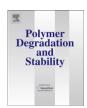
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Compatibilizing effects for improving mechanical properties of biodegradable poly (lactic acid) and polycarbonate blends

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ABSTRACT

Mechanical, morphological and rheological properties of polycarbonate (PC) and poly (lactic acid) (PLA) blends with compatibilizers have been investigated. Three types of compatibilizers were used: poly (styrene-g-acrylonitrile)-maleic anhydride (SAN-g-MAH), poly(ethylene-co-octene) rubber-maleic anhydride (EOR-MAH) and poly(ethylene-co-glycidyl methacrylate) (EGMA). The maximum value of the mechanical properties such as impact and tensile strengths of the PC/PLA (70/30, wt%) blend before or after hydrolysis was observed when the SAN-g-MAH was used as a compatibilizer at the amount of 5 phr. From the interfacial tension between PC and PLA which was determined from the weighted relaxation spectra using Palierne emulsion model, minimum value of interfacial tension (0.08 mN/m) was observed when the SAN-g-MAH (5 phr) was used. From the morphological studies of the PC/PLA (70/30) blends, the PLA droplet size showed minimum (0.19 μm) at the 5.0 phr SAN-g-MAH. From the results of mechanical, morphological and rheological properties of the PC/PLA (70/30) blend, it is suggested that the SAN-g-MAH is the most effective compatibilizer to improve the mechanical strength of the PC/PLA (70/30) blends among the compatibilizers used in this study, especially at the amount of 5 phr.

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1. Introduction

Poly (lactic acid) (PLA) is a promising polymer which is aliphatic polyester with high biodegradability and good mechanical properties such as tensile strength for industrial applications [1,2,3,4,5]. However, PLA has been limited for wide application because of brittleness and low heat distortion temperature. Polymer blending is efficient and economic method to tailor new materials with an advantageous combination of end-use properties [6,7].

Blends of PLA with a large numbers of polymers or fillers have been studied, such as polystyrene [8], poly(ϵ -caprolactone) [9,10], polyethylene [11,12], polypropylene [13,14], polypropylene carbonate [15], poly(ethylene-co-glycidyl methacrylate) [16], poly(acrylonitrile-butadiene-styrene) [17], poly(butylenes adipate-co-terephthalate) [18,19,20], poly(vinyl acetate) [21,22], poly(methyl methacrylate) [23], poly(ethylene glycol) [24], poly(aspartic acid-co-lactide) [25], starch [26,27,28] and organoclay [29,30]. However most of the blends are immiscible, adhesion between the two polymers is weak due to

high interfacial tension and weak entanglements. Interfacial tension is important to predict the mechanical properties of polymer blends.

Recently, blends of biodegradable PLA and engineering plastics such as PC are of interest in industrial application such as mobile phones. Therefore, the blends require high mechanical strength as well as biodegradability because of wastes after use. To improve mechanical strength or interfacial adhesion of the blends, compatibilizers are used to control the morphology of the blends. However, studies of PC and PLA blends are difficult to find, even though the PC/ PLA blend is an important material in industrial field. Compatibilization is often carried out to reduce the size of the dispersion phase and/or to stabilize the morphology of the blends. This technique can favor a fine dispersion by lowering the interfacial tension, stabilizing the morphology by reducing coalescence and improving the interfacial adhesion between phases [31,32]. In fact, the studies of the rheological and morphological properties of polymer blends have been carried out not only theoretically but experimentally over the last decades [33,34,35,36,37,38,39,40,41,42,43]. In the studies by Ho et al., they reported that the maleic anhydride reacts with the PLA in the presence of 4-dimethylaminopyridine [43].

In this study, polycarbonate (PC) and poly(lactic acid) (PLA) blend with three different compatibilizers such as poly(styrene-co-acrylonitrile)-g-maleic anhydride (SAN-g-MAH), poly(ethylene-co-octene)

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rubber-maleic anhydride (EOR-MAH) and poly(ethylene-co-glycidyl methacrylate) (EGMA) were investigated. The maleic anhydride which contains carbonyl group is highly polar, therefore, the MAH will interact with the polar ester group in PLA when they are blended. Also, SAN is known to be partially miscible with the PC [44]. Therefore, it is expected that compatibilizers used in this study would increase compatibility between PC and PLA. The effects of compatibilizer types and content on the mechanical, morphological and rheological properties of PC/PLA (70/30) blend were investigated. Also, the effect of compatibilizers on the degradation properties of the blends was evaluated through the hydrolysis test of the PC/PLA (70/30) blends. Interfacial tension between PC and PLA has been determined from the weighted relaxation spectra using Palierne emulsion model, and the values of interfacial tension of the blend are correlated with the degree of compatibility of the PC/PLA (70/30) blend.

