Effects of Compatibilizers on the Mechanical Properties and Interfacial Tension of Polypropylene and Poly(lactic acid) Blends

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Abstract: The effects of compatibilizers and hydrolysis on the tensile and impact strength, interfacial tension and morphology of the PP/PLA (80/20) blends were investigated. For the PP/PLA (80/20) blends before hydrolysis, the tensile strength of the blends reached a maximum when the polypropylene-*g*-maleic anhydride (PP-*g*-MAH) copolymer was added at 3 phr. For the PP/PLA (80/20) blends after hydrolysis, the tensile strength did not change appreciably with the PP-*g*-MAH content. For the blends with the styrene-ethylene-butylene-styrene-*g*-maleic anhydride (SEBS-*g*-MAH) before or after hydrolysis, the tensile strength of the blends decreased with increasing SEBS-*g*-MAH content. The interfacial tension of the PP/PLA (80/20) blend was determined from the relaxation time using the Palierne and Choi-Schowalter models, and showed a minimum value at a PP-*g*-MAH content of 3 phr in each model. For the PP/PLA (80/20) blends with the SEBS-*g*-MAH before and after hydrolysis, the increase in impact strength was more significant for the blends after hydrolysis. This suggests that PLA becomes less brittle after hydrolysis. The impact strength suggests that the SEBS-*g*-MAH is an effective impact modifier to improve the impact strength of the PP/PLA (80/20) blends.

Keywords: polypropylene, poly(lactic acid), blend, compatibility, interfacial tension, mechanical property, rheology.

Introduction

Most of plastic wastes are land-filled or incinerated and some of them are recycled. Plastics if disposed untreated are not decomposed rapidly and they are one of the causes of environmental pollution. Landfill may not be one of the ways for waste disposal any longer since landfill sites in many countries are getting full. Incineration using today's technology is not perfectly free from dioxin problems and recycling rate of plastic waste is not so high enough to reduce the pollution problem. Therefore, interest in development of new polymers having biodegradable properties has been growing since those plastics are considered as a solution for environmental pollution.[1]

Biodegradable polymers are decomposed mainly by hydrolysis of polymer main chains by microbes in water or soil and molecular weight of the polymer decreases as the breakdown proceeds. Finally, it is converted to monomers or water and carbon dioxide.[2] Even though the biodegradable polymer is desirable from an ecological stand point, there would be a problem that the service time can be shorter than expected due to decrease in mechanical strength caused by degradation. Many researches have been focused to prevent rapid decrease in mechanical strength of the eco-friendly polymers by blending of biodegradable polymers and conventional polymers.[3-5] Blending of biodegradable polymers induces gradual decomposition of conventional polymers and the phenomenon is named at biodisintegration.[6-11]

Poly(lactic acid) (PLA) is an unstable material which can be decomposed easily by various types of impurities. It especially reacts with water and it is converted to lactic acid, and the lactic acid is biodegraded by microbes.[2] Characteristics of biodegradation of PLA can be investigated by studying hydrolysis because biodegradation of PLA includes the hydrolysis reaction. The durability change of the polymer with service period can be estimated through the characteristics of hydrolysis since the reaction can be occurred by the moisture in air. Polypropylene (PP) and PLA blend may

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have biodisintegration characteristics since PLA is biodegradable. However, the blend has low mechanical strength because polar PP and nonpolar PLA is not compatible. An addition of compatibilizer to the system may improve the compatibility and mechanical strength of the polymer blends.

In this study, characteristics of mechanical property and hydrolysis of the PP/PLA (80/20) blends with various types of compatibilizers such as polypropylene-*g*-maleic anhydride (PP-*g*-MAH) copolymer and styrene-ethylene-butylene-styrene-*g*-maleic anhydride (SEBS-*g*-MAH) have been investigated. Interfacial tension of the PP/PLA (80/20) blends has been calculated from the particle size of the PLA, storage modulus and loss modulus of the PP/PLA (80/20) blends. Also, the values of the interfacial tension of the PP/PLA blends are correlated with the degree of compatibility of the PP/PLA (80/20) blends.

