Physical and Degradation Properties of Polylactic Acid and Thermoplastic Starch Blends – Effect of Citric Acid Treatment on Starch Structures

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The physical and degradation properties of polylactic (PLA)/thermoplastic starch (TPS) blends after TPS modification with citric acid (CA) were investigated. The interfacial adhesion between the PLA and TPS was expected to improve, thus enhancing the physical properties of the PLA/TPS blends. The tensile strength and Young's modulus for PLA/TPS blends at (60/40) and (40/60) blends ratio were found to increase after modification with CA. On the other hand, the elongation at break of the (60/40) blend decreased, while elongation at break of the (40/60) blend increased. Meanwhile, an additional peak at 1721 cm^{-1} was detected by the FTIR spectroscopic analysis, which indicated that the TPS had chemically interacted with the CA. The biodegradability properties of PLA/TPS blends were also improved after treatment with CA. The deterioration of PLA/TPS blends was attributed to the incorporation of CA; O_2 from the soil was attracted to the PLA/TPS blends, thus speeding up the degradation process of the blends.

Keywords: Biopolymer; Polylactic acid (PLA); Thermoplastic starch (TPS); Physical properties; Degradation properties

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INTRODUCTION

The high consumption of conventional plastics and their large-scale production have given rise to several problems, such as diminishing oil resources, increasing CO_2 discharge into the atmosphere, and pollution caused by the disposal of plastics (Markarian 2008). Interest in the use of biomaterials in plastic production has been increasing, along with a trend of increasing environmental awareness of the society. Previous researchers have found that poly(lactic acid), a thermoplastic biopolymer material, is an ideal replacement of petroleum- based plastics in extensive applications, thus mitigating solid waste disposal and lightening the dependence on petroleum resources (Zhang *et al.* 2009a). PLA has several advantages among others bioplastics such as being fully biodegradable, biocompatible, and produced from renewable resources (Arruda *et al.* 2015). As a photosynthetically renewable resource, PLA does not generate much net CO_2 emissions in its manufacturing process (Dorgan *et al.* 2001). PLA can be recyclable and compostable. It also had good stiffness and strength (Imre *et al.* 2014). However, PLA has some drawbacks, such as brittleness, moisture problems, and, most importantly, it is produced at a relatively high price (Acton 2013; Imre *et al.* 2014). To reduce these undesirable properties of PLA, researchers have attempted to modify the PLA in many ways, such as by plasticization, copolymerization, blending, and composite production, to enhance its properties and, most importantly, to lower the cost of producing the PLA itself (Auras *et al.* 2011). Starch, the main material or monomer in the production of thermoplastic starch (TPS), is inexpensive and readily available. Starch consists of amylose and amylopectin, and unlike PLA, starch is a naturally occurring polymer (Huneault and Li 2007). As a completely biodegradable polymer, starch-based products have been widely used for the food packaging industry and agricultural film industry as starch is a non-expensive material (Vikman *et al.*1999; Wang *et al.* 2007). In the presence of plasticizers such as water or glycerol, the gelatinization of starch leads to the formation of thermoplastic starch (TPS) (Huneault and Li 2007). Thus, the idea of blending TPS and PLA in this research could greatly reduce the cost and enhance the biodegradability of the biopolymer blends. Unfortunately, the incompatibility of the hydrophobic aliphatic polyesters and the hydrophilic starch makes the adhesion between the two components weak, resulting in the poor mechanical properties of the blends (Han 2005; Zhang *et al.* 2009b; Kahar *et al.* 2012). In order to improve the compatibility of PLA with other polymers, previous research works (Yuan *et al.* 2009; Lin *et al.* 2012) have focused on the use of grafting reactions, the addition of compatibilizers, and the use of reactive blending methods. In this study, the authors attempted to blend PLA with modified TPS in order to improve compatibility of the PLA/TPS blend.

