BACTERIAL CELLULOSE NETWORKS FOR REINFORCEMENT OF POLYLACTIDE

Mark P. Staiger*, Haiyuan Piao*, Seema Dean**, Peter Gostomski**
[Mark P. Staiger]: mark.staiger@canterbury.ac.nz
*Department of Mechanical Engineering, University of Canterbury, Private Bag 4800, Christchurch, New Zealand.
**Department of Chemical and Process Engineering, University of Canterbury, Private Bag 4800, Christchurch, New Zealand.

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Abstract

Cellulose microfibrils derived from bacteria (Acetobacter xylinum) are shown to be possible candidates for the reinforcement of biocomposites. Bacterial cellulose (BC) reinforced polylactide (PLA) biocomposites were prepared using a combination of solvent exchange processing and compression moulding. The microstructure and mechanical properties of BC, PLA and BC-PLA biocomposites were characterised by field-emission scanning electron microscopy (FESEM), atomic force microscopy (AFM), static tensile testing and dynamic mechanical analysis (DMA). The Young's modulus, tensile strength and storage modulus of BC-reinforced PLA composites is significantly higher than the neat polymer.

1 Introduction

Cellulosic fibres from plants have been extensively investigated as reinforcements and fillers for polymer matrix composites due to their abundance, low cost, environmental benefits and competitive specific strengths when compared with conventional synthetic reinforcements such as glass, carbon and aramid fibres [1, 2]. In addition to plant-derived cellulose, some lower animals (e.g. Tunicata sp.) and bacteria genera (e.g. Rhizobium sp., Agrobacterium sp. and Alcaligenes sp.) can also produce cellulose [3].

Bacterial cellulose (BC) such as that produced by *Acetobacter xylinum* is known to be of the Type I form of cellulose, chemically identical to plant cellulose. It has been shown by solid-state ^{13}C NMR that in its native form bacterial cellulose contains both I_α and I_β forms of cellulose with the I_α form being dominant [4]. However, the degree of polymerization (DP) of bacterial cellulose differs substantially from plant cellulose, with respective DP's in the ranges of ~2000-6000 and ~13000-14000 [5].
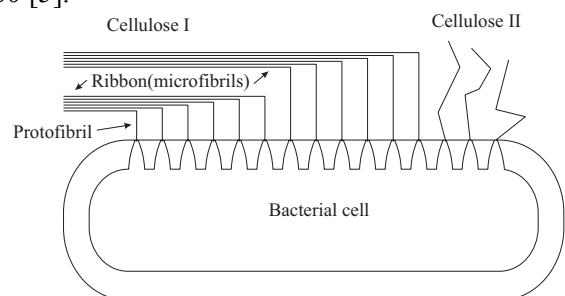

Figure 1. Schematic illustration of BC biogenesis and fibril formation [5].

Cellulose molecules are synthesised in the interior of the bacterial cell, spun out of 'cellulose export components' or nozzles to form protofibrils of ~2–4 nm in diameter and then organised into ribbon-like bundles (Figure 1) [5]. The microfibril ribbons are typically ~3-4 nm in thickness, ~100 nm in width and ~1-9 μm in length, leading to a very high aspect ratio and surface area to volume ratio. The ultra fine ribbons of BC are stabilized by extensive hydrogen bonding due to the cellulose molecule and form an open 3D network nanostructure [6]. Due to the high hydrophilicity and fine network structure of BC, the structure can hold over 99 wt.% water [7, 8]. Upon removal of the water from BC, the open structure collapses and shrinks, developing into a stiff, brittle material consisting of many thin sub-layers [9]. BC exhibits high mechanical properties with a Young's modulus of 15–18 GPa and UTS of ~260 MPa in the dried state [9]. BC has been used in a range of applications

in the food industry [10], wound healing [11], tissue engineering [7, 12] and as a reinforcement in nanocomposites [13-17].