Experimental

Materials. The polymers used in this study were PP and PLA, and they were obtained from commercial sources. The PP (grade B175H) was supplied by Samsung Total Petrochemicals Co., Korea. The PLA (grade 4032D) was supplied by NatureWorks Co., USA. The characteristics and sources of the PP and PLA are shown in Table I. The PP-*g*-MAH copolymer with a MAH content of 10 wt% and the SEBS-*g*-MAH (FG1901X) copolymer with a MAH content of 2 wt% were supplied by Hyundai EP Co. and Shell Co., respectively.

Blend Preparation. PP and PLA was blended with a weight ratio of 80/20 using a 27 mm diameter twin screw extruder (Leistritz Co.). PP-*g*-MAH and SEBS-*g*-MAH, as compatibilizers, were added in the PP/PLA (80/20, wt%) blends with 1, 3, 5, 7 and 10 phr. Before extrusion, PP, PLA, PP-*g*-MAH and SEBS-*g*-MAH were dried in a vacuum oven at 70 °C for 24 h. The temperature and screw speed of the extruder was set at 190 °C and 120 rpm, respectively.

Mechanical Properties. Impact strength of the PP/PLA (80/20) blends was investigated under the ambient condition using notched Izod impact tester (Toyoseiki DG-IB2). The impact test was performed according to the ASTM D-256 and 5 specimens were measured and averaged. Tensile strength of the PP/PLA (80/20) blends was investigated under the ambient condition using a universal testing machine (Instron 4467). Tensile test was performed according to the

Table I. Characteristics of Polypropylene and Poly(lactic acid) Used in This Study

Sample	M_w	MFI (g/10 min)	T_m (°C)	Tensile Strength (kg$_f$/cm^2)	Impact Strength (kg$_f$ cm/cm)
PP[a]	230,000	26.0	164	309.0	6.1
PLA[b]	159,700	8.0	169	770.0	2.6

[a]Supplied by Samsung Total, Korea. Grade B175H. [b]Supplied by Natureworks, USA. Grade 4032D.

ASTM D-638 and 5 specimens were measured and averaged.

Morphology. The morphology of the PP/PLA (80/20) blends was obtained by scanning electron microscopy (Hitachi S-4300) after Pt coating. The samples were fractured under cryogenic condition and etched in ethylamine 70% solution for 10 min.

Hydrolysis. The PP/PLA (80/20) blend was treated in 0.05 M hydrochloric acid solution at 85 °C for 5 days in closed glass bottles. And the blend samples were taken out after 5 days and tested for the changes in their mechanical properties.

Rheology. Rheological properties of the PP/PLA (80/20) blends were measured using advanced rheometric expansion system (ARES) in oscillatory shear at 8% strain under dry nitrogen atmosphere. The fixture used in this study was parallel-plate arrangement with 25 mm plate and the samples were fabricated in a disk with 2 mm in thickness. The frequency sweeps from 0.02 to 100 rad/s were carried out at 190 °C. The isotherm was shifted to master curves with a reference temperature 190 °C. For the measurement, the samples were tested within the linear viscoelastic strain range.

