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Biodegradability properties of chitin/polylactic acid composite films

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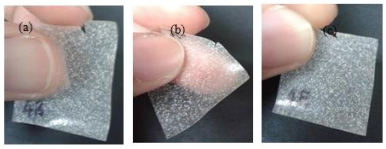
GRAPHICAL ABSTRACT



The images of crack films on (a) week 8 (PLA/C4), (b) week 10 (PLA/C3) and (c) week 10 (PLA/C4).

ABSTRACT

In this work, chitin was used as filler in polylactic acid (PLA) through solution casting method. The morphological, water absorption and biodegradability properties of chitin/PLA composite films were investigated using field emission scanning electron microscopy (FESEM), swelling test and soil burial test, respectively. FESEM images showed that there are presence of rod-like structures on the surface of PLA/chitin film possibly that of chitin particles. The biodegradability properties of the films increased as the amount of chitin increases. Fourier transform infrared spectroscopy (FTIR) was used to observe the interaction between chitin and PLA. From the spectrum, it indicates that there are no significant changes in the peak position, suggesting that there is no strong chemical interaction taking place between chitin and PLA.

Keywords: Chitin, polylactic acid, biodegradability, water absorption, soil burial test

1. INTRODUCTION

In recent years, many researchers are interested in producing polylactic acid (PLA) film as it has good biodegradability properties and has tendency to become bioplastic that is environmentally friendly. Nature Works is the major manufacturer of PLA with a production of 140, 000 tons/year [1].

However, the price of PLA at RM11.80 per kilogram which is significantly higher as compared to polystyrene (RM9.70 per kilogram) and polyethylene (RM8.60 per kilogram) [2]. PLA also has poor thermal stability, low water vapour or gas barrier properties, and inherent brittleness. So that, some modification in preparation of PLA must be done to make the films as bio-plastics. It has potential to be used worldwide to replace petroleum-based plastics.

Since the production of seafood industry increases, so does the production of prawn waste that can lead to waste pollution. Such wastes include head, shell and tail of the prawns. To reduce the pollution due to waste dumping, several studies have been done and found that prawn waste is an important source of chitin [3]. Chitin is a natural polymer that has good biodegradability and non-toxic properties as well as potential to act as filler in PLA films to enhance the properties of PLA. The developed functional films can be applied in many applications especially in bioplastic production and packaging of food, as well as in agriculture products. Therefore, finding good use of the chitin from prawn waste industry will reduce pollution problem as well as added income to the seafood industry.

Thus, this study investigated the effect of chitin loading on morphological, water absorption and biodegradability properties of resulting PLA composites.

2. EXPERIMENTAL

Materials. PLA (Nature Work TM PLA 3001D) in pellet form was obtained from NatureWork® LLC, Minnetonka, MN USA with a density of 1.24 g cm^{-3} and melt flow index (MFI) of *ca*. 15 g/10 min (190 °C, 2.16 kg^{-1}). Commercial chitin purchased from Sigma Aldrich Chemical Company in Germany, USA was used in this study. The solvent used is chloroform bought from Merck, Malaysia.

Preparation of PLA. PLA pellets (10 g) were fully dissolved in chloroform (64 mL) and it was heated in a water bath at 60°C with constant stirring. Then, the suspension was sonicated for 5 min. Immediately, the PLA solution was casted on the clean glass plates and was left for 48 h at room temperature to allow the solvent to evaporate. The thickness of the cast solution was approximately 100 µm and noted as pure PLA. This procedure was previously described by earlier publications [4, 5, 6].

Preparation of Chitin/PLA Films. The chitin/PLA biocomposite films were prepared by mixing the PLA pellets (10 g) with different amount of chitin (1, 2, 3, 4 phr) and chloroform (64 mL). The mixture was heated at 60°C with constant stirring until the PLA pellets were fully dissolved. Then, the suspension was sonicated for 5 min and immediately casted on the clean glass plate. The thickness of the cast was approximately 100 µm and coding as PLA/C1, PLA/C2, PLA/C3 and PLA/C4.

Water Absorption. The pure PLA and biocomposite films were cut into small pieces with 20 × 20 × 0.1 mm dimensions and weighed (W_0). Then, the samples were immersed into distilled water at room temperature. After 24 h, the swollen film samples were removed from distilled water and the excess water was quickly wiped out from the surface of the films. The

weight of the film samples were recorded (W_1). The sample was immersed back in water after each measurement. As described by Chuayjuljit *et al.* [7], the percent of water absorption was calculated as follows:

$$\% \text{ Water absorption} = [(W_1 - W_0)/W_0] \times 100$$

Soil Burial Test. The pure PLA and chitin/PLA composite films were cut into 25 × 25 × 0.1 mm dimensions as reported by Arjmandi *et al.* [8]. The film samples were dried in desiccator until their weight is constant (W_2). The film samples were buried in compost soil at a depth of 20 - 25 cm from the ground surface for 10 weeks. The moisture of the soil was maintained by daily sprinkling water [9, 10]. At every two week intervals, the samples were taken out. The surface of films were washed with distilled water and dried at 55 °C until their weight became constant (W_3) as originally described in earlier publication [11]. The percent weight loss was calculated using the following equation:

$$\% \text{ Weight loss} = [(W_2 - W_3)/W_2] \times 100$$

Fourier Transform Infrared Spectroscopy. Fourier transform infrared spectroscopy (FTIR) was performed using a Perkin Elmer 1600 Infrared spectrophotometer and recorded using Nicolet's AVATAR 360 at 32 scans with a resolution of 4 cm^{-1} within wavenumber of 4000 to 400 cm^{-1}.

Morphology Analysis. The morphologies of the films were characterized by field emission scanning electron microscopy (FESEM) conducted on a Carl Zeiss (Germany) Supra 35 VP using an extra high tension (EHT) of 3-5 kV. The samples were sputter-coated with gold prior to observation.

Results and Discussion

3. RESULTS AND DISCUSSION

FTIR Analysis. The FTIR spectroscopy was used to observe the intermolecular interaction and phase behavior between PLA and chitin. The FTIR spectra of the samples were illustrated in Figure 4.2. In Figure 1(a), there were absorption bands in region of 3500−3600 cm^{-1}, 2850−3000 cm^{-1} and 1759 cm^{-1} due to O–H bending and stretching vibration, C−H asymmetric stretching vibration and C=O stretching vibration, respectively [12]. The pure PLA spectra also showed a peak of C−H bending in CH_3 at 1448 cm^{-1}.

Meanwhile, no new peak was observed in the spectrum (Figure 1(b)-(c)) when chitin was added. The absence of new peak suggests that the intermolecular interaction between PLA and chitin was physically interacted rather than chemical interaction. However, the peaks at 3505 cm^{-1} shifted to a lower wavenumber and decreased in intensity when the amount of chitin was added to the PLA matrix, possibly due to some interaction between hydroxyl group of PLA and hydroxyl group of chitin. This results is similar to the one reported by Arjmandi *et al.* [8].

The peak of O−H bond stretching deformation of PLA in region 3200−3400 cm^{-1} disappeared and shifted to broad peak approximately at 3259 cm^{-1} in chitin/PLA composite (Figure 1(c)). It is interesting to note that, the peak at 1759 cm^{-1} corresponding to the C=O stretching vibration become broader when the amount of chitin added is increased. This may be due to some interaction between carbonyl group from PLA and hydroxyl group of chitin [5].

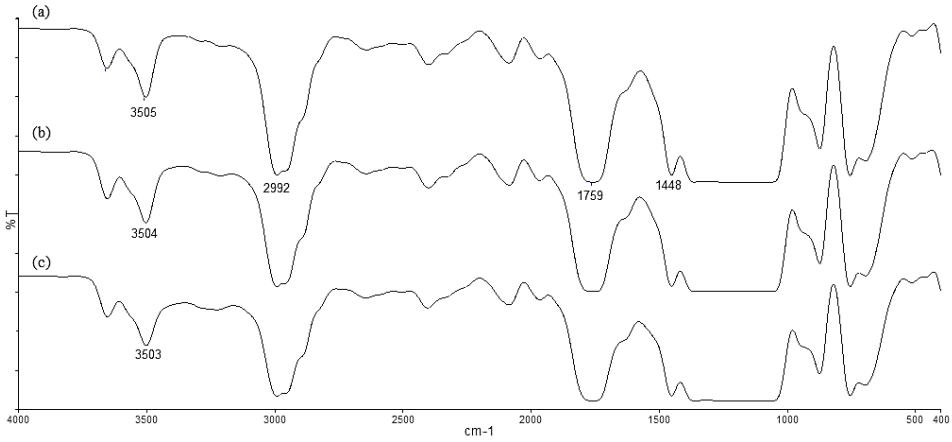


Fig. 1 FTIR spectra of (a) pure PLA, (b) PLA/C1 and (c) PLA/C2

FESEM Analysis. FESEM is a useful instrument to identify the surface morphology of the composite films. FESEM images of the films were presented in Figure 2. It can be clearly seen from Figure 2(a), pure PLA film had homogeneous structure and no defect. This observation was similar with the one reported by Bonilla *et al.* [13], when PLA matrix was filled

with chitosan powder. The presence of rod-like structure on the surface of chitin/PLA composite film (Figure 2(b)) was observed, possibly that of chitin particles.