BC can be produced in either a static, agitated or dynamic culture. Under static culture conditions, a gelatinous membrane or pellicle of BC accumulates on the surface of culture. This technology has low volumetric productivity, limited scale up potential, little or no control over process parameters such as pH and medium composition, and limited control of the product properties. Alternatively, BC can be produced in the form of a well-dispersed slurry containing irregular masses of cellulose in the form of granules and fibrous strands if the culture is agitated [4]. BC can also be produced in a dynamic set up using a rotating biological contactor (RBC) upon which BC grows on the partially submerged surfaces of rotating discs or cylinders [8, 18]. The RBC is alternately exposed to air and medium, while allowing for control over the pH and manipulation of the growth medium during the growth phase. A dynamic culture increases the production rate of BC compared with other methods due to the high surface area to volume ratio of the RBC [8, 19].

Nanoscale cellulosic microfibrils or whiskers have been isolated or extracted from plant cell walls [20-22] and shells of sea animals (e.g. tunicate) [4] with the aim of developing cellulose-based nanocomposites. However, cellulose extraction typically involves harsh chemical and mechanical processes that can degrade the properties of cellulose [23]. In contrast, cellulose produced by bacteria has the advantage of being free of lignin, pectin and hemicellulose as well as other biogenic products that are normally associated with plant cellulose, resulting in a relatively gentle extractive process that only requires some light rinsing to remove residual bacterial cells and culture media [7].

Early work on BC polymer composites was presented by Grunert et al. in which BC nanocrystal (Primacel^{TM})-polydimethylsiloxane (DS) composites were prepared by film casting. The storage modulus (E') of the pure DS was doubled by the addition of BC without any surface treatments [13]. Grunert et al. also reinforced cellulose acetate butyrate (CAB) with the same nanocrystals [14]. With the addition of 10 wt.% BC, E' of the neat CAB was increased by ~2 and ~26 times at temperatures of 81°C and 124°C, respectively.

BC reinforced composites were processed with different methods. BC (wet pellicles or dried sheet) were immersed in the polymers' solution in more cases. For example, Gindl et al. immersed BC pellicles in a CAB solution to produce BC-CAB composites [15]. Nakagaito et al. produced BC-phenol formaldehyde (PF) composites by immersing dried sheets of BC pellicles or disintegrated BC into a solution of PF, followed by hot pressing [16]. Yano et al. immersed dried BC sheets in acrylic and epoxy resin solutions to prepare composites [17]. The reported static mechanical properties of the above BC reinforced composites are listed in Table 1. The Young's modulus and tensile strength of BC-based composites were significantly increased by reinforcement with BC. By comparison natural plant fibres show poorer enhancement of mechanical properties for the amount of fibre added. For example, Joseph et al. reported that in banana fibre-PF composites, an addition of 48 wt.% fibre increased the tensile strength of PF from 7 MPa to 28 MPa [24].

Table 1 Summary of room temperature mechanical properties of various BC-reinforced polymer composites reported in the literature.

Ref	Composite system	Youngs modulus	Tensile strength
[15]	CAB 10 vol. % BC-CAB 32 vol. % BC-CAB	1.2 GPa 3.2 GPa 5.8 GPa	25.9 MPa 52.6 MPa 128.9 MPa
[25]	PF 87.6 wt.% BC-PF 87.5wt.% disintegrated BC-PF	0.375 GPa 28 GPa 19 GPa	10 MPa 420 MPa 350 MPa
[26]	epoxy 65 wt.% BC-epoxy	3-6 GPa 20 GPa	35-100MPa 325 MPa

Polylactide (PLA) has been reinforced with a large variety of plant fibres in the preparation of biocomposites [27-32]. However, the BC-PLA composite system has not been investigated till now. The present work is a preliminary investigation into the processing, microstructure and mechanical properties of BC reinforced PLA with a focus on developing a biodegradable nanocomposite. The static mechanical properties and viscoelastic behaviour of BC-PLA nanocomposites were measured and analysed. The microstructure-property relationships of the resulting BC-PLA nanocomposites are reported.