Results and Discussion

Morphology. The morphology of the PP/PLA (80/20) blends with various contents of compatibilizer was studied
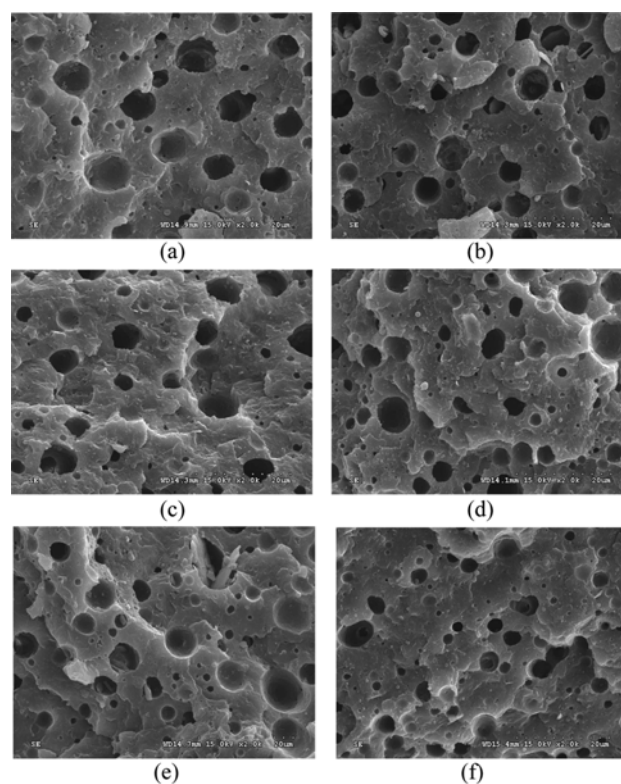
Figure 1. Scanning electron micrographs of the PP/PLA (80/20) blends with the PP-*g*-MAH content: (a) 0 phr, (b) 1 phr, (c) 3 phr, (d) 5 phr, (e) 7 phr, (f) 10 phr.
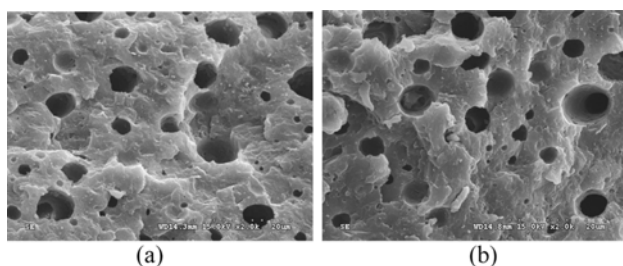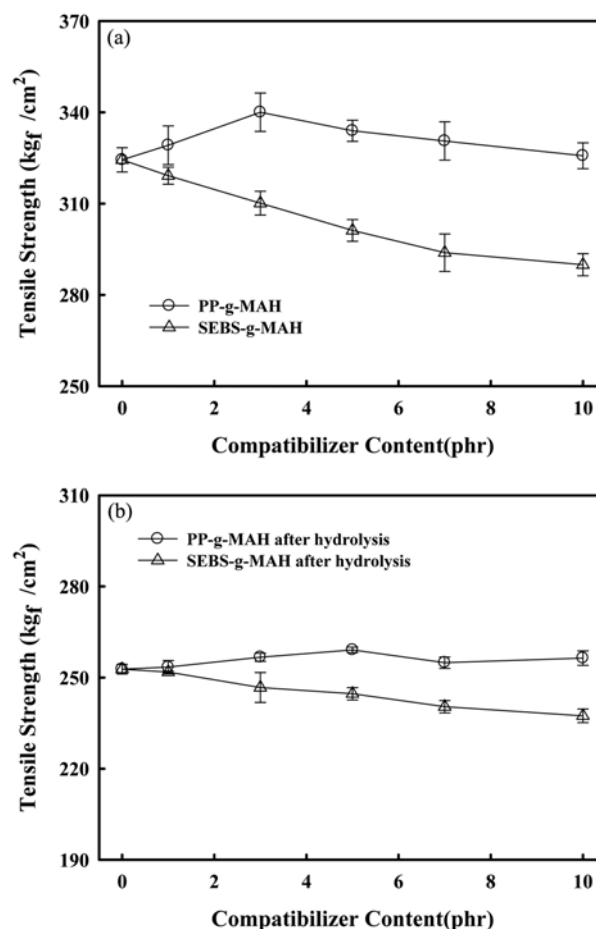
Figure 2. Scanning electron micrographs of the PP/PLA (80/20) blends with the type of compatibilizer: (a) PP-*g*-MAH (3 phr), (b) SEBS-*g*-MAH (3 phr).

using SEM. Figure 1(a-f) shows SEM images of the cryogenically fractured surfaces of the PP/PLA (80/20) blends with the PP-*g*-MAH of 0, 1, 3, 5, 7 and 10 phr, respectively. PLA was etched out from the broken surface of the specimens by ethyl amine solution and the etched sites looked like crater holes in the micrographs. As the compatibility of two polymers in the blend becomes higher, the surface tension is getting lower, and uniform dispersion is expected with tiny and uniform droplets of dispersion phases.