2. Experimentental

2.1. Materials

The polymers used in this study were obtained from commercial sources. The PLA was supplied by NatureWorks Co. (Blair, Neb., USA). The PC was supplied from LG-Dow Polycarbonate Ltd. under the trade name of PC 300-15. The characteristics and sources of the polymer samples used in this study are shown in Table 1. The SAN-g-MAH was supplied by LG Chem. Ltd., and the maleic anhydride (MAH) content was 0.5 wt%. The EOR-MAH (Fusabond® N MN493D) was supplied by Dupont Co., and MAH content of EOR-MAH was 0.5 wt%. The EGMA was supplied by Sumitomo Chemical Co. Ltd., and glycidyl methacrylate (GMA) content was 12 wt%.

2.2. Blend preparations

Blends of PC/PLA were prepared in 70/30 weight percent. Concentrations of compatibilizers (SAN-g-MAH, EOR-MAH and EGMA) were ranged from 0 to 7 phr (parts per hundred resin by weight). The PC and PLA were dried in a vacuum oven (<1 mmHg) at 80 °C for 24 h before use. The PC/PLA blends were prepared via melt processing with a Leistritz 27 co-rotating twin-screw extruder (D = 27 mm, L/D = 40) with twelve zones of temperatures, ranging from 240 to 260 °C along the barrel of the extruder. The screw speed of the extruder was set at 70 rpm. Melt processing time from inlet to outlet was about 10 min.

2.3. Mechanical properties

The impact strength of PC/PLA blends was measured by notched Izod impact strength tester (Toyoseiki DG-IB2). The impact test was performed according to the ASTM D-256. The tensile strength and flexural strength of the PC/PLA blends were investigated under the ambient condition using a universal testing machine (Instron 4467). Tensile strength test was performed according to the ASTM

Table 1Characteristics of polymers used in this study.

Sample	M _n ^a (g/mol)	M _w ^a (g/mol)	MWD ^a	Tg ^b (°C)	T _m ^b (°C)	Tensile Strength ^c (kg _f /cm ²)	Impact Strength ^d (kg _f cm/cm)
PC	14,000	38,700	2.76	151		610	87.0
PLA	82,000	159,700	1.95	69	169	770	2.6

- ^a Measured by GPC using tetrahydrofuran as eluent.
- ^b Measured by DSC at a heating rate of 10 °C/min.
- $^{\rm c}$ Measured by UTM according to ASTM D-638.
- ^d Measured by Izod notched impact tester according to ASTM D-256.

D-638 and flexural strength test was performed according to the ASTM D-790. For all of the above mechanical tests, 7 specimens were measured and averaged.

2.4. Morphology

The morphology of the cross-section of the extrudate was analyzed by scanning electron microscopy (SEM) in a Hitachi S-4300 microscope at 15 kV accelerating voltage after Pt coating. The samples were fractured with the cryogenic condition. For the calculation of average size of the dispersed phase, image analysis software (Image J) and the Saltikov's correction [45] was used to determine the cell size of the sample.

2.5. Hydrolysis

The hydrolysis test was performed in double-distilled water at $85\,^{\circ}\text{C}$ for 30 days in closed glass bottles. Samples were taken out every 5 days and dried in the vacuum oven at room temperature for 24 h. The dried samples were weighed to measure the weight loss and tested for changes in their mechanical and morphological properties.

2.6. Rheological measurements

Rheological tests of the blends were carried out at 260 °C on the Advanced Rheometric Expansion System (ARES) with a 25 mm parallel plate arrangement. The pellets were pre-dried at 80 °C in a vacuum oven for 12 h. The rheometer oven was purged with dry nitrogen during measurement to avoid degradation. A frequency range of 0.01–100 rad/s and a strain of 8% were applied during the measurement. A strain sweep was carried out to determine the strain limit for the linear viscoelastic response range. Samples for rheological tests were obtained by compression molding. The zero-shear viscosity of the individual phases necessary to calculate the interfacial tension was determined using Elise's model [46], which was fitted to the curve Eta* (Pa s) versus frequency (rad/s) obtained from dynamic frequency sweeps tests. The weighted relaxation spectra were calculated using a non-linear regression regularization method (NLREG) developed by Honerkamp and Weese [40].

3. Results and discussion

3.1. Mechanical properties

The impact strength, tensile strength and flexural strength of the PC/PLA (70/30) blends with the type of compatibilizers are shown in Figs. 1–3, respectively. In order to investigate which compatibilizer is the most effective in improving mechanical properties of the PC/PLA blends, the compatibilizers such as SAN-g-MAH, EOR-MAH or EGMA have been added in the PC/PLA blends. For the SAN-g-MAH from Figs. 1–3, it is observed that the impact strength, tensile strength and flexural strength of the PC/PLA (70/30) blends show maximum when the SAN-g-MAH is added in the amount of 5 phr, respectively.

For the EOR-MAH and EGMA from Fig. 1, the impact strength of the PC/PLA (70/30) blends increases when the compatibilizer content is at 1 phr, then, the impact strength decreases as the compatibilizer content is increased. For the EOR-MAH and EGMA from Figs. 2 and 3, it is observed that the tensile and flexural strengths of the PC/PLA (70/30) blends increases when the compatibilizers are added up to 2 phr, then, the tensile strength decreases with the increasing compatibilizer content, respectively.

