Preparation of Modified Starch-Grafted Poly(lactic acid) and a Study on Compatibilizing Efficacy of the Copolymers in Poly(lactic acid)/Thermoplastic Starch Blends

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ABSTRACT: This study has concerned preparation of polylactic acid grafted with maleated thermoplastic starch (PLA-*g*-MTPS) and a study on compatibilizing efficacy of the above copolymers in PLA/thermoplastic starch (TPS) blends. The PLA-*g*-MTPS copolymers were prepared by two-step reaction. First, maleated thermoplastic starch (MTPS) was prepared by reacting cassava starch with glycerol and maleic anhydride (MA). Second, the MTPS was grafted onto PLA molecules using peroxide as an initiator. Chemical structures of the products were characterized by using Fourier transform infrared spectroscopy and ^{1}H-NMR techniques, whereas the acid numbers of the copolymers were determined by titration. Thermal characteristic of the copolymer was also characterized by using dynamic mechanical thermal analysis. In total, 5 wt % of the graft copolymer was blended with PLA and TPS in a twin screw extruder. Mechanical, rheological, and morphological properties of the blends were evaluated via tensile test, melt flow index test, and scanning electron microscopy, respectively. It was found that mechanical properties of the blends depended on starch content and type of the PLA-*g*-MTPS. When the PLA-*g*-MTPS was prepared at low amount (0.25 pph) of peroxide, the mechanical properties of the blend was improved remarkably as compared to those of the normal blend and/or the blend containing different compatibilizers. Compatibilizing efficacy of the above copolymers became more obvious when the thermoplastic starch (TPS) blending ratio was increased. The above results were ascribed in the light of change in the viscosity and morphology of the blends. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: biopolymers; compatibilization; copolymers; initiators; polymer blends

INTRODUCTION

With the up-raising trend of oil and petrochemicals prices, as well as more public awareness and concerns about the environmental impacts of producing and dumping of plastic products, the developments and commercial uses of bioplastics have gained more and more interest worldwide. The above statement is supported by a recent forecast from European bioplastic association,[1] suggesting that global bioplastics production capacity will be increased from 724,000 ton/year, in 2010 to 1,710,000 ton/year within the year 2015. The abovementioned bioplastics include starch blends, poly(lactic acid) (PLA), poly (hydroxyl alkanoate) (PHA), other aliphatic polyesters, cellulose, and cellulose derivatives. In addition, the developments of composites and blends from the above bioplastics are also widely carried out to fulfill some demanding requirements for commercial uses of the products. For example, many research studies[2–10] have attempted to blend PLA with some bio-based, biodegradable polymers such as starches and its derivatives to reduce the material cost.

In this regard, incompatibility between PLA and starch is one of the most important factors controlling mechanical properties of the blends. To enhance the compatibility between PLA and starch, many strategies have been used. These include chemical modifications of the starch molecules before blending[2,9–12] and the use of compatibilizers. Examples of the compatibilizers include PLA-*g*-starch[6,13]

PLA-g-MA,[5,8,14] and isocyanate compounds.[4,7,15] Wang et al.[7] studied mechanical and morphological properties of PLA/wheat starch blends and found that by adding 0.5 wt % of methylenediphenyl diisocyanate (MDI), an interfacial tension between phases decreased and tensile properties of the blend (50/50% w/w) increased. Jun[15] investigated the effects of different types of isocyanates namely, toluene diisocyanate, diethylene triamine, 1,6-diisocyanatohexane (DHI), and MDI, and found that compatibilizing efficacy of DHI was the best, taking into account an increase in tensile strength of the blends. However, Schwach and Six[4] compared compatibilizing efficacy of MDI with benzoyl peroxide and PLA-g-amylose, and found that the use of peroxide and/or PLA-g-amylose was superior to the use of MDI.

Furthermore, the use of peroxide compound as a compatibilizer in PLA/starch blend systems could be even more effective if the peroxide was mixed well with maleic anhydride to form PLA-g-MA. The above-grafted polymer might be formed *in situ* and/or separately prepared before blending. Interestingly, Huneault and Li[8] studied the mechanical and morphological properties of PLA/TPS blends and found that by adding PLA-g-MA percentage elongation of the blends increased remarkably. It was also found that the use of PLA-g-MA which was separately prepared before blending (the so-called two-step modification) was more superior to the use of PLA-g-MA prepared *in situ* (one-step modification). However, the use of polymers bearing MA groups can be brought about some side reactions and side effects. This was owing to the fact that the anhydride group was very reactive, capable of inducing chain scissions of polymer which contain ester bonds via a hydrolysis.[11,16] It might also be possible that the above side reaction competes with the condensation between anhydride groups of PLA-g-MA and hydroxyl groups of the starch, lowering the efficacy of the compatibilizer.