Figure 1(a-f) shows the droplet size of the dispersed PLA decreases when the PP-*g*-MAH was added, and the size of the droplet is observed to be 5.5, 4.3, 4.2, 3.9, 3.5 and 3.4 μm, respectively. From Figure 1, the droplet size of the PP/PLA (80/20) blends with the PP-*g*-MAH is shown to be smaller than that of the PP/PLA (80/20) blend without the PP-*g*-MAH and the droplet size among the blends with the different amount of PP-*g*-MAH does not change significantly. Figure 2(a,b) shows micrographs of the PP/PLA (80/20) blends with the addition of the PP-*g*-MAH and SEBS-*g*-MAH for the content of 3 phr, respectively. From Figure 2 (a,b), the droplet size of the blends is observed to be 4.2 and 3.9 μm, respectively, and the droplet size between the blends does not change significantly.

Mechanical Properties. Figure 3(a,b) shows tensile strength of the PP/PLA (80/20) blends with the PP-*g*-MAH and SEBS-*g*-MAH before and after hydrolysis of the blends, respectively. For the PP/PLA (80/20) blends before hydrolysis, the tensile strength of the PP/PLA (80/20) blends with the PP-*g*-MAH show maximum at a content of 3 phr. This increase in tensile strength of the PP/PLA (80/20) blend is probably because that the PP-*g*-MAH may only exist at the boundary of the PP and PLA and act as a connector to hold domains, and consequently results higher mechanical strength. However, the tensile strength of the PP/PLA blends decreases with the increase of the SEBS-*g*-MAH content.

For the PP/PLA (80/20) blends after hydrolysis, the tensile strength does not change appreciably with the PP-*g*-MAH content. However, for the PP/PLA (80/20) blends with the SEBS-*g*-MAH, the tensile strength decreases with the increase of the SEBS-*g*-MAH content which may act as a plasticizer in the blends.
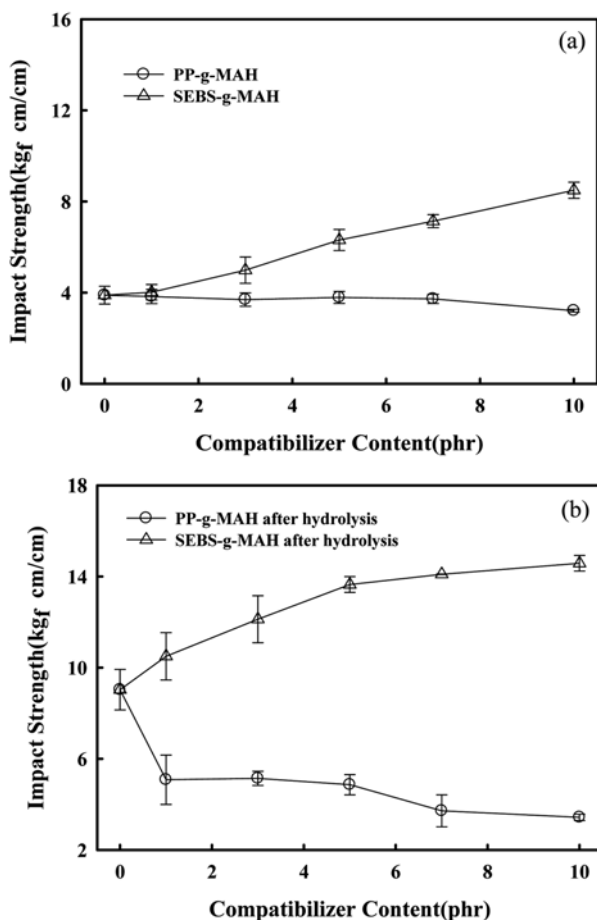

