Thermal, Mechanical, and Morphological Properties of Polylactic Acid Toughened with an Impact Modifier

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ABSTRACT: Polylactic acid (PLA) was melt-blended with different amount (0 to 50 wt %) of a commercially available ethylene acrylate copolymer impact modifier. PLA/impact modifier blends were prepared via an internal mixer and compression molded into test specimens. The thermal, mechanical, and morphological properties of the blends were investigated. The addition of impact modifier decreased the ability of PLA to crystallize and/or recrystallize. The degree of crystallinity of PLA decreased while the cold crystallization temperature shifted to higher temperatures with increasing the impact modifier content. PLA/impact modifier blends were partially miscible. This was confirmed by the dynamic mechanical analysis (DMA) tests. With increasing the impact modifier content, the blends showed some improvement in the elongation at break and notched impact strength indicating the toughening effects of the impact modifier. In contrast, the yield stress and tensile modulus decreased with the increase in the impact modifier content. Scanning electron microscopy (SEM) micrographs revealed that the toughening mechanisms among others involved shear yielding or plastic deformation of the PLA matrix induced by interfacial debonding between the PLA and the impact modifier domains. PLA with 30 wt % impact modifier showed comparable yield stress and tensile modulus and better elongation at break and impact strength (+90%) than those of polypropylene (PP). © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 2715–2725, 2012

Key words: polylactic acid; impact modifier; thermal properties; mechanical properties; morphology

INTRODUCTION

Polylactic acid (PLA) is a linear aliphatic thermoplastic polyester that can be produced from lactic acid obtained through fermentation of renewable resources such as corn starch.[1] PLA is produced either by direct condensation polymerization of lactic acid or by ring opening polymerization of cyclic lactide dimer, a diester of lactic acid. The polymer has a number of interesting properties, including biodegradability, biocompatibility, and good mechanical properties.[1] For these reasons, PLA is used in biomedical applications such as medical implants, sutures, and drug delivery systems. In addition, PLA has also been considered for commodity applications, for example, fiber and packaging products.[2] PLA has become an alternative to traditional general-purpose plastics for such applications because the polymer exhibits comparable or better mechanical properties than these petroleum-based plastics. PLA too can be melt-processed with the standard thermoplastic processing methods such as extrusion or injection molding. However, with a glass transition temperature ranging from 55 to 65°C, PLA is too stiff and brittle for room temperature applications,[3] and this brittleness limits its applications in some areas particularly as packaging materials.

The brittleness of PLA can be modified via several approaches: copolymerization of lactic acid with other monomers such as ε-caprolactone[4] and by blending PLA with a second polymer or a plasticizer.[1] Extensive efforts have been made to modify the brittleness of PLA via the first approach. Nevertheless none of these PLA copolymers are commercially available in the market.[5,6] Blending PLA with other flexible biodegradable[5–9] or nondegradable polymers[3,10,11] presents a more practical and economic way of toughening the material.[5,6,12] PLA has been blended with a number of polymers such as polycaprolactone (PCL),[7,13,14] poly(hydroxyalkaonate) (PHA),[9] and polyethylene (PE).[10,11] Many of these PLA blends are immiscible or only partially miscible and may need compatibilizers to improve their compatibility.[5,6] This will improve the dispersion of the minority phase, the adhesion between the blend components and stabilize the blend morphology[11] resulting in better mechanical properties. Compatibilizers can be introduced by adding a premade block or graft copolymer, or by *in situ* reactive

formation during melt processing.[11] The flexibility and ductility of PLA can also be improved by blending PLA with a plasticizer. Several low molecular weight compounds have been employed as plasticizers for PLA, for example, glycerol, triactine,[1,15] citrate,[15,16] and poly(ethylene glycol) (PEG).[17–19] A few problems have been reported with this approach such as migration of plasticizer to the blend surface[15,17–19] and long-term micro-phase separation[15,20] that can deteriorate the mechanical properties of the plasticized PLA.

Recently, some literatures[16,21–25] showed that PLA can be toughened by nanoparticles. According to Jiang et al.,[16] if a good dispersion is achieved, rigid nanoparticle toughening would be more beneficial than rubber toughening as both stiffness and toughness could be increased by the former. A great improvement in elongation at break has been observed by many authors[16,21–25] in addition to improvements of tensile strength and tensile modulus. Chang et al.[21] reported that the elongation at break of PLA nanocomposites was increased by 36% with the addition of 4 wt % montmorillonite. Meng et al.[22] prepared PLA nanocomposites with nanotitania coated with poly(ε-caprolactone). They reported an increase of the elongation at break to 65% (from 4%) with the addition of 26.5 wt % of the nanoparticles. Toughening mechanisms involved in PLA nanocomposites have been discussed in several literatures.[16,21–24] But, in all these research studies, the elongation at break was too low to expand the applications of PLA and the filler content was not low enough to lower the cost of composites.[22]

PLA is currently the most widely used biodegradable polymer. This has encouraged polymer additives and resin manufacturers to develop some new additives primarily for PLA to facilitate processability and improve some of its specific properties. Some examples include impact modifiers like Biostrength[TM] 130 and Biostrength[TM] 150 from Arkema, Paraloid[TM] BPM-500 from Rohm and Haas and Biomax[®] Strong 100 from DuPont; and melt strength modifiers like Cesa[®]-Extend from Clariant Masterbatches and Biostrength[TM] 700 from Arkema.[26]

There are many publications on the toughening of PLA via copolymerization,[4,27] blending of PLA with other polymers[3,5–11] as well as plasticizers.[1,17,28–30] Little information, however, is available on the toughening of PLA with impact modifiers.[31–34] In this work, the varying degrees of property modifications particularly tensile and impact properties of PLA were investigated through blending of PLA with a commercially available ethylene acrylate copolymer impact modifier, Biomax[®] Strong 100 from DuPont. This rubbery copolymer is designed with special chemistry to improve PLA impact strength and flexibility. This special chemistry refers to the presence of epoxy functionality in the impact modifier which can reactively interact with PLA[2] during melt mixing. The epoxy groups react with the hydroxyl and carboxyl groups at the chain ends of PLA.[9,11] Such interactions will increase the compatibility between the impact modifier and PLA. PLA/impact modifier blends, therefore, although immiscible is compatible. PLA/impact modifier blends of varying compositions (0–50 wt %) were prepared by melt-blending technique. The thermal and mechanical properties of the blends were investigated by means of differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), as well as tensile and impact tests. Morphological characterization was performed with scanning electron microscopy (SEM) to identify the toughening mechanisms involved. In addition, the mechanical properties of the PLA/impact modifier blends were also compared with those of a commercially available impact copolymer polypropylene (PP) to determine the maximum amount of impact modifier needed to produce toughened PLA of comparable properties with the commodity plastic.

