Effect of Acid Hydrolysis Time on Tensile and Morphological Properties of Microcrystalline Chitin Filled Polylactic Acid Biocomposites

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Abstract

The objective of this study is to investigate the effect of acid hydrolysis time on microcrystalline chitin (MCC) filled polylactic acid (PLA) biocomposites using solution casting method. MCC was produced from commercial chitin using controlled hydrolysis process at four different hydrolysis time; 15, 30, 45 and 60 min. The tensile and morphological properties of PLA/MCC biocomposites were investigated using tensile testing machine and atomic force microscopy (AFM), respectively. Tensile strength and Young's modulus of PLA/MCC biocomposites increased gradually by increasing hydrolysis time. The biocomposites with longest hydrolysis time (60 min) showed the higher tensile strength, Young's modulus and elongation at break values. AFM analysis showed homogeneous dispersion of MCC fillers with smaller particles size at longer hydrolysis time, resulted in smother surface morphology compared to biocomposites with shorter hydrolysis time.

Keywords. Microcrystalline chitin; Polylactic acid; Biocomposites; Tensile properties; Atomic force microscopy

1 Introduction

Nowadays, biodegradable polymers and biocomposites from renewable sources has become a major interest due to continuously decreasing of petroleum reserves and environmental concerns. In addition, these materials has caught great market share which grown tremendously in the plastic industry [1]. Polylactic acid (PLA) is a type of thermoplastic aliphatic polyester which can be derived from bio renewable sugar based sources such as corn starch. Due to its biodegradability properties, it is considered as a sustainable alternative to petroleum-based polymers for many application. Additionally, PLA biocomposites have essential applications on water and milk bottles, food packaging, barriers for sanitary products and diapers, pharmaceutical industries and automotive applications [2, 3]. However, it cannot be denied that PLA also has its own weakness such as low water vapor and gas barrier, its brittleness and low thermal stability properties. Due to these limitations, reinforcement with stabilizer filling such as chitin is considered as an alternative to overcome the shortcomings [2].

The abundant of natural sources motivates researchers to produce biocomposites, but it has restrictions due to its limited solubility and functionality. Chitin is a ubiquitous natural biopolymer that is mostly founded next to cellulose discovery. Chitin is a polysaccharide which found as α-crystalline form in many crustacean sources such as crabs, shrimp shells and lobsters. 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. It is a linear polymer of N-acetyl-D-glucosamine linked by α (1, 4) glycosidic bond that can be obtained from seafood industrial waste. The use of chitin in order to produce biocomposites has become more interest, due to its desirable mechanical properties [4, 5].

The present study reports the development of PLA biocomposites filled with microcrystalline chitin (MCC) filler. The tensile and morphology properties of PLA/MCC biocomposites prepared by solution casting were investigated. To the best of our knowledge, no study has been reported on the effect of acid hydrolysis time of MCC filled PLA biocomposites.

2 Materials and Methods

PLA (NatureWorkTM PLA 3001D) in pellet form was obtained from NatureWork® LLC (Minnetonka, MN USA). It had a density of 1.24 g cm^{-3} and melt flow index (MFI) of ca. 15g $10min^{-1}$ (190°C $2.16kg^{-1}$). The reagent used (hydrochloric acid), sodium hydroxide and chloroform from Merck, Malaysia.

2.1 Preparation of Microcrystalline Chitin

Microcrystalline chitin (MCC) was produced from chitin using controlled acid hydrolysis. The commercial chitin from shrimp has been used for hydrolysis process. 2.0 g of chitin was added to 60 ml of 3N HCl and hydrolyzed at four different times (15, 30, 45 and 60 min) at 100 °C using magnetic hot plate stirrer. Subsequently, the chitin suspension was centrifuged for 15 minutes with 3200 rpm rotational speed for three times. After each centrifuge period, the supernatant was replaced with distilled water in order to remove the acid from MCC filler. Then the supernatant was fully removed after final centrifuge stage. The produced chitin was then transferred to the cellulose dialysis tub with continuous water flow for 2 h in order to dialyzed and fully remove the remaining acid in the MCC filler. The dialysis process continued with distilled water for overnight period. After dialysis process, the pH of resulting solution was measured by pH meter that reached to 4 pH. Finally, produced chitin were stored in refrigerator at 4 °C.

2.2 Preparation of PLA

10 g of PLA pellets were dissolved in 64 ml chloroform by stirring the solution inside the water bath at 60 ºC for 2 h until the PLA pellets were fully dissolved. The PLA solution was immediately casted onto the clean glass plates and left for 2 hours at room temperature and then transferred to a vacuum dryer for 24 hours. The thickness of the casted film was approximately 100 μm.