Figure 3. Tensile strength of the PP/PLA (80/20) blends with the type of compatibilizer: ($\bigcirc$) PP-*g*-MAH, ($\triangle$) SEBS-*g*-MAH: (a) before hydrolysis, (b) after hydrolysis.
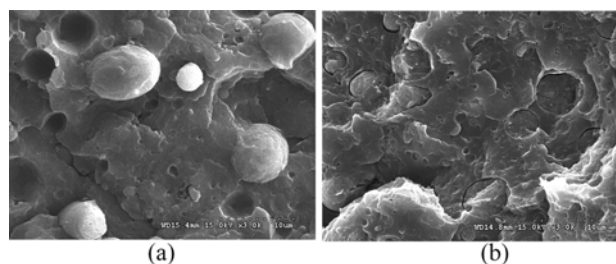
Figure 4. Scanning electron micrographs of the PP/PLA (80/20) blends: (a) before hydrolysis, (b) after hydrolysis.

Figure 4(a,b) shows SEM images of the PP/PLA (80/20) blends before and after hydrolysis, respectively. Fractured surfaces show that the PLA droplet shape well maintains before it is hydrolyzed, but after hydrolysis the shape is collapsed due to decrease in hardness and some voids are observed between the PP and PLA. From Figure 4, it is suggested that the PLA decomposes first during hydrolysis therefore the strength of the PLA after hydrolysis may decrease and probably becomes less brittle.

Figure 5. Impact strength of the PP/PLA (80/20) blends with the type of compatibilizer: (○) PP-*g*-MAH; (△) SEBS-*g*-MAH: (a) before hydrolysis, (b) after hydrolysis.

Figure 5(a,b) shows impact strength of the PP/PLA (80/20) blends with the PP-*g*-MAH and SEBS-*g*-MAH before and after hydrolysis of the blends, respectively. For the PP/PLA (80/20) blends before hydrolysis, the impact strength of the PP/PLA (80/20) blends with the SEBS-*g*-MAH increases up to 10 phr. However, the impact strength of the PP/PLA blends with the PP-*g*-MAH does not change significantly with the increase of the PP-*g*-MAH content.

For the PP/PLA (80/20) blends with the SEBS-*g*-MAH after hydrolysis, the impact strength of the blends is shown to increase with the SEBS-*g*-MAH content. This is probably because that the PLA becomes less brittle after hydrolysis, therefore the PLA resulted the increase of the impact strength of the PP/PLA blends. Also, the SEBS-*g*-MAH has high impact strength compared the PP-*g*-MAH, therefore SEBS-*g*-MAH seems to act as a impact modifier for improving the impact strength of the blends.[12] From the above results of tensile and impact strengths of the PP/PLA (80/20) blends, it is suggested that the PP-*g*-MAH acts as an effective compatibilizer to increase the tensile strength of the blends
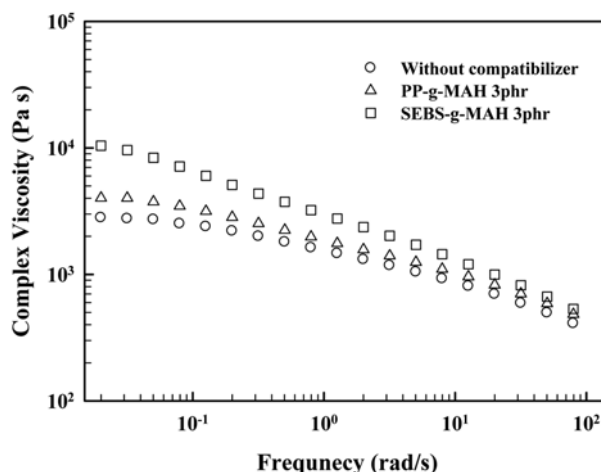
Figure 6. Complex viscosity of the PP/PLA (80/20) blends with the type of compatibilizer: (○) without compatibilizer; (△) PP/PLA/PP-*g*-MAH (3phr); (□) PP/PLA/SEBS-*g*-MAH (3phr).

at a PP-*g*-MAH content of 3 phr, while the SEBS-*g*-MAH is an effective impact modifier to increase the impact strength of the PP/PLA blends.