Wang *et al.* (2007), in their study involving the blending of TPS and LDPE, reported that using a carboxylic acid CA treatment on TPS had improved the plasticization of starch and the dispersion between PE; thus no obvious phase interface was observed in that work. Reddy and Yang (2010) also reported that cross-linking starch films with a carboxylic acid such as citric acid improves the tensile strength of the films by more than 150%. However, the optimum amount of citric acid must be below 5% to obtain a notable increase in the tensile strength. Meanwhile, Yu *et al.* (2005) reported that citric acid interacts with starch to form strong hydrogen bonds, thus improving its thermal properties and water stability while inhibiting retrodegradation. Thus, using CA to modify the TPS appears to solve the compatibility problem between PLA and TPS.

The objective of this study was to decrease the degree of polymerization (DP) of TPS and at the same time, to improve the interfacial adhesion between PLA and TPS. The authors prepared the blends using a melt-mixing method. The mechanical properties, physical properties, rheology, and biodegradability of the PLA/TPS blend were studied as a function of CA treatment of TPS.

EXPERIMENTAL

Materials

The PLA pellets used in this experimental work were purchased from Titan Chemical, Pasir Gudang, Malaysia. Cassava starch was commercially available from Thye Huat Chan Sdn. Bhd, George Town, Malaysia. Reagent-grade glycerol with a molarity of 92.10 g/mol was supplied by HmbG Chemicals, Hamburg, Germany.

Blend Preparation

Preparation of TPS-CA

Starch was premixed with 35% glycerol using a mixer (with 0%, 1%, 2%, 3%, and 4% CA) until a homogenous mixture was obtained. The mixture was left for 24 h before being processed using a Brabender plastograph EC plus (Duisburg,Germany) at 150 °C and a speed of 60 rpm with a mixing time of 10 min.

Preparation of PLA/TPS-CA blends

The blends were prepared by the melt blending of PLA with TPS using a Brabender device at a processing temperature of 180 °C, a speed of 60 rpm, and a mixing time of 10 min. The PLA was melted first for 4 min, after which TPS was added to the Brabender and processed until a plateau torque was reached. The duration of the whole process was 10 min. The blend was converted into a 1-mm sheet using a hydraulic hot press, a Gotech Testing Machine (GT-7014-P, Taichung, Taiwan). The hot press procedure involved preheating at 180 °C for 5 min, followed by 2 min of compression at the same temperature and subsequent cooling under pressure for 4 min. Table 1 shows the weight proportions of the TPS/PLA blends modified with citric acid (CA). The ratio of the treated PLA/TPS was fixed at 60/40 and 40/60, with the percentage of CA varying from 1% to 6%.

Table 1. Weight Proportion of TPS/PLA Blends (with TPS Modification by CA)

Sample	PLA (%)	TPS (%)	CA (%)
1% CA 60/40	60	40	1
2% CA 60/40	60	40	2
3% CA 60/40	60	40	3
4% CA 60/40	60	40	4
5% CA 60/40	60	40	5
6% CA 60/40	60	40	6
1% CA 40/60	40	60	1
2% CA 40/60	40	60	2
3% CA 40/60	40	60	3
4% CA 40/60	40	60	4
5% CA 40/60	40	60	5
6% CA 40/60	40	60	6

Characterization

Tensile properties

Measurements of the tensile properties were performed with an Instron Universal Testing Machine (5569 model, Pittsburgh, USA) with a crosshead speed of 10 mm/min. Dumbbell samples (1 mm thick) with a 50-mm gauge length were tested according to ASTM D 638 (2014) . The mean value was calculated and reported for the five samples.

Fourier transform infrared spectroscopy (FTIR)

The Fourier transform infrared spectra of the PLA/TPS blend were measured using a PerkinElmer Spectrum One Spectrometer (Perkin Elmer, Waltham, USA) to characterize the possible reaction between the TPS and CA. The transmittance spectra regions were obtained between 4000 and 800 cm^{-1}.

Scanning electron microscopy (SEM)

The fractured samples from the tensile testing were examined using a field emission scanning electron microscope (JEOL, JSM 6010-LV, JEOL Ltd., Japan) at an acceleration potential of 20 kV. The fractured surfaces of the specimens were sputter-coated with a thin layer of platinum using a JEOL JFC-1600 Auto Fine Coater.

