Effect of Blending Conditions on Mechanical, Thermal, and Rheological Properties of Plasticized Poly(lactic acid)/ Maleated Thermoplastic Starch Blends

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ABSTRACT: This research work has concerned a study on relationship between structure and properties of maleated thermoplastic starch (MTPS)/plasticized poly(lactic acid) (PLA) blend. The aim of this work is to investigate the effects of blending time, temperature, and blend ratio on mechanical, rheological, and thermal properties of the blend. The MTPS was prepared by mixing the cassava starch with glycerol and maleic anhydride (MA). Chemical structure of the modified starch was characterized by using a FTIR technique, whereas the degree of substitution was determined by using a titration technique. After that, the MTPS prepared by 2.5 pph of MA was further used for blending with triacetin-plasticized PLA under various conditions. Mechanical, thermal, and rheological properties of the blends were evaluated by using a tensile test, dynamic mechanical thermal analysis, and melt flow index (MFI) test, respectively. It was found that tensile strength and modulus of the MTPS/PLA blend increased with the starch content, blending temperature, and time, at the expense of their toughness and elongation values. The MFI values also increased with the above factors, suggesting some chain scission of the polymers during blending. SEM images of the various blends, however, revealed that the blend became more homogeneous if the temperature was increased. The above effect was discussed in the light of transesterification. Last, it was found that mechanical properties of the PLA/MTPS blend were more superior to those of the normal PLA/TPS blends. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 1012–1019, 2012

Key words: blends; thermoplastics; miscibility; esterification

INTRODUCTION

It has been estimated that the global bioplastic production capacity would increased from 960,000 tonnes in the year 2010 to 1,500,000 tonnes in the year 2012.[1] This indicates a promising trend for the developments and consumption of the bioplastic products. This trend has been driven by many factors including an increased public concern and awareness about the environmental impact of plastic waste, an uprising petroleum and petrochemicals prices, and stringent regulations and nontariff trade barriers.[2]

In general, bioplastics can be classified into three main categories: (i) synthetic, biodegradable plastics such as polycaprolactone, (ii) biobased, nonbiodegradable plastics such as poly(trimethylene terephthalate), and (iii) biobased, biodegradable plastics such as poly(lactic acid) (PLA). The use of biobased, biodegradable plastics has benefits of fast biodegradability and its contribution to the reducing carbon dioxide emission.[3] PLA is a kind of thermoplastic having physical and mechanical properties comparable to those of polystyrene, that is, PLA is transparent but brittle. Mechanical strength of the molten PLA also has to be improved if the PLA is needed for extrusion blown film process. In addition, price of the PLA resin is considerably high when compared with that of commodity plastics such as polyethylene and polypropylene.[4] To overcome the above limitations of PLA, it is common to modify PLA by blending with other biodegradable polymers.[5,6] Specifically, various types of starches have been used for blending with PLA. This is due to the fact that starches are renewable, biobased, and biodegradable polymers with a relatively low cost. Technically, a direct blending of PLA and starch together would yield blend product

with low mechanical properties due to a poor compatibility between the two polymers. To improve the compatilbility and the mechanical properties of the PLA/starch blend, two main strategies are used, that is, chemical modification of the polymers and/or the use of compatibilizers. Common compatibilizers for the PLA/starch blend systems include PLA-g-MA,[7] PLA-g-amylose,[8] and isocyanate compounds.[9] A study on PLA/plasticized wheat starch blends[10] suggested that the use of peroxide and/or PLA-g-MA was more effective than the use of MDI, taking into account an increase in tensile strength of the blend without scarifying percentage elongation values. Furthermore, Huneault et al.[11] demonstrated that rather than adding a peroxide compound during the blending process to induce an *in situ* formation of PLA-g-MA, direct use of PLA-g-MA, which was separately prepared before blending, was even more effective.