In this study, a new compatibilizer that was poly(lactic acid)-grafted maleated thermoplastic starch (PLA-g-MTPS) (Fig. 1) was designed and prepared. In our case, it was hypothesized that a condensation between MA and hydroxyl groups of the starch would be more effective than that between PLA-g-MA and the starch. Consequently, a better compatibility and mechanical properties of the blend could be expected. Besides, the lack of unreacted MA in the purified PLA-g-MTPS product implied that some side reaction between MA and polyester during blending could be avoided and/or suppressed.

The main aim of this study was to prepare PLA-g-MTPS and investigate the effect of the copolymers on mechanical, rheological, and morphological of various PLA/TPS blends. Finally, a comparative
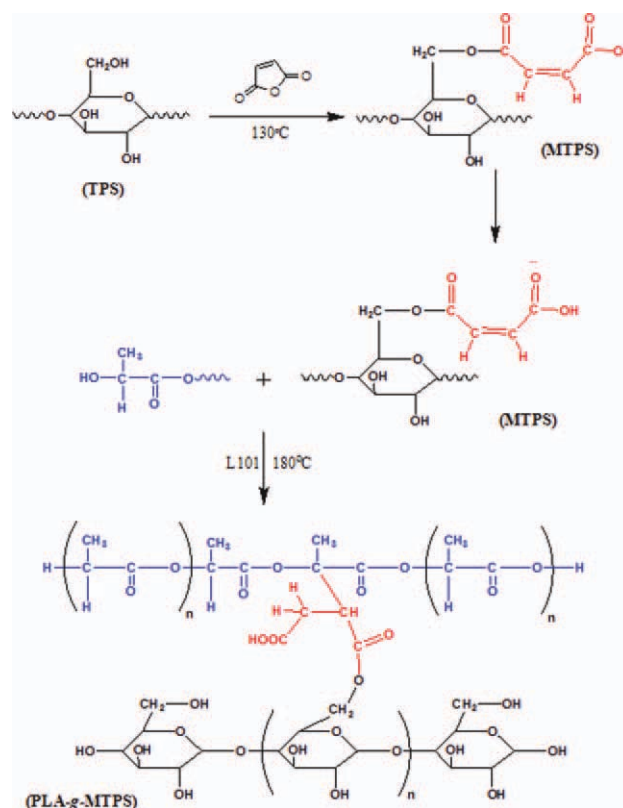

Figure 1 Condensation between maleic anhydride and starch (maleation) and grafting of maleated starch with PLA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

study between the conventional copolymer and the new one was carried out.

EXPERIMENTAL

Chemicals

PLA (2002D from NatureWork) was supplied from the Fresh Bag Co. Ltd. (Bangkok, Thailand). Cassava starch was supplied by E.C.T. International Co. Ltd. (Bangkok, Thailand). Glycerol (commercial grade) and glycerol triacetate used as plasticizers for starch and PLA were purchased from Bank Trading Co. Ltd. (Bangkok, Thailand) and Eastman (Tennessee, USA), respectively. Maleic anhydride (MA) (Laboratory grade, 98% from Fluka Co. Ltd., Missouri, USA) was supplied from ACS Xenon Co. Ltd. (Bangkok, Thailand). Peroxide compounds: namely; 1,1-di-(*tert*-butylperoxy)3,5,5-trimethyl cyclohexane (Luperox231) used for inducing PLA branching chains, and 2,5-*bis* (*tert*-butylperoxy)-2,5-dimethylhexane (Luperox 101) used to initiate grafting between PLA and maleated thermoplastic starch (MTPS) were supplied from Arkema (Colombes, France). MTPS was prepared by mixing the cassava starch with glycerol and MA in an internal mixer. More detail concerning the preparation of MTPS can be found elsewhere.[17]
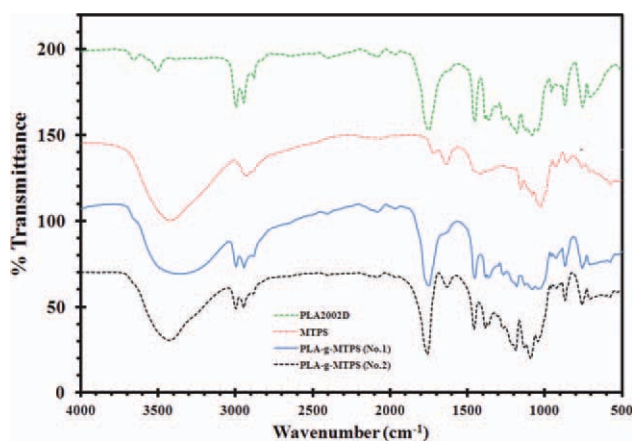
Figure 2 FTIR spectra of PLA, MTPS and PLA-g-MTPS copolymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Preparation of PLA-g-MTPS

The PLA-g-MTPS was prepared by mixing PLA resins with the prepared MTPS with the presence of Luperox101 (0.25–1.0 pph). The mixing and an *in situ* grafting reaction was carried out in an internal mixer (Brabender 350/350E, roller blade rotor type, mixing chamber, 370 cm^3), at 180°C, 40 rpm, using a fill factor of 0.86 for 5 min. After that, the product was pelletized and then purified by washing with deionized water and finally dried in an oven at 50°C until the weight was constant.

