Characteristics of Biodegradable Polylactide/Gelatinized Starch Films: Effects of Starch, Plasticizer, and Compatibilizer

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ABSTRACT: Polylactide (PLA) blends with 0–40 wt % gelatinized starches (GSs) in the presence of plasticizers and compatibilizer for improving interfacial bonding between two phases were prepared. The effects of compatibilizer, type and amount of starch, including type and concentration of plasticizer on the physical, morphological, thermal, and mechanical properties of these films were investigated. Two types of starch (corn and tapioca) were added as fillers, whereas the glycerol amount was varied from 0 to 35 wt % based on starch content. Polyethylene glycol (PEG400) and propylene glycol (PG) were added as plasticizers at four different amounts (5–20 wt %) based on PLA content, while methylenediphenyl diisocyanate was used as a compatibilizer at 1.25 wt % of GS. The results indicated that the presence of glycerol had no effect on the thermal degradation of GS. For PLA plasticization, the plasticized PLA with PEG400 had better properties than that with PG. Water absorption isotherm of the blend films increased as the amount of starches increased; in contrast, the tensile properties decreased progressively with the addition of the GS content. The blend films with gelatinized corn starch had higher tensile properties than those with gelatinized tapioca starch. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: polylactide; biodegradable; films; compatibility; starch

INTRODUCTION

Polylactide (PLA), a linear aliphatic polyester, is one of the most potential materials from renewable resources, because PLA has very low toxicity and high-mechanical performance, comparable to other commercial polymers, for example, poly(ethylene terephthalate) and polystyrene (PS).[1–3] It is highly transparent and has good barrier properties to aromas. In addition, PLA is also biodegradable and composable.[3,4] However, its major drawbacks as high cost and intrinsic characteristics (i.e. hard and brittle materials) have hindered its wide spread usages, especially in the area of packaging applications.[5–9] PLA likes most synthetic polymers from petroleum resources, which are rarely used alone by themselves, and needs to improve some properties by an inclusion of additives. Plasticizers are widely used additives for polymeric materials to enhance their flexibility, processability, and ductility. Generally, an efficient plasticizer has to reduce the glass transition temperature (T_g) and melting point of the plasticized materials.[10] Different types of plasticizers have been carried out to improve the flexible properties of PLA such as poly(ethylene glycol) (PEG),[8–12] citrate,[13–16] oligomeric lactic acid,[12] and triacetine.[14]

Starch, a hydrophilic renewable filler, is one of the well-known biopolymers and often used in order to lower the cost of the finished product and enhance the biodegradable characteristics of polymer composites.[17,18] Hence, blending starch with PLA is one of the most promising efforts to solve the limitations of PLA. Nevertheless, the immiscibility of hydrophobic PLA and hydrophilic starch renders in poor and irreproducible performances, resulting from inadequate interfacial interaction between two phases. This is a reason why a compatibilizer is becoming an important component for the PLA/starch blends. Various compatibilizers have been investigated to improve the adhesion of PLA and starch such as dioctyl maleate,[19] maleic anhydride (MA),[6] poly (vinyl alcohol),[20] especially methylenediphenyl

diisocyanate (MDI).[21] MDI is a small molecule, composed of isocyanate groups, which are highly reactive with both hydroxyl and carboxyl groups to form urethane linkages. It is more reactive than MA[22]; thus, it is expected that MDI could be a good compatibilizer between starch and PLA.

The objectives of this research were focused on the preparation of PLA/GS films compatibilized by MDI in the presence of plasticizer. Tapioca and corn starches were added as fillers, whereas glycerol, propylene glycol (PG) and PEG400 were used as plasticizers. The physical, morphological, thermal, and tensile properties of these films were evaluated through three steps comprising starch gelatinization, PLA plasticization, and blend preparation, respectively. In particular, the effects of type and content of starch and plasticizer were also emphasized.

EXPERIMENTAL

Materials

PLA resin (PLA 4042D, M_w = 130,000 Da, M_w/M_n = 1.46, T_g = 58°C, T_m = 152°C, T_d = 350°C, and density = 1.24 g/cm^3) was purchased from NatureWork LLC (Cargill-Dow, Minneapolis, MN). Glycerol with 99.5% purity, PG, PEG400, and MDI were obtained from Siam Chemical Industry Co., Bangkok, Thailand. Tapioca and corn starches containing amylose of ~ 30 and 32% by weight, respectively, were used as biodegradable additives. Percentages of amylose were determined by rapid method for estimation of amylose in maize starches.[23]

Starch gelatinization

Gelatinized starch (GS) can be obtained by gelatinization process with various content of glycerol using a high-speed mixer and a two-roll mill (Scientific, Labtech Engineering, Samutprakarn, Thailand), respectively. The mixing time and temperature in the two-roll mill were kept at 10 min and 130°C until GS was formed homogenously. Then, it was pulverized by means of a crusher and dried in an air oven at 60°C for 24 h. The GS compositions are shown in Table I.

PLA plasticization

Polylactide (PLA) pellets were dried in a vented oven at 60°C overnight before processing. Varying amounts of PG and PEG400 (5–20 wt %) were then mixed together with the PLA pellets using an internal batch mixer (Lab station Model PL2000, Brabender Plasticorder, South Hackensack, NJ) at 180°C and 60 rpm for 20 min. Neat PLA was also taken in the same way in order to use as a reference material. After that, each plasticized PLA was pulverized by means of a

TABLE I
GS Formulations Used in the Study and Glycerol Contents Obtained by TGA

Sample no.	Starch content	Water content	Glycerol content	Glycerol/ starch ratio
TG0	65	35 (6.3)	0 (0)	–
TG1	65	20 (4.0)	15 (15.5)	0.23 (0.24)
TG2	65	10 (3.4)	25 (24.0)	0.38 (0.37)
TG3	65	0 (4.4)	35 (31.0)	0.54 (0.48)
CG0	65	35 (5.9)	0 (0)	–
CG1	65	20 (4.5)	15 (14.9)	0.23 (0.23)
CG2	65	10 (2.9)	25 (24.6)	0.38 (0.38)
CG3	65	0 (4.1)	35 (34.2)	0.54 (0.53)

TG and CG refer to gelatinized tapioca starch and gelatinized corn starch, respectively. The values given in brackets are the glycerol and water contents or glycerol/starch ratio determined after processing.

crusher. Finally, plasticized PLA powder was dried in the vented oven at 60°C and stored in a desiccator.