Alternatively, many starches can be blended with PLA without the use of any compatibilizers. To enhance compatibility between the starch and PLA, however, it is important that chemical structure of the starch was modified by partially replacing hydroxyl groups of starch amylose with some less hydrophilic functional groups such as ether- and ester groups. Particularly, many esterified starches can be prepared via acylation mechanism, using anhydrides. Acetic anhydride is an effective acylating agent for modifying starch before blending with PLA.[12] However, the above anhydride cannot be imported and commercially unavailable in this region. Propionic anhydride and fatty acid anhydrides might be used as a replacement,[13] but prices of the chemicals are considerable. In our present study, chemical modification of starch by using maleic anhydride (MA) was of interest. It was expected that the modified starch containing MA-derived acidic moieties would be more compatible with PLA, and some advantage properties of the modified starch/PLA blends might be obtained. Raquez et al.[14] examined chemical structure of maleated thermoplastic starch (MTPS), which was prepared via a reactive extrusion process, and found that MA preferentially reacted with the hydroxyl groups on the C6 position of starch carbon. Of note, side reactions such as hydrolysis of starch and glucosidation also occurred, and effect of the side reactions on properties of MTPS/polyester blends should also be taken into account. Raquez et al.[15] also studied properties of the maleated starch/poly(butylenes adipate-co-terephthalate) (MTPS/PBAT) blends and found that, depending on the blend ratio, PBAT-g-MTPS might be formed through trans-esterification during the blending process. It was also found that tensile properties of the blends containing the PBAT-g-MTPS are much higher than those of the blend containing PBAT-g-TPS compatibilizer. Similarly, Shin et al.[16] studied thermal, morphological, and mechanical properties of blends of PLA and thermoplastic corn starch chemically modified with MA [CMPS] and found that the interfacial adhesion was improved by the presence of PLA-g-starch copolymers, which were formed at the interface, via a trans-esterification reaction between PLA and CMPS. It was also found that tensile strength and elongation of the blend decreased with increasing modified starch content. Noteworthy, percentage elongation values of the blends were considerably low, ranging between 0.7 and 4.0%. This is attributed to the fact that the PLA phase used for blending is a kind of brittle polymer and thus overall tensile elongation of the blends was remaining low. In this study, blends of triacetin-plasticized PLA and maleated cassava starch (MTPS) are of interested. The aim of this work is to investigate effects of blending conditions (time and temperature) on mechanical, morphological, thermal, and rheological properties of the blends.

EXPERIMENTAL

Chemicals

PLA (2002D from NatureWork) was supplied from the Fresh Bag. Cassava starch was supplied by E.C.T. International, glycerol (commercial grade), and glycerol triacetate used as plasticizers from starch and PLA were purchased from Bank Trading and Eastman, respectively. MA (Laboratory grade, 98% from Fluka) used for chemically modification of the starch was supplied from ACS Xenon. Finally, 1,1-di(*tert*-butylperoxy)3,5,5-trimethyl cyclohexane (Luperox231) used for inducing PLA branching chains was supplied from Arkema.

Preparation of maleated TPS

The cassava starch was dried in an oven at 80°C for 12 h. After that, it was mixed with 25 pph of glycerol and 2.5 pph of MA in an Internal mixer (Brabender 350/350E, roller blade rotor type, mixing chamber 370 cm³) at 130°C, 40 rpm, for 20 min, using a fill factor of 0.66. After that, the chemically modified thermoplastic starch (TPS) was purified by refluxing with acetone until pH value of the washed solution was neutral. The anticipated product from a chemical reaction between starch and MA can be illustrated in Figure 1. With the absence of MA, similar procedures were used for preparing a normal TPS.

Preparation of plasticized PLA compound

PLA compound was prepared via masterbatching. PLA resin was dried in an oven at 80°C for 12 h.
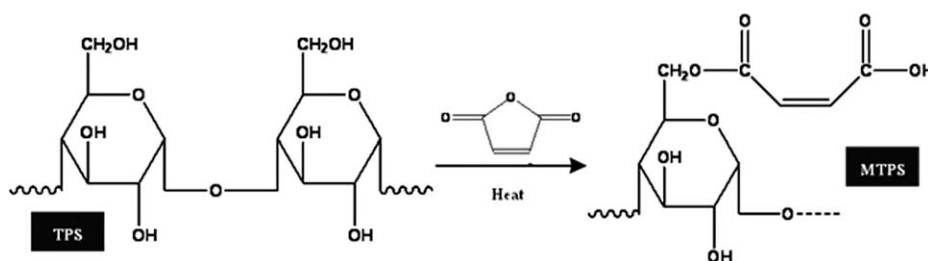
Figure 1 Reaction between starch and maleic anhydride.

