumably, early failure in these films is therefore initiated by extensive debonding at these BC/PLA interfaces during tensile loading which in turn leads to a reduction in ductility and toughness of these SR-PLA/BC films.

Failed specimens after tensile testing are shown in Figure 4 below the stress–strain curves. During tensile loading, the initially transparent nanocomposite films showed stress whitening, particularly for the highly strained films. This is as expected and due to the large amount of debonding and voiding created in these films before ultimate rupture (see Figure 5), with the presence of these debonds and/or voids causing the light to scatter and a reduction in transparency of the films.

From the SEM result, it revealed that the fracture surfaces of the PLA/BC hybrid nanocomposite films (Figure 5(c–j)) were somewhat similar to that of the neat SR-PLA film (Figure 5(a,b)). The SEM images confirmed that a multilayer structure in these SR-PLA/BC nanocomposites was still maintained after hot compaction. However, the SR-PLA structure with observable PLA nanofibers fused together in the PLA matrix was not clearly seen in these SR-PLA films with BC or MBC. Yet, the integration of BC and MBC in between the PLA layers was evident from the presence of fibrous particles at the fracture surfaces (as indicated by the white circles in Figure 5).

DSC-heating thermograms of all samples are shown in Figure 6. The isotropic PLA film and electrospun PLA nanofiber mat showed cold crystallization and a low degree of crystallinity ($\chi_c$) of around 14%–16%, which is common for PLA due to its slow crystallization rate [33]. On the other hand, there was no cold-crystallization present in all the SR-PLA nanocomposite film samples and here crystallinity was found to be greatly increased. As described in our previous work [19], upon cooling and crystallization of the partially molten PLA fiber surfaces during hot compaction, the remaining PLA fiber cores can act as nucleation sites for PLA recrystallization, leading to an increase in crystallinity. This is similar to the effect of addition of other nanofillers in PLA due to a promotion in formation of large fraction of nuclei [34]. Yet, at a BC or MBC content of 10 wt%, the crystallinity of the hybrid nanocomposite films decreased again slightly, presumably as a result of reduced chain mobility due to the high presence of BC and MBC [17,35].

TGA curves of the prepared film samples are shown in Figure 7. All PLA-based films showed a similar decomposition pattern of a one-step degradation process. From the results, it was observed that the onset degradation ($T_{onset}$) and peak degradation ($T_d$) temperatures of all the PLA-based films were in the similar ranges of 341°C–346°C and 362°C–367°C, respectively (see Table 2). However, the temperatures at 5% and 10% weight loss ($T_{5\%}$ and $T_{10\%}$, respectively) of the SR-PLA nanocomposite films seemed to slightly increase with the integration of BC or MBC [36]. For all films, the remaining char residues at 500°C were found to be around 1 wt%–5 wt% which possibly contained silicon-derived residues in the silane-treated BC/PLA films.
Since the WVTR can be one of the key characteristics for using these fully bio-based films, the WVTR of all the PLA-based films was measured and compared (Figure 8). The isotropic PLA film showed the highest WVTR value. Neat SR-PLA film showed improved barrier properties than isotropic PLA film, possibly because of the pronounced increase in crystallinity. However, with the integration of BC and particularly MBC, a further reduction in WVTR values of the hybrid nanocomposite films was observed. A higher nanocellulose content also showed a tendency to further reduce the permeability of the films. The enhanced barrier properties of SR-PLA/BC and SR-PLA/MBC films can possibly be explained by the increase in tortuous diffusion pathways for water vapor molecules due to the presence of highly crystalline nanocellulose in the films, making it less permeable. Similar results were observed and reported for systems based on PLA and cellulose nanocrystals or nanofibers.
Hybrid nanocomposite films based on MBC showed an even lower WVTR than films based on unmodified BC, presumably due to an improved interaction between both phases. Without modification, a negative effect of cellulose nanocrystal addition on water vapor barrier properties of PLA nanocomposite films has been also observed [6]. However, interestingly, when comparing our data with data for more widely studied PLA/nanoclay systems [37–41], the present SR-PLA/nanocellulose films showed a greater ability in lowering the WVTR of PLA-based films (Table 3). Previous studies on nanocomposite films based on PLA and 5 wt%–6 wt% nanoclay showed a reduction in WVTR of around 36%–50%, while in the current study we showed that the incorporation of as little as 1% BC or 1% MBC in SR-PLA can reduce the WVTR by as much as 41% or 67%, respectively. In particular, the latter number is among the highest for PLA-based nanocomposite systems. On the other hand, it has been recently reported that the addition of as little as 0.5 wt% graphene nanoplatelets can reduce the permeability of PLA-based multilayer films by as much as 53% [43]. Nevertheless, it should be noted that the comparison here was based on different PLAs and experimental conditions used in each study.

Table 2. Thermal degradation temperatures and char residue at 500°C (%) of the neat SR-PLA nanocomposite films, and SR-PLA with integrated BC and MBC films.

| Sample          | $T_{\text{onset}}$ | $T_d$  | $T_{\text{50%}}$ | $T_{\text{100%}}$ | $T_{\text{onset}}$ | Char residue at 500°C (%) |
|-----------------|-------------------|--------|------------------|-------------------|-------------------|-------------------------|
| Neat SR-PLA     | 340.7             | 364.2  | 314.5            | 326.5             | 358.0             | 3.7                     |
| SR-PLA/1%BC     | 344.5             | 366.3  | 325.0            | 335.5             | 361.0             | 3.9                     |
| SR-PLA/10%BC    | 342.8             | 361.8  | 326.5            | 335.5             | 359.5             | 5.4                     |
| SR-PLA/1%MBC    | 345.7             | 366.7  | 320.0            | 334.0             | 362.0             | 0.9                     |
| SR-PLA/10%MBC   | 344.5             | 363.0  | 329.0            | 338.0             | 361.0             | 3.5                     |
4. Conclusions

Self-reinforced poly(lactide acid) (SR-PLA) nanocomposite films incorporating 1 and 10 wt% disintegrated bacterial cellulose (BC) or MBC were successfully prepared using a processing technique based on film stacking and hot compaction of alternating layers of electrospun PLA nanofiber mats and BC. Transparent films with unique multilayered structures were obtained. It was found that the integration of BC or MBC can significantly enhance the mechanical properties of the resulting hybrid nanocomposite films. Both ultimate tensile strength and Young’s modulus of these films were noticeably increased with the introduction of BC or MBC. Between the two types of reinforcements, MBC showed itself as the better reinforcing agent due to its better interfacial interaction with the PLA phase. The ductility of most of these nanocomposite films was significantly reduced by the stiffening and embrittlement effect of the integrated nanocelluloses. However, SR-PLA films reinforced with 1 wt% MBC showed an outstanding combination of both ductility and toughness together with an effectively increase in tensile strength and modulus. Thermal properties of the SR-PLA films were slightly improved with the integration of BC or MBC. Finally, water vapor barrier properties of these PLA-based hybrid nanocomposite films were found to improve greatly, especially in the case of MBC.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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