Film preparation

GS/plasticized PLA blends and 1.25 wt % MDI (based on GS content) were hot-blended at 180°C for 4 min by the internal batch mixer. The operating screw speed of the internal batch mixer was 90 rpm. The GS level in each blend was 0, 10, 20, 30, and 40 wt %, based on the total weight of PLA and GS. Uncompatibilized blend (without MDI) was also taken in the same way in order to use as a reference material. After that, each blend specimen was pulverized by means of a crusher and was then compression-molded. Optimum holding pressure, temperature, and time of compression molding were 1500 psi, 170°C, and 15 min, respectively.

Morphological studies

Optical microscope (OM; BH2-UMA, Olympus, Tokyo, Japan) was used to observe the physical appearance of GS. Scanning electron microscope (SEM; JSM 6480, JEOL, Tokyo, Japan) was used to characterize the fractured surface of blend films. The fractured surface of the blend films was coated with a thin layer of gold (54 nm) before being scanned. The SEM was operated at 15 kV to image the films.

Crystallinity

X-ray diffractometer (D8-Advance, Bruker, Frankfurt, Germany) with Ni-filtered Cu Kα radiation operating at 40 kV and 40 mA was used to characterize starch crystallinity and confirm the changing from starch to thermoplastic at a scan speed of 5°/min with a 2θ range of 5°–40°.

Thermal properties

The thermal properties of all films were determined via a thermogravimatric analyzer (TGA/SDTA851^e, Mettler-Toledo, Greifensee, Switzerland) and a differential scanning calorimeter (DSC7, PerkinElmer, Waltham, MA). Thermogravimetric analyzer was used to evaluate glycerol quantities of GS and determine the degradation temperature (T_d) of both GS and plasticized PLA. Approximately 4 mg of sample was used for each experiment. The TGA was operated under nitrogen atmosphere using a heating rate of 20°C/min from 50 to 500°C. Before the test, the GS and plasticized PLA were dried in a vented oven at 60°C overnight. For DSC analysis, sample size with an average weight of 12 mg encapsulated in a hermetically sealed aluminum pan was prepared for each test. Thermal history of all samples was removed by first heat scanning from 25 to 200°C, followed by quenching the sample to −30°C, and finally heating again to 200°C at a heating and cooling rates of 10 and 20°C/min, respectively. The heat of fusion for 100% crystalline PLA (ΔH_f^0) is equal to 93.6 J/g.[24]

Tensile Testing

Tensile test of rectangular film specimens with the size of 15 mm wide, 150 mm long, and about 250 µm thickness was conducted with a universal testing machine (LR100K, Lloyd, Fareham, UK) at a crosshead speed of 10 mm/min and a gauge length of 100 mm, according to the ASTM D882-02. A 100-N load cell was used to measure tensile properties of the GS, platicized PLA, and blend films. At least five specimens of each film were tested, and the results were averaged to obtain a mean value.

Water absorption

The blend films (25.4 mm × 76.6 mm × 250 µm) were used for a water absorption test according to ASTM D570-98. These specimens were dried at 50°C for 24 h, cooled to room temperature, and weighed. The dried films were then immersed in distilled water at 25°C for specific intervals of time. The specimens were removed periodically from the water, blotted with tissue paper to remove excess surface water, and then weighed. Three replicates were tested for each treatment. The water absorption was calculated based on a dry basis.

RESULTS AND DISCUSSION

Characterization of GS

Quantitative analysis

TGA was used to characterize glycerol quantity after gelatinization process. The glycerol content is an im-
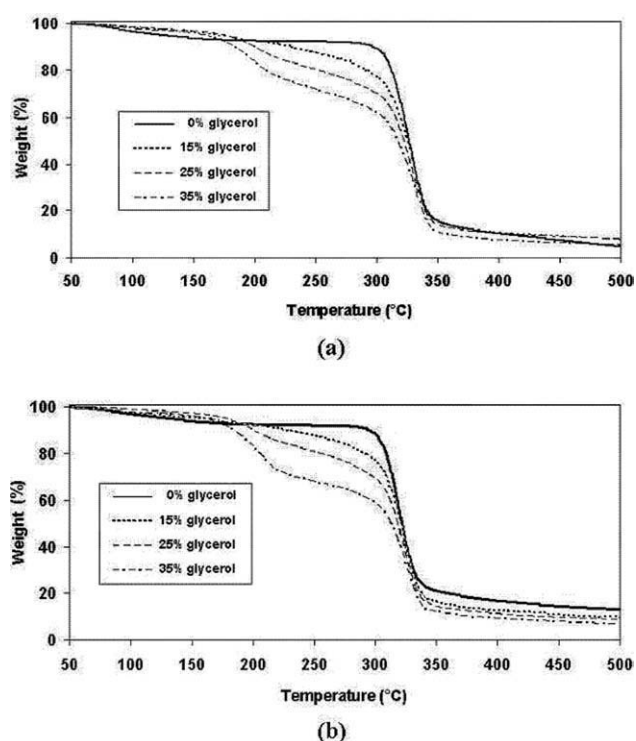

Figure 1 Effect of glycerol contents on the TGA thermograms of (a) thermoplastic tapioca starch and (b) thermoplastic corn starch.

