Preparation and characterization of LDPE/TPS blend filled with calcium carbonate

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Abstract The measurement of low-density polyethylene / thermoplastic starch (LDPE/TPS) composite with different loading of calcium carbonate (CaCO₃) as filler was conducted under several testing such as the tensile test and scanning electron microscopy. The preparation of LDPE/TPS/CaCO₃ composite was divided into three stages. The first stage involved the preparation of TPS with and without modification with carboxylic acid. The second stage, LDPE was blended with TPS to produce LDPE/TPS blend. LDPE/TPS blends with blend ratio of 100:0, 90:10, 80:20, 70:30, 60:40 and 50:50 was prepared. Each composition will undergo tensile testing to analyze their mechanical properties. The optimum LDPE/TPS blend ratio was chosen for subsequent study. Third stage involved the compounding of the chosen LDPE/TPS blend ratio with CaCO₃. The result indicate that LDPE/TPS with incorporation of CaCO₃ gave higher value of tensile properties as compared to LDPE/TPS blend. Based on the SEM micrograph, treated TPS with citric acid and ascorbic acid performed better interfacial phase as compared to untreated TPS, with no agglomeration and voids formation.

1 Introduction

Starch has widespread use since it is low cost material, and production from renewable resources. Botanical sources that contain starch such as wheat, corn, potato and rice. Biodegradable starches can be processed by using injection molding, blow molding, film blowing, foaming, thermoforming and extrusion [1-5]. Starch consists of granule and two major parts of granules are amylose and amylopectin. In addition, higher proportion of short chains gives low gelatinization temperature in amylopectin.

Starch is a hydrophilic material, brittleness and has poor mechanical strength. However, the properties of starch can be enhanced by blended with other biodegradable polymer such as polyvinyl alcohol, polylactic acid and poly (ε-caprolactone) [6-8]. The addition of plasticizer in starch film will affect the tensile strength, flexibility, elongation at break, glass transition temperature and hardness [9-12]. Commonly, plasticizers are added into polymer to reduce brittleness, reduce inter-molecular forces and increasing flexibility. Thermoplastic starch (TPS) was produced from native starch which it capable to flow and mixed with other

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synthetic polymer such as low density polyethylene. TPS is purchased from plasticized starch when the starch is mixed with plasticizer such as glycerol and conducted under mechanical process. Blending TPS with other synthetic polymers gives high ductility, high modulus with toughness, low cost, good mechanical properties, and improve biodegradability. On the other hand, crosslinking agent such as citric acid and ascorbic acid are used to form bonds between starch polymer chains in order to strengthen the material. Besides that, crosslinking agent also used to reduce the water sensitivity of starch and to improve the barrier properties of TPS [13-15]. In order to enhance the properties of product, the incorporation of filler is required. Fillers usually used to improve the performance of rubbers and other polymeric materials. Clays, talc and calcium carbonate are the types of fillers. In this study, calcium carbonate was used as filler for blending with PE/TPS blends. Calcium carbonate is used to improve mechanical properties such as strength, modulus and toughness.

2 Experimental

2.1 Materials

LDPE is a thermoplastic resin that purchased from Titan Chemical, Malaysia was used for this study. Density of LDPE is 0.91 g/cm3 and the melting point is between the ranges 105°C to 115°C. Potato starch was manufactured by ThyeHuat Chan Sdn. Bhd. Penang. The moisture content of potato starch is 20%. Potato starch is a white powder in appearance and the density is 1.5 g/cm3. Calcium carbonate was used as reinforcing filler to increase the mechanical properties of the compounding. Glycerol is made by HmBG® Chemicals and was used as a plasticizer in preparation of TPS. The density of glycerol is 1.261 g/cm3 and the melting point is 17.8°C. Citric acid is provided by SIGMA-ALDRICH and used as a crosslinking agent to reduce the water sensitivity of starch and improving the mechanical properties of TPS. Ascorbic acid is purchased from SIGMA-ALDRICH and used as a crosslinking agent to improve the properties of TPS. The melting point of ascorbic acid is between the ranges 190-194°C.

2.2 Preparation of the sample

2.2.1 Modification of TPS with citric acid and ascorbic acid

Modification of TPS was done by mixing 65% of potato starch and 35% of glycerol in the presence of 3% of citric acid or ascorbic acid. The mixtures were left at room temperature for 24 hours after preparation. Then, the mixtures were mixed by using heated two roll mill machine at temperature 150°C for 10 minutes.