EXPERIMENTAL

Materials

The materials used in this study were PLA, PP and an impact modifier. Semicrystalline PLA Grade 2002 D (4% D-lactide, 96% l-lactide content, molecular weight 121, 400 g mol^{-1}, MFR 6.4 g/10 min) was purchased from Natureworks[TM] in pellet form. Its glass transition temperature is about 63°C and melting temperature 160°C. Impact copolymer grade PP (Pro-Fax SM240) with a melt flow index (MFI) of 25 g/10 min (at 230°C and 2.16 kg) and a density of 0.894 g cm^{-3} was supplied by Titan Petchem (M) Sdn. Bhd. (Johor, Malaysia). The impact modifier, which is ethylene acrylate copolymer, was obtained from DuPont with the grade name of Biomax[®] Strong. It is a rubbery material with a glass transition temperature and melting temperature of −55 and 72°C, respectively.

Blend preparation

Prior to blending, PLA and the impact modifier were dried in a vacuum oven at 80°C for 4 h. Both materials were then premixed in a plastic container. Blends of PLA and impact modifier at varying weight ratios were prepared by melt-mixing with an internal mixer (Haake Rheomix Polydrive R 600/610 equipped with two counter-rotating blades). Melt-mixing was performed at 190°C for 5 min at a rotor speed of 50 rpm. Plates of 1 and 3 mm thickness were prepared by melt pressing chips of

PLA/impact modifier blends on a laboratory hot press at 190°C. The material was first preheated for 6 min and then compressed under a pressure of 14 MPa for 3 min. The compressed materials were then cooled in an adjacent press by circulating tap water. Test samples for tensile (narrow section: 50 mm × 6 mm × 3 mm), impact (rectangular: 75 mm × 15 mm × 3mm) were cut from these plates by using a dumbbell cutter and a band saw.

Differential scanning calorimetry

Thermal properties were investigated using a Perkin–Elmer Pyris 1 differential scanning calorimetry (DSC). Samples (about 8–10 mg) were placed and sealed in aluminum pans. The samples then were heated from 30 to 220°C at a heating rate of 10°C min^{-1} (the first heating scan) and kept at 220°C for 5 min to remove their previous thermal history. Following that the samples were quenched to −10°C at a cooling rate of 100°C min^{-1} and then were finally heated at 10 mm min^{-1} to 220°C (the second heating scan). Peak temperatures and enthalpies at glass transition, crystallization and melting were determined. The percentage crystallinity (X_c) of PLA in PLA/impact modifier specimens were estimated using baselines drawn from 95 to 190°C and a perfect heat of fusion (ΔH^0_m) of PLA of 93 J g^{-1}.[8] The X_c values of PLA in PLA/impact modifier specimens were calculated based on the following equation:

$$X_c(\%) = \frac{\Delta H_c}{(1 - \phi)\Delta H^0_m} \times 100 \qquad (1)$$

where ΔH_c is the melting enthalpy of crystallization of PLA/impact modifier specimens obtained by subtracting the enthalpy values of those of the re-crystallization exthotherms and ϕ is the weight fraction of impact modifier in the blend specimens.[8]

Dynamic-mechanical analysis

Dynamic mechanical properties were measured using a Mettler Toledo Model DMA 861 under the flexural mode of testing from −100 to 150°C. The dimensions of the samples were 60 mm × 12 mm × 3 mm. The heating rate was set at 5°C min^{-1} and a frequency of 1 Hz was employed.

Tensile testing

Tensile tests were performed at room temperature on an Instron testing machine (model 3366) according to ASTM D 638. The capacity of the load cell is 10 kN while the crosshead speed was set at
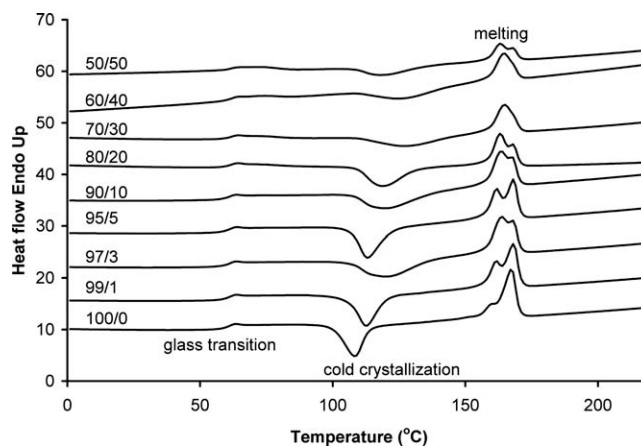

Figure 1 DSC thermograms recorded during the second heating at the rate of 10°C min^{-1} for PLA and PLA/impact modifier blends.

5 mm min^{-1}. At least five samples were tested for each reported value.

Impact testing

Notched Izod impact tests were performed using a Zwick test machine at room temperature with a pendulum hammer of 7.5 J according to ASTM D 256. A total of 10 samples for each material were tested to determine the impact strength.

