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EFFECT OF FERMENTED CHITIN NANOWHISKERS ON PROPERTIES OF POLYLACTIC ACID BIOCOMPOSITE FILMS

(Kesan Kitin Terfermentasi Terhadap Sifat Filem Biokomposit Asid Poli Laktik)

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Abstract

The fermented chitin nanowhiskers (FCNW) filled polylactic acid (PLA) biocomposite films were successfully produced using solution casting method. The biocomposite films were characterized in terms of tensile properties. The Young's modulus increased with increasing FCNW content while the tensile strength increased and reached the maximum value at 4 phr FCNW loading. Therefore it can be concluded that the optimum loading of FCNW is at 4 phr and further addition of FCNW may lead to agglomeration resulting in a decrease in tensile strength. The elongation at break of the biocomposite films decreased rapidly upon addition of FCNW into PLA. From the Atomic Force Microscopy, the surface morphology of the PLA changed upon addition of FCNW and tendency for agglomeration of FCNW at high loading was observed.

Keywords: chitin, nanowhiskers, polylactic acid, film, solution casting

Abstrak

Kitin nanowisker daripada kitin terfermentasi (FCNW) yang memenuhi filem biokomposit asid poli laktik (PLA) telah berjaya dihasilkan melalui kaedah tuangan larutan. Filem biokomposit itu kemudiannya dicirikan berdasarkan sifat kekuatan tensilnya. Modulus Young meningkat seiring dengan peningkatan kandungan FCNW manakala kekuatan tensil meningkat dan mencapai nilai maksimum pada 4 phr. Oleh yang demikian, boleh disimpulkan bahawa pengisian optimum FCNW adalah pada 4 phr dan penambahan berterusan FCNW mungkin akan membawa kepada penggumpalan yang mengakibatkan penurunan dalam kekuatan tensil. Ciri pemanjangan takat putus filem biokomposit menurun secara mendadak dengan penambahan FCNW ke dalam PLA. Daripada mikroskop daya atom, morfologi permukaan PLA berubah setelah ditambah dengan FCNW dan potensi kepada penggumpalan pada pengisian tinggi FCNW telah diperhatikan.

Kata kunci: kitin, nanowisker, asid polilaktik, filem, tuangan larutan

Introduction

Nowadays, the market share of biodegradable polymers from renewable sources has grown rapidly in the plastic industry. This is due to two major factor; i) environmental concerns and ii) consciousness that petroleum resources are limited. Generally, polymers from renewable resources can be classified into three groups; i) natural polymers including starch, protein and cellulose, ii) synthetic polymers from natural monomers such as polylactic acid (PLA) and iii) polymers from microbial fermentation including polyhydroxybutyrate (PHB). Through blending and composite formation, properties of these polymers from renewable resources can be enhanced [1].

The concept of biodegradable plastics is of a considerable interest with respect to solid waste accumulation. Bigger efforts have been made to replace petroleum-based traditional plastics by developing degradable biological materials without any environmental pollution. PLA being an aliphatic polyester and a biocompatible thermoplastic is currently considered as the 'green' eco friendly material for the future. PLA fulfill many requirements as a

packaging thermoplastic and is suitable for general packaging applications such as loose-fill packaging, compost bags, food packaging and disposable tableware [2]. However, PLA has several disadvantages including high cost production, brittleness, hydrophobic and poor thermal resistance [2]. PLA can be combined with other suitable natural sources such as the abundantly available chitin which acts as additive to enhanced its properties [3].