2.2.2 Preparation LDPE/TPS/CaCO3 composite

LDPE was blended with TPS by using heated two roll mill with the different blends ratio. The blend proportion of LDPE/TPS blend were 100:0, 90:10, 80:20, 70:30, 60:40 and 50:50. Then, LDPE/TPS blend was molded by using hot press with 1mm dimension of mould at temperature 150°C for 6 minutes. The mechanical properties of LDPE/TPS blend were investigated under tensile testing. The best optimum measured data was used to ratio for subsequent study. The chosen LDPE/TPS blend ratio was further blended with calcium carbonate. Calcium carbonate were vary from 5% to 20% relative to the LDPE/TPS blends. The compounding process was prepared by using heated two roll mill at temperature 150°C.
for 10 minutes. Next, the compounding was molded by using hot press with 1mm dimension of mould at temperature 150°C for 6 minutes.

3 Characterization and Testings

The tensile properties are determined by using Instron Machine 5569 Universal Tester. The specimens were cut from compression moulded sheets according to the ASTM D-882 standard. The samples were cut into dumbbell shape with average thickness is approximately 1mm ± 0.2mm. The crosshead speed was set 5mm/min and the gauge length was set 50mm. Three samples were taken from each of the formulation to get the average of each parameter. The morphology of the potato starch was observed under scanning electron microscopy model JEOL JSM 6460LA. SEM is used to determine the phase separation between blend components and the interaction occurred at the interphase.

4 DISCUSSION

4.1 Tensile properties

Effect of thermoplastic starch content towards the properties of LDPE can be determined by blend both materials with different TPS content. TPS has low tensile properties while LDPE pose high tensile properties. Blending of TPS with LDPE will affect the properties of LDPE which it tends to reduce the mechanical properties. The effect of TPS content on tensile strength of LDPE/TPS blends is shown in Fig. 1(a). As shown from the graph, the tensile strength of LDPE which is 9.1 MPa decrease as the TPS content increase until 4.7 MPa at 50 wt%. This results shows that increasing in TPS content can decrease the tensile strength of LDPE/TPS blends. This is due to the TPS cannot transfer stress or force applied from the outside and well distribute throughout the sample. Besides, the formation of defects such as low dispersion of thermoplastic starch will become stress concentration point and cause thermoplastic easily breaks when force is applied. The incorporation of TPS content also leads to poor adhesion with LDPE/TPS phase. The effects of these problems will cause the blends inability to support the high stress and unable to transfer the stress efficiently between phase in LDPE/TPS blends. The dispersion and distribution of TPS particles is the major factor of adhesion and tensile properties of the blends [16-17]. Therefore, as the TPS increased, the deterioration of tensile properties also increased and resulting the blends easily breaks when external force applied. Fig. 1(c) shows the effect of TPS content on elongation at break of LDPE/TPS blend. According to Kahar et.al [18], the percentage of elongation at break decreases with increasing of TPS content. The major cause to the decreases of break elongation values is due to the poor dispersion and distribution of TPS within LDPE/TPS blends. As shown in the graph, the elongation at break of LDPE which is 121.6 % decrease until 12.3 % as the TPS content increase. This is due to the weak interaction at the interphase of LDPE and TPS which leads to phase separation. Therefore, LDPE/TPS blends will break easier when the force is applied to the samples. The modulus elasticity of LDPE/TPS blends was found to be decreased as TPS content is increased. The results found that for LDPE/TPS blends at 10% TPS content is 125.8 MPa, but on 50% TPS content the value become 66.9 MPa Fig.1 (c)). The incorporation of TPS will soften the LDPE/TPS blends due to the presence of glycerol during TPS preparation. In the other words, the stiffness and rigidity of the blends will decrease as the TPS content increases [19]. At the lower TPS content, the modulus elasticity in LDPE/TPS blends is higher and possess better stiffness. From tensile properties, LDPE/TPS with blend ratio of (80:20) was chosen for subsequent study due to
acceptable tensile properties. The tensile strength of LDPE/TPS (80:20) is 7.0 MPa with 44% of elongation at break which higher than LDPE/TPS (70:30), LDPE/TPS (60:40) and LDPE/TPS (50:50).

Figs 1 (a) – (c).

