

Green polymer blends compatibilized with biomass derived-agents

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Research Paper

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ABSTRACT

The effect of soybean lecithin (SOLE) and acrylated epoxidized soybean oil (AESO) as biomass-based compatibilizer agents was studied for the purpose of enhancing the compatibility of environmentally friendly thermoplastic/elastomeric blend of poly (lactic acid) (PLA) and synthetic rubber (PI). PI was melt mixed 25:75 into PLA with and without compatibilizer agents by a twin-screw extruder. The content of compatibilizer agents was kept at 0.5 and 2%, rrespectively. The compatibility of SOLE and AESO was investigated with thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), scanning electron microscopy (SEM) and tensile test. From the thermal degradation and morphologic analysis, it was observed that SOLE was more effective in improving compatibility of PLA/PI blend in comparison with AESO. The inclusion of 0.5% SOLE into the blend system led to increment in the thermal stability, approximately, 10°C. Furthermore, a reduction of the size of PI islands distributed homogenously in the PLA matrix with the help of SOLE was observed, indicating the enhancement of interfacial adhesion. In other words, partially compatibilization took place resulting in the minimization of the dispersed PI island size.

Keywords: Polymer blend, poly(lactic acid), *cis*-1,4-polyisoprene, soybean lecithin, acrylated-epoxidized soybean oil.

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INTRODUCTION

Research is focusing on the development of biomaterials and biodegradable materials, which are two of the most popular fields of material science, due to the increasing accumulation of plastic waste (Cheng et al., 2009; Amass et al., 1998). A huge number of polymers have been already synthesized for the production of environmental friendly materials. The utilization of biodegradable polymers offers several advantages over other polymers, such as reducing the dependence on fossil fuels and easy degradation. However, one of the major problems associated with the use of these materials is to have insufficient properties that do not respond to the requests of consumers in comparison with the non-biodegradable polymers (Imre and Pukanszky, 2013). To overcome these issues faced by academic and industrial researchers, expand the scope of the application of environmental-friendly materials and besides make them a desired material which corresponds to the expectation of producer and user, the polymer blending technique can be offered as a solution which decrease the disadvantages (Ibrahim and Kadum, 2010).

Poly(lactide) (PLA) is a member of biomass derivedpolymers, which belongs to the family of polyesters (Averous, 2008; Yokohara and Yamaguchi, 2008). In the last 10 years, PLA has gained attention in the packing, textiles and environmental applications because of being a polymer mostly obtained from renewable resources and its biodegradability (Yu et al., 2010), but has not yet received the attention it deserves. The fact is that the main reason is that there are many disadvantages though they exhibit several advantages (Xiao et al., 2012). One of the major disadvantages of PLA is its brittleness (Jun, 2000). Therefore, blending of PLA with other polymers, in particular other biodegradable polymers will decrease its brittleness and keep its biodegradability property. Rubbers can be utilized as a second phase polymer in a blend system to improve the toughness of brittle PLA. They behave as stress concentrators increasing the fracture energy absorption of brittle polymers and as a result, improve the toughness of the material (Bitinis et al., 2011).

Cis-1,4-polyisoprene (PI) is an elastic-biodegradable polymer that has the same formula as natural rubber (Bridgwater, 1942; Shah et al., 2013; Linos and Steinbuchel, 2001; Simpson, 2002). Due to its benefits that whet industrial researchers' appetite, PI has been widely used in the production of some everyday materials, such as paint, gloves, hoses, tires and toys. However, it is known that a thermoplastic/elastomeric polymer system is immiscible because of weak interactions between the 2011), components (Bitinis et al., therefore, compatibilization is necessary.

Recently, there has been growing interest in the use of plasticizers and compatibilizers that are eco-friendly. It would be reasonable to suppose that these agents for biomaterials should also be biodegradable (Vieira et al., 2011). Soybean oil is one of them, which has the potential to be utilized for the purpose of improving the quality of biomaterials. It is extracted from the seeds of the soybean and its double bounded structure gives the opportunity to be functionalized.