Scanning electron microscopy

Fracture surfaces from tensile tests were examined using a field emission scanning electron microscope (FESEM SUPRA 35VP) at an acceleration voltage of 10 kV. All specimens were vacuum coated with gold prior to examination to avoid charging.

RESULTS AND DISCUSSION

DSC analysis

DSC Thermograms of PLA and PLA/impact modifier blends are shown in Figure 1 and the thermal characteristics are summarized in Table I. Pure PLA displayed a glass transition at 61.4°C. The addition of impact modifier did not result in a noticeable change in the glass transition temperature of the amorphous PLA suggesting that the PLA/impact modifier blends are immiscible. Similar trend was also reported by other studies.[32–34] In addition to the glass transition temperature, a cold crystallization temperature was also observed for both pure PLA and PLA/impact modifier blends. The cold crystallization temperatures of PLA/impact modifier blends became broaden, decreased in magnitudes and shifted to higher temperatures with increasing impact modifier content. Pure PLA showed a cold

TABLE I
Thermal Properties of Pure PLA and PLA Blends Determined by DSC (Second Heating at the Heating Rate of 10°C min^{-1a}

Sample[b]	T_g (°C)	T_{cc} (°C)	ΔH_c (J g^{-1})	T_m (°C) 1	T_m (°C) 2	ΔH_m (J g^{-1})	X_{cc} (%)	X_c (%)
100/0	61.4	108.3	27.57	159.9	167.4	36.93	29.64	39.71
99/1	61.5	112.7	29.01	161.7	168.2	38.20	31.58	41.49
97/3	61.7	120.2	25.11	163.9	167.9	35.14	27.83	38.95
95/5	61.7	113.0	30.23	161.8	168.1	35.51	34.22	40.19
90/10	61.2	119.0	22.78	163.6	167.7	30.03	27.22	35.88
80/20	61.9	118.4	24.41	163.2	168.0	27.42	32.81	36.85
70/30	62.5	126.7	9.13	164.9	–	20.95	14.02	32.18
60/40	62.5	125.2	11.58	164.6	–	18.49	20.75	33.14
50/50	61.8	116.9	7.03	163.2	168.0	16.42	15.12	35.31

[a] T_g, glass transition temperature; T_{cc}, cold crystallization temperature; T_m, melting temperatures; ΔH_c, enthalpy of crystallization; ΔH_m, enthalpy of fusion; X_{cc}, degree of crystallinity from cold crystallization, X_c, degree of crystallinity.
[b] PLA and impact modifier weight ratio.

crystallization temperature at 108.3°C. The addition of impact modifier increased the cold crystallization temperature between 4 and 18°C (Table I). The increase or decrease of the cold crystallization temperature of a component has been claimed to indicate that the crystallization of this component has become more difficult or easier, respectively, upon blending with another component.[1] It is therefore can be suggested that the addition of impact modifier decreases the ability of PLA to crystallize and/or recrystallize. Instead of facilitating nucleation of PLA molecules, the phase separated impact modifier molecules might have inhibited nucleation crystallization and/or recrystallization of PLA as these molecules (melting temperature = 72°C as determined via DSC) exist as melt state between the temperatures associated with cold crystallization of PLA.[8] According to Byrne et al.[33] the presence of epoxy functionality in the impact modifier prevents crystallization of PLA during processing. The epoxy functional groups of the impact modifier can react with the hydroxyl and carboxyl end groups of PLA[9,11] and this probably decrease the molecular segmental mobility of PLA reducing the ability of PLA to crystallize and/or recrystallize. The degrees of crystallinity of PLA/impact modifier blends from the cold crystallization were found to decrease with increasing impact modifier content as observed in Table I.

Pure impact modifier has a melting temperature at 72°C. This melting temperature of the impact modifier, however, was not observed from the DSC thermograms of the PLA/impact modifier blends. Similar trend was reported by other studies.[32,34] The heat flow that is associated with the melting of the impact modifier is probably small. Diluting this impact modifier into PLA might have reduced its heat flow in the DSC thermograms of the PLA blends. Because of the limitations of DSC, the equipment might not sensitive enough to this small

enthalpy, making the melting temperature identification difficult even at 50 wt % impact modifier content. Another possible reason is that the impact modifier becomes amorphous in the PLA/impact modifier blends. The impact modifier might not have enough time to crystallize within the cooling time frame.

Pure PLA showed a shoulder at 160.0°C and a melting peak at 167.4°C. Various researchers have reported the existence of either two distinct melting peaks or a melting peak and a shoulder during DSC measurement of either PLA, PLA blends with other polymers[5,12,35] or PLA blends with plasticizers.[1,28,29] Such observation has been attributed to lamellar rearrangement during crystallization of PLA.[1] As a result: low temperature peak formed on the melting endotherm of the original crystallites (less perfect crystal) while the high temperature peak formed on the melting endotherm of the recrystal crystallites (more stable crystal).[1] During the DSC heating scan of pure PLA, it can be suggested that some of the less perfect crystals had enough time to melt and reorganize into crystals with higher structural perfection (thicker lamellae), more stable crystals, and then remelt at higher temperature.[5,35] The addition of impact modifier separated the melting peak and the shoulder of PLA into two individual peaks (Fig. 1). The peak resulted from the shoulder became more pronounced with increasing impact modifier content suggesting the melting of relatively larger number of less perfect crystals in these blends. The restrictions to molecular segmental mobility of PLA by the impact modifier molecules would be greater with the increase in the impact modifier content. As a result, some of the less perfect crystals might not have enough time to melt and reorganize into more stable crystals. The relative number of the less perfect crystals in the PLA/impact modifier blend, therefore, would be increased with the increase in
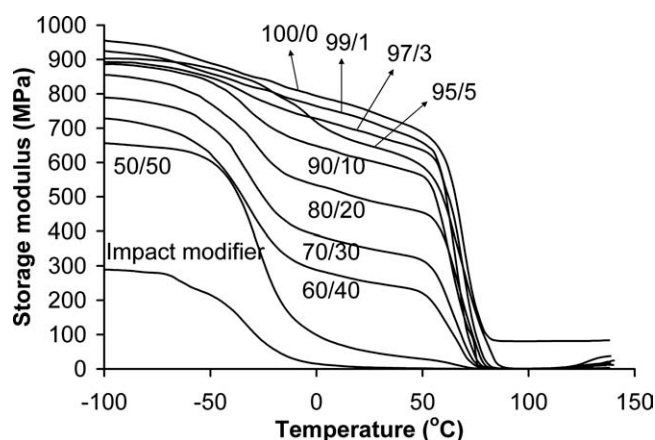
Figure 2 Storage modulus curves of pure PLA, impact modifier and PLA/impact modifier blends.