After that, the dried polymer pellets was compounded with 50 pph of glycerol triacetate (triacetin) and 0.75 pph of Luperox231 in an internal mixer (Brabender 350/350E, roller blade rotor type, mixing chamber 370 cm³) at 170°C, 40 rpm, using a fill factor of 0.86. The mixing time was 10 min, and, after that, the PLA masterbatch was diluted with PLA in a twin screw extruder (Brabender, DSE20) at a screw rotating speed of 100 rpm. Temperature profiles used from feed to die zone were 80, 160, 165, 165, 145, and 135°C, respectively. Noteworthy, the aim of using peroxide for compounding with PLA herein was to induce a branching structure of the PLA molecules and to improve melt strength of the molten PLA. This would enable a fabrication of PLA blends via an extrusion blown film processing, which is an aspect of our future work.

Blending

The dried PLA compound and TPS were premixed in a high speed mixer (Labtech Enginnering), using different weight ratios ranging from 80/20, 70/30, and 60/40. After that, the mixture was fed through a hopper of the internal mixer (Brabender) at different temperatures (170, 180, and 190°C) and at a mixing speed of 40 rpm. The blend was cooled in ambient air before undergoing pelletization process to obtain blend granules.

Fabrication

The polymer blend was fabricated into 185 × 185-mm² rectangular test pieces using a mold of 0.5-mm thick in a hydraulic compression mold (Labtech Engineering, Model T16). The sample was preheated at 160°C for 7 min before compression molded at the temperature of 160°C under a mold pressure of 150 bar for 3 min. After that, the fabricated sample was allowed to cool in the mold for 5 min before opening and removal.

Characterizations

Changes in chemical structures of the starch were examined using a Fourier transform infrared spec-

troscopy (Perkin–Elmer, Spectrum One) over the wave-number ranging from 450 to 4,000 cm⁻¹. The PLA/MTPS sample for the FTIR experiment was prepared by using KBr disc method. In addition, ATR-FTIR mode was used for characterization of the modified starch.

Degree of substitution (DS) of the modified starch was determined by using combination of saponification and titration techniques. First, 0.5 g of the modified starch was saponified by dissolving in 50 mL of distilled water and then mixed with 25 mL of an aqueous NaOH solution (0.1 mol/L). The solution was stirred at room temperature until the solution was homogeneous and transparent. Second, phenolphthalein was dropped into the solution, and then the solution was titrated with 0.1 mol/L of HCl until reaching the end point (the solution turn from pink to colorless). Finally, the DS value was calculated by using eq. (1);

$$DS = \frac{162 \times (N_{NaOH} \times V_{NaOH} - N_{HCL} \times V_{HCL})}{1{,}000 \times W - 99 \times (N_{NaOH} \times V_{NaOH} - N_{HCL} \times V_{HCL})}$$
(1)

where DS is the degree of substitution of MTPS, N_{NaOH} is the concentration of sodium hydroxide (mol/L), V_{NaOH} is the volume of sodium hydroxide (cm³), N_{HCL} is the concentration of hydrochloric acid (mol/L), V_{HCL} is the volume of hydrochloric acid (cm³), and W is the weight of starch (g).