portant parameter for producing gelatinized starch (GS), and the efficiency and appropriation of the process condition could be evaluated in terms of the remaining amount of glycerol in GSs after gelatinization. If most of glycerol content remained without vaporizing during process, it implied that processing parameters such as temperature, rotor speed, and mixing time are appropriate for starch modification. Generally, corn and tapioca starches begin to degrade at ∼ 310°C, defined as the decomposition temperature (T_d), which is in agreement with the TGA thermograms of both GS with various glycerol contents shown in Figure 1. The presence of water and glycerol in the GS was confirmed by two steps of weight loss. The first step occurred between 170 and 280°C was attributed to glycerol decomposition, and the second one at 310°C resulted from starch degradation. Because the decomposition temperatures of glycerol (evaporated slowly at 150–250°C) and starch were different more than 50°C, the content of residual glycerol in GS could be easily obtained from TGA thermograms. As expected, the weight loss of GS at 200°C increased as a function of glycerol content. The second decomposition temperature showed no significant difference when the amount of glycerol increased, because the glycerol content did not significantly affect to the T_d (onset) of GS. This thermal behavior was similarly found in both gelatinized corn and tapioca starches. From the results of TGA
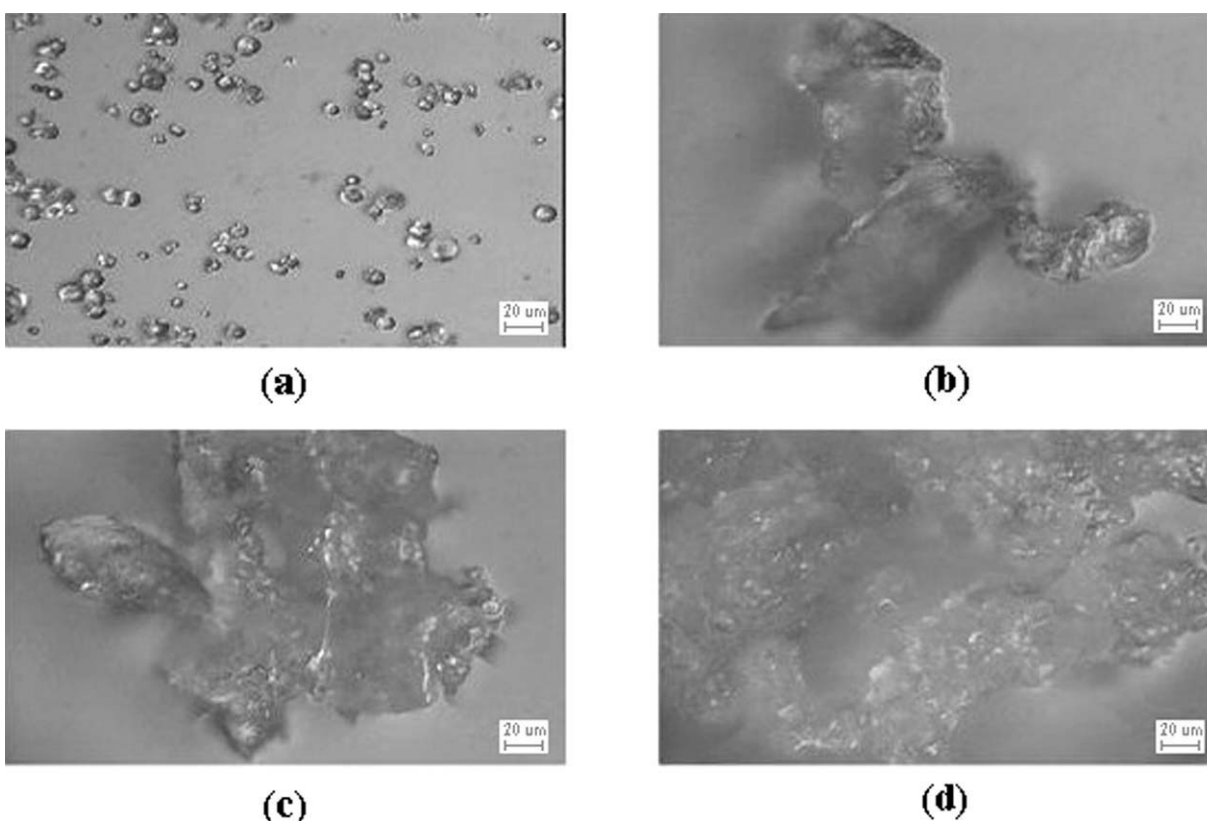
Figure 2 Optical micrographs of (a) pure and gelatinized tapioca starches with (b) 15, (c) 25, and (d) 35% glycerol (200×).

analysis, the amount of residual glycerol in GS indicated that most glycerol remained without vaporizing during process (Table I).

Morphological study

An OM was used to examine surface morphology of pure and GSs. Prepared samples were pulverized by means of a crusher and then dried in a vented oven at 60°C overnight before testing. All powdered specimens were observed at 200×.

Optical micrographs of pure and gelatinized tapioca starches are illustrated in Figure 2. In case of pure tapioca starch [Fig. 2(a)], spherical granules with diameters of about 10 μm were observed. On the other hand, the gelatinized tapioca starches [Fig. 2(b–d)] were found in irregular forms with the size being larger than that of the pure tapioca starch granules. At lower glycerol content (15 wt %) [Fig. 2(b)], the combination and aggregation of starch particles were observed, leading to abnormal shapes and larger sizes compared to pure starch granule. When the glycerol content was further increased up to 25 and 35 wt %, the granules formed at the surface of GS were obviously noticed. The size and the shape of the GS particles became larger and rougher than those of the granules with less glycerol content. This behavior is due to the swelling of granules

through water or glycerol and the diffusion of amylose out of the collapsed granules during gelatinization process.[7] In addition, the introduction of glycerol contributes to a prevention of reaggregation of starch particles, because glycerol still remains and solvates between starch polymeric chains. For corn starch, the optical micrographs of pure and GSs showed similar results to those of tapioca starches. However, the observed granules in the particles of gelatinized corn starches at 25 and 35 wt % glycerol were less than those of gelatinized tapioca starches.

Crystallinity

The starch gelatinization was defined as the melting of starch crystallites in which the complete destruction of crystalline integrity was observed. Several techniques such as DSC, DMTA, and NMR have been used to evaluate the structural changes of starch.[25] X-ray diffraction (XRD), one of the useful methods for studying starch gelatinization, is based on the determination of diffraction and reflection of crystal planes. After gelatinization or melting, these reflections disappear while broad halo appears, indicating a change from a crystalline to an amorphous (molten) stage.