Soil burial test

The biodegradation of the blend samples was checked after composting for two months. The dumbbell samples (1 mm thick) with a 50-mm gauge length were tested according to ASTM G 160 (2012). Readings were taken of the changes in the weight loss of the samples at intervals of 10 days for approximately two months. Images of the blend samples were taken every 10 days using an optical microscope to capture any enzymatic reactions or microbial attacks on the blend samples. The percentage weight loss in the PLA/TPS blend was calculated using Eq. 1,

$$\%\ \text{Weight loss} = \{(W_0 - W_t)/W_0\} \times 100 \qquad (1)$$

where W_0 is the weight of the original PLA/TPS blend and W_t is the weight of the residual films after degradation for various time intervals (Gautam and Kaur 2013).

RESULTS AND DISCUSSION

Tensile Properties

The tensile properties of the PLA/TPS with and without treatment with CA are shown in Figs. 1, 2, and 3. Improvement on compatibility of the blends was highly related to their mechanical properties. The compatibility of PLA and TPS was improved after treatment of TPS and CA. After 3% CA treatment on TPS, both (60/40) and (40/60) PLA/TPS blends showed an improvement after the TPS had been treated with up to 3% CA.

From Fig. 1, the highest tensile strength was recorded at 23.6 MPa for the (40/60) PLA/TPS; meanwhile for the (60/40) PLA/TPS the highest tensile strength was recorded at 10.4 MPa. Wang *et al.* (2007), studied TPS/PE blends system and stated that the addition of CA improves the dispersion and compatibility of TPS and PE, hence contributing to the higher mechanical properties of the blends.

This established that the compatibility of the PLA/TPS blends was enhanced by CA treatment on TPS. The blend with the highest tensile strength was the (60/40) PLA/TPS, which had a higher PLA content in the blend system. Lin *et al.* (2012) reported that pure PLA has a high tensile strength but a low elongation at break value, while TPS has good flexibility properties but low tensile strength. They also reported that the addition of a second polymer could cause a decrease in the tensile strength of the PLA/polymer blend. This explains why a higher content of TPS inside the PLA/TPS blends resulted in a lower tensile strength compared with the blends with a higher PLA content. However, when the CA content was higher than 3%, it had a negative effect on the starch (a process called acidolysis). The starch loses its rigid structure because of the severe acidolysis process, which leads to a decrease in tensile strength.

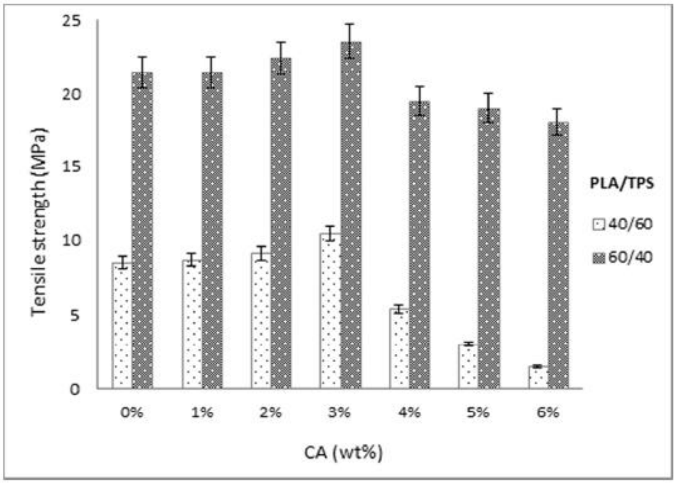

Fig. 1. Tensile strength (MPa) of PLA/TPS blends

Figure 2 shows the elongation at break for both the 60/40 and 40/60 PLA/TPS blends. The figure indicates that both blends experienced an increase in the elongation at break with the increase of CA content. It can be clearly seen that the blends with higher TPS showed a greater elongation at break as compared with the blends with higher PLA content. Treating the TPS with CA improved the flexibility of the blends in which 6% CA recorded the highest elongation at break (up to 85.3%). The acidity of CA is able to partially hydrolyze the TPS backbone and therefore allowed the TPS to elongate further. Similar work was reported by Liu *et al.* (2008), who showed that the CA treatment leads to a weaker interaction between the starch molecules, thus improving the fluidity of the TPS as well as the subsequent elongation.