the impact modifier content. In contrast, the proportion of the more stable crystals would be decreased with increasing impact modifier content and this accounts for the opposite trend observed for the peak at the higher temperature. At 30 and 40 wt % impact modifier, only the low temperature peak was observed indicating the presence of only the less perfect crystals in the PLA/impact modifier blends. During the DSC heating scan of these PLA/impact modifier blends, the less perfect crystals formed might not have enough time to melt and reorganize into crystals with higher structural perfection. This is probably due to the greater restrictions to molecular segmental mobility of PLA by the impact modifier molecules at these high impact modifier contents. Since there were no stable crystals formed, the high temperature peaks were not observed in the DSC thermograms of PLA with 30 and 40 wt % impact modifier. At 50 wt % impact modifier, in addition to the low temperature peak, the high temperature peak appeared back as a shoulder. At this high impact modifier content, the isolated impact modifier particles in the blend might have joined together and formed a continuous phase. This would limit the interactions between the carboxyl and hydroxyl end groups of PLA and the epoxy functional groups of the impact modifier. This might have facilitated some of the less perfect crystals particularly those of the PLA rich phase to melt and reorganize to more stable crystals and then remelt at higher temperature. The adverse effect of impact modifier on the ability of PLA to crystallize or recrystallize can be further confirmed from the low enthalpy of cold-crystallization (ΔH_c) and enthalpy of melting (ΔH_m) of PLA/impact modifier blends in comparison to those of pure PLA (Table I). Both enthalpies decreased continuously upon increasing impact modifier content in the blends, suggesting that the addition of impact modifier decreased the

crystallinity of PLA. The percentage of crystallinity of PLA in PLA/impact modifier blends is presented in Table I.

Dynamic mechanical analysis

The storage modulus curves of pure PLA, impact modifier and PLA/impact modifier blends are shown in Figure 2. It can be seen in Figure 2 that the addition of impact modifier decreased the storage modulus of pure PLA. As an example, the storage modulus of PLA with 20 wt % impact modifier at 25°C decreased by 35% from 751.7 to 486.9 MPa (Table II). Further decrease in the storage modulus was observed with increasing impact modifier content. The decrease in the storage modulus of PLA/impact modifier blends can be attributed to the low stiffness of the impact modifier. As shown in Figure 2 and Table II, the storage modulus of PLA/impact modifier blends gradually decreased with the increase in temperature. In the regions between −60 and 0°C, a sharp drop in the storage modulus was observed that can be associated to the glass transition of the impact modifier. This phase transition, however, was not clear for PLA/impact modifier blends with 1 wt % impact modifier content. As the amount of impact modifier increases, the storage modulus drop became more abrupt, larger in magnitude and pronounced. This observation indicates that the rigidity of PLA/impact modifier blends decreases as the impact modifier content increases. In the regions between 30 and 80°C, another sharp drop in the storage modulus was observed that can be associated to the softening or segmental mobility of PLA molecules. A slight increase in the storage modulus after this phase transition at temperature above 100°C was due to the cold crystallization of PLA during the heat scanning process.

The tan δ curves of pure PLA, impact modifier and PLA/impact modifier blends are shown in

TABLE II
Thermomechanical Properties of Pure PLA, Impact Modifier, and PLA/Impact Modifier Blends

Sample	Tan δ (°C)		Storage modulus (MPa)		
	1	2	25°C	40°C	60°C
100/0	–	69.36	751.7	713.5	606.7
99/1	–	69.36	720.7	683.5	526.7
97/3	−35.64	67.10	682.2	655.4	543.0
95/5	−35.54	70.10	647.7	617.5	486.6
90/10	−29.42	64.76	604.2	581.1	351.6
80/20	−29.64	67.85	486.9	468.3	363.5
70/30	−34.56	64.66	350.2	332.7	233.9
60/40	−33.90	62.05	253.1	237.6	148.5
50/50	−27.68	63.79	49.8	36.9	21.3
Impact modifier	−34.54	–	4.6	2.5	0.9

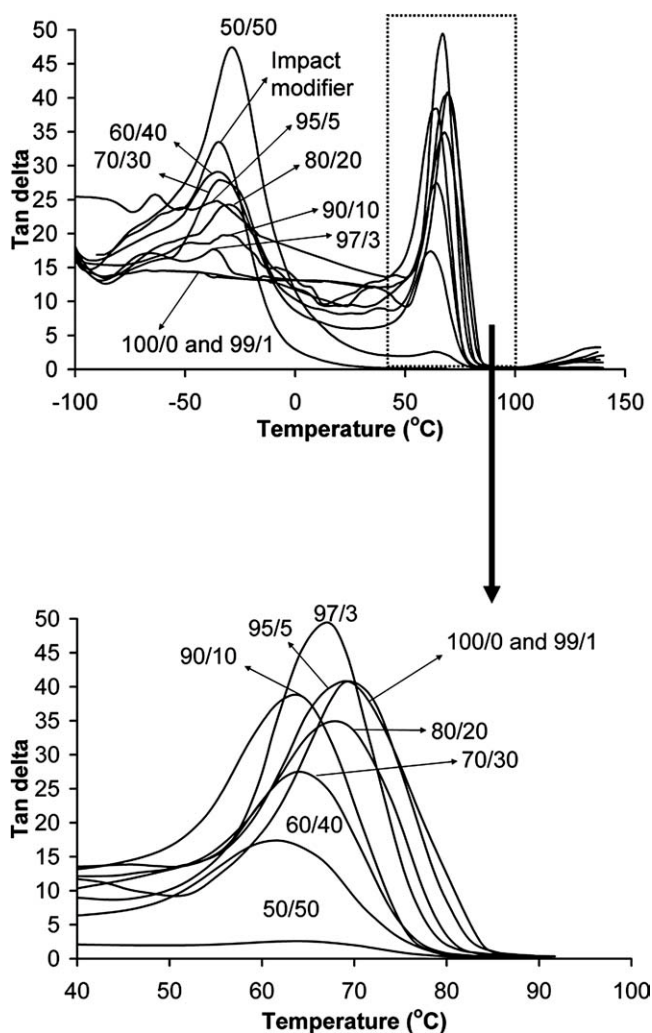**Figure 3** Tan delta curves of pure PLA, impact modifier and PLA/impact modifier blends.