Thermal analysis

Glass transition temperatures of various materials (TPS, MTPS, PLA compound, and blends) were examined by using a dynamic mechanical thermal analysis (DMTA) technique. The experiment was conducted by using Netzsch (242 model), and the sample was prepared in a form of 5 × 50 mm² rectangular with a thickness of 0.5 mm. The DMTA experiment was operated under a tension mode, at 2 N force, 1 Hz oscillating frequency, and 10 μm amplitude. The heating rate used was 3°C/min, and the sample was scanned over temperature ranging between (−70)°C and (+70)°C.
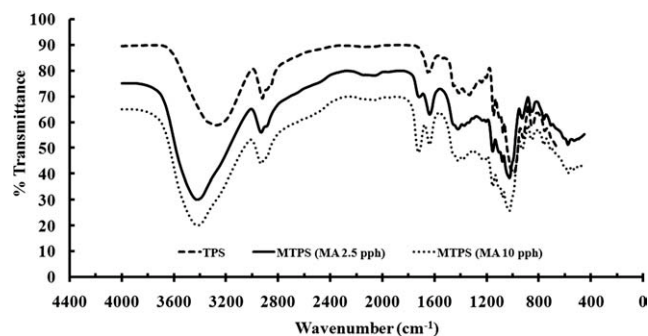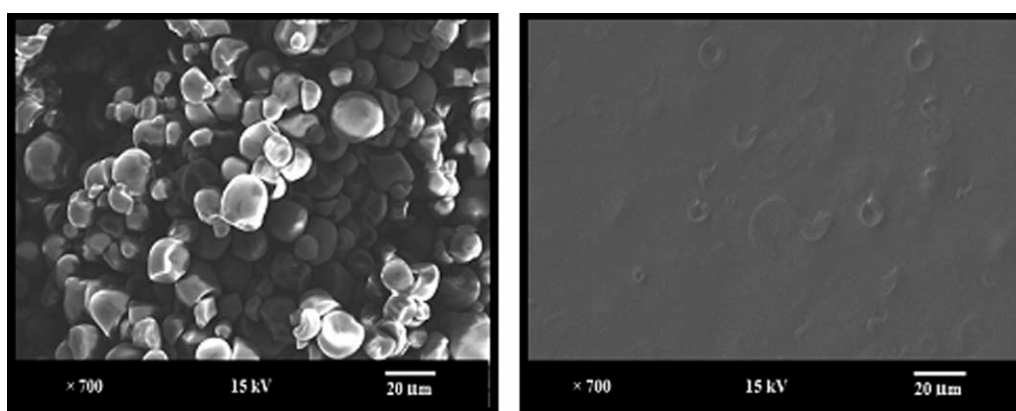
Figure 2 FTIR spectra of thermoplastic starch before and after modification with different amount of maleic anhydride.

Mechanical properties test

Mechanical properties of the various blends were evaluated by tensile test. Samples of various blends were fabricated into 3-mm thick sheets by using a compression molding at 170°C. After that, dumbbell-shape specimens were prepared by cutting the sheet using a suitable die in accordance of with an ASTM D638 standard test method. The tensile test was carried out by using a LLOYD instrument (LR 50K model) at a crosshead speed of 100 mm/min, at room temperature. At least five specimens were tested for each blend. Average values of the Young's modulus, tensile strength at break, and elongation at break were then calculated and reported. In addition, toughness values of the blends were obtained by calculating the area under the force-displacement curves of each specimen, from a tensile test.

Scanning electron microscopy

Morphologies of the various blends were examined using scanning electron microscopy (SEM) technique. The SEM specimen was prepared by cryogenic fracturing of the rectangular test-pieceS under liquid nitrogen. After that, the fracture surfaces were etched with HCl solution (0.1 mol/L) at 120°C for 20 min.

TABLE 1
Degree of Substitution of Thermoplastic Starch Before and After Modification with Different Amounts of Maleic Anhydride

Type of starch	Code	Amount of MA (pph)	DS value
Thermoplastic starch (TPS)	TPS	0	0.25
Maleated thermoplastic starch	MTPS-2.5	2.5	0.45
Maleated thermoplastic starch	MTPS-10	10.0	0.67

This was to extract the TPS phase, leaving porous PLA matrix phase to be examined. The etched specimens were washed with distilled water before drying at 50°C for 12 h. The etched surfaces of the specimens were then coated with Au, using a gold-sputtering technique (SPI-module™ coater, S/N 10081 MODEL) before SEM experiment. This was to avoid some charging effect during the electron beam scanning. The SEM experiment was operated by using a JEOL (JSM5800) machine, equipped with a secondary electron detector under an accelerating voltage of 10 kV.

