

IMPROVING THE PROPERTIES OF NANOCELLULOSE/POLYLACTIDE COMPOSITES BY ESTERIFICATION OF NANOCELLULOSE. CAN IT BE DONE?

K-Y Lee, J J Blaker, A Bismarck
Polymer and Composite Engineering (PaCE) Group
Chemical Engineering and Chemical Technology Department
Imperial College London
South Kensington Campus
SW7 2AZ London UK
Email: a.bismarck@imperial.ac.uk

SUMMARY

The effect of surface modified bacterial cellulose (BC) with hexanoic acid for the use in PLLA/BC nanocomposites was investigated. A processing strategy was developed to incorporate BC nanofibrils into the polymer matrix. It was found that the mechanical and thermo-physical properties of the nanocomposites showed significant improvement.

Keywords: Bacterial cellulose, nanocomposites, esterification, polylactide, fatty acid

INTRODUCTION

Recent interests in green nanocomposites and public demand for more environmental friendly products have sparked the development of nanocomposites derived from renewable sources. One of the most studied renewable sources is cellulose. Cellulose I can be derived either from plant or synthesised by bacteria, such as from the *Acetobacter* species. The use of plant based cellulose such as natural fibres in the production of composite materials has been well documented. Major automotive makers in Germany are currently switching from conventional plastics to natural fibre reinforced composites to replace their door panels and boot linings [1]. Such action is a direct result of the distinct advantages of natural fibres over conventional glass fibres; low cost, low density, high toughness and biodegradability [2].

In addition to natural fibres, bacterial cellulose has also been studied extensively. As a matter of fact, bacterial cellulose possesses similar advantages to natural fibres but with the exception of carbon neutrality [3]. However, the mechanical properties between natural fibres and bacterial cellulose are somewhat different. Bacterial cellulose possesses significantly higher Young's modulus over natural fibres. The Young's modulus of

bacterial cellulose was found to be 114 GPa [4]. This value is comparable to glass fibres (70 GPa) given that bacterial cellulose has a lower density (1.25 g cm^{-3}) compared to glass fibres (2.5 g cm^{-3}). Natural fibres, on the other hand, possesses much lower Young's moduli; cotton (12.6 GPa), flax (27.6 GPa), sisal (22.0 GPa) and jute (26.5 GPa) [5]. Bacterial cellulose exists naturally as a nano-sized material (diameter of between 24 to 86 nm and a length of several micrometres) [6, 7] and therefore, it has a high surface area to volume ratio. This implies that for the same amount of material, the interface will be larger for bacterial cellulose compared to natural fibres. Such property is highly advantageous in composites production. In addition to this, the highly crystalline structure [8] of bacterial cellulose ($\sim 90\%$) is also highly favourable to be used as reinforcement in nanocomposite materials. However, the extremely hydrophilic nature of bacterial cellulose poses a problem. The interfacial adhesion between hydrophilic bacterial cellulose and hydrophobic polymer is often poor. Therefore, it can be anticipated that by modifying the surface of bacterial cellulose, the highly crystalline structure can be retained whilst the surface will be modified to become hydrophobic. Combining this with biodegradable polymer matrices, truly green or renewable nanocomposites can be produced.

In the present study, bacterial cellulose was modified on the surface via a fatty acid esterification reaction. It was then subsequently used as a filler to produce cellulose reinforced polylactide. The potential of this modification to the overall performance of the nanocomposites was then investigated.

MATERIALS AND METHODS

Poly(L-Lactic Acid) (PLLA) was purchased from Biomer (L9000, MW ≥ 150 kDa, D-content $\approx 1.5\%$) and used as the polymeric matrix. 1,4-Dioxane (Sigma-Aldrich ACS Reagent, $\geq 99\%$ purity) was used as the solvent for PLLA. Pyridine (analaR NORMAPUR, purity $\geq 99.7\%$) and ethanol (GPR, purity $\geq 99.7\%$) were purchased from VWR. Hexanoic acid (Aldrich, $\geq 99.5\%$ purity), dimethyl carbonate (Aldrich Reagent Plus, purity $\geq 99\%$) and *p*-toluenesulfonyl chloride (Aldrich, $\geq 99\%$ purity) were purchased from Sigma-Aldrich. All the materials were used as received without further purification. Bacterial cellulose was extracted from commercially available *Nata-de-Coco* (CHAOKOH coconut gel in syrup, Ampol Food Processing Ltd, Nakorn Pathom, Thailand).