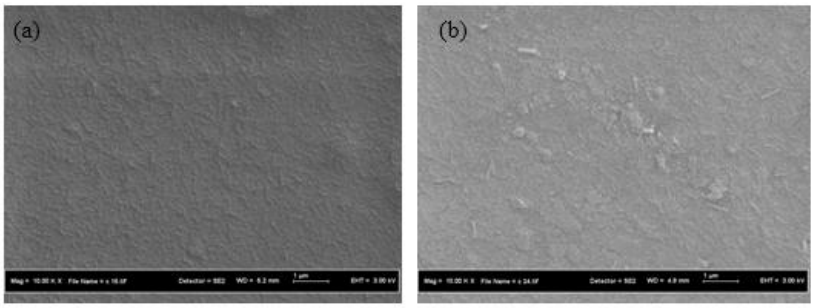


Fig. 2 FESEM images of (a) pure PLA and (b) PLA/C1

Water Absorption. Swelling test of pure PLA film and chitin/PLA films were carried out to investigate water absorption properties by calculating the percentage of water absorption. It can be seen from Figure 3 that the percent of water absorption of the films increased with increasing amount of chitin in PLA matrix. Since PLA is strongly hydrophobic [14] and chitin has absorption ability [15, 16], the water absorption of the films is mainly due to the chitin. The film with higher water absorption is usually experiencing microorganism attack such as bacteria and fungi, where they used water as a medium to access into the interior of the matrix. It suggests that film with high content of chitin would exhibit biodegradability ability [7].

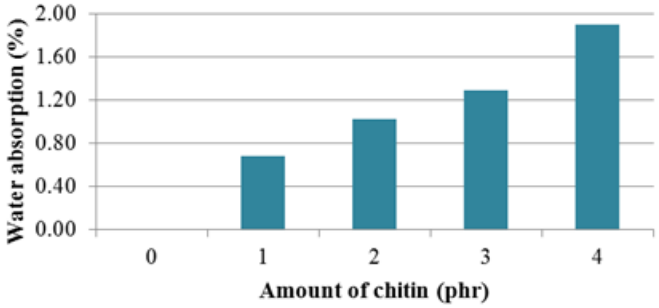


Fig. 3 Percentage of water absorption of pure PLA film and chitin/PLA composite films

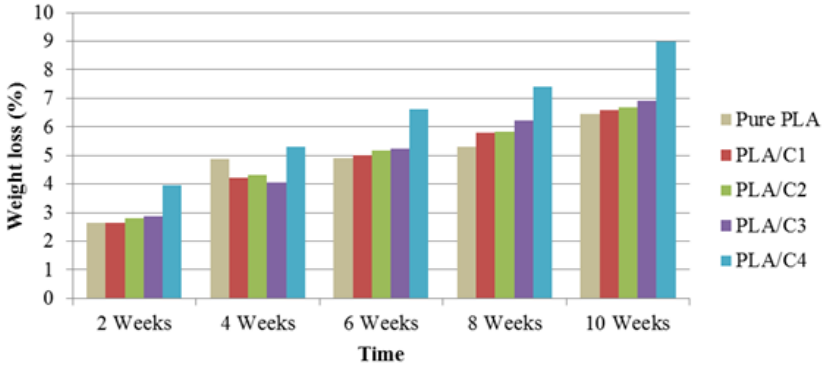


Fig. 4 Percentage of weight loss of pure PLA and chitin/PLA composite films

Soil Burial Test. Soil burial test had been used to estimate the biodegradable properties of chitin/PLA composite films. Figure 4 shows the percentage of dry weight loss of pure PLA and chitin/PLA composite films for every two weeks. Figure 5 illustrates the images of the films before and after soil burial test. From Figure 4, it can be seen that percent of weight loss increased with the increasing of chitin content. It is possibly due to the presence of microorganisms such as fungi and bacteria, consuming the chitin materials on the surface of films as nutrient source [17].

The finding revealed no single crack or hole on the surface of pure PLA film and chitin/PLA composite films (with chitin content 1-3 phr) up to 8 weeks (Figure 5). However, there was initial crack on the surface of PLA/C4 and PLA/C3 film

on week 8 and week 10, respectively (Figure 6). Therefore, prolonging the burial time and increasing the amount of chitin in PLA matrix lead to a short induction and faster degradation of the PLA films. This observation was similar to that reported by Arjmandi *et al*. [17], when PLA matrix was filled with microcrystalline cellulose (MCC) and cellulose whiskers. They found that the presence of high content of cellulose whiskers can enhance the biodegradability properties of PLA.