Melt flow index test

Flow rate of polymer melt was determined using a melt flow index (MFI) tester, in accordance with an ASTM D-1238. The melt indexer was preheated at a specified time and then the polymer blend granules were loaded into the cylinder. The specific weight of 2.16 kg was then placed on a piston. The sample was preheated and compressed for 2 min, before being extruded for 10 min. The extrudate after 10 min was weighed and reported as a MFI value (g/10 min).

RESULTS AND DISCUSSION

Characterization of MTPSs

Figure 2 shows overlaid FTIR spectra of TPSs before and after reacting it with different amounts of MA.

Figure 3 Scanning electron micrographs of starch (left) and thermoplastic starch (right).
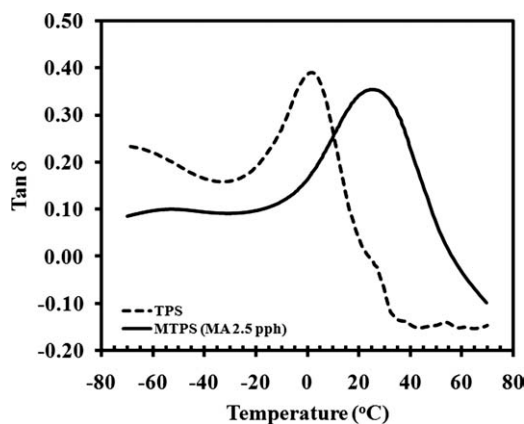
Figure 4 DMTA thermograms of thermoplastic starch (TPS) and maleated thermoplastic starch modified with 2.5 pph MA.

A broad peak at 3400 cm^{-1} corresponding to O—H stretching of starch amylose and amylopectin can be observed. More importantly, the peak at 1787 cm^{-1} representing carbonyl bond of the anhydride group emerged after the chemical modification and that tended to increase with the amount of MA.

Table I shows degree of substitution (DS) values of various types of TPSs. DS values of the modified TPSs were higher than that of the normal TPS. In addition, the higher the amount of MA used the greater the DS values. Based on the above results from FTIR and titration, it might be concluded that the MTPS with different degrees of substitution was successfully prepared.

Figure 3 shows scanning electron micrographs of the normal starch and the TPS. It can be seen that the starch particles disappeared after compounding with a glycerol plasticizer. This suggests that the TPSs were successfully obtained. Similar morphological aspect was also observed for the MTPS.

Figure 4 shows DMTA thermogram of TPS and the MTPS (modified with 2.5 pph of MA). Tan δ

TABLE II
Tensile Properties of Various PLA/MTPS Blends, Prepared at 190°C for 12 min

PLA/MTPS blending ratio (% w/w)	Tensile strength (MPa)	Elongation at break (%)	Modulus (MPa)	Tensile toughness (J)
80/20	17.3 (0.6)	556 (12)	188 (20)	5.3 (0.5)
70/30	13.0 (0.7)	79 (20)	141 (18)	0.5 (0.1)
60/40	15.5 (0.9)	56 (4)	151 (8)	0.4 (0.1)

peak of the TPS occurred at 2°C, referring to the glass transition temperature (T_g) of the TPS whereas that of the MTPS occurred at 25°C. This indicates that T_g value of the TPS has shifted after the chemical modification. It was apparent that the presence of some MA-derived acidic groups on the starch molecules (Fig. 1) increased the chain rigidity of the starch molecules via a steric effect and a greater intermolecular interaction. For the MTPS modified by 10 pph of MA, its DMTA thermogram could not be obtained, because the material was very tacky. This implies that the above material does not have any practical usability. Therefore, only the starch modified with 2.5 pph of MA was further used for blending with PLA.