Extraction and purification of bacterial cellulose

Bacterial cellulose was extracted from 5 jars of *Nata-de-Coco*. Firstly, the coconut gels were rinsed three times with de-ionised water and blended for 1 min using a laboratory blender (Waring Blender LB20EG, Christison Particle Technologies, Gateshead UK). The resulting blend of bacterial cellulose was then homogenised for 2 min using a homogeniser (Polytron PT 10-35 GT, Kinematica.CH, Switzerland) and centrifuged to remove the excess water. To further purify the bacterial cellulose, the centrifuged bacterial cellulose product

was re-dispersed in 5 L of de-ionised water and boiled in 0.1 M sodium hydroxide solution at 80 °C for 20 min to remove any remaining microorganisms and soluble polysaccharides [9]. This purified bacterial cellulose was then successively centrifuged and homogenised to neutral pH.

Modification of bacterial cellulose via esterification

2 g (dry weight) of the extracted and purified bacterial cellulose was solvent exchanged from water through methanol into pyridine at a concentration of 0.3% (g mL⁻¹). The mixture was homogenised at 20,000 rpm for at least 1 min at each stage to completely disperse the bacterial cellulose in the solvent. Bacterial cellulose was retained through centrifugation at 14,000G for 15 min before re-dispersing it again in the subsequent solvent. In the final solvent exchange step, the concentration of bacterial cellulose in pyridine was adjusted to 0.5% (g mL⁻¹). The bacterial cellulose-pyridine mixture was then poured into a 1 L 3-neck round bottom flask and stirred using a magnetic stirrer. 92 g of *p*-toluenesulfonyl chloride was added into this mixture and an equimolar amount of hexanoic acid was added after the addition of *p*-toluenesulfonyl chloride. The reaction was conducted at 50°C for 2 h under nitrogen atmosphere and it was subsequently quenched with 1.5 L of ethanol. The product was solvent exchanged from ethanol to water using the previously described centrifugation-homogenisation steps. In order to use the bacterial cellulose in later stages, the neat and modified bacterial cellulose were dispersed in water and dimethyl carbonate respectively at a concentration of 0.4% (g mL⁻¹) and subsequently freeze dried (Edwards modulyo freeze dryer, West Sussex UK).

Preparation of porous composite microspheres with 5 wt% cellulose reinforcement

In order to ease the processing of BC and PLLA in an extruder, a method based on thermally induced phase separation (TIPS) to produce porous composite microspheres in the absence of water was adopted from literature [10]. Such microspheres can be fed directly into the extruder. 395 mg of freeze-dried cellulose was added into 90 mL of 1,4-dioxane and homogenised at 20,000 rpm to disperse the cellulose in the solvent. 7.5 g of PLLA was then added into this mixture (1:12 g mL⁻¹) and the polymer was left to dissolve overnight at 60°C under magnetic stirring. The resulting mixture was then poured into a 50 mL syringe and added drop wise into a bath of liquid nitrogen to rapidly induce phase separation. The frozen microspheres were then transferred into a 500 mL one-neck round bottom flask and subsequently freeze-dried to remove the solvent and produce porous composite microspheres.

Processing of composite microspheres and the production of composite films

5.6 g of microspheres were fed into a 5 cm³ twin screw micro-extruder (DSM Research BV, The Netherlands) kept at a melt temperature of 180 °C and rotating at 10 rpm. After all the microspheres had been fed into the micro-extruder, the screw rotation speed was

increased to 40 rpm for 30 min to promote mixing of cellulose in the polymer melt. The polymer melt was then extruded at a screw rotational speed of 20 rpm. These extruded products were pelletized and compression moulded into films in a hot press (George E Moore and Sons, Birmingham UK) at 180 °C and 2 t for 2 min. The resulting film was then left to cool down to room temperature naturally.