Rheology. Figure 6 shows the complex viscosity of the PP/PLA (80/20) blends with PP-*g*-MAH (3 phr) and SEBS-*g*-MAH (3 phr). The results show that the complex viscosity of the blends with the PP-*g*-MAH and SEBS-*g*-MAH is always higher than that of the blends without compatibilizer. The changes of the complex viscosity of the blends depend on the degree of compatibility between the components and the complex viscosity of the compatibilizer itself. Actually, the complex viscosity of the SEBS-*g*-MAH copolymer is higher than that of the PP-*g*-MAH. Also, it is known that the increased viscosities of the blends suggest the increased compatibility between the components. Therefore, from the results of Figure 6, it is suggested that the PP-*g*-MAH and SEBS-*g*-MAH act effectively to increase the viscosities of the PP/PLA blends.

Interfacial Tension of PP/PLA Blends. Compatibility of polymer blends can be studied by the measurement of interfacial tension of the blends. Interfacial tension can be obtained by Palierne emulsion model[13] and Choi-Schowalter model[14] using relaxation time which are shown in eqs. (1) and (2), respectively.[15-19]

$$\tau_1 = \frac{R_v \eta_m}{4\alpha} \frac{(19K+16)(2K+3-2\phi(K-1))}{10(K+1)-2\phi(5K+2)} \quad (1)$$

$$\tau_1 = \frac{R_v \eta_m}{4\alpha} \frac{(19K+16)(2K+3)}{40(K+1)} \times \left[1 + \phi \frac{5(19K+16)}{4(K+1)(2K+3)}\right] \quad (2)$$

where τ_1 is the form relaxation time due to the relaxation of the interface, η_m is the viscosity of the matrix, α is the interfacial tension of the blend, ϕ is the volume fraction of

the dispersed phase, and $K=\eta_i/\eta_m$ is the zero shear viscosity ratio of the droplet and matrix. Relaxation time is obtained basically from weighted relaxation spectrum ($\tau H(\tau)$). Weighted relaxation spectrum ($\tau H(\tau)$) was calculated by eqs. (3) and (4), and storage modulus (G') and loss modulus (G'') were measured by ARES.[17-20]

$$G'(\omega) = \int_{-\infty}^{\infty}\left[\frac{H(\tau)\omega^2\tau^2}{1+\omega^2\tau^2}\right]d(\ln\tau) \quad (3)$$

$$G''(\omega) = \int_{-\infty}^{\infty}\left[\frac{H(\tau)\omega\tau}{1+\omega^2\tau^2}\right]d(\ln\tau) \quad (4)$$