XRD patterns of pure and various GSs are showed in Figure 3. For both pure starches, single peaks at
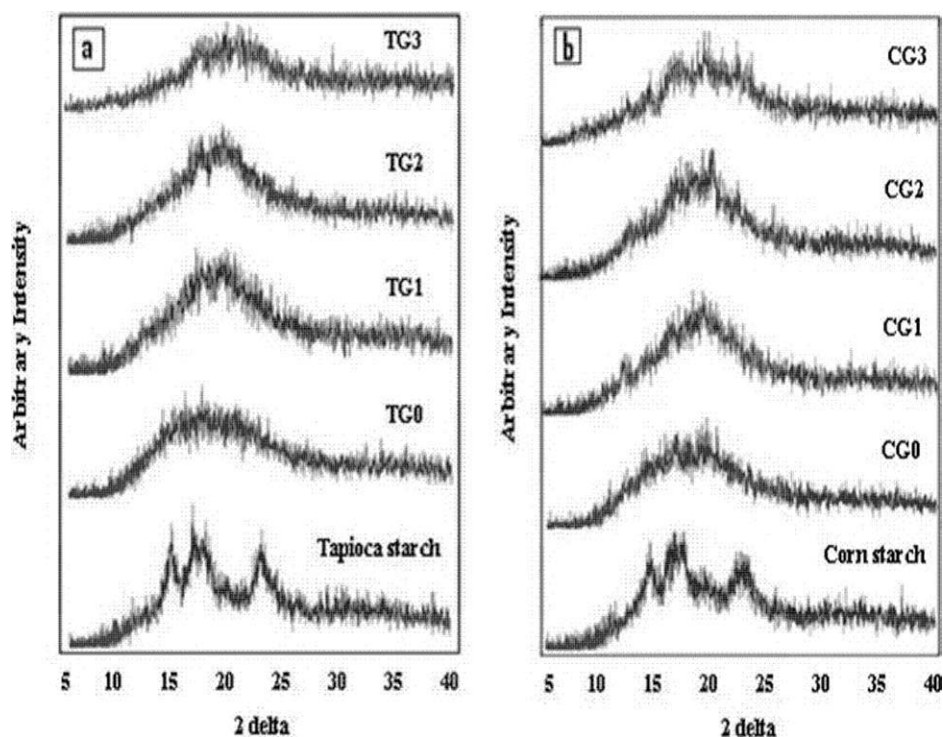
Figure 3 Wide angle X-ray diffraction patterns of (a) pure and gelatinized tapioca starch and (b) pure and gelatinized corn starch at various glycerol contents.

2θ of 15° and 22° and double peaks at 17° and 18° were observed. In the case of GS, the areas of the peaks, which correspond to the crystalline region, decreased in comparison with those of pure starch. These behaviors are resulted from the disruption of the crystalline region or a decrease in the degree of crystallinity during gelatinization in which the glycerol molecules destroy intermolecular hydrogen bondings between starch molecules and form hydrogen bonds instead. The disappearance of intermolecular hydrogen bondings leads to a decrease in the crystallinity as well as increases chain mobility of starch molecules. These results confirm that the increasing glycerol contents affected the structure of starch leading to the structural change from crystalline to amorphous. It is a transformation from semi-crystalline starch to completely thermoplastic starch, where the GS can be molded into different shapes by melt-processing techniques.

Tensile properties

Figure 4 shows the tensile properties of GS films having 25 and 35 wt % glycerol content. It can be seen that the tensile strength and elongation at break of the GS films with 25 wt % glycerol were higher than those of the GS films with 35 wt % glycerol. The GS films containing 35 wt % glycerol were too soft and easy to disrupt due to overloading plasticizer content. In contrast, those GS films with 20 and

35 wt % water (i.e., 15 and 0 wt % glycerol, respectively) were too brittle and could not be pressed into absolute films, because water, one of important plasticizer in the system, is easy to evaporate during processes leaving the GS films with low or without plasticizer content. These results indicate that the amount of glycerol and water or the ratio between these two plasticizers is an important factor in determining the processability and also tensile properties of the GS films. The appropriate ratio of each plasticizer leads to the GS films with desirable processability and properties. Excess amount of glycerol (35 wt %) makes the films too soft; whereas, extra water content (35 wt %) causes the brittleness of the GS films.
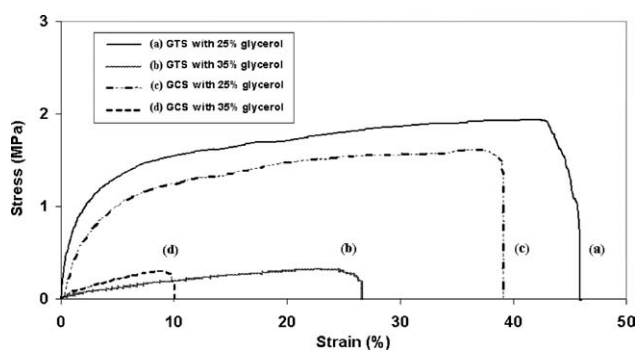

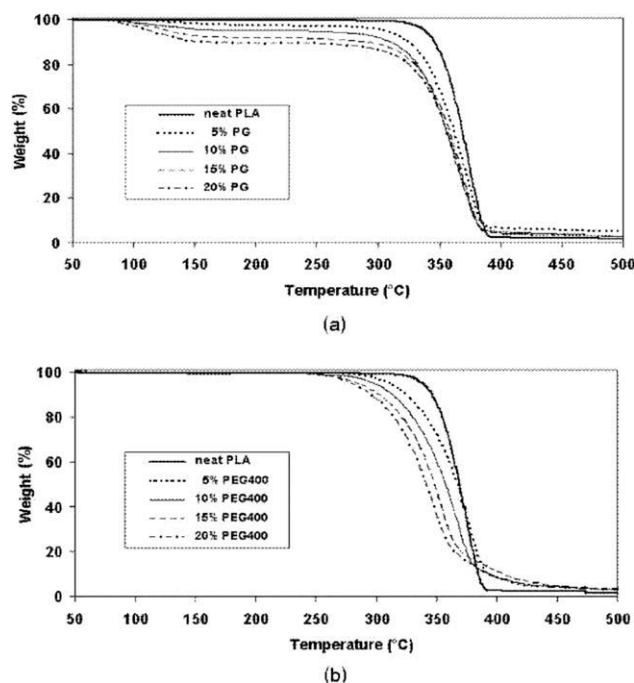**Figure 4** Stress–strain curves of GS films at 25 and 35% glycerol.