Tensile testing of composite films

In order to perform mechanical tests, the composite films were cut into dog-bone shaped specimens using a Zwick cutter (Zwick GmbH and Co. KG, Ulm, Germany). These dog-bone shaped specimens had an overall length of 75 mm, a gauge length of 30 mm and the narrowest part of the specimen was 4 mm. All the tensile tests were conducted in accordance to BS EN ISO 527: 1996 using an Instron universal material testing machine (Instron 4502, Instron Corporation, Massachusetts, USA). The testing speed and load cell used were 1 mm min⁻¹ and 1 kN, respectively. At least five specimens were tested for each sample.

Scanning electron microscopy (SEM)

SEM was conducted using a high resolution field emission gun scanning electron microscope (LEO Gemini 1525 FEG-SEM, Carl Zeiss NTS GmbH) and used to characterise the composite microspheres. The accelerating voltage used was 5 kV. All the samples were fixed onto the SEM stubs using carbon tabs. Prior to the SEM, the microspheres were frozen in liquid nitrogen and trisected to enable observation of their porous interior before coating with chromium for 1 minute at 75 mA.

Differential scanning calorimetry (DSC)

The melting and crystallisation behaviour of the polymer and nanocomposite materials were investigated using DSC (DSC Q2000, TA Instruments, UK) under helium atmosphere using a sample mass of 6 mg. A heat-cool-heat regime was applied. It was heated from room temperature to 210 °C at a rate of 10 °C min⁻¹ before cooling down to room temperature at a rate of 50 °C min⁻¹ to erase the samples' thermal history. The samples were then re-heated from room temperature to 210 °C at 10 °C min⁻¹.

Thermal gravity analysis (TGA)

The thermal degradation behaviour of the composite materials was characterised using TGA (TGA Q500, TA Instruments, UK). The sample size was approximately 5 mg and the samples were heated from room temperature to 500 °C at a rate of 10 °C min⁻¹. An inert (nitrogen) atmosphere was used in this characterisation.

Dynamic mechanical analysis (DMA)

The viscoelastic behaviour of the composite materials was measured using Triton 2000 DMA (Triton Technology Ltd, Keyworth UK). DMA was performed in tension mode (gauge length and sample width of 10 mm and 4 mm respectively) at a frequency of 1 Hz. The storage modulus, loss modulus and tan delta were measured from 30 °C to 120 °C at a heating rate of 2 °C min⁻¹.

RESULTS AND DISCUSSIONS

The morphology of the composite microspheres

Figure 1 shows the scanning electron micrographs of the composite microspheres prepared by TIPS. It can be seen that the microspheres produced has a channel-like porous structure (figure 1b). This is a direct result of the solvent freezing from the outside towards the centre of the microspheres. In addition to this, the pores act like a three dimensional fingerprint where the solvent-rich phase used to be as a result of the phase separation. It can also be observed that the pore structure is highly anisotropic. This is a characteristic of solid-liquid phase separation induced by TIPS [11]. Large air pockets are also seen inside the microspheres (see figure 1a). This might be due to the entrapment of air during the dropping of polymer solutions into the liquid nitrogen bath. Similar results were also observed in literature [10, 12]. As mentioned earlier, these composite microspheres were directly fed into an extruder for further processing.