Chitin is one of the most abundant natural polymers after cellulose that exist in nature but its functionality and limited solubility have restricted its applications. Chitin is a polysaccharide and is found in many crustacean sources such as crabs, shrimp shells and lobsters in the α-crystalline form while β-chitin is found in squid pens. Chitin, a linear polymer of *N*-acetyl-D-glucosamine linked by α (1,4) glycosidic bond [4,5] can be obtained from seafood industrial waste such as prawn waste. Both chitin and its derivatives chitosan, possess huge range of useful properties; such as biocompatibility, antibacterial and environmentally friendly polyelectrolyte [6]. In contrast, its derivatives chitosan has been commercialized for a variety of applications such as waste water treatment, textile and paper industry, cosmetic, medicine and agriculture [7]. However, interest in chitin has been recently revived because chitin is found to have desirable mechanical property due to their natural stacks of chitin nanocrystals which have a Young's modulus as high as 41 GPa measured by X-ray diffraction [8].

However, their industrial applications are scarce largely due to high prices. Chitin is usually obtained through chemical treatments which discard large amount of chemical wastes. In the last decade, a biotechnological approach using lactic acid fermentation to purify chitin from crustacean waste is gaining its popularity due to its environmentally clean approach and cheaper production cost. Previous research [9] has successfully extracted a rich protein liquor and a partially purified chitin from tiger prawn waste through solid state bacterial fermentation process. If chitin can be converted into potential new material such as forming polylactide-chitin composite, it would be a very great advantage to the prawn processing industries which discarded nearly 50% of the whole processed prawn.

Materials and Methods

Materials

Polylactic acid (NatureWork^{TM} PLA 300ID) in pellet form was obtained from NatureWork® LLC, Minnetonka, MN USA. The density of PLA is 1.25 g/cm^3, melting temperature of 145-155°C, glass transition temperature of 55-58°C, cystallinity of up to 37% and it has average molecular weight of M_w: 220 kDa and M_n: 101 kDa. Fermented chitin nanowhiskers (L=50 nm, D=10 nm) was produced from chitin obtained from prawn waste fermentation through acid hydrolysis [10]. The reagent used was hydrochloric acid and chloroform from Merck, Malaysia.

Preparation of PLA and PLA/FCNW biocomposites

A 10 wt% solution of PLA pellets in chloroform was prepared by stirring the solution in water bath at 60ºC until the pellets were fully dissolved. The PLA solution was immediately cast on clean glass plates and left for the solvent to evaporate at ambient temperature for 48 hours. The cast solution noted as pure PLA.

For the preparation of PLA/FCNW biocomposites, 10 wt% solution of PLA was mixed with different amount of FCNW (2, 4 and 6 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 cast on a clean glass plate to remove the solvent. The composites were designated as PLA/FCNW2, PLA/FCNW4 and PLA/FCNW6.

Characterization

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

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

Results and Discussion

Atomic Force Microscopy (AFM) analysis

Surfaces of PLA and PLA/FCNW biocomposites were observed using AFM to further explore the nature of interactions between PLA and FCNW. The surface morphology of PLA and PLA/FCNW biocomposite with various contents of FCNW are shown in Figure 1.

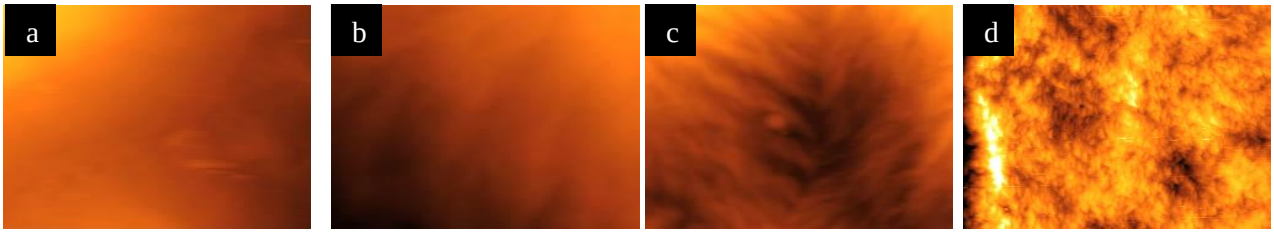

Figure 1. AFM images of a) PLA composite and PLA/FCNW composite with different FCNW loading (b) 2 phr, (c) 4 phr and (d) 6 phr