Effects of PLA/MTPS blend ratios

Table II shows averaged tensile parameters of the various PLA/MTPS blends. Tensile strength at break, percentage elongation, and tensile toughness values of the blends decreased when the starch content was increased from 20 to 30 pph. After that, the above tensile parameters rarely decreased with the starch content, taking into account the standard deviation values. Scanning electron micrographs of the various blends (Fig. 5) reveal that the polymer blends are immiscible, containing starch particles of
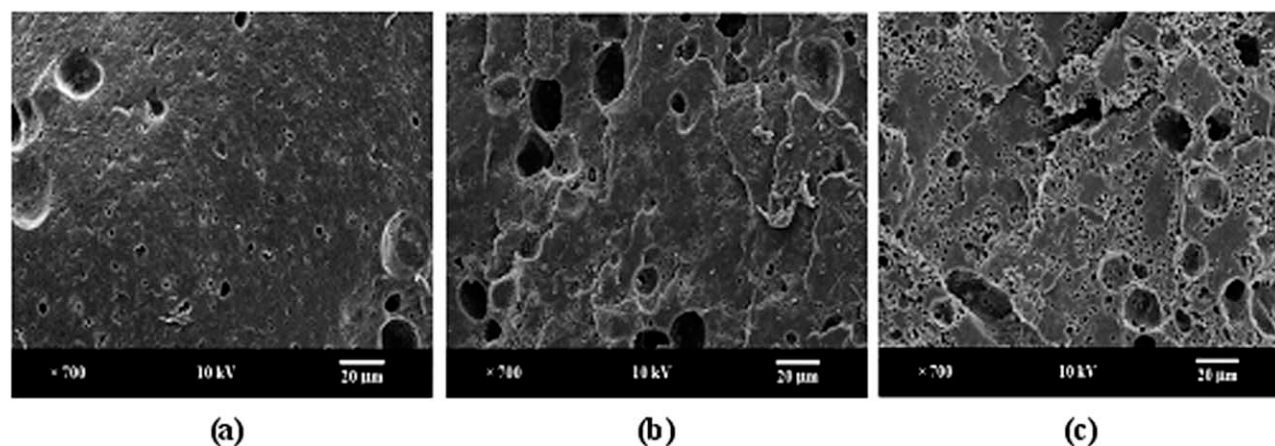
Figure 5 Scanning electron micrograph of various PLA/MTPS blends; (80/20% w/w) (a), (70/30% w/w) (b), and (60/40% w/w) (c).
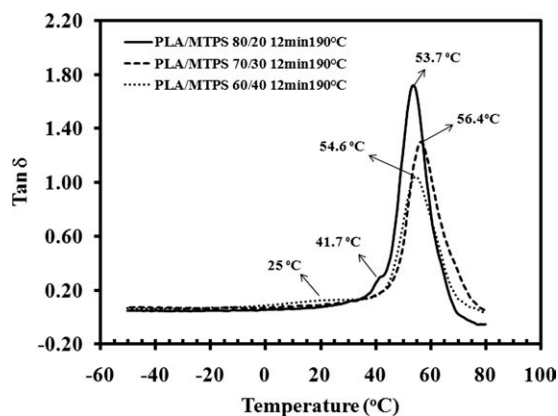
Figure 6 DMTA thermograms of various PLA/MTPS blends.

various sizes being dispersed in a continuous PLA matrix. The amount of starch particle size increased remarkably when the starch content was increased from 20 to 30 pph. This morphological change contributed to the decrease in tensile properties of the blend as was discussed earlier. Similar trends were observed by Shin et al.[16] in a study on mechanical and morphological properties of blends of PLA and chemically modified corn starch. By further increasing the starch content to 40 pph, the SEM image shows that amount of starch particles with a relatively small particles size increased.