From the preliminary result, LDPE/TPS blends with 80/20 blend ratio was selected due to the acceptable mechanical with optimum TPS content. For the subsequent study, LDPE/TPS blends was prepared by treated TPS with citric acid and ascorbic acid. Citric acid and ascorbic acid was added in LDPE/TPS blends to acts as a crosslink agent in order to improve the compatibility between LDPE/TPS interphase. Based on the Fig. 2, the tensile strength of LDPE/TPS, LDPE/TPSCA and LDE/TPSAA improves steadily as calcium carbonate is added. The tensile strength is improved which increased from 6.9 MPa to 7.5 MPa for LDPE/TPS, 7.4 MPa to 9.3 MPa for LDPE/TPSCA and 7.1 MPa to 8.9 MPa for LDPE/TPSAA. The initial increase in strength of the composite is due to good filler-matrix interaction. Thus, it enables more stress to be transferred from the matrix to the filler during external loading. However, further increase in calcium carbonate loading was decreased in the tensile strength of LDPE/TPS, LDPE/TPSCA and LDPE/TPSAA. The tensile properties decrease along with further addition of calcium carbonate. The increasing filler loading will attributed to the formation of filler aggregates, which are made up of particles held together by weak forces [20-21]. The aggregates are easily debond from the matrix and resulted in decrease the tensile strength of the composite. The increase in strength of LDPE/TPS composite at lower calcium carbonate loading are attributed by the homogeneity dispersed of calcium carbonate particles. The well dispersed particles made the crack propagation path longer, absorb a portion of energy and enhanced the plastic deformation [22]. However, with the increased of calcium carbonate loading, the detachment of the filler particle from the LDPE/TPS matrix caused voids which increased the size to form crack. In addition, the
agglomeration of calcium carbonate results decrease in mechanical strength due to low strength of agglomerates itself. On the other hand, the tensile properties of LDPE/TPS blends that treated with citric acid and ascorbic acid increased as compared to untreated LDPE/TPS blends. As can be seen from the graph, the addition of citric acid and ascorbic acid in TPS was improved the tensile strength of the LDPE/TPS blends. Citric acid and ascorbic acid was improved the interaction of the starch molecule as the citric acid and ascorbic acid increased the slippage of starch molecule. The acidity of citric acid and ascorbic acid was induced to fragmentation of starch and rupture of starch granules that weaken the chain entanglements.

Fig. 2. Effect of filler loading on tensile strength of LDPE/TPS, LDPE/TPSCA and LDPE/TPSAA.

4.2 Morphology analysis

Fig. 3 (a) – (c) show the SEM images of LDPE/TPS, LDPE/TPSCA and LDPE/TPSAA blends. The images from both 100x and 300x magnification shows that there are significant voids between the interphase of LDPE and TPS. The voids in LDPE/TPS blends indicating poor degree of interfacial interaction between LDPE and TPS. This is due to compatibility problem between hydrophilic TPS and hydrophobic LDPE. TPS particle does not tend to disperse homogeneously in LDPE. In the Fig. 3 (a), thermoplastic starch particles were found around 100 μm – 150 μm which indicating poor dispersion and higher degree of phase separation. On top of that, a large particle size will weaken the adhesion bonding between LDPE/TPS blends [23-24]. On the other hand, as can be seen from Fig. 3(c) and (d), the SEM micrographs for LDPE/TPSCA and LDPE/TPSAA blends shows good interfacial phase as compared to LDPE/TPS blends. The interfacial phase and adhesion was found to be improved by well dispersed of TPS particles that was treated with citric acid and ascorbic acid in LDPE/TPS blends. The size range of thermoplastic starch particle that treated with citric acid and ascorbic acid were found around 30 μm – 50 μm. As can be seen from the Figs. 3 (b) and (c), the smaller TPS particles that treated with citric acid and ascorbic acid are homogeneously dispersed throughout the LDPE/TPS matrix. Besides, the voids formation between polymer phase also reduced and no agglomeration was found in LDPE/TPSCA and LDPE/TPSAA blends. Continuity of a phase was favoured by citric acid and ascorbic acid may attributed to low interfacial tension.
The thermoplastic starch that treated with citric acid and ascorbic acid was dispersed and dissolves in LDPE phase, thus reducing the voids on the blends surface. These TPSCA and TPSAA well dispersed in LDPE in smaller size of particles due to LDPE phase was adhered well with TPS particles. The agglomeration of TPS in LDPE also found to be reduce and approved that citric acid and ascorbic acid has been improved the adhesion of LDPE/TPS blends. The breakdown of TPS particles due to citric acid and ascorbic acid contributed to homogeneous dispersion and well embedded in LDPE/TPS blends. In order to study the interaction between matrix and dispersed phase of LDPE/TPS/CaCO₃, SEM micrographs of fracture surface was observed under 100x and 300x magnification. Fig. 4 (a) – (c) show the SEM micrograph of LDPE/TPS, LDPE/TPSCA and LDPE/TPSAA blends with 20% of calcium carbonate. The images from both 100x and 300x magnification shows that there are clear voids between the interphase of CaCO₃ and LDPE/TPS matrix blend as compared to CaCO₃ filled LDPE/TPSCA matrix and LDPE/TPSAA matrix. The voids in LDPE/TPS/CaCO₃ composite indicates poor degree of interfacial interaction between LDPE.
and TPS as well as between CaCO$_3$ and LDPE/TPS matrix. This is due to the compatibility problem between hydrophilic TPS and hydrophobic LDPE.