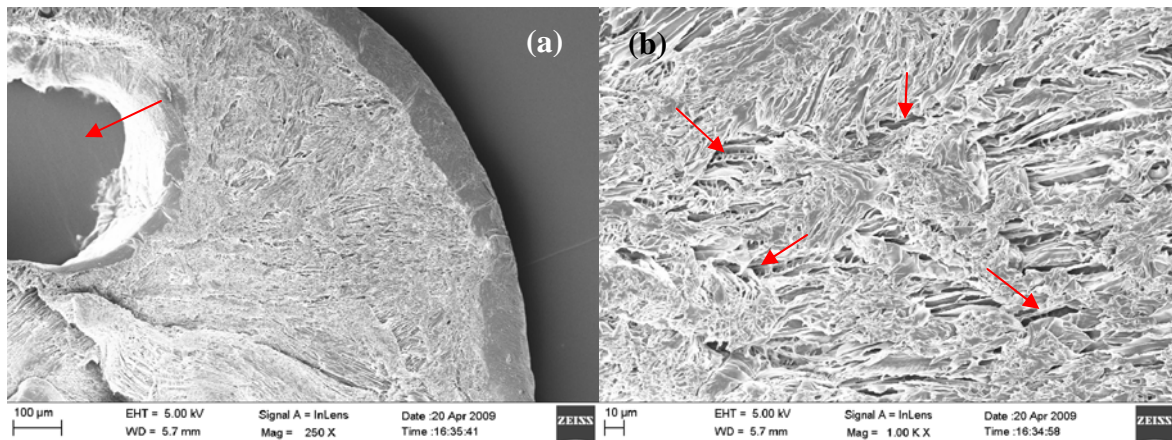


Figure 1: Scanning electron micrographs showing the morphology of the composite microspheres. (a) at low magnification (b) at high magnification

Mechanical properties of cellulose nanocomposites

The mechanical properties of neat PLLA and cellulose reinforced PLLA nanocomposites are shown in table 1. It can be seen that both the tensile modulus and tensile strength of the nanocomposites increased when compared to neat PLLA. The tensile modulus of the BC

reinforced nanocomposites increased by 40% but the tensile strength remained constant. On the other hand, the tensile modulus and tensile strength of hexanoic acid modified bacterial cellulose (C₆BC) reinforced nanocomposites improved by 33% and 10% respectively.

Table 1: Tensile properties of cellulose/modified cellulose reinforced PLLA nanocomposites

Polymer/Cellulose (wt %)	Tensile Modulus (GPa)	Tensile Strength (MPa)	Elongation at Break (%)
Neat PLLA	1.35 ± 0.10	60.3 ± 1.9	3.6 ± 0.2
PLLA/BC (5 wt%)	1.87 ± 0.04	61.3 ± 0.6	2.5 ± 0.1
PLLA/C ₆ BC (5 wt%)	1.80 ± 0.04	65.9 ± 1.3	2.7 ± 0.1

The improvement seen in the tensile modulus of the nanocomposites can be explained by the rule of mixture of nanocomposites materials. Cox's model [13] can be used to calculate the Young's modulus of the nanocomposites. Equation 1 and 2 shows the model where f is the fibre volume fraction, ν is the Poisson's ratio, l , d , E , E_m , E_f are the length and the diameter of the fibre, moduli of the nanocomposites, polymer and fibre, respectively, It can be deduced from this equation that as the reinforcing phase's volume fraction increases, the tensile modulus of the nanocomposites will no doubt increase.

$$E = E_m(1 - f) + \left(\frac{1}{6}\right)\left(1 - \frac{\tanh(\beta)}{\beta}\right)E_f \quad [1]$$

$$\beta = \frac{l}{d} \sqrt{\frac{E_m}{(1 + \nu)E_f \times \ln(\pi/4f)}} \quad [2]$$

At first glance, the tensile strength of PLLA/BC seemed to improve compared to pure PLLA. However, when the errors from the tensile strength measurements are taken into account, the tensile strength between neat PLLA and PLLA/BC are the same. Even though the tensile strengths are the same, the increment in the tensile modulus of PLLA/BC nanocomposites is enough to justify the improvement in its mechanical properties. It can also be seen from table 1 that the PLLA/C₆BC nanocomposites showed significant improvement in both tensile strength and modulus. This improvement can be attributed to the improved interaction between modified BC and PLLA. In addition to this, the surface modification of the bacterial cellulose retains its highly crystalline structure and this contributed to the increment in mechanical properties of the nanocomposites as well.