2 Experimental methods

2.1 Materials

NatureWorks™ polylactide (PLA) film was obtained from Cargill Dow LLC. The L/D ratio of

the PLA was 24:1 to 30:1. 1,4-dioxane and yeast extract were supplied by Sigma Aldrich NZ. Ammonium sulfate, citric acid, ethanol, glucose, glycerol, magnesium sulfate, sodium hydrate and sodium phosphate were supplied by Biolab Scientific NZ.

2.2 Preparation of bacterial cellulose

Acetobacter xylinum, ICMP 15569 was grown in a rotating (7 rpm) biological contactor for 192 hrs, using a 120 mm diameter cylinder that was partly submerged in culture medium - a modified method after Serafica *et al.* [19]. A litre of medium contained 50 g glucose, 5 g ammonium sulfate, 2.7 g sodium phosphate, 1 g magnesium sulfate, 0.5 g yeast extract 1.5 g citric acid, 14 mL ethanol and 2 mL of a trace element solution [33]. Cellulose pellicles were harvested and boiled in 1 M NaOH solution for 15 minutes to remove cell debris and medium. Pellicles were rinsed twice and soaked in deionised water (DIW) for 48 hrs. A ~2 mm layer of BC pellicle was peeled off from the thick pellicle to prepare the composites. Excess water on the surface of BC pellicle was removed with tissue paper and then the pellicle was cut into ~10×50 mm^2 pieces. BC pellicles were immersed in pure 1,4-dioxane for 15 min. The immersion of the pellicles was carried out three times to ensure exchange of the water with solvent.

2.3 Preparation of BC-PLA composites

Initially, PLA was dissolved in 1,4-dioxane to obtain a 10 wt.% PLA solution. In some cases, glycerol was also added to the polymer solution to act as a plasticizer [34]. Glycerol was dissolved in 1,4-dioxane first, followed by dissolution of the PLA to prepare a solution containing 9 wt.% PLA and 1 wt.% glycerol. The BC pellicles were immersed in the polymer solution for 24 hrs. The resulting BC-PLA pellicles were placed on a glass plate and dried at room temperature for a further 12 hrs, followed by drying at 50ºC under vacuum (100 mbar) for 12 hrs to remove any residual water or solvent. The dried BC-PLA pellicles were hot pressed at 180ºC for 3 min using 1.5 MPa of pressure. Pure PLA and PLA-glycerol solutions were also cast into films and hot pressed as above. The designations and fibre content of the prepared materials are given in Table 2.

Table 2 Designations and fibre content of the prepared materials.

Material	Designated name	Fibre content (wt. %)
PLA	PLA	-
Blend of PLA-glycerol	PLAG	-
BC reinforced PLA	BC-PLA	11.39
BC reinforced PLA-glycerol	BC-PLAG	11.28

2.4 Thermomechanical Analysis

Differential scanning calorimetry (DSC) (Calorimetry Sciences Corp. MS-DSC 4100) was used to measure the melting point of PLA and the blend of PLAG for optimisation of the hot pressing step. 0.1 g of sample was scanned over the temperature range of 20-200ºC at a rate of 0.4ºC/min. Dynamic mechanical analysis (DMA) (Perkin Elmer Instruments Inc. Diamond) was performed in tension mode at a frequency of 1 Hz, amplitude of 5 μm and tensile preload of 10 mN. DMA specimens had a thickness of ~0.1 mm, gage length of 10 mm and width of 3-8 mm. The storage modulus (E'), loss modulus (E") and tan δ (E"/E') were measured over the range of -50 to 150°C using a heating rate of 5°C/min. For plasticized samples (*i.e.* PLAG), the heating rate was reduced to 1°C/min. Static tensile testing (MTS858 Systems Corp.) was carried out on specimens with the same dimensions as for DMA using a 2.5 kN load.