Acrylated-epoxidized soybean oil is one of the modified sovbean oil derivates that have hydrophilic hydroxyl groups in its chemical structure, although, it is a hydrophobic molecule (Lopez and Santiago, 2013). Another agent is lecithin, which is used for a wide variety of applications in food, paint, medical and pharmaceutical industries as emulsifier agent due to its two-tailed amphiphilic compound. It is commercially manufactured from egg yolk, soybean, or corn at low cost and thereby minimizes chemical pollution (Boye et al., 2010). In our previous article (Eksiler et al., 2017), we proposed biodegradable filmmade of polycaprolactone and synthetic rubber as a joining tape which is flexible, transparent and durable and can be used for agricultural applications. The blend was compatibilized with lecithin, thereafter, degradation test was conducted in soil. It was found that the addition of lecithin accelerates the degradation of the blend. In this regard, the addition of lecithin might also cause a quick degradation of PLA since the degradation of PLA takes years (Shogren et al., 2003). Until now, although there have been few publications of PLA/natural rubber blend in literature (Bitinis et al., 2011; Chumeka et al., 2013; Jaratrotkamjorn et al., 2011; Suksut and Deeprasertkul, 2011; Liu and Zhang, 2012; Tanrattanakul and Bunkaew, 2014), PLA/synthetic rubber blend has not been widely studied as much as PLA/natural rubber (Niaounakis, 2015; Kowalczyk, 2012; Eawwiboonthanakit et al., 2014). Furthermore, to the best of our knowledge, there has been no publication that investigates improvement of the incompatibility of PLA/synthetic rubber blend with a compatibilizer which is biodegradable

and non-reactive.

The objective of this study is to investigate the effect of SOLE and AESO compounds as compatibilizer on mechanical, thermal and morphological properties of the PI toughened PLA. The influence of compatibilizer content on the blend was also evaluated. Moreover, the characterization of the blends was carried out by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), scanning electron microscopy (SEM) and their mechanical properties were determined.

MATERIALS AND METHODS

Polylactic acid (PLA) was obtained in pellet form from Toyota Co. (Product code: U'zS-09, Aichi, Japan) [weight averaged molecular weight (M_w)=106,000]. The polyisoprene (PI) used in the present work was provided by Zeon Cooperation, Japan [(Mw=10 × 10⁵calculated by GPC). Soybean lecithin (SOLE) was supplied from Kanto Chemical Co. Inc. (Tokyo, Japan). Acrylated-epoxidized soybean oil (AESO) with monomethyl ether hydroquinone content of 4,000 ppm as inhibitor was purchased from Aldrich Company.

PLA/PI blends preparation

Blends containing SOLE or AESO were fed into the twinscrew extruder (IMC-1979, Imoto Machinery Co., Japan). The ratio between PLA and PI was 75:25 by weight. The compatibilizers were weighted according to parts per 100 parts of the blend. The rotation speed, temperature and residence time for melt mixing are controlled as 40 rpm, 190°C and 5 min, respectively. The films were prepared using a hydraulic hot-press (IMC-180C, Imoto Machinery Co., Japan) at 180°C for 10 min under a pressure of 30 MPa, and then cooled to room temperature. The thickness of the sheets was about 0.2 mm.

Characterization

Thermogravimetric analysis (TGA)

TGA was carried out using EXSTAR TG/DTA7000 (SII Nanotechnology Inc., Japan) with scan range from 30 to 550°C at a constant heating rate of 10°C /min and continuous nitrogen flow to determine the degradation behavior and thermal stability of PLA, PI and their blends.

Differential scanning calorimetry (DSC)

DSC of the samples were performed in an EXSTAR DSC6220 (SII Nanotechnology Inc., Japan). The samples were analyzed in a heat-cool-heat made with the rate of



Figure 1: TGA curves of neat PLA, PI, PLA/PI and compatibilized PLA/PI blends.

10°C min⁻¹. Temperature scan was performed in the range of -120 to 230°C.

Scanning electron microscopy (SEM)

The morphology of the blends was examined by a scanning electron microscope (JCM-6000, JEOL, Japan) using a backscattered electron imaging (SEM/BSE) at 10 kV. The blend films were broken liquid nitrogen. SEM micrographs were taken at 400x magnification.

Tensile testing

Tensile testing was carried out with a Compact tensile and compression tester (IMC-18E0, Imoto Machinery Co., Japan). The composite sheets were cut into strip samples ($40 \times 5 \times 0.2$ mm). Five samples for each blend composition were tested. The measurements were made at 10 mm/min cross-head speed in a room adjusted to 25° C.

RESULTS AND DISCUSSION

Thermal properties of neat PLA, neat PI and their blends including SOLE or AESO

In this study, 50:50 and 75:25 ratio of PLA/PI blends were

prepared to evaluate the mechanical, thermal and morphological properties of biodegradable compatibilized PLA/PI blend. Nevertheless, due to the unfavorable physical condition of 50:50 blend system, such as being sticky and PLA-PI phase separation seen even through naked eyes, 50:50 blend system was eliminated and 75:25 ratio of PLA/PI blend was used for the characterization. TGA was carried out for ascertaining the thermal degradation behaviors of PLA/PI blends with and without compatibilizer, neat PLA and PI (Figure 1). The neat PI was more thermally stable than the neat PLA, which the temperature at the level of 50% weight loss ($T_{d50\%}$) of PI was 382.1°C, whereas $T_{d50\%}$ of PLA was 364.0°C. From the curve of the PLA/PI blend without compatibilizer, it was obviously seen that the thermal stability of PLA/PI was lower than that of both neat PLA and neat PI due to the lack of compatibility, 353.6°C.