Figure 5 Effect of (a) PG and (b) PEG400 content on the TGA thermograms of neat and plasticized PLA films.

Conclusively, the physical appearance and tensile properties of the GS films indicate that the appropriate amount for starch gelatinization process is 25 wt % glycerol, leading to absolute films with acceptable tensile properties. Hence, the GS with 25 wt % glycerol was selected to use for blending with PLA in film preparation step.

Characterization of plasticized PLA

Thermal properties

Thermal gravimetric analysis. The effect of PG and PEG400 content on the thermal degradation behavior of plasticized polylactide (PLA) is illustrated in Figure 5(a,b). The plasticized PLA with different amount of PG showed two decomposition stages. The first stage at around 97°C was attributed to the loss of PG content, because it was similar to the decomposition temperature of pure PG. The second stage appearing around 320–360°C was associated with the thermal degradation of plasticized PLA. This stage was the main step resulting from completely thermal decomposition of the PLA backbone. Table II summarized the onset of the degradation temperature [T_d (onset)] for each stage and the percentage of weight loss for all the PG-plasticized PLA samples.

As listed in Table II, the PG content affected the amount of weight loss of the films at the first stage. Weight loss of the films increased as a function of the PG content. These results confirm that the first

step of weight loss must be due to the decomposition of PG. The second weight loss occurred from the degradation of PLA. Considering the thermal stability of the plasticized PLA films, it was obviously seen that the thermal degradation temperature of plasticized PLA films with PG decreased about 10°C compared to the neat PLA film. These data imply that the addition of PG slightly decreased the thermal stability of the PG-plasticized PLA films compared to the neat PLA film. For PEG 400, because the degradation temperature of PEG400 is close to that of PLA (280–350°C), the one step of weight loss for each PEG400-plasticized PLA can be observed, as shown in Figure 5(b), due to the overlapping of their thermal decomposition stages. The thermal degradation behavior of plasticized PLA films with PEG400 also indicated the decreasing thermal stability of plasticized PLA films as increasing plasticizer content. Obviously, upon increasing the amount of PEG400, weight loss of the films increased, and the onset of the thermal degradation temperatures was decreased.

Differential scanning calorimetry. The second heating of differential scanning calorimetry (DSC) thermograms for neat PLA and plasticized PLA with PG and PEG400 is displayed in Figure 6(a,b), respectively. The neat PLA showed a clear glass transition temperature at 58.5°C, and a small melting endotherm at 152.1°C, corresponding to residual crystallinity, as also reported by Martin and Averous.[12] The introduction of PG and PEG400 led to a decrease in the glass transition temperature (T_g), melting temperature (T_m), and crystallization temperature (T_c) of PLA, indicating that PG and PEG400 played a significant role as a plasticizer in the PLA. This is a typical behavior for plasticized thermoplastics, where plasticizers can reduce the glass transition temperature by increasing the free volume and thus chain mobility of the polymeric molecules as well as may also promote their crystallinity due to those enhanced chain mobility.

TABLE II
Onset of Degradation Temperature and Percentage of Weight Loss for Plasticized PLA Films with Various PG and PEG 400 Contents

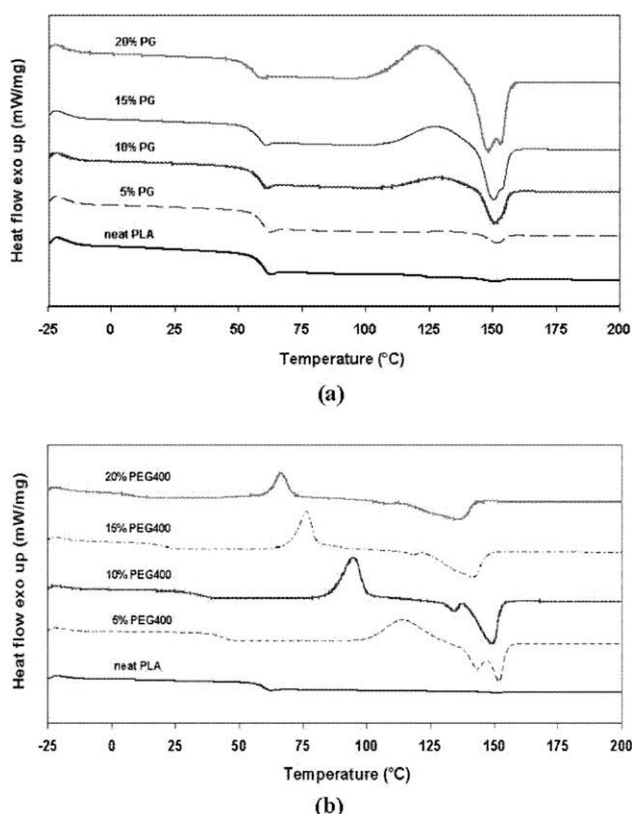| Sample ID	T_d (°C) (onset)		Weight loss (%)	
	First	Second	At 120°C	At 360°C
Neat PLA	–	349.87	0.00	29.06
PLA + 5% PG	97.78	335.57	0.91	47.56
PLA + 10% PG	98.25	331.63	2.22	57.51
PLA + 15% PG	98.65	338.94	4.03	53.20
PLA + 20% PG	98.96	334.35	6.19	55.93
PLA + 5% PEG400	–	341.67	–	40.23
PLA + 10% PEG400	–	329.82	–	54.31
PLA + 15% PEG400	–	320.69	–	70.77
PLA + 20% PEG400	–	314.21	–	77.04

Figure 6 DSC thermograms of neat and plasticized PLA films with various (a) PG and (b) PEG400 content.