Preparation of plasticized PLA compound

PLA compound was prepared via a masterbatching technique. First, PLA resin was dried in an oven at 80°C for 12 h. After that, the dried polymer pellets were compounded with 50 pph of glycerol triacetate (triacetin) and 0.75 pph of Luperox231 in the internal mixer (Brabender 350/350E, roller blade rotor type, mixing chamber, 370 cm^3) at 170°C, 40 rpm, using a fill factor of 0.86. The mixing time was 10 min and the PLA masterbatch was then diluted with PLA in a twin screw extruder (Brabender, DSE20) using a screw rotating speed of 100 rpm. Temperature profiles used from the extruder feed to die zones were 80, 160, 165, 165, 145, and 145°C. Noteworthy, the aim of using Luperox231 peroxide for compounding with PLA herein was to induce branching structure of the PLA molecules, and to improve melt strength of the molten PLA. This would allow fabrication of PLA blends via an extrusion blown film processing, which will be another aspect of our future study.

Blending

The plasticized PLA compound, TPS, was premixed in a high speed mixer (Labtech Engineering), using different weight ratios ranging from 80/20, 70/30, to 60/40. In addition, 5 wt % of the prepared PLA-g-MTPS was also added to serve as a compatibilizer for this blend system. After that, the mixture was fed through a hopper of a twin screw extruder (Brabender DSE20), at a screw rotating speed of 100 rpm. Temperature profiles used from the extruder feed to die zones were 80, 160, 165, 165, 145, and 135°C. The extrudate was then cooled in a water bath before undergoing pelletization process to obtain blend granules.
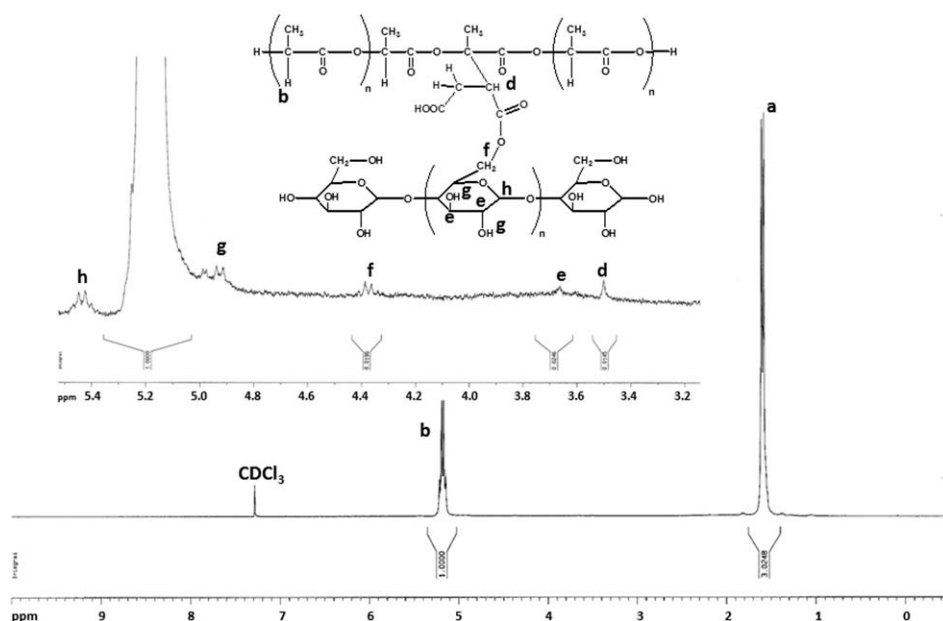

Figure 3 ^{1}H-NMR spectra of PLA-g-MTPS copolymer No.1, prepared by using 1.0 pph peroxide.

TABLE I
Acid Numbers of PLA and PLA-*g*-MTPS Copolymers

Samples	HCl (mL)	Acid No. (mg NaOH/g)
PLA	8.4	332
PLA-*g*-MTPS (No. 1)	5.1	359
PLA-*g*-MTPS (No. 2)	3.1	364

Fabrication

The blend extrudate was fabricated into 185×185 mm^2 rectangular test pieces by using a 0.5-mm thick mold in a hydraulic compression molding machine (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 kg/cm^3 for 3 min. After that, the fabricated sample was allowed to cool in the mold for 5 min before demolding.

