Study on polylactic acid/acrylonitrile butadiene styrene composites filled with micro-crystalline cellulose

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Abstract The effect of surface treatment by using silane coupling agent with varying ratio of micro-crystalline cellulose (MCC) on polylactic acid (PLA) / acrylonitrile butadiene styrene (ABS) blend system were investigated. The study had focused on the blend modification onto the mechanical, structural, morphological and biodegradability properties of PLA/ABS blends. The study showed that the tensile properties of the PLA/ABS blends were deterioriated with increasing in MCC content. The interfacial adhesion was approach by using silane treatment caused by the incorporation of MCC and coupling agent. According to the results, the addition of MCC and surface treatment s howed an increasing better in tensile properties as compared to the standardized counterpart. On top of that, the morphological analysis by using scanning electron microscopy (SEM) found out that the interfacial adhesion of MCC was improved in both systems which is with and without silane treatment. Both of the systems was obtained having a weight loss during the soil burial test and the biodegradation process in PLA/ABS/MCC blends as proven in biodegradability analysis.

1 Introduction

Nowadays, plastics are used commonly in our daily life which inflates the necessity of plastics, hence will increasing the demands for plastics. Due to the demands of consumers is high, the production of plastics rapidly over the past few decades. Every year the world production of plastic is estimates to be more than 100 million tonnes. However, most conventional plastic used are polyethylene, polypropylene, polystyrene, polystyrene, polystyrene, polyvinyl chloride and polystyrene terephthalate which are non-biodegradable or their recycling process is either difficult or not economical [1-5]. According to Ibrahim et al. [6] predominant biopolymers such as polylactic acid (PLA), polyglycolic acid (PGA) polycaprolactone (PCL) and polyhydroxyalkanoate (PHA) has been studied as one of the biodegradable based plastics. Among those biopolymers, PLA was getting most attention as it made from renewable agricultural sources and also can maintain its transparency after processing [8-9].

However, even PLA was selected as good choice in the biopolymer processing, it has to overcome the problems such as low drawability, insufficient toughness and limited gas barrier [10]. To serve as a solution to the aforementioned problems, PLA may be blended with other polymers such as acrylonitrile butadiene styrene (ABS) in order to impart toughness properties on the blend.

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In terms of improving, bio-based content, this work was aimed to blend PLA with acrylonitrile butadiene styrene (ABS) and filled with micro-crystalline cellulose (MCC). This may allow for a good balance of performance, from the toughness properties of ABS and bio-based content from PLA. Furthermore, the idea of blending PLA/ABS blends with MCC was introduced as it can reduce the price of highly cost PLA and at the same time can retain equivalent biodegradability [11]. However, the major problem with this blending system is the poor interfacial interactions between the blend’s components. Thus by carried the silane treatment onto MMC filler is expected to overcome this blending problems.

2 Experimental

2.1 Materials

PLA was purchased from the Titan Chemicals Corp located in Pasir Gudang, Johor. It is in granules form and has melting temperature at 160 °C. ABS is an amorphous plastic consisting of three monomers; acrylonitrile, butadiene and styrene. The ABS was purchased from Titan Chemicals Corp located in Pasir Gudang, Johor. It is in pellet form and has glass transition temperature at around 105 °C. MCC is a white powdery fibers and high purity cellulose powders. It has a micro size, odourless and combustible. It was purchased from Sigma Aldrich, United States.

Silane coupling agent, γ-methacryloxypropyltrimethoxysilane (γ-MPS) with an approximate purity of 97%, was provided by Sigma Aldrich, United States.

2.2 Preparation of the sample

2.2.1 MCC modification with silane coupling agent

MCC was silanized with γ-MPS in a mixture of ethanol/water (80/20) [12]. The γ-MPS was added into the solution and the pH was adjusted to 4 by adding a few drops of acetic acid. The mixture was mechanically stirred for 4 h under ambient temperature. Then, MCC was filtered and washed with ethanol followed by distilled water to drive out any excess silane. Later, the silanized MCC was dried at room temperature for 2 days, and heated in oven at 80°C for another 4h to promote the actual chemical coupling.

