Structural and dimensional analysis of LDPE/TPS blend filled with calcium carbonate

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Abstract This study aims to investigate the changes in structural, thermal stability and water absorption properties of thermoplastic starch (TPS) before and after modification with citric acid and ascorbic acid. The first stage of study involved the preparation of TPS from native potato starch. Starch will be converted into thermoplastic like in the presence of glycerol as plasticizer. For the second stage, LDPE was blended with TPS to produce LDPE/TPS blend with and without modification. Then, the influence of calcium carbonate as particulate filler on the properties of LDPE/TPS blends was also investigated. Structural findings based on the FTIR analysis showed the formation of new ester bond on the TPS backbone after the modification, which correspond to the formation of crosslinking network in TPS phase. Water absorption test was used to determine the effectiveness of TPS modification in term of physical interaction between the phases.

1 Introduction

There is increasing developments in the use of partial biodegradable polymer in daily applications resulting in highly demand of natural sources such as starch [1-3]. Since plastics are very important in daily life, production of biodegradable plastics to make plastics more compatible with the environment is necessary [4-5]. According to Katarzyna et.al, [6], primary degradation mechanism of biodegradable polymer involves the action of microorganism such as bacteria, fungi and algae. Biodegradable materials degrade into biomass, carbon dioxide and methane under aerobic or anaerobic conditions. In addition, cellulose, chitin, starch, polyhydroxyalkanoates, polylactide, polycaprolactone, and collagen are one of the types of biodegradable polymers [7].

Most researcher use biodegradable polymer in their studies as its exhibit more benefits which are sustainable, low cost and environmental. Thermoplastic starch is processing from native starch which it capable to flow and mixed with other synthetic polymer such as low density polyethylene. 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

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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 [8-11].

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 case, native potato starch undergoes the plasticization process with glycerol and treated with carboxylic acid, namely; citric acid and ascorbic acid. Calcium carbonate was used as a particulate filler in order to improve the dimension and thermal stability of LDPE/TPS blends, as well as their resistance to the moisture absorption.

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 Thye Huat Chan Sdn. Bhd. Penang and was chosen in this study. 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. CaCO₃ was used 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 moulded 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 moulded by using hot press with 1mm dimension of mould at temperature 150°C for 6 minutes.
3 Characterization and Testings

Thermogravimetric analysis (TGA) is used to determine the thermal behaviour of the thin film. TGA is used to measure the weight loss of the sample as a function of temperature and time. The experiment was conducted according to standard ASTM D258. 10mg of specimen was put in the platinum pan. The samples were heated at 20°C/min from 30°C to 600°C. The data were collected using Perkin-Elmer TGA 7. The decomposition of composite and its thermal stability was observed based on the curves produced. The structure of polymer blends was investigated by using FTIR Spectroscopy. Water absorption test was conducted according to standard ASTM D570. The samples were cut in dimension 30mm × 30mm. Then, the samples were dried in the oven at a temperature 50°C for 24 hours. After that, the samples were allowed to cool in room temperature and each of the samples was weighted using electronic balance. The samples were immersed in distilled water at room temperature for 30 days. The water absorption measurements were taken for every 3 days. Three samples were prepared for each of the formulation.

4 DISCUSSION

4.1 Structural analysis

Fig. 1 shows the TPS, TPSCA and TPSAA spectra in range of 4,000–650 cm⁻¹ region. The IR spectrum of The peaks at 3,485 cm⁻¹ and 2,928 cm⁻¹ in potato starch was attributed to O–H and C–H bond stretching [12] while the peaks at 1,406 cm⁻¹ was attribute to the bending modes of H–C–H and C–H [13]. The characteristic peaks 1078 cm⁻¹ and 1150 cm⁻¹ in TPS indicate the C–O bond stretching of C-O-H group [14]. Another two peaks at 1650 cm⁻¹ was attributed to C=O bond [15]. Besides, the spectrum also shows the effect of citric acid and ascorbic acid modification on TPS. The existence of new shoulder peak at 1709 cm⁻¹ in TPSCA and 1729 cm⁻¹ in TPSAA illustrates that the ester bond existed [16]. Peak at 1729 cm⁻¹ reflect the possible of chemical reaction between TPS with citric acid and ascorbic acid. It is noted that, the citric acid and ascorbic acid is capable to form covalent bond with TPS by detecting the appearance of new ester peak. Similar results were reported by Bower and Maddams [17] which states that the C=O stretching was resulted from the formation of ester groups between TPS and carboxylic acid. The functional groups of LDPE/TPS/CaCO₃, LDPE/TPSCA/CaCO₃ and LDPE/TPSAA/CaCO₃ composite were presented in Fig. 1(b). The presence of calcium carbonate was identified by assigned of O-C-O bond at absorption peak of 925 cm⁻¹ [18]. No additional peak was observed after the addition of CaCO₃ which confirmed the only physical interaction occurred between CaCO₃ and LDPE/TPS matrix.
4.2 Water absorption