2.3 Preparation of PLA/MCC composites

10 g of PLA pellets were mixed with 2 phr of MCC and dissolved in 64 ml chloroform and then the mixture was kept at 60 ºC inside the water bath with strong agitation for 2 h until the PLA pellets were fully dissolved. The suspension was then sonicated for 10 min and was immediately casted onto a clean glass plates. The casted films were dried for 2 hours at room temperature and then transferred to a vacuum dryer for 24 hours. The thickness of the casted film was approximately 100 μm and biocomposite films were designated as PLA/MCC 15, PLA/MCC 30, PLA/MCC 45, and PLA/MCC 60.

3 Characterization

Mechanical test was done using the LRX Lloyd 2.5 kN Tensile 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 12.5 mm min^{-1} was utilized in all cases and the results were taken as an average of ten samples.

The morphology of samples were observed using Atomic Force Microscopy (AFM). AFM observation were performed using SPA-300HV atomic force microscopy with a SPI 3800 controller and the samples (1.0 × 1.0 cm) were analyzed directly.

4 Results and Discussion

4.1 Tensile properties

The effect of hydrolysis time of MCC on the tensile strength and Young's modulus of PLA/MCC biocomposites are given in Figure 1a. As can be observed from Figure 1a, incorporation of MCC with hydrolysis time of 15, 30 and 45 min into PLA caused to decrease the tensile strength of PLA biocomposites compared to neat PLA. These decreases could be attributed to the relatively big particle size of MCC which decreased the interaction between the MCC and PLA matrix. It was also observed that the tensile strength of PLA/MCC biocomposites increased with increasing hydrolysis time of MCC and reached a maximum value of approximately 25 MPa for MCC with 60 min hydrolysis time. This increase in tensile strength is due to the smaller particle size of MCC filler and homogeneous dispersion of MCC filler throughout the PLA at longer hydrolysis time. As can be seen in Figure 1a, Young's modulus of PLA/MCC biocomposites also increased with increasing hydrolysis time of MCC. This improvement in Young's modulus was due to the stiffening effect of the high modulus MCC filler, which caused to decrease the mobility of polymer chains. Similar observation has been reported by Syazeven et al. [6]. Additionally, the decrease in Young's modulus of PLA/MCC biocomposites with shorter hydrolysis time (15 and 30 min) is due to the big particle size of MCC filler, which caused to create voids in the biocomposites. As shown in Figure 1b, the elongation at break of PLA/MCC biocomposites with 15 and 30 min hydrolysis time decreased compared to the neat PLA, due to the restricting the segmental chain movement of PLA. However, PLA/MCC biocomposites at 45 and 60 min hydrolysis time did not show significant change in elongation at break compared to the neat PLA. It can concluded that the biocomposites with longest hydrolysis time (60 min) showed the best mechanical properties in terms of tensile strength, Young's modulus and elongation at break.

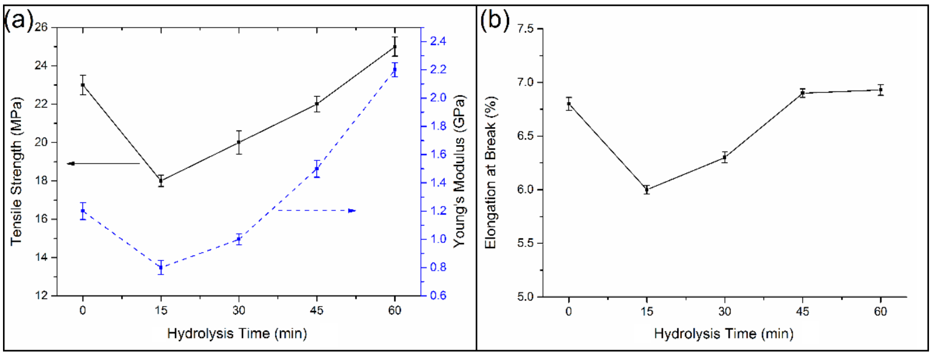

Figure 1. a) Tensile strength, b) Young's modulus and c) elongation at break of PLA/MCC biocomposites at different period of hydrolysis time.