While the (40/60) PLA/TPS showed greater improvement in the elongation at break, the (60/40) PLA/TPS showed a slower increase in the elongation at break value as the amount of CA increased. At a (60/40) PLA/TPS ratio, TPS acts as a dispersion phase in PLA. The effect of CA on fluidity of TPS is overwhelmed by the brittleness properties of the PLA itself. PLA has an inherent brittleness as evidenced by its relatively low tensile strain at break, and toughness (Shirai *et al.* 2016). Only a slight improvement could be observed on the PLA/TPS (60/40) blends, even after the blend was treated with CA.

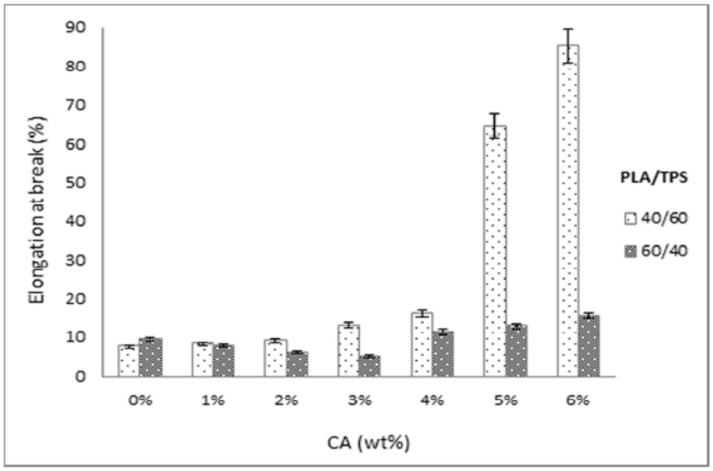

Fig. 2. Elongation at break (%) of PLA/TPS blends

Figure 3 shows that the Young's modulus of the (60/40) PLA/TPS blend continuously increased from 870.3 MPa (0% CA, 60/40) up to 1119.5 MPa (3% CA). However, after the blend was treated with 4% CA, the Young's modulus value decreased to 933.7 MPa because of the severe acidolysis of the TPS, which resulted in the loss of rigidity in the TPS structure. Meanwhile, the lower value of Young's modulus of the (40/60) PLA/TPS blend was attributable to the effect of incorporating a higher loading of TPS into the PLA matrix system. The use of 35% glycerol in the preparation of TPS had a softening effect on the blend, thus decreasing the Young's modulus. Similar works reported by Godbole *et al.* (2003) and Reis *et al.* (2008) reported that blends with an addition of thermoplastic starch (TPS) in a thermoplastic system have a decreased Young's modulus and tensile strength. Huneault and Li (2007) also reported that the Young's modulus of PLA/TPS blends decreased markedly with the addition of TPS.