Furthermore, $T_{d50\%}$ of all the blends was compatibilized with AESO, ~355°C was similar to that of noncompatibilized PLA/PI, indicating that AESO did not remarkably improve the interactions among the blend components. In contrast, a significant improvement in the thermal stability of the blends including SOLE was observed. $T_{d50\%}$ of the PLA/PI/0.5% SOLE and /2% SOLE blends shifted to higher temperatures by means of SOLE and reached almost the same temperature at which 50% weight loss of neat PLA, ~365°C. This result shows that SOLE is more efficient to enhance the compatibility between PLA and PI than AESO because the thermal



Figure 2: (a) DSC curves of neat PLA, PI, PLA/PI and compatibilized PLA/PI blends during the cooling scan and (b) the second heating scan.

Table 1: The effect of compatibilizers on the transition temperature of PLA/PI blends.

Material	Cooling scan		2 nd Heating scan				
	T _{cc} (°C)	$\Delta H_{cc}(j/g)$	Tg (°C)	T _m (°C)	∆Hm(j/g)	Tc (°C)	ΔH _c (j/g)
PLA	97.40	4.58	61.33	175.77	57.40	94.73-158.82	30.60/6.86
PI	-	-	-63.34	-	-	-	-
PLA/PI	97.20	9.76	60.92/-64.98	174.43	44.50	94.95/158.23	14.60/5.65
PLA/PI/0.5%AESO	99.00	0.70	60.07/-72.22	174.57	41.60	98.28/158.08	22.70/6.03
PLA/PI/2%AESO	96.10	0.80	60.12/-62.52	174.55	43.50	95.14/157.62	24.00/6.29
PLA/PI/0.5%SOLE	95.80	6.65	60.10/-73.55	174.97	39.10	98.20/158.73	19.50/6.84
PLA/PI/2% SOLE	95.90	6.47	60.01/-73.20	175.10	38.90	101.65/158.61	14.30/4.76

stability is strongly influenced by the interaction between blend components (Lizymol and Thomas, 1993).

Figure 2 shows the results from DSC thermograms and a detailed evaluation of the DSC graph was listed in Table 1. From the cooling scan, small cold crystallization temperature (T_{cc}) peaks were found in the PLA/PI blends non-compatibilized and compatibilized with SOLE, apart from PLA/PI compatibilized with AESO. According to the heat of cold crystallization (ΔH_{cc}) values of the PLA/PI/SOLE, it can be suggested that the SOLE partially interacts with the blend components, whereas the addition of AESO to the blend system led to inhibition of PLA crystallization during the cooling scan. The reason why AESO inhibited the crystallization in the cooling scan is possibly that after the polymer blend melted, just before cooling scan started, phase separation of PLA and PI took place and AESO left the PLA. This finding supports the crystallization temperature (T_c) peaks of PLA/PI/AESO

blends recorded in the second heating.

When the T_c of non-compatibilized PLA/PI blend was compared with that of PLA/PI/AESO blends, it was found that the existence of AESO did not affect the crystallization of PLA since AESO was already removed from PLA when melted before the cooling scan. However, in the case of addition of SOLE into the blend, it slightly inhibited the crystallization in the second scan and acted as a compatibilizer, although two glass transition temperature $(T_{\rm g})$ peaks appeared, proving that the blend is still immiscible (El-Hadi, 2014). The findings earlier mentioned can be confirmed with the changes in the heat of fusion $(\Delta H_{\rm m})$ values of the blends. The presence of PI in the PLA led to an increment in the crystallization of PLA because amorphous PI caused a decrease in the mobility of the PLA molecular chains, thus, PLA/PI blend exhibited a higher $\Delta H_{\rm m}$ value according to the proportion of PLA in the blend, in comparison with neat PLA. As expected, from the $\Delta H_{\rm m}$



Figure 3: Tensile strength (A) and modulus, (B) graphs of PLA/PI, (a) PLA/PI, (b, d) compatibilized with AESO and (c, e) SOLE.

values of the blends, it was found that the addition of AESO did not provide notably changes, whereas the inclusion of SOLE caused a drop in the $\Delta H_{\rm m}$ values, indicating SOLE has better interaction than AESO between PLA and PI.