Figure 3. While only one tan δ peak was observed for pure PLA and PLA/impact modifier blend with 1 wt % impact modifier, two distinct tan δ peaks were observed for other PLA/impact modifier blends suggesting that PLA and impact modifier phase-separated and formed immiscible blends when the impact modifier content was more than 1 wt %. The tan δ peak at the lower temperature was due to the glass transition of the impact modifier. Its magnitude as well as the corresponding glass transition temperature was observed to increase slightly with increasing impact modifier content. The latter is clear from Table II. As for the tan δ peak observed at the higher temperature, it can be associated to the glass transition temperature of PLA. This tan δ peak decreased in the magnitude and shifted to lower temperature with increasing impact modifier content (Fig. 3 and Table II). Such behaviors observed for both of the glass transition temperatures suggest that PLA and impact modifier are partially miscible and that there are some
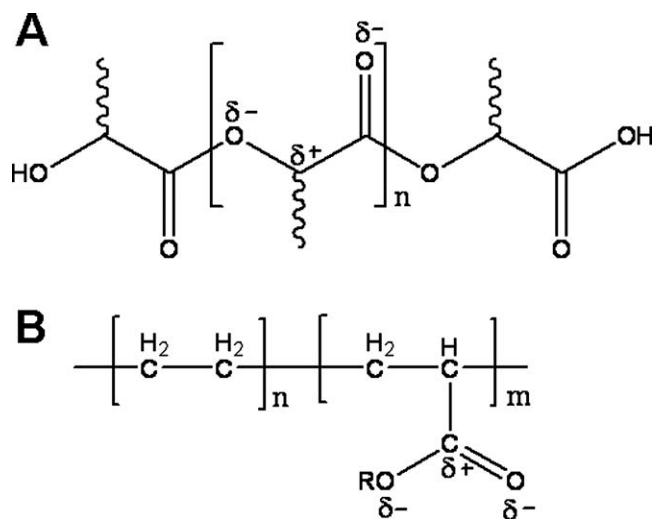
Figure 4 Ester polar groups of (A) PLA and (B) impact modifier.

interactions between PLA and impact modifier at the molecular level particularly when the impact modifier content was more than 1 wt %. These interactions refer to the reactions between the epoxy functional groups of the impact modifier and the carboxyl and hydroxyl end groups of the PLA. Other possible interaction is through the polar interactions between the ester groups of PLA and those of impact modifier. Figure 4 shows the ester polar groups of PLA and impact modifier.

Tensile properties

Figure 5 shows tensile stress-strain curves of PLA and PLA/impact modifier blends. Generally the stress-strain curves were shown to be very dependent on the composition of the blends. At low impact modifier content (1, 3, and 5 wt %), the PLA/impact modifier blends exhibited brittle fracture as the pure PLA. Well defined yields points were observed and
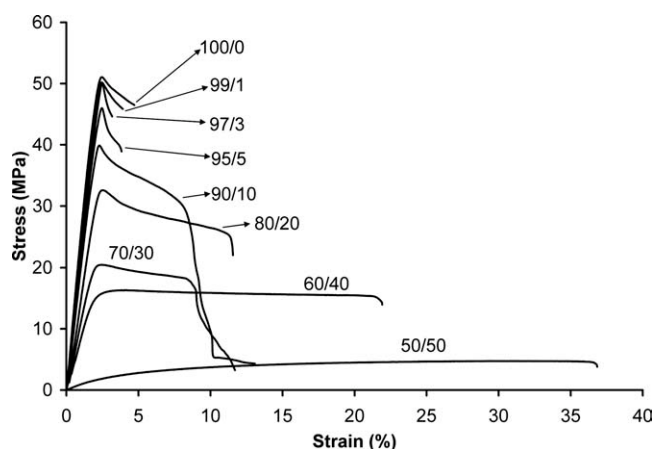

Figure 5 Tensile stress-strain curves of PLA and PLA/impact modifier blends.

Figure 6 Visualization of break behavior of the tensile test specimens of PLA/impact modifier blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the materials failed at low strain at break of 4.5, 4.0, 3.3, and 3.6%, respectively, for pure PLA and PLA with 1, 3, and 5 wt % impact modifier. Broadening of the yield peaks as well as more visually observable stress whitening in the test specimens (Fig. 6) were observed for PLA blends with 10, 20, 30, and 40 wt % impact modifier. Extensive stress whitening of these blends resulted in larger strain at break than the blends with lower impact modifier contents. A distinct yield peak was hardly observed for PLA with 50 wt % impact modifier and the stress-strain curve for the blend resembled that of rubbery materials like polycaprolactone (PCL). These results clearly suggest that the inherent brittle fracture behavior of PLA can be successfully improved with the addition of appropriate amounts of impact modifier.