As shown in Figure 6, plasticized PLA systems of both PG and PEG400 indicated a single T_g lower than that of neat PLA, which decreased with increasing plasticizer content. The lowest T_g values of 54.6 and 8.8°C were obtained with the addition of 20 wt % PG and PEG400, respectively. A significant decrease in the T_m of plasticized PLA compared to pure PLA of $\sim$ 5–15°C was also observed. The depression of T_m for PG-plasticized PLA did not seem to be much dependent on the PG concentration in contrast to that of plasticized PLA with PEG400 in which its T_m was related mostly to plasticizer contents. Similar results have been reported by Xiao et al.,[26] which indicated that the presence of plasticizer increased the chain segment mobility of PLA molecules, leading to the decrease in the crystallization temperature of PLA. For this reason, the T_m of PLA decreased with the addition of plasticizer. Moreover, it was found that some melting endotherms of plasticized PLA were split into two distinct peaks as previously reported by several researches.[27–29] For example, Pennings et al.[27] reported that this result was due to the lamellar rearrangement during crystallization of PLA: a lower temperature peak was formed on the melting endothermic peak of original crystallites. In addition, Piorkowska et al.[28] explained that the additional melting peak on the thermograms of plasticized PLA

occurred from the reorganization of crystal structure as related to the stability of lamellae.

In case of the T_c, the DSC thermogram of neat PLA did not show any T_c. This result is in accordance with several researches.[12,30] However, the T_c was affected by the addition of plasticizers, in particular when PEG400 was added into neat PLA. This is because plasticized PLA can crystallize with more ease at lower temperatures resulting from the enhanced chain mobility. The PG, which gradually induced T_g, T_c, and T_m shifts (even at 20% loading), had limited effect on the thermal transitions of PLA. Hence, the thermal characteristics of plasticized PLA compared to neat PLA demonstrated that PEG400 can be regarded as the efficient plasticizer for PLA more than PG due to the significant decrease in T_g, T_c, and T_m. These results are supported by their tensile properties.

Tensile properties

Neat PLA film has high Young's modulus (2 GPa) and tensile strength (70 MPa); however, it is a brittle material with an elongation at break of 7%. Thus, it is needed to be improved by some additives. Table III illustrates the effect of PG and PEG400 contents on the tensile properties of PLA films. Obviously, tensile properties of plasticized PLA films depended on the PG content. Unexpectedly, the addition of PG caused a significant decrease in an elongation at break. Whereas the tensile strength and Young's modulus of plasticized PLA films were decreased with increasing amount of PG as well.

The reduction in tensile properties of plasticized PLA films with PG was not related to general function of plasticizer used for improving elongation of material. This behavior may be occurred from lacking of compatibility between PLA and PG. The decrease in elongation at break did not mean that the films were still brittle; in fact, they were too soft and easy to disrupt. These results are in agreement with their thermal properties, implying that the PG

TABLE III
Tensile Properties of Neat and Plasticized PLA

Film samples	Tensile strength (MPa)	EB (%)	Young's modulus (MPa)
Neat PLA	70.22 ± 1.97	7.36 ± 0.44	1915.11 ± 72.49
5% PG	42.79 ± 2.51	4.99 ± 0.38	1854.73 ± 81.88
10% PG	37.06 ± 0.88	4.51 ± 0.19	1661.09 ± 83.11
15% PG	27.57 ± 0.81	3.70 ± 0.40	1616.39 ± 118.91
20% PG	23.09 ± 1.89	2.87 ± 0.09	1411.97 ± 28.97
5% PEG400	32.43 ± 2.29	4.04 ± 0.46	1594.63 ± 65.32
10% PEG400	17.08 ± 0.47	40.58 ± 3.58	958.08 ± 54.87
15% PEG400	5.14 ± 0.59	2.21 ± 0.39	570.36 ± 52.39
20% PEG400[a]	–	–	–

[a] Plasticized PLA with 20% PEG400 cannot be detected, because it is too soft and easy to disrupt.
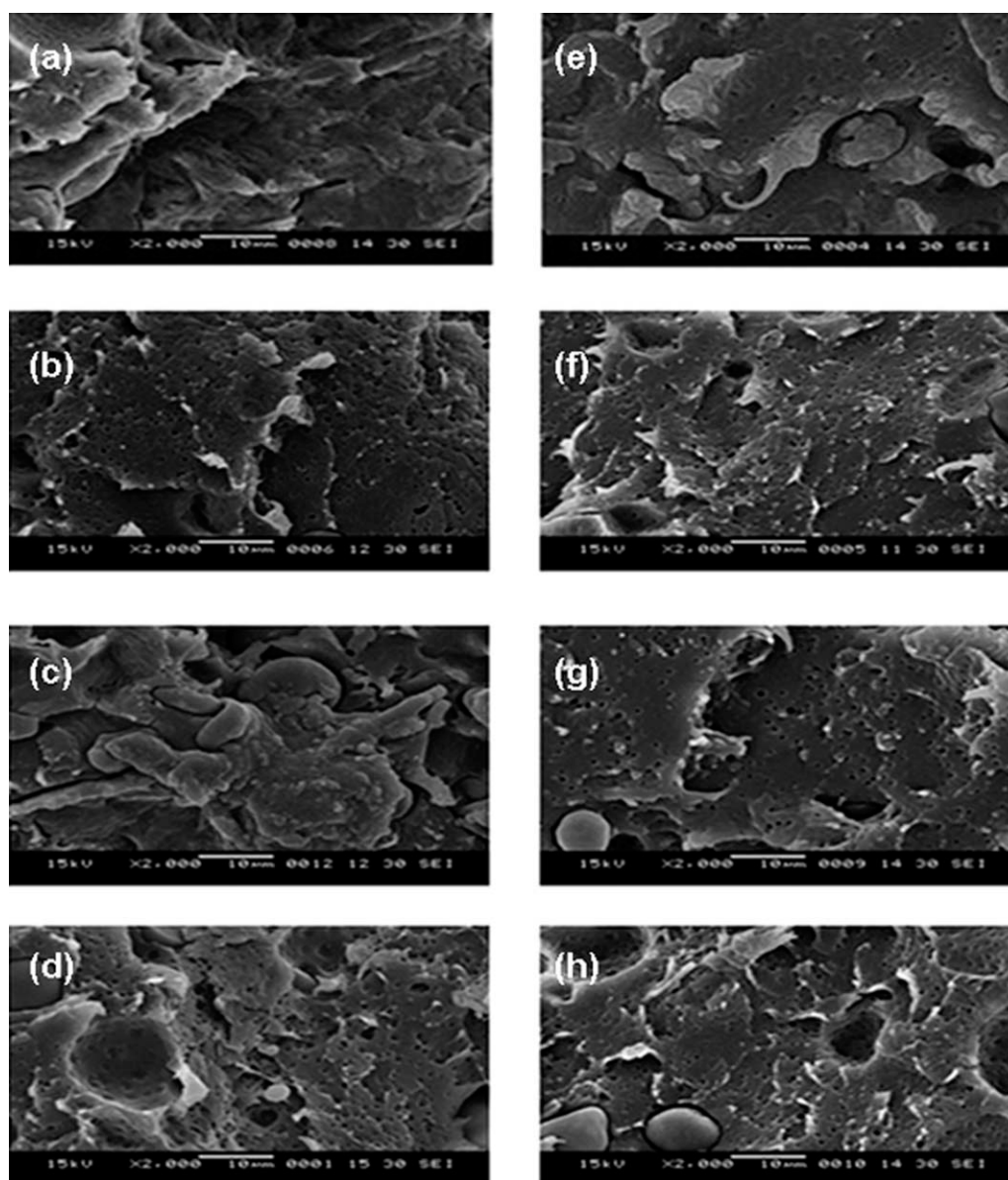
Figure 7 SEM micrographs of the fractured surface of plasticized PLA blend films (1.25 wt % MDI) with (a) 10, (b) 20, (c) 30, and (d) 40% gelatinized tapioca starches and (e) 10, (f) 20, (g) 30, and (h) 40% gelatinized corn starches.