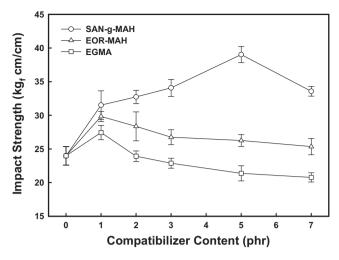


Fig. 1. Impact strength of the PC/PLA (70/30) blends with the type of compatibilizer: (\bigcirc) SAN-g-MAH; (\triangle) EOR-MAH; (\square) EGMA.

3.2. Morphology

Mechanical and rheological properties of polymer blends are closely related to the particle size of the dispersed phase and interfacial tension between the two phases. Fig. 4(a)-(f) shows SEM images of the cryogenically fractured surfaces of the PC/PLA (70/30) blends with the SAN-g-MAH content from 0, 1, 2, 3, 5 to 7 phr, respectively. From Fig. 4(a)-(f), the particle size of the PLA in the blends decreases with the increase of SAN-g-MAH content, and shows minimum when the SAN-g-MAH is added in the amount of 5 phr. Table 2 shows the number-average droplet radius (R_n) of the dispersed PLA which are 1.42, 1.32, 0.42, 0.34, 0.19 and 0.21 μ m with the SAN-g-MAH content of 0, 1, 2, 3, 5 and 7 phr, respectively. Table 2 also shows the volume-average droplet radius (R_v) of the particles of the PC/PLA blends. R_n and R_v can be written as Eqs. (1) and (2), respectively [38]:

$$R_n = \sum n_i R_i / \sum n_i \tag{1}$$

$$R_{\nu} = \sum n_i R_i^4 / \sum n_i R_i^3 \tag{2}$$

where n_i is the number of particle and R_i is the radius of particle in the blends. From Table 2, it can be seen that the size of the

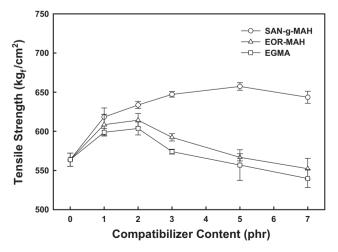


Fig. 2. Tensile strength of the PC/PLA (70/30) blends with the type of compatibilizer: (\bigcirc) SAN-g-MAH; (\triangle) EOR-MAH; (\square) EGMA.

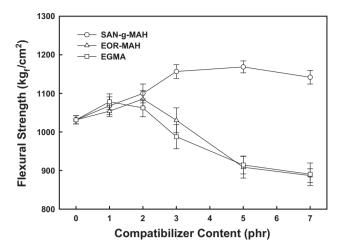


Fig. 3. Flexural strength of the PC/PLA (70/30) blends with the type of compatibilizer: (\bigcirc) SAN-g-MAH; (\triangle) EOR-MAH; (\square) EGMA.

dispersed phase of PC/PLA (70/30) blends compatibilized with the SAN-g-MAH decreases most significantly when the SAN-g-MAH content is at 5 phr. This result is consistent with the results of mechanical properties of the PC/PLA (70/30) blends which is that the maximum mechanical strength is observed when the SAN-g-MAH is added in the amount of 5 phr. Therefore, the decrease in particle size of the blends suggests the increase of the compatibility between the PC and PLA components.

Fig. 5(a)—(c) shows the morphology of the PC/PLA (70/30) blends with the three different compatibilizers such as SAN-g-MAH, EOR-MAH and EGMA, respectively. The compatibilizer content was set at 5 phr. From Fig. 5, the PLA droplet in the PC/PLA (70/30) blend with the SAN-g-MAH shows uniform and the droplet size is the smallest among the samples. From Fig. 5(a)—(c), the number-average droplet radius (R_n) of the dispersed PLA is observed to be 0.19, 1.03 and 1.93 μ m (Table 2), respectively. From this result, it is suggested that the SAN-g-MAH is more efficient compatibilizer than the EOR-MAH or EGMA for the PC/PLA blend. This result is consistent with the results of the mechanical properties of the PC/PLA (70/30) blends shown in Figs. 1—3.

3.3. Hydrolysis

Blending of biodegradable polymers such as PLA may cause gradual decomposition of petroleum based polymers such as PC and the phenomenon is named biodisintegration. When PLA reacts with water, it is converted to lactic acid, and the lactic acid is biodegraded by microbes. Characteristics of PLA biodegradation can be investigated by studying hydrolysis because biodegradation of PLA may include the hydrolysis reaction [14]. In this paper, the biodegradation was observed by Eq. (3), measuring the ratio of weight loss to the initial weight of the sample.

Weight loss (%) =
$$\frac{(W_0 - W_1)}{W_0} \times 100$$
 (3)

where W_0 and W_1 are the weights of the samples before and after the hydrolysis test, respectively.