The tensile properties of PLA and PLA/impact modifier blends are shown in Figure 7. The addition of low amount of impact modifiers, i.e., 1 and 3 wt % did not significantly affect the yield stress of PLA. Beyond 3 wt % impact modifier, the yield stress of PLA decreased dramatically with increasing impact modifier content. A decrease of 91% (Table III) of the yield stress from 51 (pure PLA) to 4 MPa was observed for the blend with 50 wt % impact modifier. The tensile modulus of PLA also decreased with increasing impact modifier content. It decreased by 97% when 50 wt % impact modifier was added to PLA. The decrease in the yield stress and the tensile modulus with increasing impact modifier content was expected and can be attributed to 1) the lower yield stress and tensile modulus of the impact modifier as compared to those of PLA, 2) the presence of impact modifier domains in PLA acting as stress concentrators, which results in yielding

at an overall stress lower than that of the pure PLA,[36] 3) the decrease of the actual volume of the stronger and stiffer PLA with the introduction of impact modifier which leads to a decrease in the effective load bearing phase (PLA) of the polymer blend[37] and 4) the lowering of the crystallinity of the blends in relation to pure PLA[38] as evident from Table I. A lower degree of crystallinity means higher content of free volume which leads to a decrease in stiffness. Both the yield stress and the tensile modulus of the PLA/impact modifier blends showed a linear variation with impact modifier content with high coefficient of determination (R-squared) values of 0.995 and 0.986, respectively.

The elongation at break of PLA slightly decreased with the addition of 1, 3, and 5 wt % impact modifier. At these low contents of impact modifier, all the applied stress were mainly bear by the matrix PLA resulting in brittle failure.[34] The low elongation at
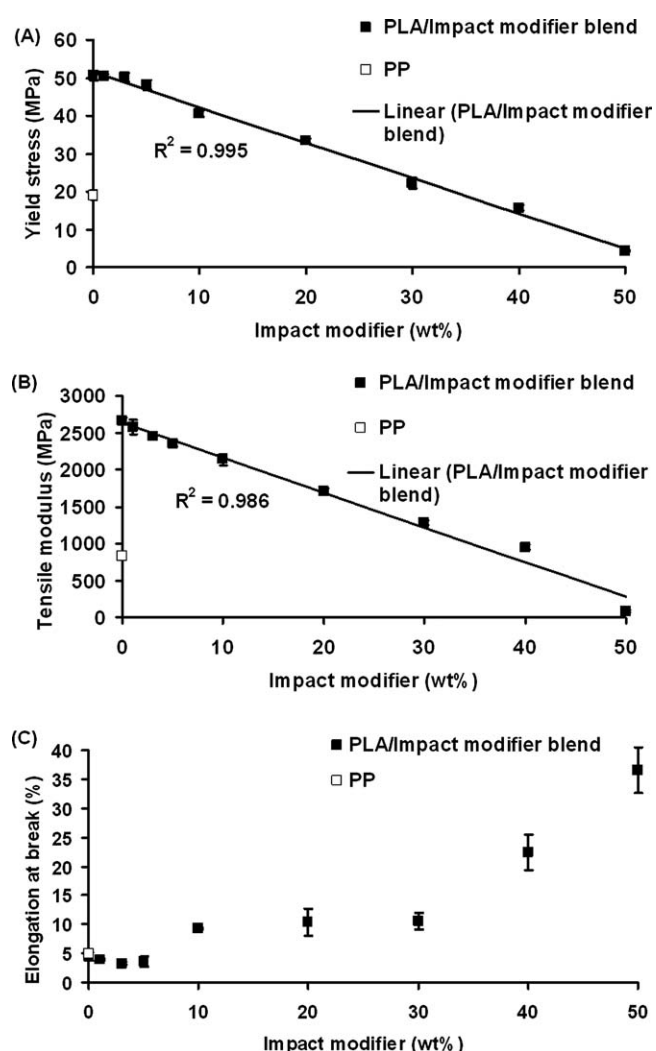

Figure 7 Tensile properties of PLA and PLA/impact modifier blends. (A) Yield stress; (B) tensile modulus; and (C) elongation at break.

TABLE III
Percent Decrease or Increase in the Mechanical Properties of PLA with the Addition of Impact Modifier[a]

Sample	Yield stress (MPa)	Tensile modulus (MPa)	Elongation at break (%)	Notched impact strength (kJ m^{-2})
99/1	−0.5[a]	−3.3[a]	−11.5[a, b]	0.7[a]
97/3	−1.0[a]	−7.8[b]	−28.0[b]	39.0[a, b]
95/5	−4.9[b]	−11.8[c]	−21.1[a, b]	75.5[b]
90/10	−20.0[c]	−19.9[d]	105.5[c]	274.8[c]
80/20	−34.1[d]	−36.0[e]	128.2[c]	695.8[d]
70/30	−56.3[e]	−51.9[f]	134.6[c]	314.5[c]
60/40	−69.0[f]	−64.4[g]	393.6[d]	186.7[e]
50/50	−91.2[g]	−96.8[h]	705.9[e]	878.7[f]

[a] Values are all in percentage. Values of the same letter shows no significant difference at alpha level = 0.05.

break of these PLA/impact modifier blends could also be attributed to the high degrees of crystallinity of these blends (Table I).[1,33] A significant increase in the elongation at break (105%) was observed at 10 wt % impact modifier, it then leveled off up to 30 wt % impact modifier. The elongation at break increased remarkably when 40 and 50 wt % impact modifier contents were added in PLA with improvements of 394 and 706%, respectively. The increase in the elongation at break can be attributed to the extensive shear whitening in the test specimens (Fig. 6) in addition to the low degrees of crystallinity of the blends (Table I) as compared to pure PLA.

Generally, PLA with up to 30 wt % impact modifier showed better tensile properties than impact copolymer polypropylene (PP). At 30 wt % impact modifier, PLA showed 16.7, 13.4 and 112.6% higher respectively, for yield stress, tensile modulus and elongation at break than those of PP. At 40 wt % impact modifier, although the blend still showed better tensile modulus and obviously higher elongation at break than PP, the yield stress, however, suffered a decreased of 17.1%. It can be suggested that the maximum amount of impact modifier to be incorporated inside PLA so as to produce a blend of better tensile properties than PP is 30 wt %.