2.5 Microstructural characterisation

Scanning electron microscopy was performed with a field-emission scanning electron microscope (FE-SEM)(JEOL JSM-7000F) in ultra high vacuum mode at an accelerating voltage of 2 kV. The fracture surfaces of the specimens were prepared for FE-SEM by sputter coating with gold. Atomic force microscopy (AFM) was performed with a Digital Instruments 3100 with a Nanoscope IIIa controller to investigate the morphology of the BC. Ambient atmosphere measurements were made in contact mode using an oxide-sharpened silicon nitride tip on a triangular cantilever with a soft spring constant of ~0.06 N/m (Veeco SPN-20). Load forces for the samples were on the order of 5 nN, and no image

degradation was observed during scanning. Scan speeds ranged from 1 to 5 Hz. Contact mode was chosen above tapping mode as it demonstrated much higher lateral resolution of the samples.

3 Results and Discussion

After dissolution and recasting, the melting point of PLA and PLAG were determined from DSC to be 159 and 148ºC, respectively. A temperature of 180ºC was used during hot pressing to ensure complete melting of the PLA while taking care to minimise cellulose degradation. The molecular weight of PLA may decrease by as much as 25-37% if held for 30 min at 160ºC in air [35]. Thus, the use of vacuum and short cycle times (3 min) during hot pressing was used to minimise degradation of the PLA.

Freeze-dried BC pellicle was observed by FE-SEM (Figure 2). The BC pellicles consisted of an ultrafine layered network structure (Figure 2). The layered morphology appears to be caused by a periodic agglomeration of microfibrils through the thickness of the pellicle. A highly networked structure at the outer surface of the BC pellicles was also observed with AFM (Figure 3). The microfibrils of the native BC were 5-10 μm in length and ~50 nm in diameter. At higher magnifications (Figure 3b), these microfibrils are observed to be agglomerates of smaller fibrils, having diameters in the order of 10 to 20 nm.
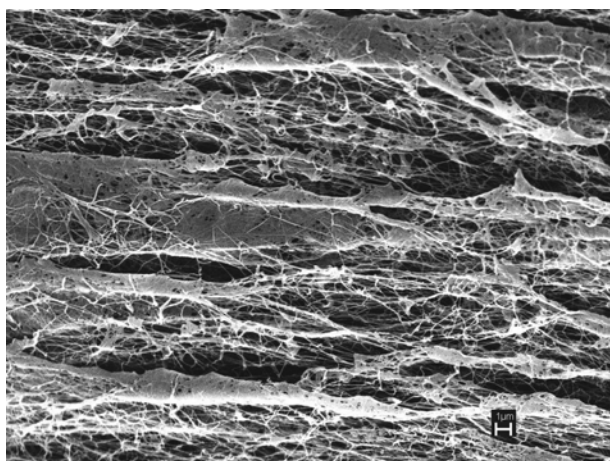

Figure 2. An FE-SEM micrograph of a freeze-dried BC pellicle, showing the fine network structure and layered morphology (10,000 ×).
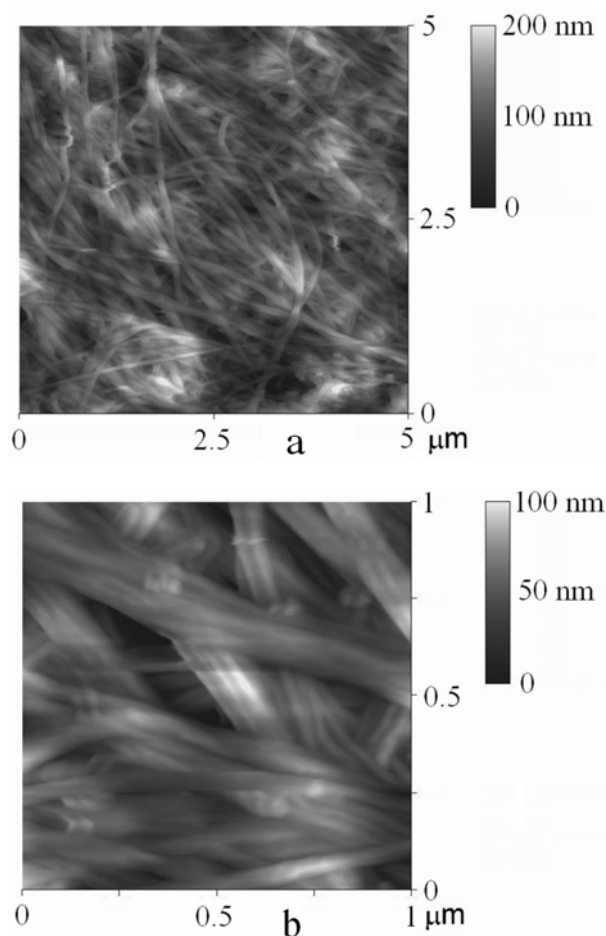