Tensile properties of neat PLA, neat PI and their blends including SOLE or AESO

Figure 3 shows the strength and modulus results obtained from tensile test depending on the compatibilizer and its content in the polymer blends. The evaluation of the tensile test of the non-compatibilized blend film exhibited that PLA/PI blend had a tensile strength of 25.49 MPa. It decreased with the addition of 0.5 and 2% AESO and, indicated there is no notable interaction among the blend components. This might be due to the phase separation of PLA and PI, as earlier mentioned in the DSC findings. On the other hand, the tensile strength of PLA/PI blends compatibilized with SOLE were higher than those of PLA/PI/AESO. However, the amount of SOLE limit in the PLA/PI blend was 0.5%. Increasing SOLE content up to 2% decreased tensile strength of the blend, which is 29.6% lower compared to the blend with 0.5% SOLE. It was also found that the trend of tensile strength graph is similar with the tensile modulus.

It can be concluded that SOLE as a compatibilizer helped PI to be distributed better in PLA, hence, the blend including SOLE gave better mechanical properties in comparison with the non- and compatibilized with AESO PLA/PI blends. In Figure 4, the stress-strain curves of the neat PLA, non-compatibilized and compatibilized PLA/PI blends were presented. Apparently, PLA is a hard and brittle polymer. When 25% PI was added into PLA, the resulting blend underwent extensive plastic deformation. In addition 0.5% SOLE into PLA/PI blend exhibited higher elastic modulus and modulus of toughness. From stressstrain curves of the samples, their toughness energy was calculated and evaluated. Toughness energy were found as follows: PLA/PI > PLA/PI/0.5% SOLE > PLA/PI/2% SOLE > PLA > PLA/PI/0.5% AESO> PLA/PI/2% AESO. PLA/PI blend displayed the topmost toughness from the stressstrain curve in the tensile test. The modulus of toughness value decreased with the increase in the addition of AESO to PLA/PI due to the immiscibility of the material.

Morphology of neat PLA, neat PI and their blends including SOLE or AESO

SEM micrographs of fractured cross sections of PLA/PI blends with and without compatibilizer taken in the backscattered electron mode (BSE) were depicted in Figure 4. SEM/BSE photos exhibited that PI particles dispersedly occurred as big islands in the PLA phase, indicating the poor interfacial interaction and strong incompatibility between PLA and PI from a sea-and-island morphology (Bitinis et al., 2011; Pongtanayut et al., 2013). In the case of the blend compatibilized with AESO, the compatibility of the blends in Figure 5b and d was not even as good as that of the non-compatibilized blend.

PLA/PI blend with 0.5 and 2% AESO led to the phase separation and obviously showed the worst morphology among all the samples, having the large sphere size of PI. On the contrary, the compatibilized blend with 0.5% SOLE (Figure 5c) indicated a finer dispersion of PI component in the PLA matrix attributed to the decrease in the PI particle



Figure 4: Stress-strain curves of PLA, non-compatibilized and compatibilized PLA/PI blends.



Figure 5: SEM/BSE micrographs for fracture surfaces of PLA/PI (a), PLA/PI compatibilized with 0.5% AESO, (b) 0.5% SOLE, (c) 2% and (d) AESO.

size.

It is a widely-held view that the presence of compatibilizer stabilizes the blend morphology by

suppression of coalescence and decrement of interfacial tension (Chen et al., 2014). This result supports the finding of the TGA, DSC and tensile studies earlier discussed. In

addition, the inclusion of more SOLE (2%) into the blend negatively affected the blend morphology. As a result, the size of PI islands increased, and besides, homogenous dispersion turned into heterogeneous. Therefore, it could be concluded that the amount of compatibilizer utilized has an optimal limitation (Si et al., 2008), 0.5%.

Conclusion

A biodegradable blend made from PLA and PI was prepared through melt blending. In order to improve miscibility of the blend, SOLE and AESO, which are biomass-based compounds, were added to the blend system. As a non-reactive compatibilizer for PLA/PI blend, SOLE was more effective than AESO. Thermal degradation analysis demonstrated that existence of SOLE led to a remarkable increase in the thermal stability of PLA/PI blend when compared with non-compatibilized, ~10°C. In contrast, the thermal stability of PLA/PI did not change in the presence of AESO. From the results of DSC and SEM analysis, it was found that the blends including 0.5% SOLE exhibited the best morphology among all the blends. The size of PI islands in the PLA matrix decreased and the PI islands were homogenously distributed as compared with others, revealing the enhancement of interfacial adhesion. Furthermore, the addition of compatibilizers represented different effects on tensile strength and modulus of the blends, in order of 0.5% SOLE > 2% SOLE > and 0.5% AESO > 2% AESO.

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