2.2.2 Preparation of PLA/jackfruit seed starch blend

PLA/ABS blends were prepared by using heated two roll mill at 170ºC with rotation rate of 10 rpm. Firstly, the PLA was added to the nip of the heated two roll mill and processed until it melts. Then, the ABS was added and mixed with PLA until homogeneous. Lastly the MCC filler was added until completion of the mixing. The PLA/ABS/MCC composites was then undergoing the hot press molding to produce a 1 mm sheet. The hot press molding process was take place at 170ºC for 6 minutes.

3 Characterization and Testings

The Instron universal testing machine (Model 3366) was to examine the mechanical properties of each PLA/ABS/MCC blend by setting the crosshead speed of 10mm/min under an ambient temperature. An average value was taken for at least 5 samples in order
to get precise value for tensile strength, elongation at break, and modulus of elasticity for each blend formulation. The morphological studies was carried out on the tensile fracture surface by using the analytical Scanning Electron Microscope (SEM) (Model JEOL JSM-6460 LA) with the supply of accelerating voltage at 10kV. The purpose of this testing was to analyze the topographic imaging of samples such as the fracture surfaces, homogeneity of filler in the PLA/ABS composites and the distribution and dispersion of MCC embedded in PLA/ABS composites. To prevent the charging effect on the surface morphology which would affect the testing results, the fracture samples were required to be coated with platinum layer about 1.5-3.0 nm thickness with aid of utilizing the Auto Fine Coater (Model JEOL JFC 1600). The biodegradability of PLA/ABS composites filled with MCC could be determined by soil burial test under laboratory scale. Rectangle shape samples with the dimension of 3cm x 2cm were prepared from each type of blend ratio. The soil was filled up a container and it was exposed to the environmental condition during the whole testing duration. Gardening soil was used in this experiment. The samples were then buried into the soil with 10cm depth from the soil surface to allow the microorganisms action for 50 days. The buried samples were watered everyday for 1000mL into the container to keep the soil moist. After 50 days, they were then collected and cleaned with distilled water before taking for surface analysis by using optical microscope.

4 DISCUSSION

4.1 Tensile test

Figures 1 (a) – (b) show the effect of MCC loadings on the tensile properties of PLA/ABS blends. PLA is generally known to have high tensile strength, but facing the inferior toughness properties. The addition of ABS was to improve the brittleness of PLA. On the other hands, a polymer matrix with incorporation of filler will increase or decrease the tensile strength depending on the on type of filler. Form the figures it can be seen that the increasing in MCC loadings will increase tensile strength of the PLA/ABS/MCC composites. This due to the incorporation of reinforcing filler on the blends that could form the good mechanical interlocking between filler-matrix prevent the PLA/ABS chains movement [13].

Furthermore, for PLA/ABS composites with silane treatments exhibited higher tensile properties as compared to untreated MCC counterparts as results from the better PLA/ABS – MCC interfacial interaction. The highest tensile strength of PLA/ABS-30% MCC was 22.5 MPa, while for untreated PLA/ABS-30% MCC as merely 20.7 MPa. The better in tensile strength was due to the improvement in interfacial interaction between MCC and PLA/ABS matrix. The Similar trend was observed on the Young’s modulus graph for both composites. The Young’s modulus for untreated composites at 30% MCC was 1920 MPa and the value was increased for silane treatment composite counterpart to 2175 MPa. The treatment could prevent the chains slippage and provide better PLA/ABS blend’s dimensional stability [14]. Furthermore, the formation of interfacial bonding between MCC and PLA/ABS matrix also reduced the flexibility of the blends since the network restricted the movement of blends.
4.2 Morphological analysis