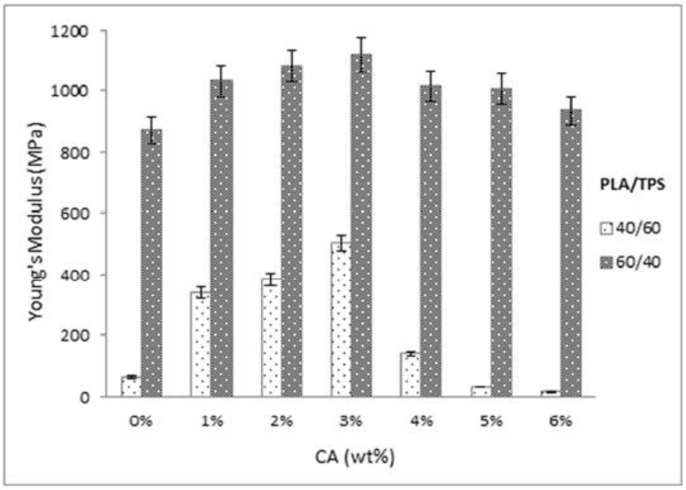

Fig. 3. Young's modulus (MPa) of PLA/TPS blends

FTIR Spectroscopic Analysis

The FTIR spectra of the 0% CA-treated (60/40) PLA/TPS blend and 3% CA-treated (60/40) PLA/TPS blends are shown in Fig. 4. After the modification of the TPS, the changes in the TPS structure were confirmed by means of IR spectral analysis. The acidolysis of the starch backbone and the esterification process between starch and CA were also determined. Based on Fig. 4, the peak observed at 3338 cm^{-1} was referred to the vibration stretching of inter- and intra-molecular bonds between the starch and glycerol hydroxyl groups (Orozco *et al*. 2009; Yuan *et al.* 2009). The peak at 2945 cm^{-1} was imputed to belong to the C–H stretching band from the TPS backbone (Han 2005; Orozco *et al*. 2009). The stretching of the C=O bonds came from the backbone of the PLA found at a frequency of 1754 cm^{-1} (Orozco *et al*. 2009). The C–OH group peak, found at a frequency of 1043 cm^{-1}, was believed derive from the TPS hydroxyl substituent (Han 2005). From Fig. 4, it was found that almost all the similar functional groups were still attached to the TPS backbone after the TPS had been modified by CA. Figure 4 also presents an additional peak at 1721 cm^{-1} that was found on the treated PLA/TPS 3%CA blend. The peak was identified as the carboxyl and ester carbonyl groups (Reddy and Yang 2010; Kahar *et al.* 2012). Previous works by Reddy and Yang (2010) and Kahar *et al.* (2012) reported that this peak is due to the esterification reaction that occurs between TPS and CA. Thus, the linkages formed by the reaction between citric acid and starch were confirmed by the presence of the carbonyl peak in the FTIR spectra.

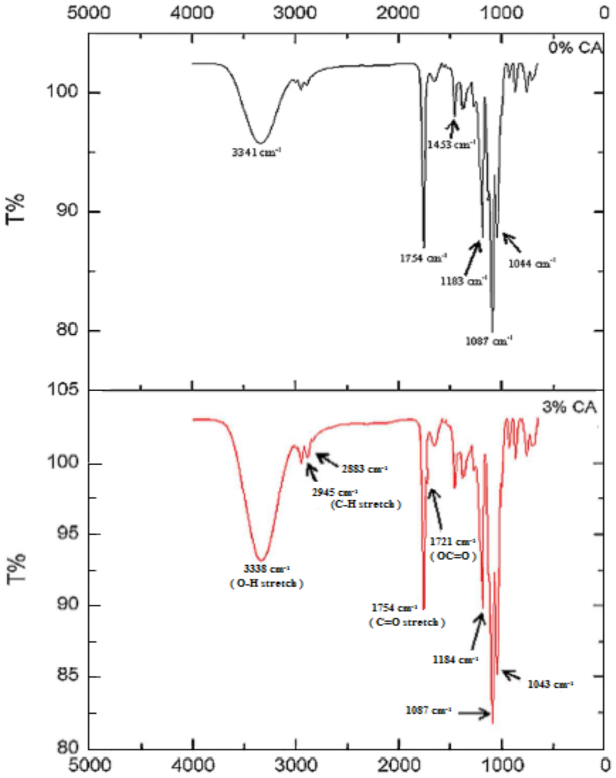

Fig. 4. FTIR spectra of PLA/TPS (60/40) with 0% CA and 3% CA blend

To strengthen the finding that a reaction occurred on the TPS after treatment with 3% of CA, a schematic of this reaction is shown in Fig. 5. Based on the reaction shown in Fig. 5, after the heating of the CA, the carbonyl group from the CA was dehydrated to form citric anhydride. Later, the citric anhydride reacted with the hydroxyl group in starch to form starch acetate (Zhang *et al.* 2009a). The other end of the CA yielded cross-linked starch acetate (Kumar *et al.* 2010). Additionally, the peak at 1721 cm^{-1} also pointed out the efficiency of the acetylation process that occurred between the hydroxyl group in starch and citric acid.