4.2 Surface morphology

Surface morphology of the PLA/MCC biocomposites were observed using AFM in order to explore the dispersion of MCC in the PLA. AFM micrographs of PLA/MCC biocomposites at four different hydrolysis times (15, 30, 45 and 60 min) are shown in Figure 2a-d, respectively. As can be seen in Figure 2a, PLA/MCC biocomposite at 15 min hydrolysis has very rough surface. This can be explained by the big size of MCC particles, which unable to uniformly disperse in the PLA. This observation is consistent with tensile properties results, which it was decreased at 15 min hydrolysis time (Figure 1a). Figure 2b indicated slightly smoother surface morphology compared to the PLA/MCC biocomposites with 15 min hydrolysis time (Figure 2a), due to smaller particle size and better dispersion of MCC in the PLA. Figure 2c and d are shown further improvement in the morphology and smoother surface morphology compared to the PLA/MCC biocomposites with shorter hydrolysis time. This could be due to the produced smaller size of MCC particles by longer hydrolysis time. In the PLA/MCC biocomposites with 60 min of hydrolysis time (Figure 2d), it seems that MCC particles have been changed from micro to nano size. Due to this significant changes in the size of MCC particles, the filler dispersed homogeneously throughout the PLA and resulted in smooth surfaces morphology compared to PLA/MCC biocomposites with shorter hydrolysis time (15, 30 and 45 min).

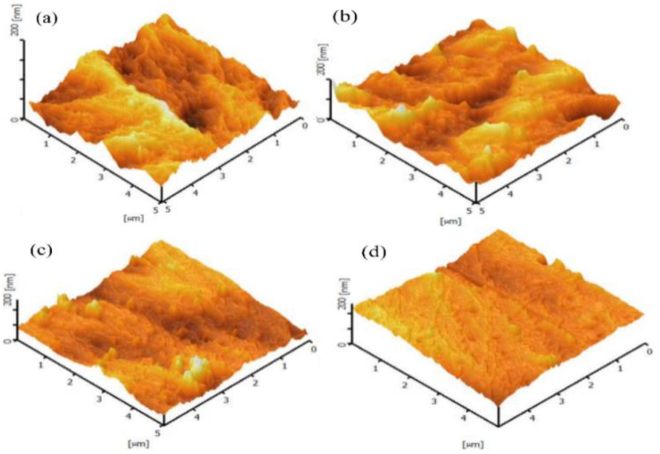

Figure 2. AFM micrographs of PLA/MCC biocomposites at hydrolysis period of a) 15, b) 30, c) 45 and d) 60 min.

5 Conclusion

Microcrystalline chitin was produced using four different hydrolysis time (15, 30, 45 and 60 min). The MCC fillers were incorporated into PLA and the effect of hydrolysis time on the tensile and morphological properties of PLA/MCC biocomposites were investigated. The tensile strength of PLA/MCC biocomposites increased with increasing MCC hydrolysis time due to the smaller particle size of MCC fillers, which increased the interaction between MCC and PLA. Young's modulus of PLA/MCC biocomposites also increased at longer MCC hydrolysis time, while decreased at shorter hydrolysis time (15 and 30 min). MCC hydrolysis time did not influence elongation at break of PLA/MCC biocomposites significantly. AFM analysis confirmed the smoother surface morphology at longer MCC hydrolysis time, which indicates homogeneous dispersion of MCC fillers and smaller particles size. It was found that hydrolysis time influenced the tensile and morphological properties of PLA/MCC biocomposites with MCC filler at 60 min hydrolysis time producing biocomposites with better properties in terms of tensile and morphology properties compared to PLA/MCC biocomposites containing MCC with shorter hydrolysis time.

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References

1. Kricheldorf, H. R. "Syntheses and application of polylactides," Chemosphere, vol. 43, pp. 49-54, 2001.
2. Haafiz, M. K. M., Hassan, A., Zakaria, Z., Inuwa, I. M., Islam, M. S. and Jawaid, M. "Properties of polylactic acid composites reinforced with oil palm biomass microcrystalline cellulose," Carbohydrate Polymer, vol. 98, pp. 139-145, 2013.
3. Nampoothiri, K. M., Nair, N. R. and John, R. P. "An overview of the recent developments in polylactide (PLA) research," Bioresource Technology, vol. 101, pp. 8493-850, 2010.
4. Chaussard, G. and Domard, A. "New Aspects of the Extraction of Chitin from Squid Pens," Biomacromolecules, vol. 5, pp. 559-564, 2004.
5. Chandumpaia, A., Singhpibulpornb, N., Faroongsarngc, D. and Sornprasita, P. "Preparation and physico-chemical characterization of chitin and chitosan from the pens of squid species, Loligo lessoniana and Loligo formosana," Carbohydrate Polymers, vol. 58, pp. 467-474, 2004.
6. Syazeven, E. A. M. A., Zakaria, Z., Hassan, A. and Haafiz, M. K. M. "Effect of fermented chitin nanowhiskers on properties of polylactic acid biocomposite films," The Malaysian Journal of Analytical Sciences, vol. 18, pp. 385-390, 2014.