Figure 3. AFM micrographs of the outer surface of the dried BC pellicle at (a) lower magnification where details of the fine network structure can be observed and (b) higher magnification where the structure of individual fibres is seen.

The tensile behaviours of PLA and its composites are shown in Figure 4 and Figure 5. Brittle fracture was observed for pure PLA as shown by the linear stress-strain behaviour (Figure 4) and smooth appearance of the fracture surface (Figure 6 a). The elongation before failure of neat PLA was increased 64% with the addition of glycerol. Plastic deformation could be observed on part of the fracture surface of PLAG (Figure 6 b). The fracture surface of PLAG also presented regions of brittle behaviour, suggesting that glycerol may be limited in its effectiveness as a plasticizer for PLA - a conclusion also made by Martin *et al.* [36]. Furthermore, a large number of voids were present in PLAG compared with pure PLA which may be due to the volatilisation of the glycerol during hot pressing.

The combination of BC and PLA greatly enhanced the modulus and strength of neat PLA even with relatively low fibre contents. The BC and PLA appear to be well bonded as evidenced by the observed lack of microfibril pull-out even in the absence of any compatibilizers. Compatibilizers are normally required in natural fibre thermoplastic composites due to the incompatibilities between the hydrophilic cellulose and hydrophobic polymer matrix [37]. However, in the case of the BC-PLA composites the lack of fibre pull out (Figure 7a and b) is likely to be due to the network structure of the BC. It is proposed that the network structure hinders fibre pull out since the removal of a single microfibril from the matrix under an applied load would require the cooperative debonding of many microfibrils.

BC-PLAG composites contained numerous small voids which greatly reduced tensile strength. However, PLAG and BC-PLAG had rougher fracture surfaces indicating higher ductility is obtained with additions of glycerol when compared with neat PLA or BC-PLA.
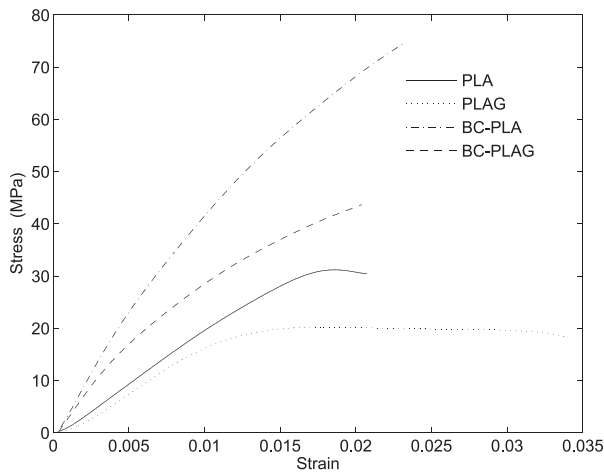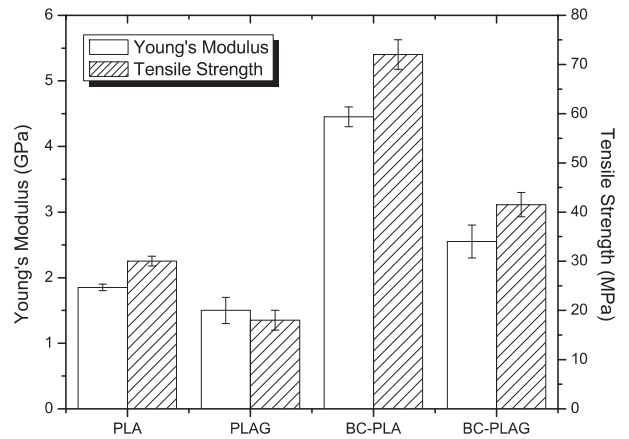