is not an efficient plasticizer for PLA films comparing with PEG400. In case of PEG400-plasticized PLA films, the rapid decreasing of tensile strength and Young's modulus compared to the neat PLA with the addition of 15 wt % PEG400 was observed. On the other hand, the elongation at break of plasticized PLA film as high as 41% was obtained when 10 wt % PEG400 was compounded into those films, indicating that the tensile properties of PLA films can be improved by PEG400. Table III summarizes the tensile strength, elongation at break, and Young's modulus for all neat and plasticized PLA films. Thus, comparatively, PEG400 showed greater efficiency as a plasticizer for PLA film than PG.

Conclusively, the thermal and mechanical properties of the plasticized PLA films confirmed that the

appropriate type and content of the plasticizer for the PLA films was 10 wt % PEG400. This 10 wt % PEG400-plasticized PLA will be used to blend with 25 wt % glycerol-GS in the next step.

Characterization of blend films

Morphological studies

The fractured surface of GS and PLA blends with 1.25 wt % MDI (Fig. 7) is rough, which is a typical characteristic of a compatible structure. For 10 wt % GS blend [Fig. 7(a,e)], most of the GS were well enveloped by the PLA matrix and fractures occurred through the PLA matrix. When the GS level increased greater than 20 wt %, more starch granules
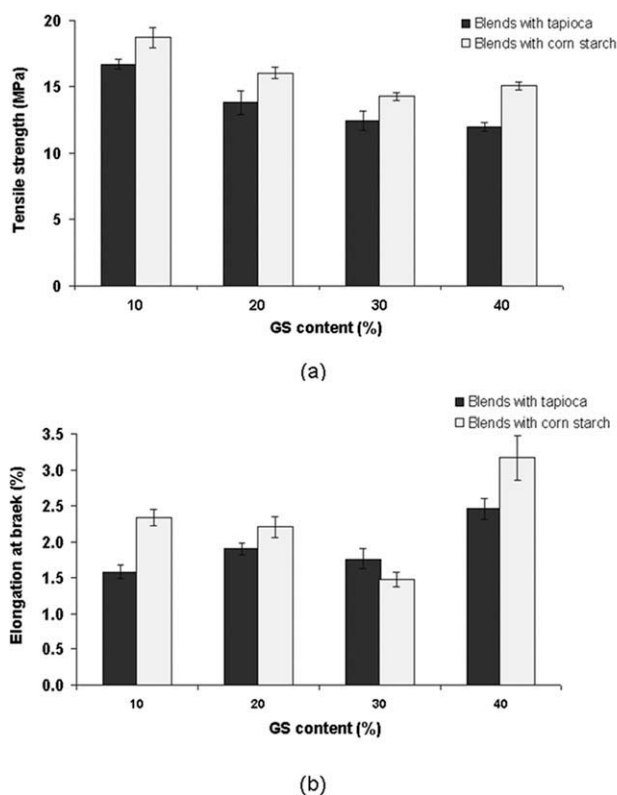
Figure 8 Tensile properties of plasticized PLA blend films with various GS content: (a) tensile strength and (b) elongation at break.

were observed clearly in the matrix and the fractures occurred at some of the interfaces between the PLA matrix and starch granules, suggesting that the GS was not well wetted by the PLA matrix. For example, at 40 wt % GS content [Fig. 7(d,h)], starch aggregations were observed clearly, and the starch granules were seemingly detached from the PLA matrix as a result of fracture mechanism.

According to Wu,[31] for a particulate-filled composite containing a coupling agent, the wetting and bonding at the interface significantly influenced the properties of the composite. To form an adhesive bond, the first step requires an interfacial molecular contact by wetting. Because of the wetting, the molecules diffuse across the interface and react chemically to establish covalent bonds across the interface. The diffusion is usually accelerated by low-surface tension, which enhances wetting and increases the adhesion bond strength and, consequently, the fracture energy. Any interfacial defects may result in poor wetting and poor adhesive bond strength.

As discussed earlier, molecular diffusion and absorption are two critical factors to the wetting property. In a well-wetted blend, there are few voids and entrapped air bubbles due to the reduced surface tension of the matrix. Because MDI has a boiling temperature of about 208°C,[32] which is higher

than the mixing temperature (180°C), and the isocyanate groups are highly polar, it thus seems possible that the surface tension of GS could be reduced in the presence of MDI during mixing. However, the amount of MDI was fixed at 1.25 wt %, which probably was insufficient to wet all the starch. It seems that 40 wt % GS and 1.25 wt % MDI was an optimum combination which is consistency with mechanical properties. This result suggested that each starch level may have its own optimum MDI content.