Thermal behaviour of the cellulose reinforced nanocomposites

DSC curves are used to obtain thermal information such as the glass transition temperature, crystallization temperature and melt temperature. Figure 2 shows the DSC curves of pure PLLA and cellulose reinforced PLLA nanocomposites. From these curves, it is clear that the addition of cellulose/modified cellulose to PLLA has certain impact on the nanocomposites' thermal behaviour. It can be seen that the glass transition temperature of the nanocomposites did not change significantly due to the addition of cellulose ($\sim 59^\circ\text{C}$). However, the addition of cellulose and modified cellulose did affect the crystallisation behaviour of the polymer. The crystallisation temperature decreased up to 20°C due to the addition of cellulose nanofibrils. This is because the cellulose nanofibrils aided the crystallisation of the polymer [14]. However, the ability of nucleating new crystals seems to be decreasing with modification. Such results can be implied from the crystallisation temperature of the modified cellulose nanocomposites ($\sim 106^\circ\text{C}$) and the non-modified cellulose nanocomposites ($\sim 99^\circ\text{C}$). The appearance of two melt peaks in the pure PLLA polymer is not surprising. Usually, annealing of crystallisable PLLA will produce two melt peaks, as seen in figure 2 [15]. It is also worth noticing that the addition of cellulose/modified cellulose did not affect the melt temperature significantly.

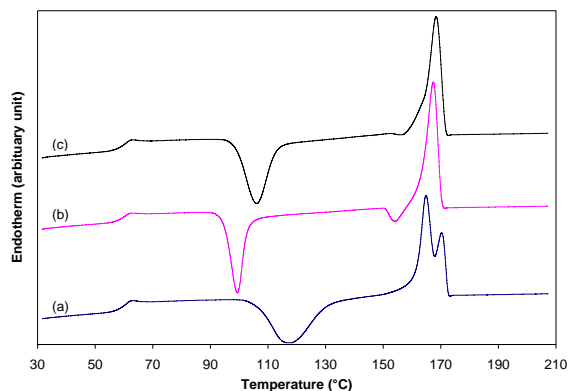


Figure 2: DSC curves (second heating curve) of cellulose reinforced PLLA nanocomposites. (a) Pure PLLA (b) PLLA/BC (c) PLLA/C₆BC

Viscoelastic properties of the nanocomposites

Figure 3 shows the DMA results of the produced nanocomposites; the storage moduli of cellulose/modified cellulose reinforced PLLA nanocomposites are higher than that of pure PLLA. This can be explained by the reinforcing effect of cellulose. In addition to this, the storage modulus of PLLA/C₆BC is significantly higher than PLLA/BC. Such results are not surprising as the modified bacterial cellulose is expected to have better interaction with the hydrophobic PLLA. From figure 3, it can also be seen that the peak of tan delta decreased with cellulose/modified cellulose reinforcement. Generally, tan delta measures the amount of energy used to deform the material dissipated as heat [16]. The decrease in the height of the tan delta peak implies that the nanocomposites experienced a decrease in molecular chain mobility due to the addition of cellulose/modified bacterial cellulose.