Figure 6 shows DMTA thermogram of the various blends. For the blend containing 40 pph MTPS, a tan δ peak located at about 25°C could be ascribed to the glass transition temperature of the modified starch. This peak, however, disappeared when the starch content was decreased from 40 to 30 pph. Another tan δ peak located at 54°C represented the glass transition temperature of plasticized PLA. The value is slightly higher than that of the PLA before blending (50°C). It was believed that this discrepancy could be attributed to the presence of some bulky PLA-g-MTPS molecules produced from a trans-esterification between MTPS and PLA during blending. The formation of PLA-g-starch has been observed by Shin et al.[16] in a study on blends of chemically modified thermoplastic corn starch and PLA. In that case, results from FTIR spectra were

used to support the copolymer formation. Similarly, Raquez et al.[10] reported that PBAT-g-MTPS occurred via trans-esterification between MTPS and PBAT. Of note, DMTA thermogram of the blend-containing 20 pph MTPS also shows a small peak at 42°C. In our opinion, the above peak might be attributed to a migration of glycerol from the TPS phase into the PLA phase. This would yield the plasticized PLA with a lower T_g value. The above DMTA peak, however, was not observed when the starch blend ratio increased.

Table III shows averaged tensile properties of the PLA/MTPS blends (70/30% w/w) experienced different blending temperatures. It can be seen that by increasing the temperature, tensile strength of the material increased at the expense of percentage elongation and tensile toughness values. Similarly, Table III shows that percentage elongation and toughness of the PLA/MTPS blend (70/30% w/w), prepared at 170°C, decrease with increasing blending time. It was quite obvious that tensile properties of the blends are sensitive to blending time and temperature. This implied that the there might be some chemical reaction during blending. The above-mentioned reactions include chain scission of both PLA and MTPS molecules via a hydrolysis, which was induced by the presence of carboxylic group in the MTPS.

The above hypothesis could be supported by the results from a MFI test of the various blends. From Table IV, it can be seen that MFI value of the blend increased with blending time. Similarly, the MFI value rapidly increased with blending temperature. These results indicate that viscosities of the blend decreased with the blending temperature and time. The decreases in viscosity values were attributed to the chain scission of polymers via a hydrolysis as discussed earlier.

Scanning electron micrographs of the various blends [Fig. 7(a–d)] reveal that phase separation between the dispersed modified starch and the PLA matrix became less obvious if the blending temperature was increased. The above morphological change reflected a better homogeneity between two polymeric phases. However, change in morphology of the blends with the blending time was not obvious.

TABLE III
Tensile Properties of Various PLA/MTPS Blends (70/30% w/w), Prepared Under Various Time and Temperature

Blending conditions		Tensile properties			
Temperature (°C)	Time (min)	Tensile strength (MPa)	Elongation at break (%)	Modulus (MPa)	Tensile toughness (J)
170	7	9 (0.8)	377 (32)	135 (14)	2.3 (0.3)
170	12	8.7 (0.5)	212 (11)	92 (5)	1.2 (0.1)
180	12	13.8 (0.7)	149 (25)	113 (25)	0.6 (0.4)
190	12	13.0 (0.7)	79 (20)	141 (18)	0.5 (0.1)

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<tr><td colspan="3" align="center">TABLE IV
Melt Flow Index of Various PLA/MTPS (70/30% w/w)
Blends</td></tr>
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Time (min)	Temperature (°C)	Melt flow index (g/10 min)
7	170	23.3 ± 3.3
12	170	29.0 ± 5.1
12	180	44.7 ± 6.3
12	190	57.0 ± 6.2

TABLE V
Tensile Properties of PLA/TPS and PLA/MTPS Blends (70/30% w/w)

| Tensile properties | Type of blends | |
	PLA/TPS (70/30% w/w)	PLA/MTPS (70/30% w/w)
Tensile strength (MPa)	13.50 (± 0.80)	9.0 (± 0.78)
Elongation (%)	8.7 (± 0.34)	376.9 (± 31.86)
Modulus (MPa)	296.24 (± 20.90)	134.9 (± 13.77)
Tensile toughness (J)	0.06 (± 0.01)	2.3 (± 0.29)

This means that the above changes in tensile properties of the blend with time were predominated by the effect of chain scission.

Last but not least, it is worth comparing tensile properties of the above PLA/MTPS blends (70/30% w/w) to those of normal TPS/plasticized PLA blend. From Table V, it can be seen that, by changing from TPS to MTPS, percentage elongation and toughness of the blend increased at the expense of its tensile strength and modulus. This could be attributed to side chemical reactions that occurred during the blending, including the chain scission and the trans-esterification. The greater tensile elongation and toughness of the MTPS/PLA blend system indicated benefit effects obtained from the use of the modified starch reported in this work.