Fig. 6 shows weight loss of the PC/PLA (70/30) blends containing different types of compatibilizers after hydrolysis. From Fig. 6, it is observed that weight loss of the blends with or without compatibilizer increases continuously with the increase of hydrolysis time up to 30 days. PC/PLA blend with 5 phr of SAN-g-MAH shows the lowest weight loss after hydrolysis compared the blends with EOR-MAH and EGMA. From Fig. 6, it shows that degradation rate of the

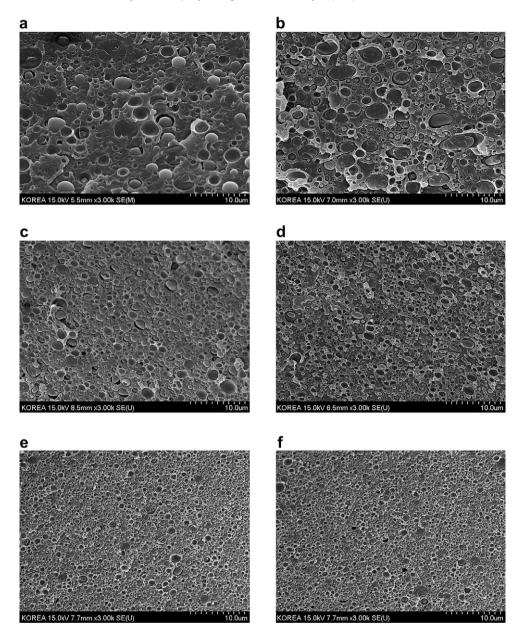


Fig. 4. Scanning electron micrographs of the PC/PLA (70/30) blends with the SAN-g-MAH content: (a) 0 phr; (b) 1 phr; (c) 2 phr; (d) 3 phr; (e) 5 phr; (f) 7 phr.

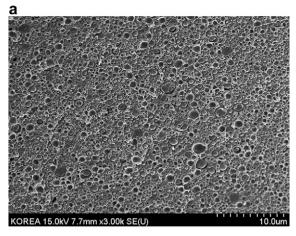
Table 2 Average particle radius and particle polydispersities of the PC/PLA (70/30) blends with Compatibilizer.

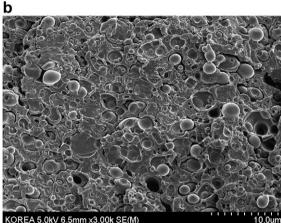
Blend composition	Compatibilizer	Content (phr)	R _n a (μm)	R _ν ^b (μm)	R_{ν}/R_n
PC/PLA	SAN-g-MAH	0	1.42	1.53	1.08
(70/30)		1	1.32	1.61	1.22
		2	0.42	0.64	1.52
		3	0.34	0.56	1.65
		5	0.19	0.26	1.37
		7	0.21	0.30	1.43
	EOR-MAH	5	1.03	1.28	1.24
	EGMA	5	1.93	2.27	1.18

^a $R_n = \sum n_i R_i / \sum n_i$ (n_i : the number of particles, R_i : the radius of particles). ^b $R_v = \sum n_i R_i^4 / \sum n_i R_i^3$.

PC/PLA (70/30) blend with SAN-g-MAH (5 phr) is slower than the blends without compatibilizer or adding other compatibilizers such as EOR-MAH and EGMA, because degree of compatibility between PC and PLA is improved by adding SAN-g-MAH as we have seen in Figs. 1-3.

The impact and tensile strengths of the PC/PLA (70/30) blends after hydrolysis for 30 days are shown in Figs. 7 and 8, respectively. For the PC/PLA (70/30) blend with 5 phr of SAN-g-MAH, the impact strength decreased up to 17% after 5 days, while the impact strength of the blend without compatibilizer decreased steeply up to 75%. The tensile strength of the PC/PLA (70/30) blend which shows in Fig. 8 indicates a similar tendency to the impact strength of the PC/PLA (70/30) blend shown in Fig. 7. An important thing to point out is that the values of impact and tensile strengths of the PC/PLA (70/30) blends with and without compatibilizers do not change significantly after 10 days of hydrolysis time. However, the weight loss of the blends increased steadily with the hydrolysis time (Fig. 6). This result may suggest that mechanical properties of





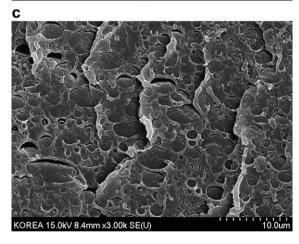


Fig. 5. Scanninig electron micrographs of the PC/PLA (70/30) blends with the 5 phr of compatibilizer: (a) SAN-g-MAH; (b) EOR-MAH; (c) EGMA.

the PLA already lose its property mostly when the hydrolysis time is 10 days in such a hydrolysis condition.