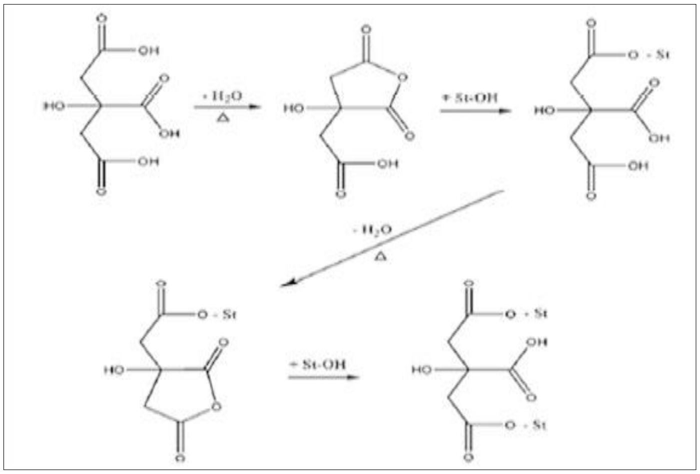

Fig. 5. Schematic reactions from esterification process between TPS and CA (Kahar *et al*. 2012)

Blend Morphology

Figures 6a and 6b present SEM micrographs of the untreated (40/60) PLA/TPS blend at magnifications of 150 and 300, respectively. From Fig. 6a, although TPS was dominant in the PLA/TPS blends at a ratio of 60 wt.%, the TPS remained in a granular form and existed as a dispersed phase in the PLA matrix. Furthermore, Fig. 6b also shows that the TPS granules had been completely separated from the PLA matrix. The size of the TPS particles was approximately 20 to 25 µm. The large size of TPS granules showed that untreated TPS had failed to improve the interfacial interaction between the hydrophobic PLA and the hydrophilic TPS, thus producing immiscible blends of PLA/TPS blends. Imre *et al.* (2014) reported that a heterogeneous structure from immiscible blends could weaken the interaction between the blends in the system. Thus, a large phase separation could be seen in the SEM micrograph. At the blend interphase, a large volume of voids was observed. This indicated that the blend was incompatible.

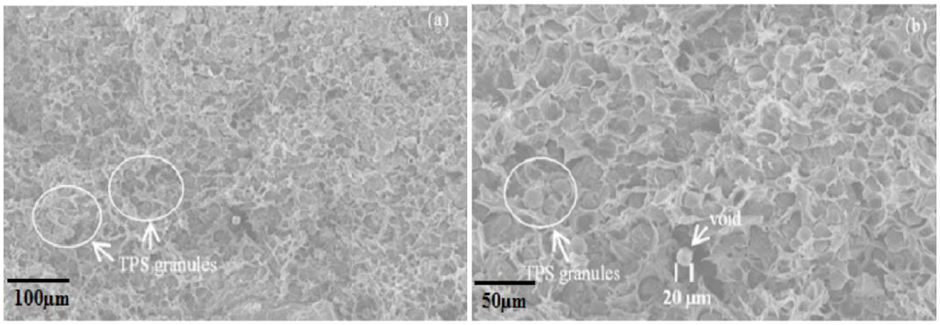

Fig. 6. SEM micrographs of untreated PLA/TPS (60/40) blend at (a) 150X and (b) 300X

Figure 7a shows PLA/TPS blends with 3% of CA, where the TPS granules were less visible. The granules were mostly melted and fused together with the PLA matrix to form a co-continuous phase. This showed that a compatible blend had been achieved. Figure 7b shows that fine TPS particles were well embedded in the PLA matrix, with the size of the TPS particles decreasing to approximately 10 µm. The appearance of fewer voids in the treated PLA/TPS interphase showed that after the TPS had been treated with CA, adhesion improved between the PLA and TPS.