In addition, a large particle size will weaken the adhesion bonding between LDPE/TPS/CaCO$_3$ composites. The size range of calcium carbonate particle were found around 10 μm – 20 μm and the size range of thermoplastic starch particle that were found around 100 μm – 150 μm. Besides, as can be seen from Fig. 4 (b), the SEM micrographs for LDPE/TPSCA/CaCO$_3$ composites shows better interfacial phase as compared to LDPE/TPS/CaCO$_3$ composites. The interfacial phase and adhesion has been improved by well dispersed of TPSCA particles and calcium carbonate particles in LDPE phase. The size range of thermoplastic starch particle that treated with citric acid is smaller compared to the size of untreated thermoplastic starch. The size of TPSCA particles were found in SEM micrograph is around 20 μm – 50 μm. Based on the Figs. above, the smaller TPS particles that treated with citric acid is homogeneously dispersed throughout the LDPE/TPSCA/CaCO$_3$ matrix. For the LDPE/TPSAA/CaCO$_3$ composites, SEM micrograph exhibit good interfacial phase as compared to LDPE/TPS/CaCO$_3$ composites. The adhesion phase of LDPE/TPSAA/CaCO$_3$ composites has been improved by addition of ascorbic acid in TPS particles. TPS particle well embedded in LDPE phase. Therefore, the micrograph found there is no agglomeration and voids formation occurred in LDPE/TPSAA/CaCO$_3$ composites. The size of TPSCA particles were found in SEM micrograph is around 20 μm – 50 μm and the size of CaCO$_3$ particle were found around 10 μm – 20 μm. On the other hand,
the presence of CaCO\textsubscript{3} also can be observed in SEM micrograph. Increasing of CaCO\textsubscript{3} content in LDPE/TPS matrix causes voids which increase in size to form a crack. Agglomerate of CaCO\textsubscript{3} form by the interaction between the filler particle. The particle tends to attract each other cause it grouping together forming the agglomerations. In addition, the agglomeration of CaCO\textsubscript{3} particle results in a decrease in tensile properties of LDPE/TPS composite compared to LDPE/TPSCA and LDPE/TPSAA composite due to low strength of the agglomerates itself.

5 Conclusions

TPS had been blended with LDPE to produce a partial biodegradable polymer. According to the study, several composition between LDPE and TPS are prepared with different LDPE/TPS blend ratio. Each composition provided different characteristics based on the amount of TPS content. Tensile test demonstrated that high TPS content will give low mechanical properties of LDPE/TPS blends. From tensile properties, LDPE/TPS with blend ratio of 80:20 was chosen for subsequent study due to the acceptable tensile properties. In order to achieve better properties of LDPE/TPS blend, TPS was treated with citric acid and ascorbic acid to improve the mechanical properties. Calcium carbonate filler was added in LDPE/TPS, LDPE/TPSCA and LDPE/TPSAA at different weight percentage which are 5%, 10%, 15% and 20% in order to performed better properties. Based on the SEM micrograph, treated TPS performed better mechanical and thermal properties as compared to untreated TPS. This is due to the TPS particle well embedded in LDPE phase. On the other hand, the micrograph was found there is no agglomeration and voids formation occurred in LDPE/TPSCA/CaCO\textsubscript{3} composites and LDPE/TPSAA/CaCO\textsubscript{3} composites.

The authors wish to gratefully acknowledge the School of Materials Engineering, as well as Research and Innovation Department under Universiti Malaysia Perlis and Kementerian Pengajian Tinggi Malaysia (Ref: FRGS/1/2016/TK05/UNIMAP/02/9) for supporting this research project.

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