Figure 5. Young's modulus and tensile strength of PLA and its composites with BC reinforcement.

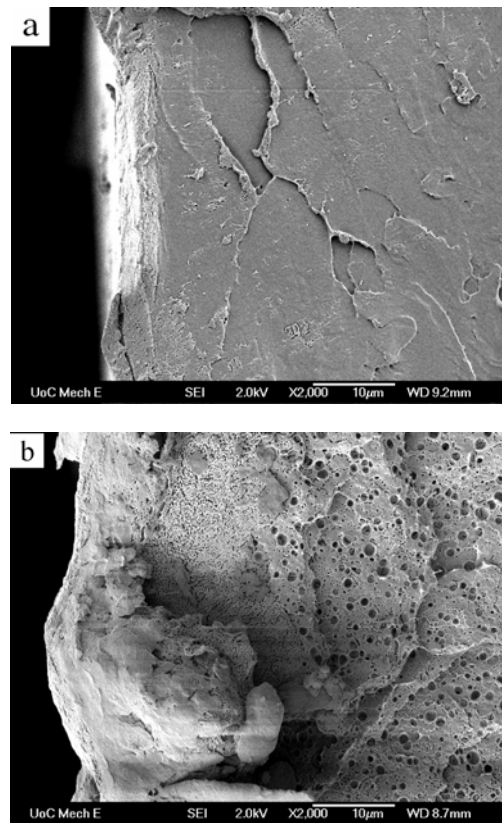Figure 4. Tensile stress-strain behaviour of neat PLA and BC-PLA composites.

Figure 6. Scanning electron micrographs of tensile fractured cross sections of (a) neat PLA and (b) PLAG.
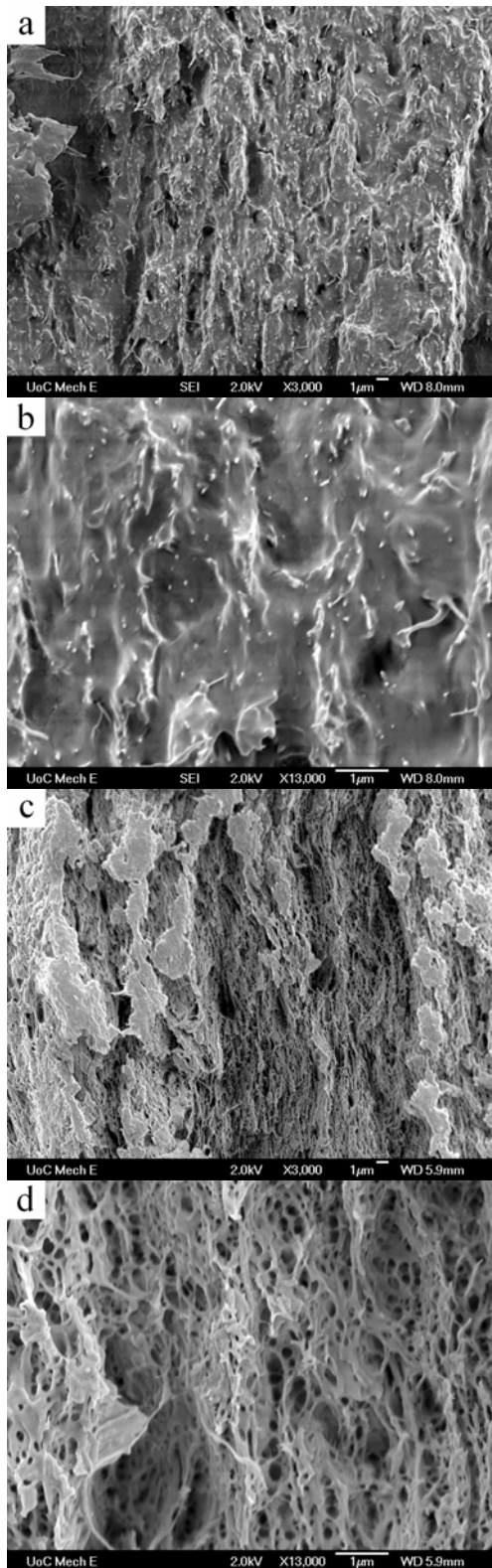
Figure 7. Scanning electron micrographs of the tensile fractured surfaces of BC-PLA composites at (a) 3000 × and (b) 13000 × and BC-PLAG composites at (c) 3000 × and (d) 13000 ×.