Characterizations

Chemical structures of MTPS and PLA-*g*-MTPS were examined by using a Fourier Transform Infrared Spectroscopy (FTIR) (PerkinElmer, Spectrum One) over the wavenumbers ranging from 450 to 4000 cm^{-1}. The sample for the FTIR experiment was prepared by a KBr disk method.

^{1}H-NMR technique was used to characterize the chemical structure of PLA-*g*-MTPS. Sample for the NMR analysis was prepared by dissolving about 5 g of the PLA-*g*-MTPS in 15 mL of CDCl$_3$. The spectrum was recorded using a Bruker instrument (DPX300 Ultrashield), with TMS as a reference at 20°C.

In addition, the amount of MTPS grafting chains in the PLA-*g*-MTPS copolymer was evaluated from acid number, determined by using a back titration technique. First, 0.5 g of the PLA-*g*-MTPS was
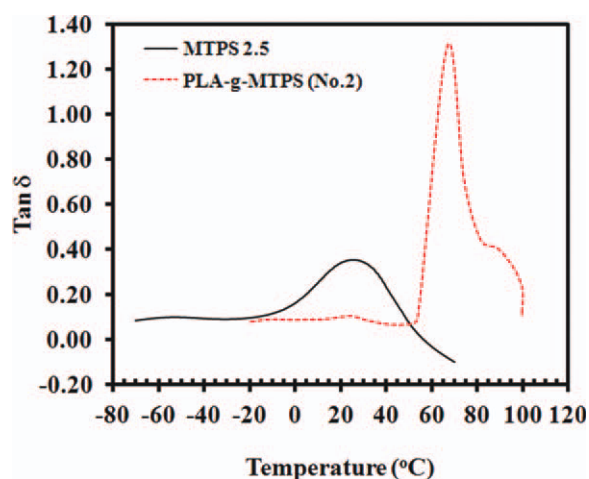

Figure 4 DMTA thermograms of MTPS before and after grafting with PLA using 1.0 pph of peroxide. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
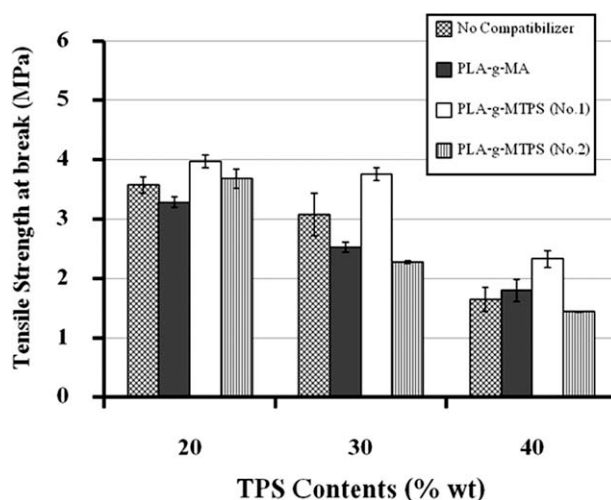

Figure 5 Tensile strength of various PLA/TPS blends containing different compatibilizers.

dissolving in 50 mL of THF and then mixed with 50 mL of an aqueous NaOH solution (0.1 mol/L). The solution was stirred at 70°C until the solution was homogeneous. Then, 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 turning from pink to colorless). Finally, acid number of the polymer sample was calculated by using eq. (1):

Acid number(mg NaOH/g)

$$= \frac{V_{\text{NaOH}}(\text{mL}) \times C_{\text{NaOH}} \times 40}{\text{Polymer blend}(\text{g})} \quad (1)$$

where $V_{\text{NaOH}} =$ volume of sodium hydroxide solution (mL)

$C_{\text{NaOH}} =$ concentration of sodium hydroxide solution (mol/L)

Thermal analysis

Glass transition temperatures of various materials (MTPS and PLA-*g*-MTPS) were examined using dynamic mechanical thermal analysis (DMTA) technique. The experiment was conducted using GABO (EPLEXOR QC 25) and the sample was prepared in a form of 5×50 mm^2 in rectangular with a thickness of 0.5 mm. The DMTA experiment was operated under a tension mode, at 2N force, 1 Hz oscillating frequency, 1.0% static strain, 0.05% dynamic strain, and 10 μm amplitude. The heating rate used was 3°C/min and the sample was scanned over temperatures ranging between (-70) and $(+70)$°C.