Fig. 9(a)—(b) shows SEM images of the fractured surface of the PC/PLA (70/30) blends without and with 5 phr of SAN-g-MAH after hydrolysis for 10 days, respectively. After hydrolysis test for 10 days, fractured surface of the blends underwent degradation which increased the formation of cavities, rough surface with large holes and increased droplet radius especially in the PC/PLA blend without compatibilizer. For the PC/PLA blend without compatibilizer (Fig. 9 (a)), surface revealed erosion and more cavities and holes than that of PC/PLA blend with 5 phr of SAN-g-MAH (Fig. 9(b)). From the

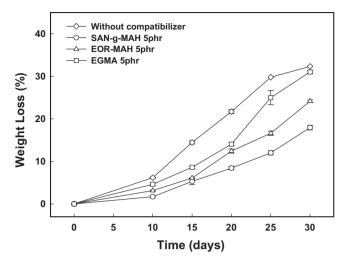


Fig. 6. Weight loss of the PC/PLA (70/30) blends after hydrolysis for 30 days: (\diamondsuit) without compatibilizer; (\bigcirc) SAN-g-MAH (5 phr); (\triangle) EOR-MAH (5 phr); (\Box) EGMA (5 phr).

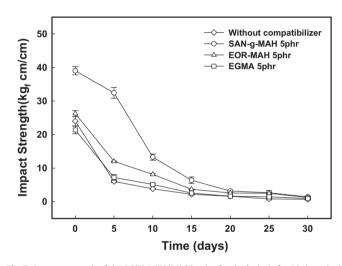


Fig. 7. Impact strength of the PC/PLA (70/30) blends after hydrolysis for 30 days; (\diamondsuit) without compatibilizer; (\bigcirc) SAN-g-MAH (5 phr); (\triangle) EOR-MAH (5 phr); (\square) EGMA (5 phr).

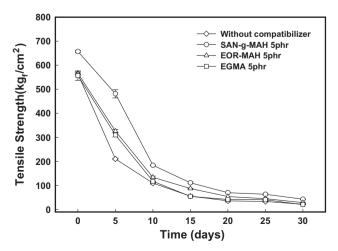
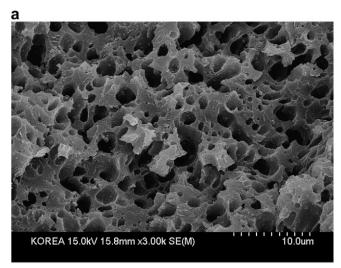


Fig. 8. Tensile strength of the PC/PLA (70/30) blends after hydrolysis for 30 days: (\diamondsuit) without compatibilizer; (\bigcirc) SAN-g-MAH (5 phr); (\triangle) EOR-MAH (5 phr); (\square) EGMA (5 phr).



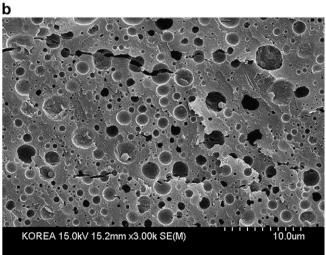


Fig. 9. Scanninig electron micrographs of the PC/PLA (70/30) blends after hydrolysis for 10 days: (a) without compatibilizer; (b) SAN-g-MAH (5 phr).

results of mechanical properties and morphology of the PC/PLA (70/30) blends after hdrolysis, it is suggested that SAN-g-MAH (5 phr) acts as a good compatibilizer for the PC/PLA blend, therefore, the rate of degradation of the PC/PLA blend with the SAN-g-MAH is slower than the blends with the EOR-MAH or EGMA.

3.4. Rheology

Fig. 10 shows complex viscosity of the PC/PLA (70/30) blends with the SAN-g-MAH content from 1 to 7 phr. From Fig. 10, when the SAN-g-MAH content is 5 and 7 phr, complex viscosity of the blends compatibilized with the SAN-g-MAH shows appreciably higher compared the PC/PLA (70/30) blends without adding compatibilizer. At the frequency of 1.0 rad/s, the complex viscosity of the blends is observed to be 940, 882, 977, 909, 1029 and 1014 Pa s when the SAN-g-MAH content is 0, 1, 2, 3, 5 and 7 phr, respectively. The viscosity of the blends with 5 phr SAN-g-MAH appears to be the highest value among the samples. It is known that the increased viscosities of the blends suggest the increased compatibility between the dispersed and continuous phases.

As we have seen in Fig. 4, when the SAN-g-MAH content is 5 phr, the number-average droplet radius (R_n) of the dispersed PLA is found to be 0.19 μ m which is the smallest value among the samples.

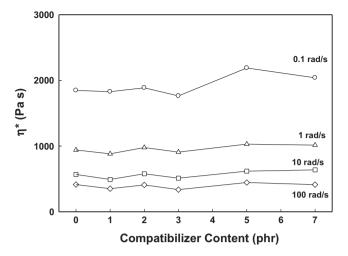


Fig. 10. Complex viscosity of the PC/PLA (70/30) blends with the SAN-g-MAH content: (\bigcirc) 0 ph; (\triangle) 1 phr; (\bigcirc) 2 phr; (\bigtriangledown) 3 phr; (\diamondsuit) 5 phr; (\bigcirc) 7 phr.