In general, the storage modulus (E') of BC-PLA was higher than neat PLA (Figure 8). The increase in E' due to the addition of BC to PLA was found to be greater at higher temperatures. For example, E' was doubled with the addition of BC to PLA with an increase from 4.66 to 8.49 GPa at ~25°C, while E' increased from 0.337 to 4.092 GPa at ~100°C – an increase of ~12 times. The large increase in E' at higher temperature for BC-PLA is due to cold crystallisation *via* molecular rearrangement [38]. Apparently, the BC microfibrils provide favourable nucleation sites for crystallisation since a similar crystallisation peak did not appear for neat PLA or PLAG. A similar phenomenon has been observed for poly(trimethylene terephthalate) (PTT) with the addition of nano-clay. The value of E' after T_g for the nanocomposite is higher about 10 times than that of pure PTT, which is the result of the improvement in crystallization capability of the PTT matrix. [38]. E' for PLAG was reduced due to the addition of glycerol. Similarly, BC-PLAG exhibited higher E' values than PLAG, especially at higher temperatures where BC promoted crystallisation of the PLAG.
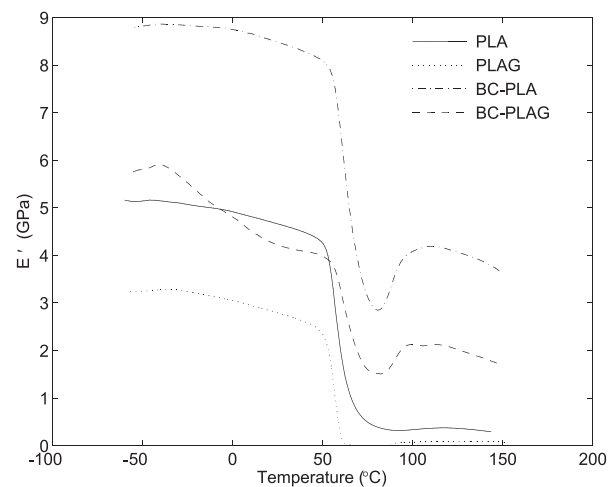

Figure 8. Storage modulus (E') of neat PLA and BC-PLA composites as a function of temperature.