Mechanical properties test

Mechanical properties of the various blends were evaluated by tensile test. Samples of various blends
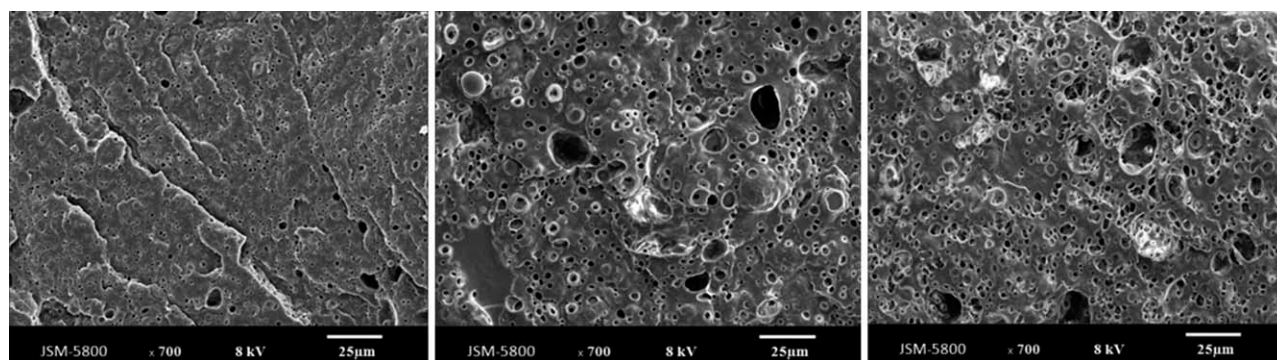
Figure 6 SEM micrographs of various PLA/TPS blends; 80/20% w/w (left), 70/30% w/w (center), 60/40% w/w (right).

were fabricated into 3-mm thick sheets by using a compression molding at 160°C. After that, dumbbell shape specimens were prepared by cutting the sheet to comply with an ASTM D638 standard test method. The tensile test was carried out using a LLOYD instrument (LR 50K model) at the crosshead speed of 100 mm/min at room temperature. At least five specimens were tested for each run. 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 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 room temperature for 24 h. This was to extract the thermoplastic starch (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^{TM} coater, S/N 10081 MODEL) prior to SEM experiment. This was to avoid a charging effect during the electron beam scanning. The SEM experiment was operated using a JEOL (JSM5800) machine, equipped with a secondary electron detector under an accelerating voltage of 8 kV.

Melt flow index test

Melt flow rate of polymer blend was determined using a melt flow index tester, in accordance with an ASTM D1238-10.

RESULTS AND DISCUSSION

Characterizations of MTPS and PLA-g-MTPS

Figure 2 shows overlaid FTIR spectra of PLA and MTPS (both before and after grafting with PLA). A broad peak at 3400 cm^{-1} corresponding to O—H stretching of starch amylose and amylopectin could be observed in the spectrum of MTPS. Peak at 1718 cm^{-1} represents C═O stretching vibration of the
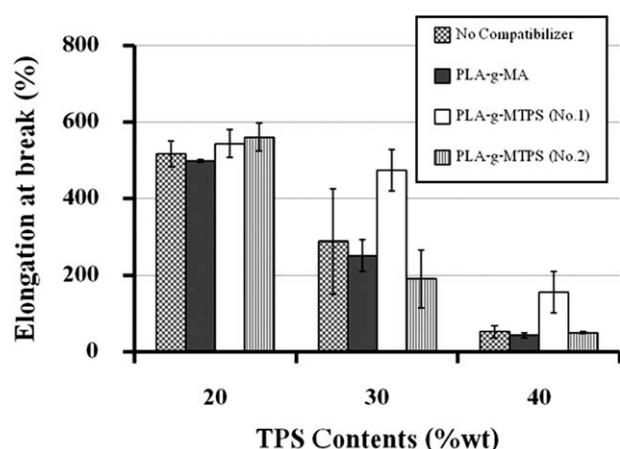

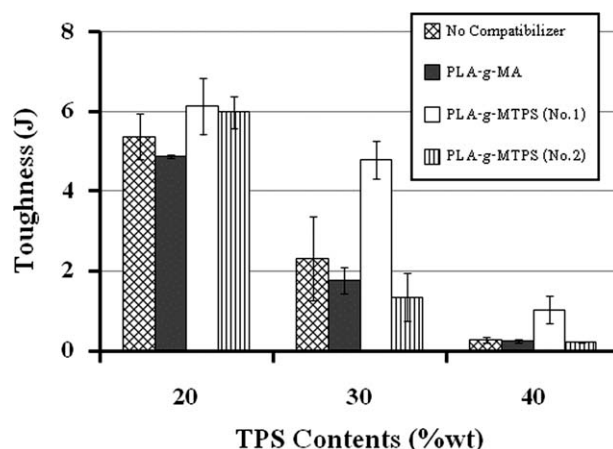**Figure 7** Tensile elongation of various PLA/TPS blends containing different compatibilizers.