The decrease in particle size is maybe due to the increased compatibility between the two components, and this result is consistent with the result of complex viscosity of the PC/PLA (70/30) bends. From the results of Figs. 4 and 10, it is suggested that the SAN-g-MAH acts most effectively among the compatibilizers used in this study for the PC/PLA (70/30) blends, especially the SAN-g-MAH is added 5 phr.

3.5. Interfacial tension of PC/PLA blends

One of the most striking properties of emulsions is that particles change shapes under a shear stress. The balance between the two types of forces exerted on the particles, viscous forces and Laplace pressure originating from the interfacial tension, dictates their equilibrium form. The process during which a deformed particle is regaining its spherical form is called the form relaxation process. This process has characteristic relaxation time (τ_1), the form relaxation time. Gramespacher et al. [41] observed that the relaxation spectrum of the blend is combination of three peaks. Two of them are related to the relaxation time of each of the blend components. The remaining peak can be related to the form relaxation time (τ_1) due to the relaxation of the interface between the two components.

Compatibility of the polymer blends can be investigated from the interfacial tension of the two components. To get the interfacial tension of the PC/PLA (70/30) blends, we have used Palierne emulsion model [35] shown in Eq. (4):

$$\tau_1 \, = \, \frac{R_{\nu} \eta_m}{4\alpha} \frac{(19 K + 16)(2 K + 3 - 2 \phi(K-1))}{10(K+1) - 2 \phi(5 K + 2)} \tag{4}$$

where $K = \eta_d/\eta_m$ is the viscosity ratio between the dispersed phase (η_d) and the matrix (η_m) , α the interfacial tension between the components of the blend, φ the volume fraction of the dispersed phase and R_v the radius of the monodispersed droplets. In addition, for each blend studied here, the polydispersity (R_v/R_n) of the inclusions does not exceed 2.0 as we can see in Table 2. This condition is essential if one wants to use the blend viscoelastic data to determine the interfacial tension between its components.

In Table 3, the effect of compatibilizer addition on the interfacial tension between the PC and PLA was evaluated using the weighted relaxation spectra (τ H(τ)) of the PC/PLA (70/30) blends compatibilized with SAN-g-MAH, EOR-MAH and EGMA from a non-linear regression regularization method (NLREG) developed by Honerkamp

Table 3 Form relaxation time (τ_1) and interfacial tension (α) of the PC/PLA (70/30) blends with different types of compatibilizers and concentrations.

Compatibilizer	Content (phr)	τ ₁ (sec)	α ^a (mN/m)
SAN-g-MAH	0	3.00	3.34
	1	4.94	2.14
	2	13.4	0.31
	3	13.4	0.27
	5	20.2	0.08
	7	13.4	0.15
EOR-MAH	5	8.15	1.03
EGMA	5	8.15	1.82

^a α was calculated from the Palierne emulsion model.

and Weese [40]. To get the weighted relaxation spectra of the PC/PLA blends, Eqs. (5) and (6) are introduced, which is related to the experimental values of storage modulus (G') and loss modulus (G''), respectively. The G' and G'' were measured using ARES in this study [39,47]:

$$G'(\omega) = \int_{-\infty}^{\infty} \left[H(\tau)\omega^2 \tau^2 / \left(1 + \omega^2 \tau^2 \right) \right] d(\ln \tau)$$
 (5)

$$G''(\omega) = \int_{-\infty}^{\infty} \left[H(\tau)\omega\tau / \left(1 + \omega^2 \tau^2 \right) \right] d(\ln \tau)$$
 (6)

where ω is the frequency and τ is the relaxation time.

Fig. 11 shows the weighted relaxation spectra of PC, PLA and PC/PLA (70/30) uncompatibilized blend calculated directly from storage modulus raw data. The mathematical method is available in the ARES RSIOrche600 software package from Rheometrics. It can be seen from Fig. 11 that three peaks are identified from the weighted relaxation spectrum of the PC/PLA (70/30) blend without adding compatibilizer (SAN-g-MAH). The first relaxation spectrum peak is related to the PC component and the second relaxation spectrum peak corresponds to the PLA component. The value of the relaxation time (3.1 s) corresponding to the remaining peak is therefore associated to the form relaxation time due to the relaxation of the interface between the PC and PLA blend.

Fig. 12 shows the weighted relaxation spectrum of the PC/PLA (70/30) blend with the SAN-g-MAH $(5~\rm phr)$. When the SAN-g-MAH

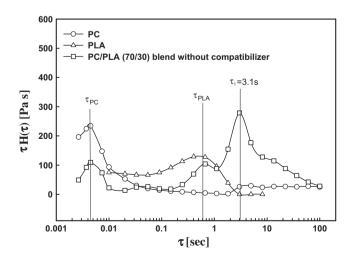


Fig. 11. Weighted relaxation spectrum of the PC, PLA and PC/PLA (70/30) blend without compatibilizer: (\bigcirc) PC; (\triangle) PLA; (\square) PC/PLA (70/30) blend without compatibilizer.

