EFFECTS OF CHITIN NANOWHISKERS ON TENSILE PROPERTIES OF POLYLACTIC ACID BIOCOMPOSITE FILM

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Abstract
Chitin nanowhiskers prepared through acid hydrolysis using commercial chitin (CCNW) and chitin obtained from fermented prawn waste (FCNW) were compared in the formation of polylactic acid (PLA) biocomposites. The chitin nanowhiskers filled PLA biocomposite films were successfully produced using solution casting method and were characterized in terms tensile properties. The tensile strength of both PLA-CCNW and PLA-FCNW increased with increasing of CCNW and FCNW loading up to 3phr and 1phr respectively. The Young's modulus of both biocomposites increased with increasing of nanofiller loading but elongation at break decreased with increasing of nanofiller loading. From the Atomic Force Microscopy, the surface morphology of the PLA changed upon addition of chitin nanowhiskers and tendency for agglomeration of CNW at high loading were observed.

1. Introduction

Biodegradable polymers and biocomposites from renewable resources are fast becoming the current interest in the plastic industry due to dwindling petroleum reserves and environmental and end-of-live issues. Properties of the polymers made from renewable resources such as polylactic acid (PLA) can be enhanced through blending and composite formation [1]. PLA fulfills several requirements as a packaging thermoplastic. PLA is significantly flexible hence a continuous series of products can be prepared similar to poly (vinyl chloride) (PVC), polystyrene (PS) or polypropylene (PP). PLA is suitable in the production of loose-fill packaging, compost bags, food packaging and disposable tableware due to its biodegradability [2]. Polymer nanocomposite is described as a multiple phase materials consisting polymer matrix and nanofillers. The reinforcement of polymers using nanofillers has shown potential to increase mechanical properties of the polymer even with low filler content. Most natural polymers including chitin, cellulose and starch are hydrophilic which can result in increasing of degradability of one polymer [3].

Many semi-crystalline natural polymers consist of both crystalline and amorphous region. The amorphous region can be removed during acid hydrolysis [4] process while the crystalline region remained intact producing chitin rodlike whiskers at nanoscales which can be used as reinforcing nanofiller in polymer nanocomposites [5]. Use of chitin nanowhiskers as fillers to improve mechanical properties of biocomposites started a decade ago and is promising as chitin is easily and widely available from seafood processing industries as low cost waste products which could further decrease cost of production of PLA biocomposites.

This paper reports on the use of chitin nanowhiskers obtained from fermented prawn waste chitin and its effect as nanofillers in PLA. Fermentation of prawn waste is an-ongoing process in our laboratory to recover protein for aquaculture feed [6] and the partially purified chitin is a potential by-product. Finding use to the produced chitin will benefits the industry as well as reducing solid pollution caused by seafood industry. In frozen headless prawn industry nearly 50% of the whole prawn is discarded as waste material. Our previous work on chitin recovery from fermented prawn waste has produced a partially purified chitin almost similar to commercial chitin [7]. Conventionally chitin is chemically treated via acid and alkali treatments to purify chitin from calcium carbonate and protein from the crustacean exoskeleton. This harsh treatment usually produces high volumes of chemical waste and an alternative fermentation method reduces this polluting materials and is also able to recover the rich protein content in the prawn waste. At present Malaysia is discarding about …. tones of seafood waste [8] which is normally discarded as it is or been used as it is as feed. Using prawn waste as it has its disadvantages as it contains high fibre and reduces the protein content which is needed as feedmeal [9]. It is envisaged that the use of fermented chitin as chitin nanowhiskers is comparable to cellulose nanowhiskers as both contain the same parent compound, the glucose units having many hydroxyl functional groups important for intermolecular attractions between PLA and chitin nanowhiskers [10].

2. Materials and methods

2.1 Materials

Polylactic acid (PLA) was supplied by NatureWorks (specific gravity:1.25, melting temperature of 145-155°C, glass transition temperature of 55-58°C).

Chitin nanowhiskers (L=50 nm, D=10 nm) was produced through acid hydrolysis [4]. The chitin used obtained from prawn waste fermentation is designated as fermented chitin (FC) while commercial chitin (CC) was purchased from Sigma Aldrich, Malaysia. All other reagents (HCl, NaOH and chloroform) were from Merck, Malaysia.

2.2 Preparation of PLA, PLA/FCNW and PLA/CCNW biocomposite film

A 10 wt% solution of PLA pellets in chloroform was prepared by stirring the solution inside the water bath at 60ºC for 3hours until the pellets were fully dissolved. The PLA solution was immediately cast on clean glass plate and left to dry for 48 hours. The thickness of the cast solution was approximately 100µm and noted as PLA.

For the preparation of PLA/FCNW biocomposite film, 10 wt% solution of PLA was mixed with different amount of FCNW (1, 2, 3 and 4 phr) and the mixture was kept at 60ºC with strong agitation until the PLA pellets were fully dissolved. The suspension was then sonicated for 5 min and was immediately casted on a clean glass plate. The biocomposite films were designated as PLA/FCNW1, PLA/FCNW2 PLA/FCNW3 and PLA/FCNW4. This process was repeated using CCNW.