Figure 8 Tensile toughness of various PLA/TPS blends containing different compatibilizers.

TABLE II
Melt Flow Index Values of Various PLA/TPS (80/20% w/w) Blends Containing Different Compatibilizers

Compatibilizers	MFI (g/10 min)
No compatibilizer	19.3 ($\pm$1.5)
PLA-g-MA	27.1 ($\pm$3.1)
PLA-g-MTPS No. 1	22.3 ($\pm$1.7)
PLA-g-MTPS No. 2	18.7 ($\pm$2.7)

MA moiety in the maleated starch was also noted. After grafting the PLA with MTPS, the FTIR peak at 1759 cm^{-1}, corresponding to C=O stretching vibration of PLA backbone emerged. In addition, the absorption peak at 1630 cm^{-1} representing C=C bond in the nongrafted maleic acid moiety can also be noted. Noteworthy, it was found that the relative height of this peak (1630/1759 cm^{-1}) increased with the amount of peroxide used for inducing the formation of PLA radical during grafting. This implies that the greater the amount of peroxide used, the higher the extent of grafting between PLA and MTPS.

^{1}H-NMR spectrum of a product (Fig. 3) also reveals the presence of characteristic peaks representing methyl protons (1.57, 1.61 ppm, doublet) and methane protons (5.14, 5.16, 5.19, 5.21, quartet) of the PLA backbone. Furthermore, by enlarging the spectrum, additional peaks representing the MTPS grafting chains can be seen. These include methine protons (3.5 ppm) of the ring opening MA moiety in the maleated starch molecules and amylose/amylopectin ring protons at 3.66, 4.36, 4.93, and 5.44 ppm.

In addition, by carrying out a back titration for various graft copolymers, it was found that the acid number values of PLA-g-MTPS copolymers increased with the peroxide content (Table I). Noteworthy, titration of a control PLA sample (without grafting) was also carried out and the results revealed that acid number of the PLA is much lower than that of the graft copolymers. The latter was owing to the presence of some carboxylic acid groups at the chain ends of PLA homopolymer. The acid number was mainly attributed to the presence of carboxylic acid in the MA moiety of the PLA-g-MTPS. The above results imply that the amount of grafting chains increased with the peroxide content.

Figure 4 shows DMTA thermograms MTPS before and after grafting with PLA by 1.0 pph of peroxide. From the thermogram of the grafted copolymer
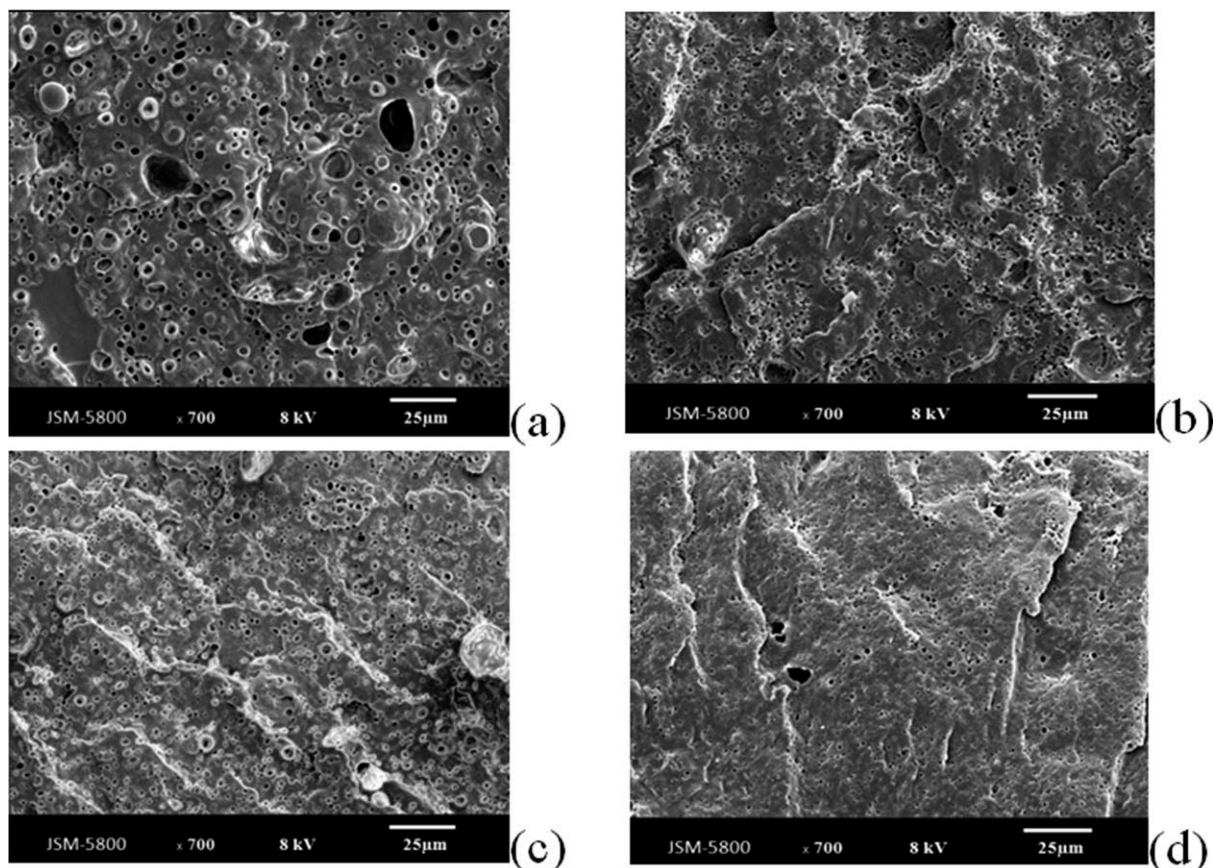