Properties of the polymer composites are strongly dependent on the uniform distribution of the fillers. Hence, Scanning Electron Microscope (SEM) testing of the biocomposites were performed in order to investigate the level of distribution of MCC in PLA/ABS matrix. The SEM micrographs of fractured surfaces of PLA/ABS/MCC composites at 5% and 30% were shown in Figure 2 and 3. From the morphology of the fracture surface (Figure 2), there is a little compatibility between the PLA/ABS matrix with MCC phase. It could be observed the smooth surface of MCC particles without being adhere with PLA/ABS matrix. This was due to the incompatibility problem arise from hygroscopic nature of the MCC and PLA/ABS matrix [15]. Meanwhile, there was slight level of agglomeration with 30wt% MCC contents in PLA/ABS matrix. Poor interfacial adhesion have been created between the MCC and the PLA/ABS blend and it contributed to weak interfacial regions [16]. As the MCC content was higher, the poor mixing creating aggromerations of MCC filler and lead to the void formations [17]. In figure 3, MCC particles have better interfacial interaction and imbedded inside the PLA/ABS matrix as a result from the silane treatment. The micrographs were being more compact, and thus the void formations were less for both 5% and 30% MCC composites.

Fig. 2. SEM micrographs of untreated 5% and 30% MCC-filled PLA/ABS composites.
4.3. Biodegrability analysis

The biodegradability properties is one of the interesting criteria in biopolymers composites. This is due to the service lifetime of the biomaterial must be known to make sure whether it is biodegraded and lost its performance during the application period or not, thus it can perform its optimum usefulness for the certain period for safety. The polymer degradation is an irreversible process that can be induced by several environmental factors. The factors influence the rate of degaradation, including the type of chemical bond in the polymer backbone, hydrophilicity, molecular weight, copolymer composition, crystallinity and presence of low molecular weight compounds [18,19]. PLA is biocompatible and undergo hydrolytic scission to lactic acid when implanted. To study the effect of MCC into the PLA/ABS composites, the MCC loading with 0% and 30% for treated and untreated samples was undergo testing after 50 days burying into the soil. As shown in the figure 4, the increasing of MCC content up to 30wt%, it was apparently more obvious to observe the surface erosion by the microorganisms. The higher the fillers loading, the higher the weight loss in soil burial and could be reduce time to degrade in polymer applications. Incorporation of reinforce fillers and biodegradable polymer, there were more prone to bacterial attack despite presence of ABS in composites. The cellulose were degraded first and leaving vacant space, which increases the surface area for the onwards biodegradation of the polymer matrix. This is due by the formation of voids and cavities, which were more concentrated in the location where the filler attaches to the PLA/ABS matrix. Image of MCC 5% and MCC 30% illustrate that with the addition of silane coupling agent onto MCC, less degradation was observed and that specimen without silane coupling agent had rougher surfaces. This is indicated there was noticeable effect of bacterial action in specimen due to the strong biopolymer-filler interaction by the silane. The poor interaction adhesion was indicated by the large amounts of filler extracted after the soil burial.
Conclusions

The effect of micro-crystalline cellulose (MCC) loading on polylactic acid (PLA)/acrylonitrile butadiene styrene (ABS) with and without surface treatments by silane coupling agent were investigated. The main purpose of choosing MCC in this study was to produce a partial bio-based plastics with the wish to partially replace the conventional petroleum-based plastics which have some disposing issues. In this study, the incorporation of MCC has been show that by adding reinforce filler capable to improve the tensile properties. The higher the MCC content in the PLA/ABS composite, the tensile strength and Young’s modulus show good increment in its value especially for silane treated MCC composites. It is due to the better interacial interaction between PLA/ABS matrix and MMC. In morphology analysis, silane treated MCC was well dispersed and embedded in the PLA/ABS matrix and have less void formation as compared to untreated MCC counterparts. In soil burial test, it was found that increasing in MCC content in the matrix would be enhance the degradation kinetics and thus increased the weight loss. It was observed that more adhering microorganisms colonizing onto the surfaces as more as MCC content was added. As the MCC filler content increased, the formation of voids, cracks and cavities become more prominent.

Fig. 4. Optical microscope image for treated and untreated at magnification of x80 for 5% MCC and 30% of compost in soil burial after 50 days.
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