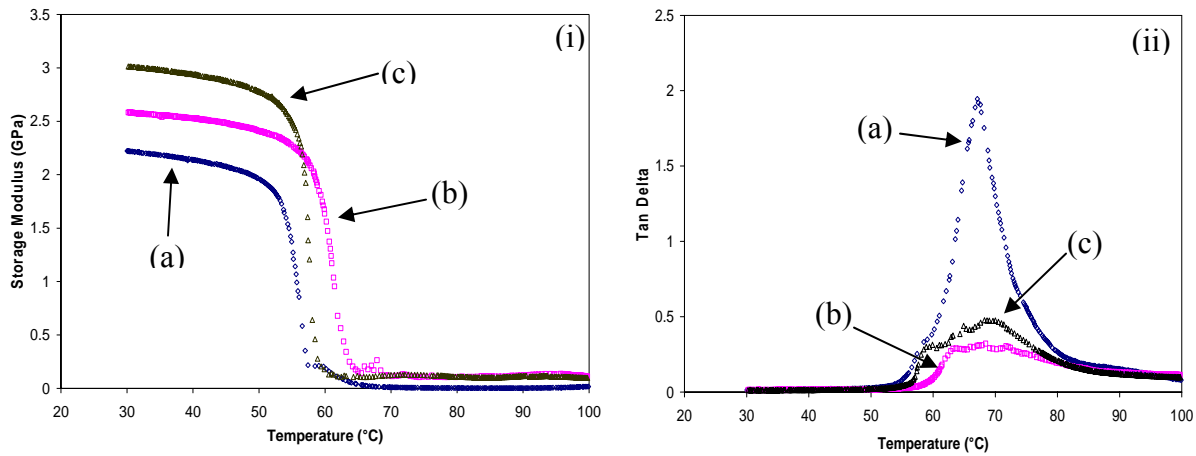


Figure 3: Graphs showing the temperature dependency of (i) storage modulus and (ii) tan delta of the nanocomposites. (a) Pure PLLA, (b) PLLA/BC, (c) PLLA/C₆BC

Thermal degradation behaviour of the cellulose reinforced nanocomposites

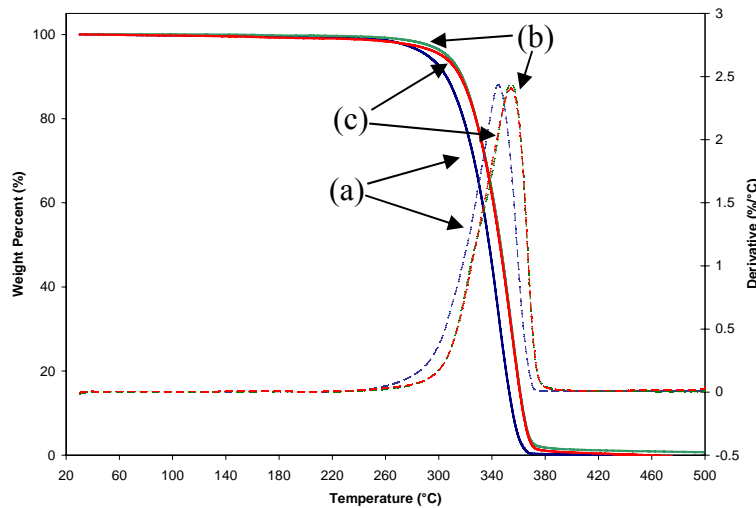


Figure 4: TGA curves of (a) Pure PLLA, (b) PLLA/BC and (c) PLLA/C₆BC. Solid line indicates percentage weight loss; dotted line indicates the derivative of weight loss.

The thermal stability of the nanocomposites is of importance as it will determine the applications of the end product. Figure 4 shows the TGA curves of PLLA and cellulose reinforced PLLA nanocomposites. It can be seen that all the materials underwent single step degradation. The 25% weight-loss temperature occurred around 323°C for pure PLLA and 332°C for PLLA/BC and PLLA/C₆BC. The 50% and 75% weight-loss temperature occurred around 338 °C and 348 °C respectively for pure PLLA. On the other hand, the

50% and 75% weight-loss temperature for PLLA/BC and PLLA/C₆BC nanocomposites occurred around 347 °C and 357 °C respectively. In addition to this, the degradation of pure PLLA occurred between 250 °C and 370 °C but the degradation of the nanocomposites occurred between 280 °C and 400 °C. Therefore, it can be concluded that the thermal stability of the nanocomposites improved by approximately 30 °C and the effect of bacterial cellulose modification did not improve the thermal stability relative to the effect observed for the non-modified bacterial cellulose nanocomposites.