Figure 9 SEM micrographs of various PLA/TPS blends (70/30% w/w); the blend without a compatibilizer (a), the blend with PLA-g-MA(b), the blend with PLA-g-MTPS No.1 (c), the blend with PLA-g-MTPS No.2 (d).
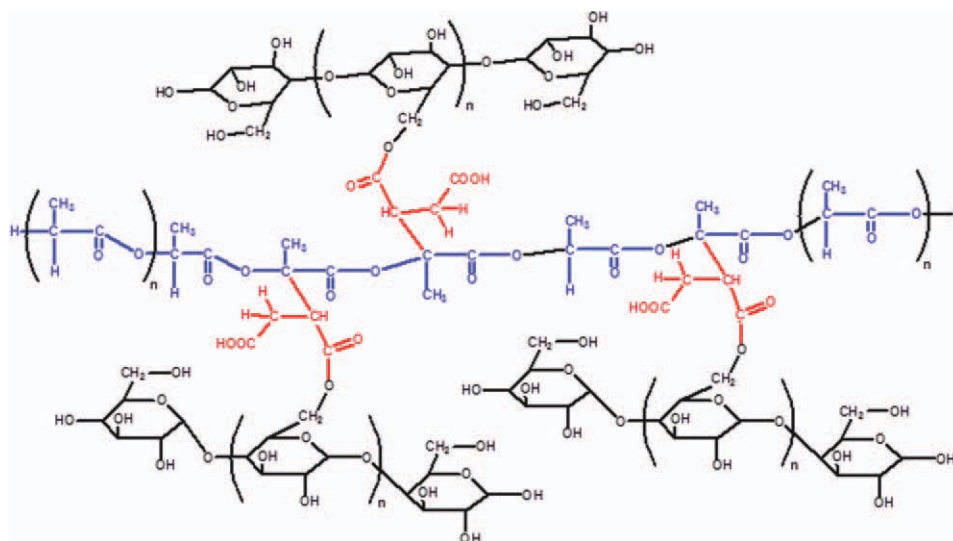
Figure 10 Possible structure of the PLA-*g*-MTPS copolymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

product, two tan δ peaks can be observed. The higher temperature peak at about 67°C represents a glass transition temperature (T_g) of the PLA backbone, whereas a broad peak at 25°C corresponds to T_g of the MTPS grafting chains. Similar characteristics were observed from the DMTA thermograms of copolymers prepared by using lower amount of the peroxide. Based on the above results from FTIR, titration, ^{1}H-NMR, and DMTA, it might be concluded that the PLA-*g*-MTPS copolymers with different levels of grafting were successfully prepared.

Figure 5 shows the changes in tensile strength of the PLA/TPS blends as a function of TPS content and types of compatibilizers. In overall, tensile strength, elongation, and toughness of the normal blends seemed to decrease with increasing TPS content. The effects can be ascribed to the changes in morphological properties of the blend which are shown in Figure 6. It was found that phase separation between the PLA matrix and the dispersed TPS become more obvious when the starch content was >20 wt %. It can also be noted that the higher the starch content, the greater number of the starch particles. This is owing to the fact that PLA is incompatible with the more hydrophilic TPS.

Similarly, Figure 5 also shows that tensile strength of the blend, containing copolymers as a compatibilizer decreased with the starch content. It is interesting that the tensile properties of the blends also depended on the types of the copolymers used. When PLA-*g*-MA was added, the tensile strength of the PLA/TPS blend (80/20% w/w) slightly decreased as compared to that of the normal blend (without any compatibilizer). This was not the case when the PLA-*g*-MTPS was used. In this case, the

tensile strength of the blend did not decrease, but tended to increase if the PLA-*g*-MTPS copolymer No. 1 was used. The compatibilizing efficacy of the above copolymer became more pronounced when the starch content was further increased to 30 and 40 wt %. In this case, only the PLA-*g*-MTPS copolymer No. 1 led to a remarkable improvement in tensile strength of the blend.