Tensile properties

To investigate the effect of interfacial modification on the mechanical performance of the PLA and GS blends, the tensile stress–strain behavior was characterized. From our previous work,[33] the results showed that the tensile properties of 40/60 (w/w) GS/plasticized PLA blend films containing 1.25 wt % MDI were significantly enhanced compared to those films without MDI. In this research, we thus studied the effect of various GS contents of the blends in the presence of 1.25 wt % MDI. In all cases, the gelatinized corn and tapioca starches comprised 25 wt % glycerol. The tensile strength and elongation at break of blend films with various GS contents are demonstrated in Figure 8(a,b), respectively. The tensile strength of blend films with 1.25 wt % MDI decreased progressively with the addition of the GS content. In terms of the elongation at break, a similar decrease with increasing GS content was observed. As the starch content increased, the effective cross-sectional area of the PLA continuous phase was reduced, resulting in decreased tensile strength and elongation at break. Elongation decreased as starch content increased; however, at 40 wt % GS content, elongation at break slightly increased. In addition, tensile properties of GCS/plasticized PLA blend films were slightly higher than those of GTS/plasticized PLA blend films. It might be occurred from the difference of amylose content in starches. Starch with high amylose content (corn starch) gave high crystallinity, which led to higher mechanical properties compared to that with low-amylose content (tapioca starch). Similar results have been reported by Chinnaswamy and Hanna,[34] which indicated that shear strength of starch extrudate increased with increasing amylose content, and the starch extrudate with 100% pure amylose content had the greatest shear strength.

Water absorption

Figure 9(a,b) illustrates water absorption isotherms as a function of time for neat PLA and GS/plasticized PLA blend films at various GS content. MDI
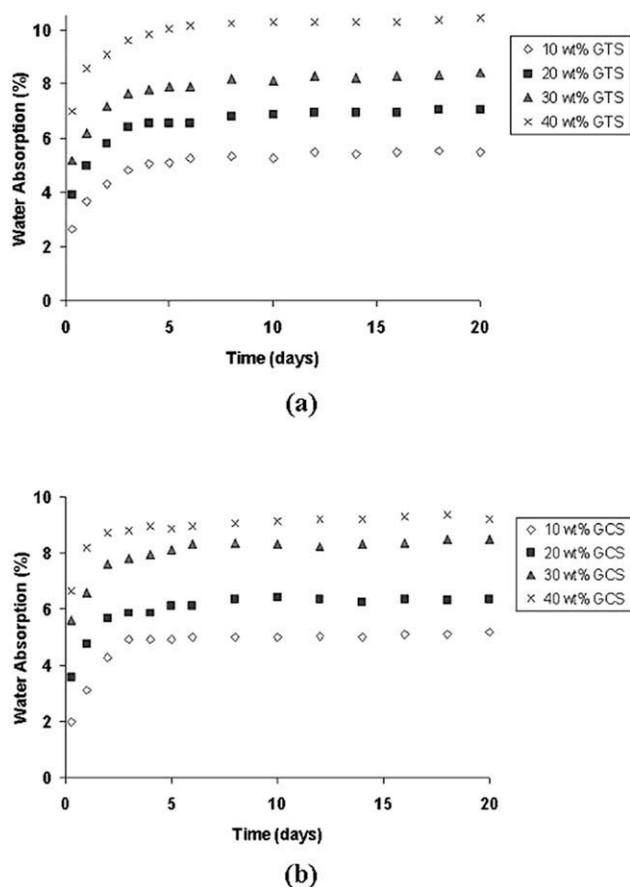
Figure 9 Water absorption isotherms of plasticized PLA blend films with various GS content: (a) tapioca starch and (b) corn starch.

content of all the blend films was 1.25 wt %. Clearly, the water absorption in the blends depended on both exposure time and GS content. Unlike the neat PLA film that can absorb about 1% water absorption, the blend films absorbed more water as the amount of GS increased. The water absorption isotherms of all blend films increased rapidly during first 5 days and then leveled off. The plasticized PLA films with 40 wt % GS had the highest water absorption compared to the others. These results can be concluded that the rate of water uptake depended upon the GS content.

At 10 wt % GS, the plasticized PLA blend films gradually absorbed water until it reached an equilibrium value of about 5%. At higher volume fraction of GS, water uptake increased. The blend with 40 wt % GS had the highest water uptake of 9 and 10% for GCS and GTS, respectively. These results ensure that both GS are more hydrophilic than PLA matrix, leading to an enhancement of hydrogen bond formation between hydroxyl groups in the GS and water; as a result, the water uptake of the blend films increased as a function of GS content. This behavior can be similarly found in both starches. Nonetheless, the water absorption isotherms of GTS/plasticized

PLA blend films were slightly higher than those of GCS/plasticized PLA blend films, resulting from the difference in amylose content between tapioca and corn starches (30.79 and 32.35 wt %, respectively).[23] The starch with low-amylose content is well known to absorb more water upon soaking than the one with high-amylose content due to its higher amount of large branched amorphous molecules of amylopectin. As a result, the blend films with gelatinized tapioca starch exhibited higher water absorption than its counterpart due to its lower amylose content (higher amylopectin). The crystalline region of starch was melted upon gelatinization, and swelling of amylopectin played a main role in water absorption.

CONCLUSION

Tapioca starch is an interesting material that can be an efficient candidate for blending with the other polymers to make biodegradable plastics. Both gelatinized tapioca and corn starches exhibited similar thermal, physical, and tensile properties. From the TGA results, the amount of glycerol did not significantly affect to the thermal degradation of GSs. However, the physical and tensile properties indicated that glycerol is a crucial factor for gelatinization and processability of starch. For PLA plasticization, thermal and mechanical analysis demonstrated that PEG400 gave the best results. The DSC thermograms revealed the significant depressions of the glass transition temperature and melting temperature of PEG400-plasticized PLA films. The tensile strength of PEG400-plasticized PLA was seen to decrease as the concentration of plasticizer increased. In the meantime, elongation at break reached up to 41%. Thus, comparatively, PEG400 has a greater efficiency as a plasticizer for PLA film than PG. The PLA/GS blend films gave good properties when small amount of MDI was added. The morphological analysis of the compatibilized blends showed that most of the GS particles were melted and formed a continuous phase with PLA matrix. However, their tensile strength and elongation at break decreased slowly when the GS content increased. This behavior occurred in both PLA blend films with GTS and GCS. However, the blend films with GCS had higher tensile properties than those with GTS.

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