From Figure 1(a), smooth surface of neat PLA was observed while the inclusions of FCNW into the PLA matrix change the surface topography of the pure PLA (Figure 1 (b)-(d)). It interesting to note that at lower FCNW content (2 phr), the filler was well dispersed inside the PLA with no sign of agglomeration. However at higher FCNW contents (4 and 6 phr) the FCNW has started to agglomerate. The presence of these FCNW agglomerations provides evidence of the poor filler dispersion in matrix which affect the tensile properties of PLA biocomposite as discussed in detail in the next section. Similar observation was also reported [11] when using microcrystalline cellulose as filler in PLA.

Tensile properties

The tensile properties of PLA/FCNW were investigated in order to determine the effect of FCNW loading on PLA. The tensile strength, Young's modulus and elongation at break of PLA/FCNW biocomposite at different FCNW loading are shown in Figure 2, 3 and 4 respectively and the results are summarized in Table 1.

Table 1. Mechanical properties of PLA/FCNW biocomposite film

Material Code	Tensile Strength (MPa)	Elongation at Break (%)	Young's Modulus (GPa)
PLA	11.2 ± 0.7	90.0 ± 14.7	1.36 ± 0.6
PLA/FCNW2	11.3 ± 0.8	20.1 ± 1.1	2.22± 0.5
PLA/FCNW4	12.4 ± 0.6	22.8 ± 1.8	2.997 ± 0.3
PLA/FCNW6	8.8 ± 0.7	7.2 ± 1.2	3.73 ± 0.6

Figure 2 shows the tensile strength of PLA/FCNW biocomposites. Tensile strength of PLA/FCNW showed improvement when incooperating with FCNW loading up to 4 phr before decrease with further addition of FCNW. The reduction in tensile strength for the PLA/FCNW at higher FCNW loading may be attributed to aggregation of FCNW due to Van der Waal's forces. The results seem support the microscopy analysis discussed in previous section. On the other hand at the low filler content, the reinforcing effect of FCNW is 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. This may likely to be the explanation for the decrease recorded in the tensile strength.

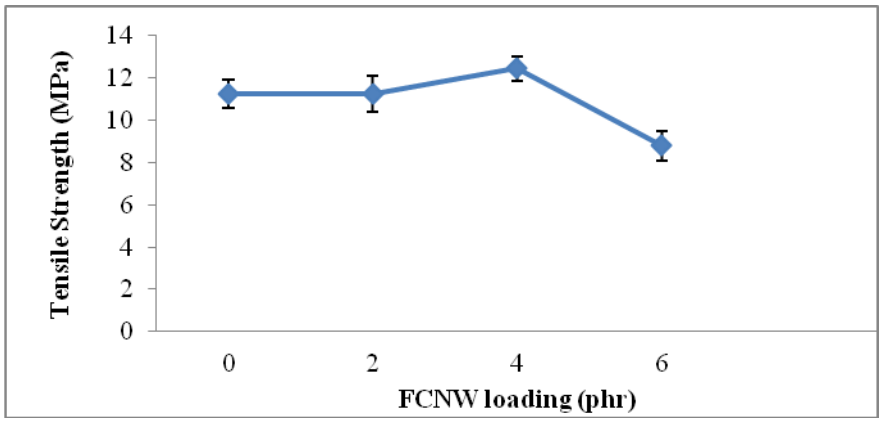

Figure 2. Tensile strength of PLA/FCNW biocomposite film

The Young's modulus of PLA/FCNW biocomposite was increased with increasing of FCNW loading as shown in Figure 3. 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 [12].