2.3 Characterization

Mechanical test was done using the Instron 4400 Universal Tester to measure the tensile strength at the point of breakage for each sample. Tensile tests were carried out at room temperature, according to the ASTM D882. A fixed crosshead rate of 10mm/min was utilized in all cases and the results were taken as an average of eleven tests.

The morphology of samples were observed using Atomic Force Microscopy (AFM). AFM observation was performed using SPA-300HV atomic force microscopy with a SPI 3800 controller, the PLA and the composite samples (0.1 mm x 0.1 mm) were analyzed directly.

3. Results and discussions

3.1 Mechanical properties

The results of tensile mechanical tests on PLA and biocomposites are shown in Table 1. It can be seen that the addition of chitin nanowhiskers in PLA increased the Young’s modulus of biocomposites at all content. This behaviour is attributed to stiffening effect of filler which decrease the polymer chains mobility and consequently enhanced the modulus of biocomposite. The increase in modulus with increasing filler loading can be explained by increased in hydrogen bonding, stiffening effect and high crystallinity index of the filler which is a typical characteristics of filler/polymer composite [11].

Tensile strength of PLA/FCNW showed improvement upon addition of 1 phr FCNW before decreasing with further addition of FCNW whereas PLA/CCNW showed increment of tensile strength up to 3 phr loading. The reduction in tensile strength for both biocomposites at higher loading may be attributed to aggregation of chitin nanowhiskers due to Van der Waal’s forces. On the other hand at low filler content, the reinforcing effect of FCNW and CCNW are dominant but as the filler content increased, the filler-filler interaction become dominant compared to filler-matrix interaction which lead to poor interfacial adhesion between FCNW and PLA.

Table 1 shows that the elongation at break decreased rapidly upon addition of FCNW and CCNW and decreased gradually as the concentration of filler increased for all formulations which makes the PLA more brittle. These observations may be attributed to the stiffening action of the filler that restricted the segmental chain movement of PLA during tensile testing.

Material Code	Tensile Strength (MPa)	Elongation at Break (%)	Young's Modulus (GPa)
PLA	11.95 ± 1.37	115.87 ± 59.47	1.75 ± 0.83
PLA/FCNW1	15.41 ± 1.15	22.15 ± 6.55	2.81 ± 0.66
PLA/FCNW2	13.49 ± 0.95	29.11 ± 5.15	3.10 ± 1.26
PLA/FCNW3	11.43 ± 1.27	12.92 ± 2.69	3.70 ± 1.76
PLA/FCNW4	9.49 ± 2.18	4.67 ± 1.71	3.96 ± 0.96
PLA/CCNW1	15.08 ± 1.15	99.6 ± 34.34	1.59 ± 1.13
PLA/CCNW2	16.85 ± 0.70	26.61 ± 13.11	3.15 ± 1.43
PLA/CCNW3	21.36 ± 1.01	33.62 ± 9.20	3.35 ± 2.66
PLA/CCNW4	18.02 ± 0.99	22.87 ± 12.01	5.40 ± 2.42

Table 1. Tensile properties of PLA and its biocomposites

The results also showed that the performance of FCNW and CCNW as fillers is almost comparable but further investigations are on-going to obtain more informations on the potential of using fermented chitin (without treatment) to produce CNW as further treatment will increase production cost of PLA nanocomposites. Fermented chitin is a low cost product obtained from waste material and is easily available from seafood industries in Malaysia.

3.2 Atomic force microscopy (AFM) analysis of biocomposites

The surface morphology of PLA, PLA/FCNW and PLA/CCNW biocomposite with 4 phr loading is shown in Figure 1. In Figure 1(a), a smooth surface of neat PLA was observed while the inclusions of FCNW and CCNW in PLA matrix changes the surface topography of PLA (Figure 1 (b) and 1 (c)). At higher contents (4 phr), FCNW showed agglomeration while CCNW homogenously dispersed inside the PLA matrix with limited formation of agglomerates. The presence of these agglomerations provides evidence of the poor filler dispersion in matrix which affect the tensile properties of PLA biocomposite. Similar observation was also reported when using microcrystalline cellulose as filler in PLA [12].

Figure 1. AFM images of a) PLA biocomposite, (b) PLA/FCNW (4 phr) and (c) PLA/CCNW (4 phr)

4. Conclusion

The effect of chitin nanowhiskers on the tensile properties of PLA biocomposite were investigated by using two types of chitin; chitin obtained from prawn waste fermentation and commercial chitin. Young's modulus increased with increasing of filler content while elongation at break of the biocomposites film decreased sharply upon addition of chitin nanowhiskers for both PLA/FCNW and PLA/CCNW. However, the tensile strength of PLA/FCNW increased up to 1 phr loading whereas PLA/CCNW increased up to 3 phr loading. Better dispersion of chitin nanowhiskers was observed in PLA/CCNW compared to PLA/FCNW. Future works involved the effect of treatment of chitin prior to forming CNW on the properties of the biocomposites.

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