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

Calculation of the weighted relaxation spectrum ($\tau H(\tau)$) was carried out using RSIOrche600 software, and weighted relaxation spectrums of the PP, PLA and the (PP/PLA) (80/20) blends with and without the PP-g-MAH and SEBS-g-MAH are shown in Figures 7-9. For the relaxation spectrum of the PP/PLA (80/20) blend shown in Figure 7, two relax-
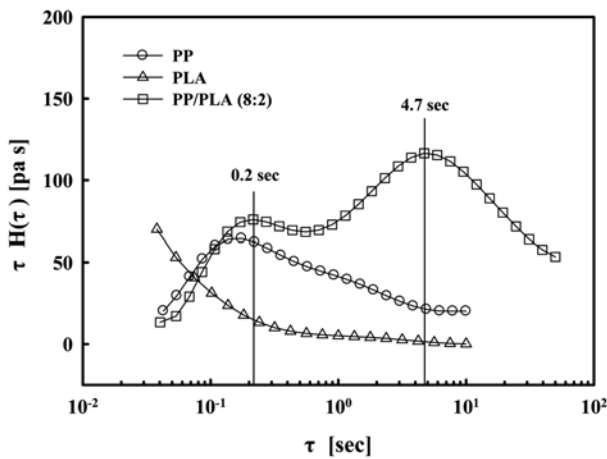
Figure 7. Weighted relaxation spectrum of the PP, PLA and PP/PLA (80/20)) blend: (○) PP; (△) PLA; (□) PP/PLA.
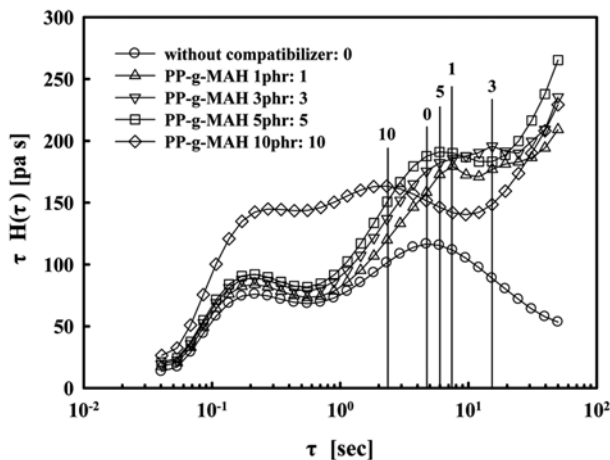
Figure 8. Weighted relaxation spectrum of the PP/PLA (80/20) blend with the PP-g-MAH content: (○) 0 phr ; (△) 1 phr ; (▽) 3 phr; (□) 5 phr; (◇) 10 phr.

Table II. Form Relaxation Time (τ) and Interfacial Tension (α) for the PP/PLA (80/20) Blends with Compatibilizer Content

| Compatibilizer	Compatibilizer Content (phr)	τ (s)	α_1^a (mN/m)	α_2^b (mN/m)
PP-g-MAH	0	4.7	3.96	6.99
	1	7.6	1.96	3.45
	3	12.1	1.16	2.05
	5	5.9	2.23	3.94
	10	2.3	4.49	7.92
SEBS-g-MAH	1	4.7	3.10	5.48
	3	4.7	2.87	5.07
	5	4.7	2.77	4.88
	10	4.7	2.45	4.32

$^a\alpha_1$ was calculated from the Palierne model. $^b\alpha_2$ was calculated from the Choi-Schowalter model.

ation spectrum peaks are observed at about 0.2 and 4.7 sec, respectively. The first peak (0.2 sec) is related to the phase of the component (PP) and the second peak (4.7 sec) corresponds to the long relaxation time which is associated with the contribution of the interphase of the PP and PLA blend.

Figure 8 shows the weighted relaxation spectrum of the PP/PLA (80/20) blends with 0, 1, 3, 5 and 10 phr PP-g-MAH. When the PP-g-MAH is added to the PP/PLA (80/20) blend up to 3 phr, the second relaxation time is increased from 4.7 to 12.1 sec (Table II). From Figure 8 and Table II, it is also shown that the relaxation time decreases from 5.9 to 2.3 sec when the PP-g-MAH was added from 5 to 10 phr to the PP/PLA (80/20) blends, respectively. When the second relaxation time of the blend is increased, the degree of compatibility of the blend is known to be increased. When the PP-g-MAH exists at the boundary of the PP and PLA, consequently results higher values of second relaxation time for the interphase of the PP and PLA blend since the PP-g-MAH may act as a connector to hold the PP and PLA phases.

Figure 9 shows the weighted relaxation spectrum of the PP/PLA (80/20) blend with the SEBS-g-MAH. When the SEBS-g-MAH is added to the PP/PLA (80/20) blends, the second relaxation time is observed to be constant at 4.7 sec. As a result, the interfacial tension of the PP/PLA (80/20) blends changes very small with the amount of SEBS-g-MAH (Table II). This result suggests that the compatibility of the PP/PLA (80/20) blends does not change appreciably with the amount of the SEBS-g-MAH. However, from the results of the impact strength of the PP/PLA (80/20) blends, it is suggested that the PP-g-MAH may act as an impact modifier because of increasing the impact strength of the PP/PLA (80/20) blend with the amount of SEBS-g-MAH.