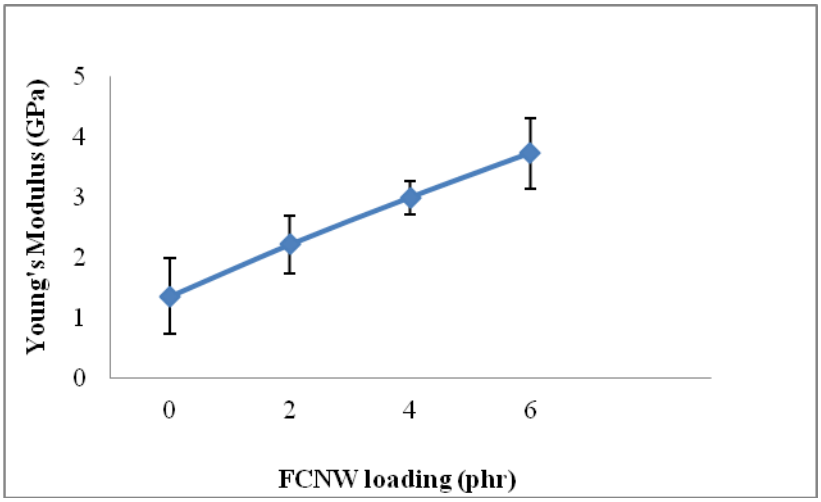

Figure 3. Young's modulus of PLA/FCNW biocomposite film

It also revealed that the addition of FCNW in the PLA matrix give the negative impact to the elongation at break for biocomposites. The elongation at break of PLA/FCNW decrease dramatically as compared to the PLA as shown in Figure 4. It can be clearly seen that the elongation at break decreased gradually as the concentration of filler increased for all formulations of PLA becomes more brittle. These observations may be attributed to the stiffening action of the filler by restricting the segmental chain movement of PLA during tensile testing. Similar result has been reported by Bulota et al. [13] in study of mechanical behaviour of PLA reinforced TEMPO-Oxidized cellulose and by Wang et al. [14] in cooperating cellulose whisker with soy protein thermoplastic.

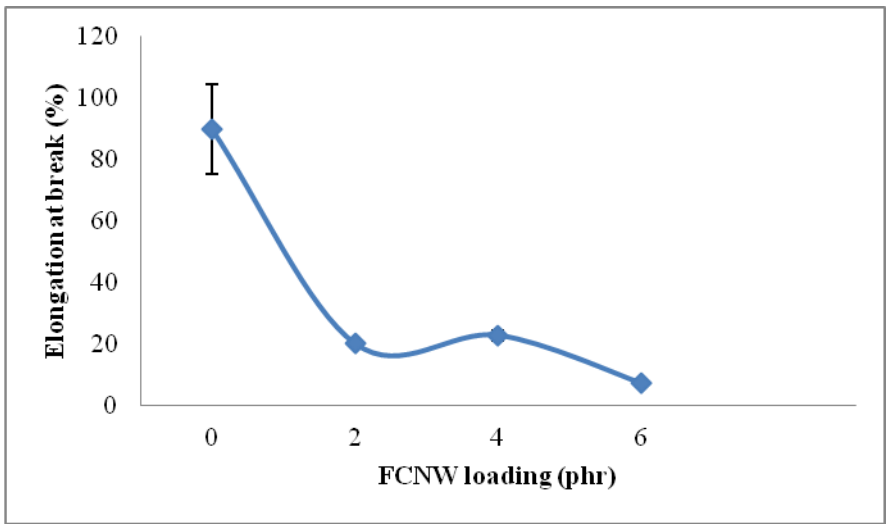

Figure 4. Elongation at break of PLA/FCNW biocomposite film

Conclusion

PLA/FCNW biocomposite film was successfully produced using solution casting method. AFM showed that at 2 phr FCNW content, the filler was well dispersed with no evidence of agglomeration. Agglomeration of FCNW started to be observed at 4 phr. which indicates poor filler dispersion in matrix. Young's modulus increased with increasing of FCNW content while tensile strength increased up to a maximum value at 4 phr FCNW loading. Elongation at break of the PLA/FCNW biocomposite film decreased sharply with addition of FCNW.

Acknowledgement

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