CONCLUSIONS

The mechanical properties, thermal behaviour and viscoelastic properties of bacterial cellulose nanofibrils reinforced PLLA nanocomposites have been investigated in the present study. It was found that the surface modification of bacterial cellulose with hexanoic acid via esterification reaction modified the extremely hydrophilic surface of bacterial cellulose to hydrophobic surface. FTIR confirmed this modification (data not shown) as an ester carbonyl peak (1750 cm^{-1}) was observed in the modified sample and this peak was not observed in the unmodified sample. Such modification proved to be effective in terms of improving the mechanical properties of the nanocomposites produced due to the improvement in the interfacial adhesion between the cellulose and PLLA. The tensile modulus and tensile strength of PLLA/C₆BC nanocomposites increased by 33% and 10% respectively when compared to neat PLLA. From the DMA results, the storage modulus of PLLA/C₆BC was 20% higher than that of PLLA/BC. Moreover, the storage modulus of PLLA/C₆BC nanocomposites was 36% higher than that of neat PLLA. These results have demonstrated the reinforcing ability of surface modified bacterial cellulose nanofibrils. The TGA results revealed an improvement in the thermal stability of both PLLA/BC and PLLA/C₆BC nanocomposites with respect to neat PLLA. Therefore, it can be concluded that the idea of heterogeneous modification of bacterial cellulose to improve the properties of bacterial cellulose reinforced PLLA nanocomposites can work. However, more characterisation still needs to be done in search of the best fatty acid modification that will provide optimum interfacial adhesion between bacterial cellulose and PLLA. Future studies focus on the search for the most suitable long chain fatty acids that will maximise interfacial adhesion, leading to the production of truly green and renewable bacterial cellulose reinforced PLLA nanocomposites with improved mechanical and thermo-physical properties.

ACKNOWLEDGEMENT

The authors would like to thank the UK Engineering and Physical Science Research Council (EPSRC) for their financial support in the project (EP/F032005/1).

References

1. B C Suddel, W J Evans, 2005, in *Natural Fibers, Biopolymers and Biocomposites*, A K Mohanty, M Misra, L T Drzal (CRC Press), pg 237 – 266.
2. R Karnani, M Krishnan, R Narayan, *Polymer Engineering and Science* 1997 (37), pg 476 – 483.
3. W Gindl, J Keckes, *Composites Science and Technology* 2004 (64), pg 2407 – 2413.
4. Y C Hsieh, H Yano, M Nogi, S J Eichhorn, *Cellulose* 2008 (15), pg 507 – 513.
5. A K Mohanty, M Misra, G Hinrichsen, *Macromolecular Materials and Engineering* 2000 (276/277), pg 1 – 24.
6. E Chanliaud, K M Burrows, G Jeronimidis, M J Gidley, *Planta* 2002 (215), pg 989 – 996.
7. M Iguchi, S Yamanaka, A Budhiono, *Journal of Materials Science* 2000 (35), pg 261 – 270.
8. W Czaja, D Romanovicz, R M Brown Jr, *Cellulose* 2004 (11), pg 403 – 411.
9. H Toyosaki, T Naritomi, A Seto, M Matsuoka, T Tsuchida, F Yoshinaga, *Bioscience, Biotech and Biochemistry* 1995 (59), pg 1498 – 1502.
10. J J Blaker, J C Knowles, R M Day, *Acta Biomaterialia* 2008 (4), pg 264 – 272.
11. C Schugens, V Maquet, C Grandfils, R Jerome, P Teyssie, *Polymer* 1996 (37), pg 1027 – 1038.
12. V Maquet, A R Boccaccini, L Pravata, I Notingher, R Jerome, *Biomaterials* 2004 (25), pg 4185 – 4194.
13. G G Tibbetts, J J McHugh, *Journal of Materials Research* 1999 (7), pg 2871 – 2880.
14. A P Mathew, K Oksman, M Sain, *Journal of Applied Polymer Science* 2006 (101), pg 300 – 310.
15. D M Bigg, *Advances in Polymer Technology* 2005 (24), pg 69 – 82.
16. M S Huda, L T Drzal, A K Mohanty, M Misra, *Composites Science and Technology* 2006 (66), pg 1813 – 1824.