Similar effects were observed for tensile elongation values (Fig. 7) and tensile toughness values (Fig. 8) of the various blends. Noteworthy, the tensile toughness of the PLA/TPS (70/30% w/w) blend containing PLA-*g*-MTPS copolymer No. 1 was comparable to that of the PLA/TPS (80/20% w/w) blend without any compatibilizer. This means that one can increase the starch content in the blend product, for the purpose of cost reductions, without scarifying tensile properties of the material.

The differences in compatibilizing efficacies of the various graft copolymers can be related to changes in melt flow index (MFI) of the blends. Table II lists the MFI values of the PLA/TPS blends (80/20% w/w) containing different types of compatibilizers. It can be seen that MFI value of the normal blend (without any compatibilizer) increased from 19.3 to 27.1 g/10 min when the PLA-*g*-MA was added. On the other hand, MFI values of the blends containing PLA-*g*-MTPS copolymers did not change significantly, taking into account the standard deviation values.

In this regard, the above effects could be explained in the light of chemical structure of the copolymers. In the case of PLA-*g*-MA, its molecules contain some anhydride moieties, capable of activating chain scissions of the PLA molecules, during melt blending, via a hydrolysis mechanism.[18] This means that molecular

weight of the PLA will be decreased and hence MFI of the blend increased. The reduction in chain length of the PLA phase in the blend was then contributed to a decrease in tensile properties of the blends. On the other hand, the PLA-*g*-MTPS molecules contain some carboxylic acid groups, generated from a ring opening of the MA when reacting with starch during the maleation and lack of anhydride moieties (Fig. 1). In this regard, it is known[19] that catalytic reactivity of the carboxylic acid group is inferior to that of the anhydride group. Therefore, it is possible that amount and reactivity of acid groups in the PLA-*g*-MTPS copolymer molecules are not sufficiently strong to induce the above side reaction.

In addition, some changes in morphology of the PLA/TPS blends upon an addition of copolymers were worth considering. Figure 9 shows scanning electron micrographs of the various PLA/TPS blends (70/30% w/w). SEM image of the normal blend (without any compatibilizer) reveals that the two phases were poorly miscible. Similar results were observed by Huneault and Li[8] and Jang et al.[20] By adding the copolymers, the particle size of the starch minor phase significantly decreased. This indicates that the copolymers are capable of acting as a compatibilizer by reducing coalescence and surface tension of the minor phase during blending. Similar morphological change was noted for the blends containing different amounts of starch.

Last but not least, differences in compatibilizing efficacy between the PLA-*g*-MTPS copolymer No. 1 and the copolymer No. 2 deserve examination. This can be explained in the light of differences in molecular architectures between these two copolymers. Figure 1 shows that the MTPS prepared first is a kind of modified starch having multifunctional groups, that is ring opened maleic anhydride moieties. After grafting it onto PLA molecules, the obtained PLA-*g*-MTPS is actually a kind of network molecules (Fig. 10). The higher of the peroxide content (used for grafting), the more complex of the copolymer structure. In this regard, molecular weight and bulkiness of the PLA-*g*-MTPS copolymer No. 2 became higher, owing to the fact that the copolymer was prepared by using a larger amount (1.0 pph) of peroxide. Consequently, the chain mobility and diffusion rate of the copolymer molecules toward the interface between PLA and TPS can be retarded and/or restricted as was suggested by the reputation model.[21,22] This means that the actual amount of the copolymer oriented at the interface could be lower. The above factor contributes to the lower compatibilizing efficacy of the copolymer.

CONCLUSIONS

PLA-*g*-MTPS copolymers were successfully prepared by reacting maleic anhydride with TPS, followed by grafting the maleated TPS with PLA, using a peroxide compound as an initiator. Compatibilizing efficacy of the above copolymers for PLA/TPS blends depend on the blending ratio and type of the copolymers used. By adding 5 wt % of the copolymer, prepared by using low peroxide content (0.25 pph), tensile strength, elongation, and toughness of PLA/TPS blends increased. Efficacy of the above copolymer is also superior to that of the PLA-*g*-MA compatibilizer provided the same blending conditions. The above effects became more obvious when the starch content in the blends was increased from 30 to 40 wt %. These results are related to a decrease in MFI values of PLA/TPS blends which was suppressed when PLA-*g*-MTPS was used as a replacement of PLA-*g*-MA.

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