Impact properties

Figure 8 shows the notched Izod impact strengths of PLA and PLA/impact modifier blends. A moderate improvement of the impact strength was observed with the addition of up to 5 wt % impact modifier. The impact strength was significantly increased from 3.6 kJ m^{-2} for the neat PLA to 13.6 and 28.9 kJ m^{-2}, respectively, for PLA with 10 and 20 wt % impact modifier. At 20 wt % impact modifier, a "partial break" was observed for the PLA/impact modifier blend test specimen. The impact strengths of the blends with 30 and 40 wt % impact modifier

were higher than that of the neat PLA. The values, however, were significantly lower than the value obtained for the blend with 20 wt % impact modifier. This can be explained by the low values of the yield stress and tensile modulus of PLA blends at high impact modifier content. If blends have a low modulus and low yield stress, the stress can not be transferred far from the crack tip. Thus, the crack propagates without a large deformation of the matrix component near the crack tip[39,40] resulting in low impact strength. Another possible reason is the presence of only less perfect crystals in these PLA/impact modifier blends as evident from the DSC thermograms (Fig. 1). Usually, imperfect or less perfect crystals containing cracks or microcracks are typical of a brittle matrix, whereas perfect crystals may contribute to the improved toughness.[41] At 50 wt % impact modifier, the PLA/impact modifier blend test specimen again showed a 'partial break' after the impact test. As compared to PP, PLA/impact modifier blends showed better impact strength when the impact modifier content was equal to and greater than 10 wt %. At 30 wt %
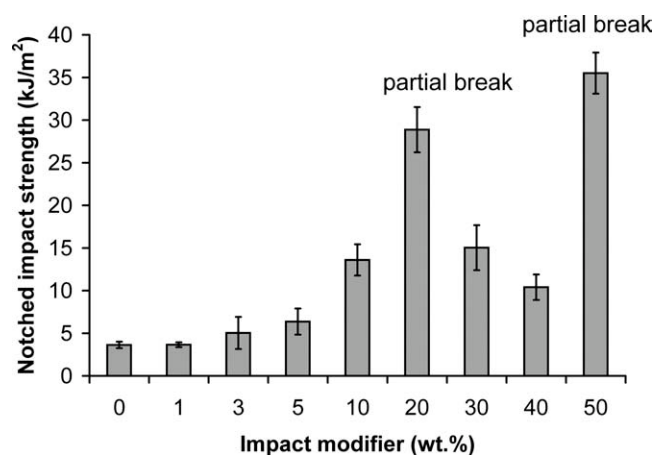

Figure 8 Notched impact strength of PLA and PLA/impact modifier blends. Notched impact strength for PP = 7.81 ± 1.50 kJ m^{-2}.
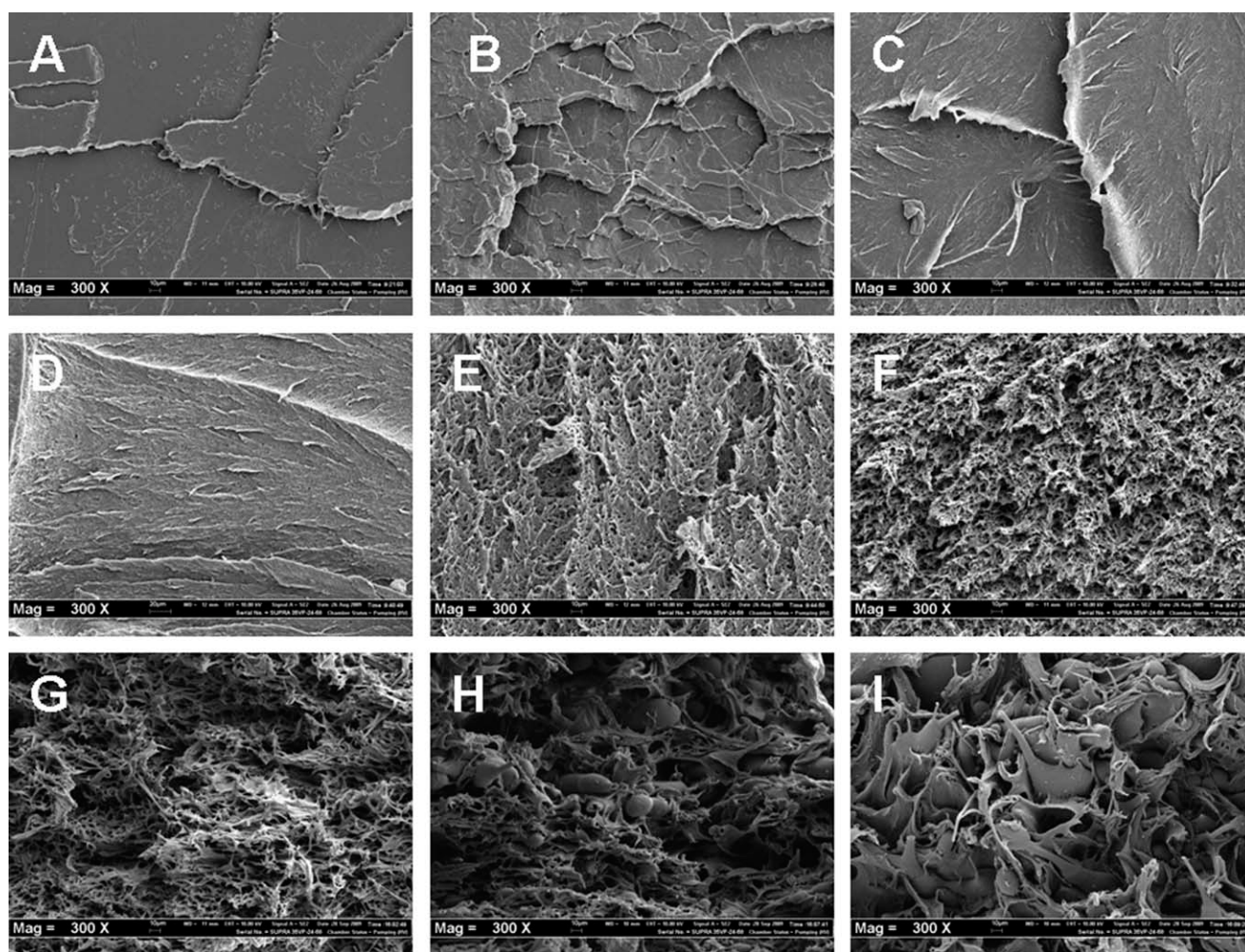
Figure 9 SEM Micrographs of tensile fractured surfaces of PLA and PLA blends with different impact modifier contents. (A) Neat PLA; (B) 1 wt %; (C) 2 wt %; (D) 5 wt %; (E) 10 wt %; (F) 20 wt %, (G) 30 wt %; (H) 40 wt %; (I) 50 wt % impact modifier.