The peak of the loss modulus (E'') was used as a measure of the T_g. Neat PLA was found to have a T_g of 58.68°C, which increased to 63.87°C with the addition of BC as found for BC-PLA. T_g of neat PLA decreased slightly to 56.69°C with the addition of glycerol (Figure 9). Similar T_g values were reported by Martin *et al.* using thermal analysis [36]. Similarly, the addition of BC to PLAG increased the T_g to 63.06°C for BC-PLAG.
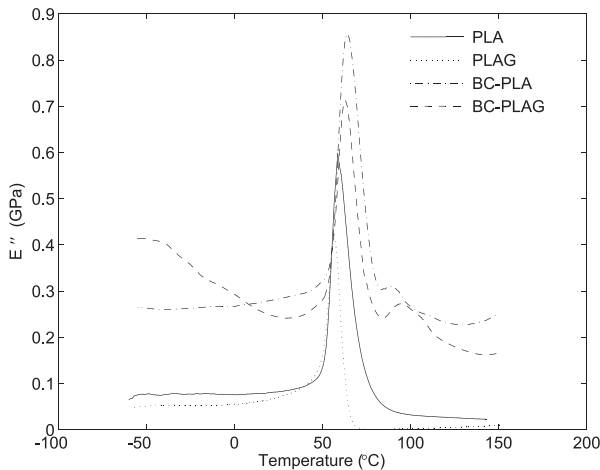
Figure 9. Loss modulus (E") of neat PLA and BC-PLA composites as a function of temperature.

The addition of BC to PLA or PLAG dramatically reduced the height of the tan δ peak (Figure 10), indicating a large decrease in damping capacity for the BC-PLA and BC-PLAG composites. Energy dissipation will occur in the polymer matrix and at the interface with a stronger interface characterized by less energy dissipation [39]. BC-PLA exhibited the lowest damping capacity caused by the apparent bonding between the BC microfibrils and PLA matrix which must originate from the network structure of the BC. Similarly, a lack of microfibril pull out was observed for BC-PLAG (Figure 7c and d), suggesting that the BC network structure has a similar reinforcing effect in BC-PLAG composites and leading to a lower damping capacity compared with PLAG. Further, the large damping capacity of PLAG is attributed to its highly porous structure [40].
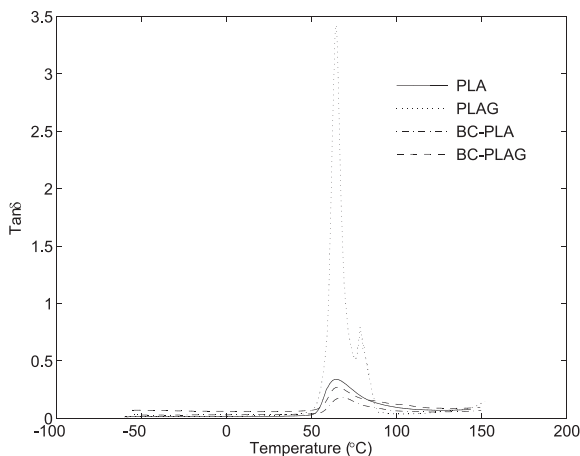

Figure 10. Tan δ of neat PLA and BC-PLA composites as a function of temperature.

4 Conclusions

This preliminary study of BC-PLA nanocomposites showed that this composite system of materials has the potential to offer great mechanical properties in the form of a biodegradable nanocomposite. The SEM results showed that the PLA appears to be integrated with the nano-scale network of the BC. Tensile properties were strongly enhanced by the addition of BC reinforcement. The Young's modulus value of BC-PLA was up to ~2.4 times that of neat PLA with similar increases observed for BC-PLAG. The tensile strength value of BC-PLA was up to ~2.4 times that of neat PLA; the tensile strength value of BC-PLAG was up to ~2.16 times that of PLAG. PLAG exhibited lower tensile properties, and larger tensile failure strains up to 1.5 times that of neat PLA. However, glycerol was not an appropriate plasticizer of PLA due to the formation of voids. Similarly, the storage modulus (E') of the neat PLA and PLAG was improved by the addition of BC. Finally, the DMA results showed that the presence of BC reinforcement significantly reduced the damping capacity of the BC-PLA and BC-PLAG composites.

5 Acknowledgements

6 References

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