CONCLUSIONS

This work has shown that, besides the blending ratio, time and temperature affect mechanical, rheological, and morphological properties of the MTPS/plasticized PLA blends. Tensile strength and modulus of the blends increased with blending temperature and time at the expense of their percentage elongation and tensile toughness values. The above effects were discussed in the light of hydrolysis and
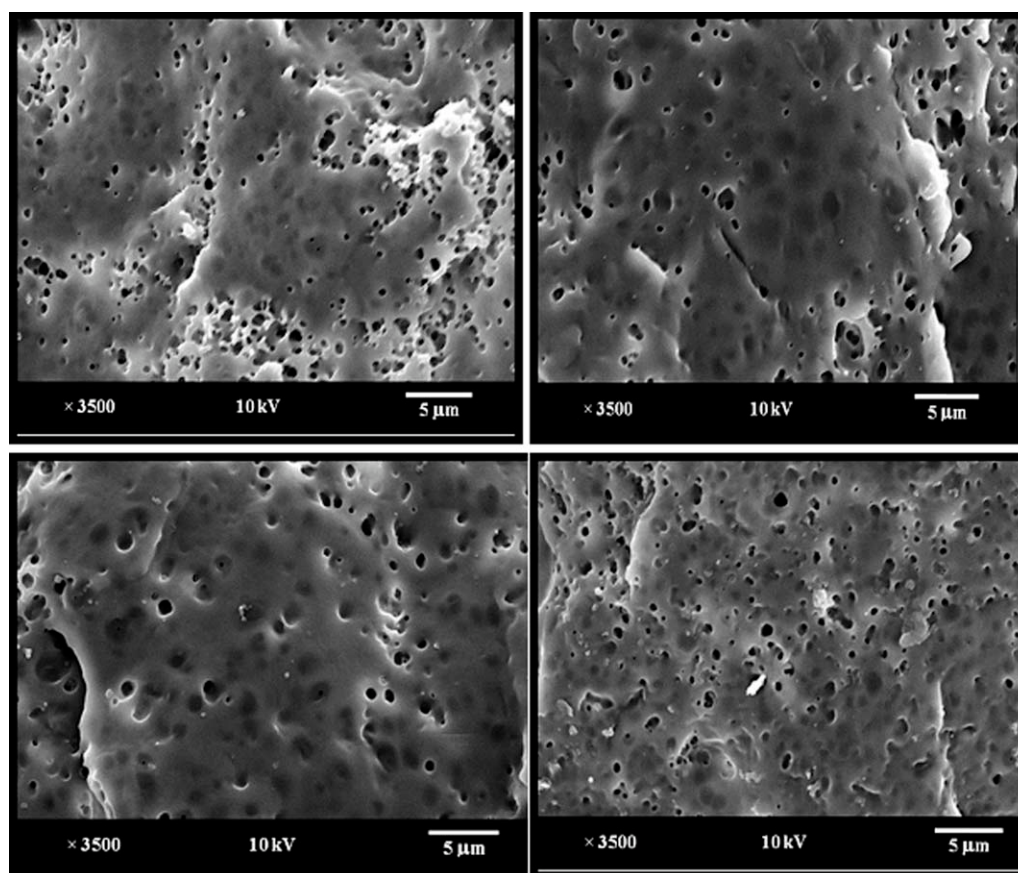
Figure 7 Scanning electron micrographs of various PLA/MTPS blends (70/30% w/w) prepared at different conditions; 170°C, 12 min (top left), 180°C, 12 min (top right), 190°C, 12 min (bottom left), and 170°C, 7 min (bottom right).

a trans-esterification occurred during the blending process. This was supported by the results from MFI test and SEM images of the various blends. It was also found that the mechanical properties of the PLA/MTPS (70/30% w/w) blends were greater than those of the PLA/TPS (70/30% w/w) blends under the same blending conditions.

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