Fig. 2(a) shows the percentage of water uptake or water absorption of LDPE/TPS, LDPE/TPSCA and LDPE/TPSAA blends. As can be seen from the graph, the water absorption for the first 3 days was increased rapidly for all the series. This phenomenon was due to the water molecule start to penetrate inside the voids exist in LDPE/TPS blends. Then, the graph show steady increase after water molecule start to interact with hydroxyl groups from TPS (Stage 2) before its become saturated with surrounding (Stage 3). On the other hand, the graph for LDPE/TPS blend shows higher water absorption when compared to LDPE/TPSCA and LDPE/TPSAA blends. There was significant voids between the LDPE and TPS interphase that allows the water molecule to penetrate and occupied inside. The formation of voids between LDPE and TPS molecules indicating to poor interfacial interaction between LDPE and TPS. In addition, high content of hydrophilic nature in TPS will affected the quantity of water absorption. Potato starch are hydrophilic and having OH
group that can interconnect with the water molecule through the hydrogen bonding [19]. On contrary, the weight of water absorption for LDPE/TPSCA and LDPE/TPSAA blends were lower than LDPE/TPS blends. The modified TPS with citric acid and ascorbic acid were able to improve the adhesion at the interphase and thus lower the possibility of voids formation. Besides, citric acid and ascorbic acid also react as a crosslink agent [20] that can prevent the swelling of starch as well as restricts the penetration of water molecules inside the starch.

Fig. 2(b) shows the effect of water absorption on LDPE/TPS/CaCO$_3$, LDPE/TPSCA/CaCO$_3$ and LDPE/TPSAA/CaCO$_3$ composites. The water absorption of LDPE/TPS/CaCO$_3$ composite, LDPE/TPSCA/CaCO$_3$ composite and LDPE/TPSAA/CaCO$_3$ composite stage 1 was show similar trend with the blends without CaCO$_3$ due to the of water molecule occupied the voids at the interphase LDPE/TPS matrix and CaCO$_3$. The diffusion of water molecules into the miniaturized voids and micro gaps in the polymer matrix, was due to the lack interfacial interaction between phases [21]. In stage 2, the water uptake slowly increase due to the hydrophilicity of TPS could form strong interaction with water molecule. In the third stage, the graph become saturated and reach the equilibrium with the surrounding. In all series, the water absorption for LDPE/TPS/CaCO$_3$ composite was found to have significant water uptake as compared to another systems. The formation of voids between LDPE and TPS molecules indicating to poor interfacial interaction between CaCO$_3$ with LDPE/TPS matrix. On the other hand, there is less apparent voids formation between the LDPE/TPSCA and LDPE/TPSAA with CaCO$_3$ which reflects lower water absorption as compared to LDPE/TPS system.

Fig. 2 (a). The effect of water absorption on LDPE/TPS, LDPE/TPSCA and LDPE/TPSAA blends.
Fig. 2(b). The effect of water absorption on LDPE/TPS, LDPE/TPSCA and LDPE/TPSAA with 20% calcium carbonate.

4.3 Thermal stability

The TGA thermograms observed in Fig. 3(a) shows the thermal decomposition for LDPE/TPS blends and LDPE/TPSAA blends. There were three decomposition stages found for LDPE/TPS blends and LDPE/TPSAA blends which are corresponding to their compound’s degradation. The degradation temperature observed at 38.61ºC to 110ºC was correspond to volatilization of moisture and another degradation occurred at the range of 110ºC to 250ºC due to the of glycerol that used in preparation of TPS [22]. The first major weight loss is referring to the degradation of thermoplastic starch at about 250ºC to 350ºC [23]. Another major weight loss for LDPE/TPS blends and LDPE/TPSAA blends occurred at 331.5ºC and 298.9ºC respectively, which attributed to the decomposition temperature for LDPE phase.

Based on the degradation temperature curves, LDPE/TPS blends shows higher thermal stability as compared to LDPE/TPSAA blends. This due to the presence of ascorbic acid in TPS will partially hydrolyse the TPSAA chains and thus lowering its thermal stability. Fig. 3(b) shows the TGA thermogram for LDPE/TPS/CaCO3 composite and LDPE/TPSAA/CaCO3 composite at 20% CaCO3 loading. The thermograms graph for both composites exhibit almost similar characterization. First stage decomposition start at temperature 150°C–250°C which related the evaporation of glycerol in TPS phase. For the second stage, at temperature 250°C–350°C was attributed to decomposition of TPS in the composite. At temperature 350°C–470°C was attributed to LDPE decomposition [24]. Although, TPS and LDPE was completely decomposed at 500°C, the remaining residue above that temperature was attributed to calcium carbonate. The decomposition temperature for calcium carbonate was reported at 850°C–900°C [25].

By comparing the thermal decomposition of both series, the weight loss of LDPE/TPSAA/CaCO3 composite is lower than LDPE/TPS/CaCO3 composites. LDPE/TPS/CaCO3 composite indicate poor degree of interfacial interaction between LDPE and TPS as well as between calcium carbonate and LDPE/TPS matrix and thus lowering their thermal stability. Better interfacial interaction between LDPE/TPSAA matrix with CaCO3 was believed to contribute better thermal stability for LDPE/TPSAA/CaCO3 composite. Good interaction at the interphase allows CaCO3 to prevent LDPE/TPS chain movement and therefore give resistance to the thermal decomposition.
5 Conclusions

In order to achieve better thermal and water resistance properties, TPS were treated with citric acid and ascorbic acid. Treatment with citric acid and ascorbic acid creating new functional groups as confirmed with FTIR analysis. Ester bonding that appeared after the treatment could initiate the crosslink network within the TPS phase. This would lead to the better thermal stability and better resistance to the water absorption. Moreover, CaCO₃ as a particulate filler was added in LDPE/TPS, LDPE/TPSCA and LDPE/TPSAA in order to improved the targeted properties. Treated TPS with citric acid and ascorbic acid were found to have better compatibility with CaCO₃ as its reflected to their thermal and water resistance properties.

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