impact modifier, the blend showed higher impact strength than PP by 92.6%.

SEM observation

Figure 9 shows SEM micrographs of tensile fractured surfaces of PLA and PLA/impact modifier blends. Brittle fracture surface with little plastic deformation or fine fibrils were observed on the fractured surface of PLA. In contrast, a large amount of plastically deformed material was observed on the fractured surfaces of PLA/impact modifier blends. The presence of plastic deformation in the form of matrix drawing or shear yielding due to rubber cavitations is believed to be responsible for the ductility of PLA/impact modifier blends. Plastic deformation became more apparent when the impact modifier content in the blends was equal to or more than 10 wt %. PLA with 20 wt % impact modifier

showed relatively the highest degree of plastic deformation or fibrillation of the PLA matrix. This may explain for the incomplete fracture of the blend after the impact test (Fig. 8).

PLA with 40 and 50 wt % impact modifier, however, showed different surface morphologies as compared to other PLA/impact modifier blends. PLA with 40 wt % impact modifier showed little sign of plastic deformation. Some rod-shape domains as well as large voids created due to pulled out of large impact modifier particles were observed on the fractured surface [Fig. 9(H)]. The formation of rod-shape domains and large impact modifier particles can be attributed to coalescent of small impact modifier particles during the melt-blending. Large impact modifier particles can facilitate fracture crack propagation by exfoliation at the interface between the PLA matrix and the impact modifier particles.[3] This can partially explain for the low impact strength of PLA with 40 wt % impact modifier (Fig. 8). Instead

of rubber particles or rod-shape domains, domains of continuous irregular shapes of the impact modifier were observed on the fractured surface of PLA with 50 wt % impact modifier [Fig. 9(I)]. This suggests that at this impact modifier content, the PLA/impact modifier blend formed cocontinuous structure. The dominant properties of a polymer blend are dictated by the continuous phase and properties of the continuous phase.[42] The properties of the blend, therefore, are determined not only by the properties of PLA but also by the properties of impact modifier. Extensive plastic deformation of the PLA and impact modifier phases was clear from Figure 9(I). This may explain for the 'partial break' of PLA with 50 wt % impact modifier after the impact test (Fig. 8).

Cavities resulted from debonding of impact modifier particles were also obvious from Figure 9(E–G). These cavities were enlarged in the stress direction along with shear yielding of PLA.

Toughening mechanism of PLA with the addition of impact modifier can be described as follows. In rubber-toughened polymeric materials, there exist two types of cavitations either formation of internal cavitations in the rubber domains when there is a strong interfacial bonding between the components or debonding cavitations at the interface when the tensile stress is higher than the interfacial bonding strength. Since impact modifier has different elastic properties compared to PLA, its particles act as stress concentrators under tensile stress. The stress concentration developed gives rise to high triaxial stress in the impact modifier particles. Because there was insufficient interfacial adhesion between impact modifier and PLA, interfacial debonding took place under this triaxial stress. The voids caused by debonding altered the stress state in PLA surrounding the voids, and triaxial tension was locally released and shear yielding was allowed. With the debonding progress, PLA strands between impact modifier particles deformed more easily to achieve the shear yielding. This toughening mechanism has been described for other systems.[5,6,35,38,42,43] Rubber cavitations via interfacial debonding and shear yielding induce energy dissipation mechanisms in PLA, which will retard crack initiation and propagation, leading to an improve impact strength of the brittle PLA as evident from Figure 8.

CONCLUSIONS

Blends of PLA and a commercially available impact modifier at different weight ratios were prepared and characterized. DSC results showed that the addition of impact modifier decreased the ability of PLA to crystallize and/or re-crystallize resulting in a decrease of degree of crystallinity of PLA and shifting of the cold crystallization temperature to higher temperatures with increasing impact modifier content. Two phase systems of PLA/impact modifier blends were confirmed by the DMA results. Although phase-separated, PLA and impact modifier are partially miscible as shifting of the glass transition temperatures of both components slightly towards each other were observed with increasing impact modifier content. The stress-strain curves showed that the brittle behavior of PLA changed to ductile failure with the addition of impact modifier. Yield stress and tensile modulus of PLA were decreased while elongation at break and notched impact strength increased with the incorporation of increasing amount of impact modifier. Morphological observation via SEM revealed that a debonding-initiated shear yielding mechanism was involved in the toughening of PLA/impact modifier blends. At 50 wt % impact modifier, both PLA and impact modifier formed continuous phases. In addition to shear yielding of PLA, extensive deformation of the impact modifier domains was observed on the fractured surface which accounts for the 'partial' break of the blend after the impact test. PLA with 30 wt % impact modifier showed comparable yield stress and tensile modulus and better elongation at break and impact strength (+90%) than those of PP.

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