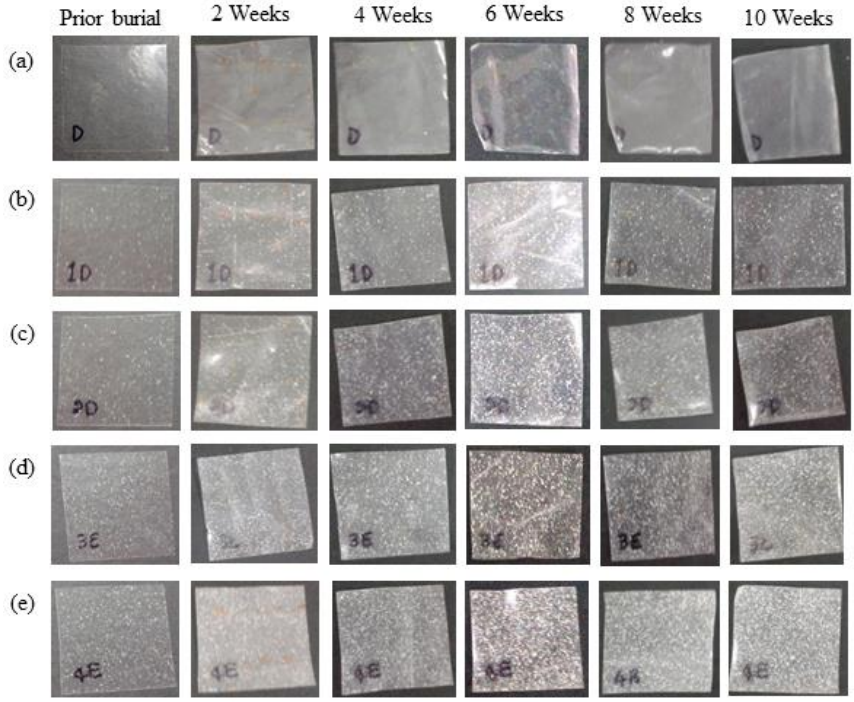


Fig. 5 Biodegradable images of the films prior and after soil burial test; (a) pure PLA, (b) PLA/C1, (c) PLA/C2, (d) PLA/C3 and (e) PLA/C4.

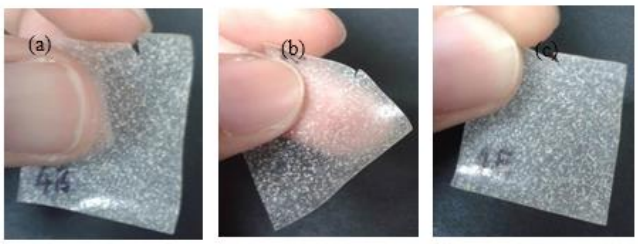


Fig. 6 The images of crack films on (a) week 8 (PLA/C4), (b) week 10 (PLA/C3) and (c) week 10 (PLA/C4).

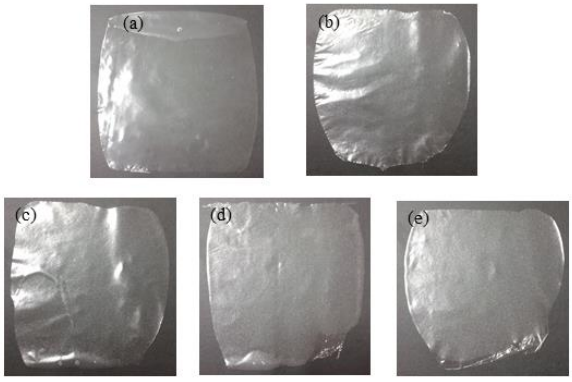


Fig. 7 Visual comparison of the transparency of (a) pure PLA, (b) PLA/C1, (c) PLA/C2, (d) PLA/C3 and (e) PLA/C4

Film Transparency. Pure PLA and chitin/PLA composite films with different loading of chitin were successfully prepared by solution casting method. The pure PLA film (Figure 7(a)) produced was transparent and have smooth surface. The transparency of chitin/PLA composite films also can be categorized as transparent. But as clearly observed in Figure 7(b)-(e), as the chitin content was increased, there were some white spot presenct in the composite films. That expected to be chitin

aggregates in the PLA matrix. The similar finding has been reported earlier by Haafiz *et al*. [5], when microcrystalline cellulose (MCC) reinforced PLA composite.

4. CONCLUSION

The chitin/PLA composite films were successfully prepared by solution casting method. FTIR analysis revealed that there are slight changes in the position and broadness of O–H peak suggesting small interaction taking place between chitin and PLA. Interestingly, FESEM images showed the presence of rod-like structures on the surface of chitin/PLA film, possibly that of chitin particles. Chitin/PLA composite had higher water absorption compared to pure PLA, due to microorganism used water as a medium to access into the interior of the PLA matrix. Since chitin was natural biodegradable material, with high content of chitin in PLA matrix and prolonging the soil burial time can lead to the improvement of its biodegradable properties of PLA.

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