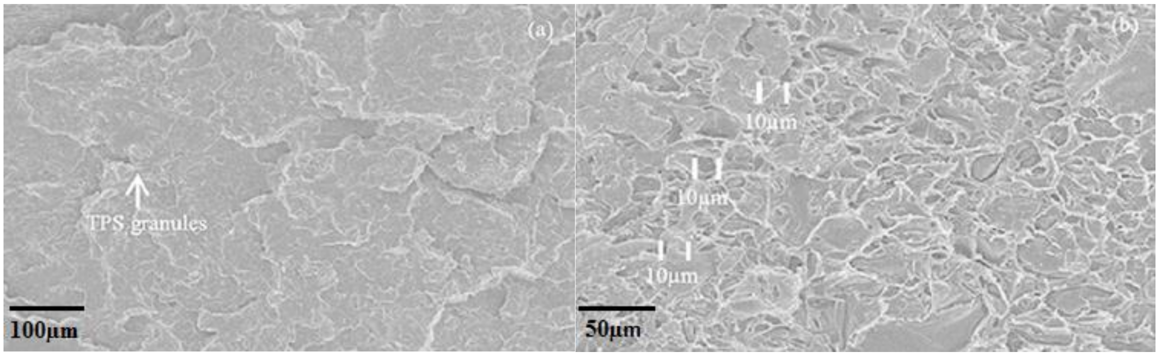

Fig. 7. SEM micrographs of treated PLA/TPS (60/40) blend with 3% CA at (a) 150X and (b) 300X

Biodegradation of the Blends

Table 2 shows the biodegradability of the PLA/TPS, as evaluated by weight loss during biodegradation in soil. The (40/60) PLA/TPS treated with 0%, 3%, and 6% CA was used as test samples. As shown in Fig. 8 and Table 2, the PLA/TPS blend treated with a higher content of CA recorded the highest biodegradation rate, up to 26.2%. The samples with modified TPS showed a faster degradation rate compared with the blends with unmodified TPS because the CA accelerated the biodegradation rate. Kahar *et al*. (2011) implied that CA-modified starch underwent partial molecular degradation during TPS preparation. With reference to Fig. 8, the increment of weight loss after the addition of CA was around 4% to 6% higher than untreated TPS. Therefore, a high amount of CA can severely hydrolyze the TPS chain and hence, the TPS experienced partial degradation via an acidolysis process. A high concentration of CA accelerated the biodegradation rate of PLA/TPS blends. Thus, the percentage of weight loss in the blends increased as the CA content is increased. In previous research (Shi *et al.* 2011), a similar result was reported, where the weight loss rate of the PLA/starch composite was higher than that of the pure PLA. From the observation of the previous FTIR spectroscopic analysis in Fig. 4, the PLA/TPS treated with 3% CA had a higher peak for the OH group. Thus, the treated blends degraded faster than the control blend because the higher hydroxyl content inside the treated PLA/TPS blends was more easily attracted to O_2 from the soil environment. Microbial attack from microorganisms can colonize polymeric surfaces (Mohan and Srivastava 2010). The microorganisms will attack the enzymes or radicals of biological origin in the polymer, leading to embrittlement and loss of mechanical stability.

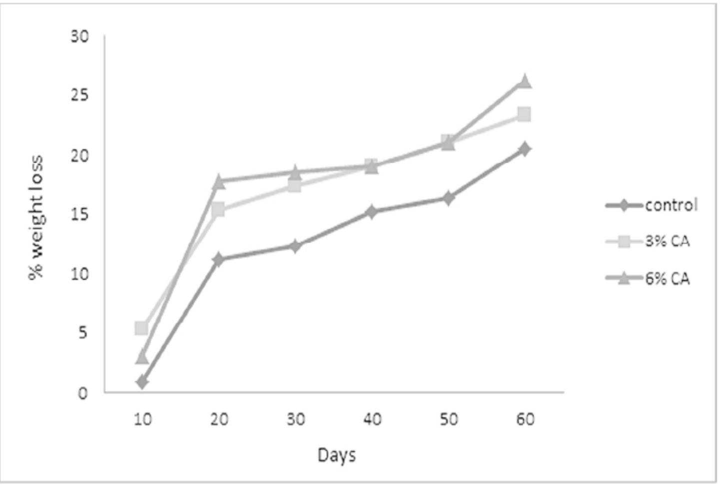

Fig. 8. % Weight loss after two months of soil burial testing of PLA/TPS (40/60) blends