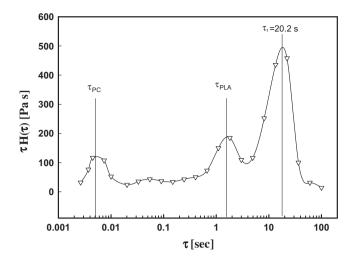


Fig. 12. Weighted relaxation spectrum of the PC/PLA (70/30) blend with the SAN-g-MAH (5 phr).

(5 phr) is added to the PC/PLA (70/30) blend, the third peak which represents the form relaxation time of the interface between the PC and PLA is increased from 3.1 to 20.2 s (Table 3). When the relaxation time is increased, the degree of compatibility of the blend is known to be increased. For the pure PLA and the PLA after blend with PC shown in Figs. 11 and 12, the form relaxation time is increased slightly from 0.6 to 1.6 s, respectively. The increase in the form relaxation time of the PLA after blend with PC is maybe affected by the slow relaxation of the interface between the PC and PLA, especially when the PLA is dispersed phase in the PC/PLA (70/30) blend.

Table 3 shows the form relaxation time (τ_1) due to the relaxation of the interface and interfacial tension (α) between PC and PLA obtained from the weighted relaxation spectra of the compatibilized PC/PLA (70/30) blends with the SAN-g-MAH, EOR-MAH and EGMA. From Table 3, it shows that the form relaxation time is shifted to higher values, when the SAN-g-MAH content is increased up to 5 phr. Then, the form relaxation time is decreased when the SAN-g-MAH content is at 7 phr. It can be expected that the form relaxation time (τ_1) due to the relaxation of the interface between PC and PLA will be increased when the compatibility between the two phases is increased. Also, it can be thought that the interfacial tension (α) between PC and PLA will be decreased when the compatibility between the two phases is increased. From the Palierne emulsion model, the interfacial tension of the PC/PLA (70/30) blend shows minimum value (0.08 mN/m) at the 5.0 phr of the SAN-g-MAH content. From this result, it is suggested that the optimum content of SAN-g-MAH for PC and PLA blend is found to be 5 phr. These results are consistent with the results of the mechanical properties of PC/PLA blend and morphological studies which shows minimum dispersed droplet size especially in the amount of 5.0 phr SAN-g-MAH.

4. Conclusion

In this study, mechanical, morphological and rheological properties of the PC/PLA (70/30) blends compatibilized with SAN-g-MAH, EOR-MAH and EGMA were investigated. From the results of mechanical properties such as impact, tensile and flexural strengths, the PC/PLA (70/30) blends with the SAN-g-MAH (5 phr) showed maximum mechanical strengths among the compatibilizers used in this study. This result suggests that the SAN-g-MAH is the most effective compatibilizer than the others to improve the mechanical

strengths of the PC/PLA blends. From the morphological studies of the PC/PLA (70/30) blends, the minimum value (0.19 $\mu m)$ of PLA droplet size was observed at the 5.0 phr SAN-g-MAH, which is consistent with the results of mechanical strengths of the PC/PLA (70/30) blends. From the results of hydrolysis of the PC/PLA (70/30) blends, degradation rate of the blend with SAN-g-MAH (5 phr) showed slower than compared to the blends without compatibilizer or adding other compatibilizers such as EOR-MAH and EGMA, and this result is also consistent with the results of impact and tensile strengths of the PC/PLA (70/30) blends after hydrolysis.

From the weighted relaxation spectra of the PC/PLA (70/30) blends using Palierne emulsion model, the interfacial tension between PC and PLA showed minimum value (0.08 mN/m) at the amount of 5.0 phr SAN-g-MAH. This result is consistent with the results of mechanical properties of PC/PLA (70/30) blend and morphological studies which shows minimum dispersed droplet size especially at the amount of 5.0 phr SAN-g-MAH. From the above results of the mechanical, morphological and rheological studies, it can be concluded that SAN-MAH is the most effective compatibilizer to improve the mechanical strength of the PC/PLA (70/30) blends, especially at the amount of 5 phr.

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References

- [1] Drumright RE, Gruber PR, Henton DE. Adv Mater 2000;12(23):1841-6.
- [2] Tsuji H, Miyauchi S. Polymer 2001;42(9):4463-7.
- 3] Grijpma DW, Pennings AJ. Macromol Chem Phys 1994;195(5):1633-47.
- [4] Doi Y, Fukuda K. Biodegradable plastics and polymers. Amsterdam: Elsevier; 1994.
- [5] Ray SS, Yamada K, Okamoto M, Ueda K. Polymer 2003;44(3):857-66.
- [6] Nugroho P, Mitomo H, Yoshii F, Kume T, Nishimura K. Macromol Mater Eng 2001;286(5):316–23.
- [7] Lunt J. Polym Degrad Stab 1998;59(1):145–52.