Table II shows the interfacial tension of the PP/PLA (80/20) blend calculated by the Palierne and Choi-Schowalter models. From the Palierne model, the interfacial tension of
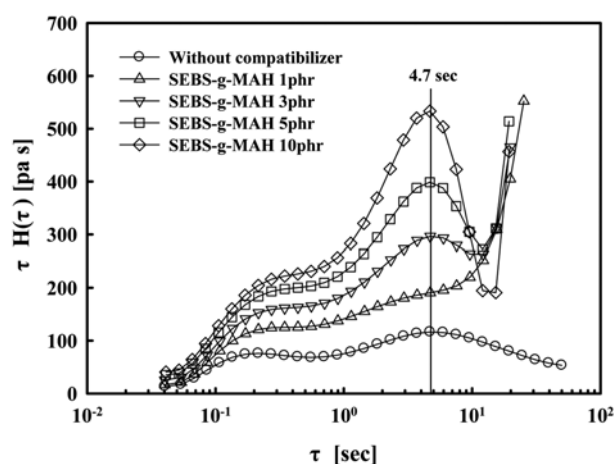
Figure 9. Weighted relaxation spectrum of the PP/PLA (80/20) blend with the SEBS-*g*-MAH content: (○) 0 phr; (△) 1 phr; (▽) 3 phr; (□) 5 phr; (◇) 10 phr.

the PP/PLA (80/20) blends with the PP-*g*-MAH shows minimum value (1.16 mN/m) at the 3 phr content, which suggests that the compatibility increases at the 3 phr of the PP-*g*-MAH. From the Choi-Schowalter model, the interfacial tension of the PP/PLA blends with PP-*g*-MAH shows also the minimum value (2.05 mN/m) at the 3 phr content, which represents the similar trend with the result obtained by Palierne model. At 3 phr of the PP-*g*-MAH, the second relaxation time shows maximum value from Table II, therefore, the interfacial tension of the blend shows minimum at 3 phr of the PP-*g*-MAH since the interfacial tension of the blend can be obtained from the second relaxation time due to the relaxation of the interphase of the PP and PLA blend. When the interfacial tension of the blend is decreased, the degree of compatibility of the blend is known to be increased. From the above results, it is suggested that the PP-*g*-MAH is an effective compatibilizer at the amount of 3 phr to improve the compatibility of the PP/PLA (80/20) blends, and this result is consistent with the results obtained from the tensile strength of the PP/PLA (80/20) blends.

Conclusions

In this study, the effects of compatibilizers and hydrolysis on the tensile and impact strengths and interfacial tension of the PP/PLA (80/20) blends with the amount of the PP-*g*-MAH and SEBS-*g*-MAH were investigated. From the results of tensile strength of the PP/PLA (80/20) blends before hydrolysis, the tensile strength of the PP/PLA (80/20) blends with the PP-*g*-MAH showed maximum at the amount of 3 phr which can be concluded that the PP-*g*-MAH is an effective compatibilizer to improve the tensile strength of the blends.

For the PP/PLA (80/20) blends before and after hydrolysis, the impact strength of the blends increased with the SEBS-

g-MAH content. The increase in impact strength was more significant for the PP/PLA (80/20) blends after hydrolysis, which suggested that the PLA became less brittle after hydrolysis. From the results of impact strength of the PP/PLA (80/20) blends, it is concluded that the SEBS-*g*-MAH is an effective impact modifier to improve the impact strength of the PP/PLA (80/20) blends.

From the above results, it is suggested that the optimum amount and effectiveness of the compatibilizer for the PP/PLA blends can be correlated when the mechanical strength, interfacial tension and relaxation time of the blends are obtained, and this results can be applied to other polymer blends as well.

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