Table 2. Percent (%) Weight Loss of PLA/TPS Blends

Days / Sample	10	20	30	40	50	60
Control	0.9	11.1	12.3	15.2	16.4	20.5
3%	5.3	15.3	17.3	19.0	21.0	23.3
6%	3.1	17.7	18.5	19.0	21.0	26.2

Figures 9a and 9b show the embrittlement of the PLA/TPS after the blend samples were composted in the soil. The excretion of lipophilic microbial pigments that led to unwanted colors in the polymer could also be detected under an optical microscope (Mohan and Srivastava 2010). From Fig. 9a, the colonization and embrittlement at the surface of the untreated blends were different than that of the modified PLA/TPS-CA blends. As mentioned earlier, the high hydroxyl content within the modified PLA/TPS blends attracted attack from more colonies. As a result, the modified PLA/TPS with 3% CA deteriorated easily and had a higher percentage of weight loss compared to the unmodified blends as shown in Fig. 9b. Thus, modification of TPS with CA can increase the biodegradability properties of PLA/TPS blends.

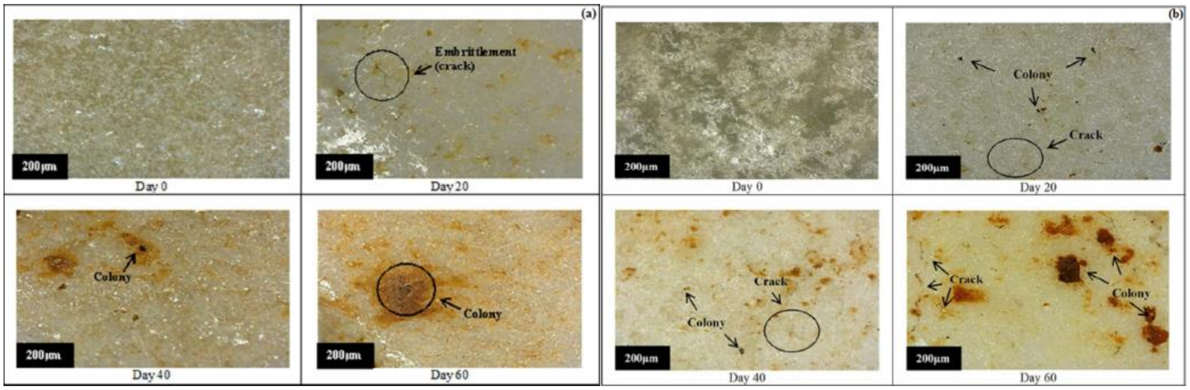

Fig. 9. Optical micrographs of (a) PLA/TPS-CA 0% and (b) PLA/TPS-CA 3%

CONCLUSIONS

1. The chemical modification of thermoplastic starch (TPS) using citric acid (CA) results in blends with improved tensile properties and interfacial adhesion between the poly-(lactic acid) (PLA) and TPS phases. The additional peak (1725 cm^{-1}) from the FTIR analysis demonstrated that the CA interacted chemically with the TPS.
2. From the SEM micrographs, the changes at the interphase of the PLA/TPS blends after the modification of TPS with CA can be confirmed. The formation of voids within the PLA matrix was minimized, which indicated that after the treatment of TPS with CA, the interfacial adhesion between the PLA/TPS blends improved.
3. A higher content of CA accelerated the degradation of the PLA/TPS blends, increasing the percentage weight loss of these fully biodegradable blends.

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