- [8] Biresaw G, Carriere CJ. J Polym Sci B Polym Phys 2002;40(19):2248-58.
- [9] Semba T, Kitagawa K, Ishiaku US, Hamada H. J Appl Polym Sci 2006;101 (3):1816–25.
- [10] Yeh JT, Wu CJ, Tsou CH, Chai WL, Chow JD, Huang CY, et al. Polym Plast Technol Eng 2009;48(6):571–8.
- [11] Anderson KS, Hillmyer MA. Polymer 2004;45(26):8809-23.
- [12] Wang Y, Hillmyer MA. J Polym Sci A Polym Chem 2001;39(16):2755-66.
- [13] Reddy N, Nama D, Yang Y. Polym Degrad Stab 2008;93(1):233-41.
- [14] Yoo TW, Yoon HG, Choi SJ, Kim MS, Kim YH, Kim WN. Macromol Res 2010;18 (6):583–8.
- [15] Ma X, Yu J, Wang N. J Polym Sci B Polym Phys 2006;44(1):94–101.
- [16] Oyama HT. Polymer 2009;50(3):747-51.
- [17] Zhizhong S, Li Q, Liu Y, Hu G, Wu C. Eur Polym J 2009;45(8):2428–33.
- [18] Jiang L, Wolcott MP, Zhang JW. Biomacromolecules 2006;7(1):199–207.
- [19] Signori F, Coltelli M-B, Bronco S. Polym Degrad Stab 2009;94(1):74-82.
- [20] Coltelli M-B, Bronco S, Chinea C. Polym Degrad Stab 2010;95(3):332-41.
- [21] Gajria AM, Dave V, Gross RA, McCarthy SP. Polymer 1996;37(3):437–44.
- [22] Park JW, Im SS. Polymer 2003;44(15):4341–54.
- [23] Eguiburu JL, Iruin JJ, Fernandez-Berridi MJ, San Roman J. Polymer 1998;39 (26):6891–7.
- [24] Sheth M, Kumar RA, Dave V, Gross RA, Mccarthy SP. J Appl Polym Sci 1997;66 (8):1495–505.
- [25] Oyama HT, Tanaka Y, Kadosaka A. Polym Degrad Stab 2009;94(9):1419–26.
- [26] Huneault MA, Li H. Polymer 2007;48(1):270-80.
- [27] Zhang JF, Sun X. Biomacromolecules 2004;5(4):1446-51.
- [28] Petinakis E, Liu X, Yu L, Way C, Sangwan P, Dean K, et al. Polym Degrad Stab 2010;95(9):1704–7.
- [29] Fukushima K, Abbate C, Tabuani D, Gennari M, Camino G. Polym Degrad Stab 2009;94(10):1646–55.
- [30] Zaidi L, Kaci M, Bruzaud S, Bourmaud A, Grohens Y. Polym Degrad Stab 2010;95(9):1751–8.
- [31] Wu S. Polymer interfaces and adhesion. New York and Basel: Marcel Dekker Inc: 1982.
- [32] Lepers JC, Favis BD, Tabar RJ. J Polym Sci B Polym Phys 1997;35(14):2271-80.
- [33] Homg KM, Noolandi J. Macromolecules 1981;14(3):736–42.
- [34] Fredrickson GH, Milner ST. Macromolecules 1996;29(23):7386-90.
- [35] Palierne JF. Rheol Acta 1990;29(3):204-14.
- [36] Almusallam AS, Larson RG, Solomon MJ. J Rheol 2004;48(2):319-48.
- [37] Schulze SJ, Cernohous JJ, Hirao A, Lodge TP, Macosko CW. Macromolecules 2000;33(4):1191–8.
- [38] Shi D, Hu GH, Ke Z, Li RKY, Yin J. Polymer 2006;47(13):4659-66.
- [39] Sung YT, Han MS, Hyun JC, Kim WN, Lee HS. Polymer 2003;44(5):1681-7.
- [40] Honerkamp J, Weese J. Rheol Acta 1993;32(1):65-73.
- [41] Gramespacher H, Meissner J. J Rheol 1992;36(6):1127-41.
- [42] Graebling D, Muller R, Palierne JP. Macromolecules 1993;26(2):320-9.
- [43] Ho CH, Wang CH, Lin CI, Lee YD. Polymer 2008;49(18):3902-10.
- [44] Kim WN, Burns CM. Polym Eng Sci 1988;28(17):1115–25.
- [45] Underwood EE. Quantitative stereology. Reading, MA: Addision Wesley; 1970.
- 46] Elise A. SPE international symposium on oilfield chemistry; 1995. p. 279–289.
- [47] Ferry JD. Viscoelastic properties of polymers. New York: Wiley; 1980.