

Effects of Compatibilizers on the Mechanical Properties of ABS/PLA Composites

Mi Yeong Jo, Yeon Jong Ryu, Jun Hee Ko, Jin-San Yoon

Department of Polymer Science and Engineering, Inha University, Yonghyun-Dong, Nam-Gu, Incheon 402-751, Korea

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ABSTRACT: Composites composed of acrylonitrile-butadiene-styrene copolymer (ABS) and poly(lactic acid) were prepared to develop ABS-based automobile console boxes with improved environmental friendliness. ABS/PLA composites without any additives showed extremely poor mechanical properties. However, increase in the content of polybutadiene moiety of ABS and introduction of proper compatibilizer and heat stabilizer enhanced the mechanical properties of ABS/PLA composites significantly. Thermal

stabilization effect of the heat stabilizer was assessed by determining the activation energy of thermal degradation, by measuring the molecular weight variation of PLA and by observing the morphology of the fractured surface. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: composites; mechanical properties; bio-materials; compatibility

INTRODUCTION

Recently human beings are facing serious crisis due to the depletion of natural resources including crude oil and the climate change provoked by the global warming. These led to the world-wide enactment of many environmental regulations such as the Kyoto and Montreal Protocols. In this respect, enhancement of car fuel efficiency and development of eco-benign materials have become crucial for the competitiveness of autoindustries.

Acrylonitrile-butadiene-styrene copolymer (ABS) is frequently used for the automobile interior parts due to its excellent impact strength in combination with good balance of other requisite properties. These unique properties are originated from the specific components in the copolymer. ABS contains rubber-rich phase composed of polybutadiene (PB) and PB grafted with styrene-acrylonitrile random copolymer (SAN) which is dispersed in rigid SAN-rich matrix. The PB moiety mainly determines the toughness of ABS, while the tensile and flexural strength depends on primarily on the SAN matrix.¹

The amount of SAN grafted to PB backbone as well as the content and domain size of the rubber phase has a vital influence on the impact strength of ABS.^{1–4} ABS has also been applied as ingredient for

impact modification of many commodity plastics such as polycarbonate (PC),^{5–7} nylon^{8,9} and poly(butylene terephthalate) (PBT).^{10–12}

Poly(lactic acid) (PLA) has good mechanical properties comparable to those of polypropylene in many aspects.¹³ PLA is considered to be an environmentally benign material, because it is usually synthesized by polymerizing lactic acid produced through the fermentation of renewable resources such as corn.^{14–18} Because a lot of corn is to be consumed to produce bioethanol, which should provoke serious environment concern about the indiscreet deforestation to expand the arable land for the corn cultivation running counter to the CO₂ reduction, efforts are under way to investigate to use grass instead of grain as the source of the lactic acid production.¹⁹ Fermentation by using genetically engineered microbes is another interesting route for a direct PLA synthesis.²⁰

Replacement of part of ABS with PLA may reduce the consumption of petroleum-based resources and thereby enhance the eco-friendliness of the material. Increasing the content of renewable resources in automobile interior parts may also help to overcome the trade barriers imposed by the environmental regulations. The replacement is beneficial also in the cost aspect because the price of ABS is higher than that of PLA.

However, the incompatibility between PLA and ABS as well as the brittleness of PLA makes difficult to achieve the desired material properties.

It is certain that a complete prevention of the deterioration of the material properties of ABS as a result

Correspondence to: J.-S. Yoon (jsyoon@inha.ac.kr).

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of the incorporation of PLA is unavoidable.² However, since the material properties of ABS are far superior to those required for many car interior parts, ABS/PLA composites can be used for the same purpose instead of ABS alone, if the material properties meet the target values. For example, the impact strength of ABS with butadiene content of 25 wt % is as high as 480 J m^{-1} , while 80 J m^{-1} of impact strength is enough for car console boxes which are usually made of ABS. In this study, ABS/PLA composites were prepared for autointerior parts by toughening of PLA and interfacial adhesion improvement through proper selection of heat stabilizers and compatibilizers.^{21,22}

EXPERIMENTAL

Materials

Acrylonitrile-butadiene-styrene copolymer (ABS, butadiene content of 25 wt %) and grafted-ABS (G-ABS, butadiene content 58%) were donated from Cheil Industries (Korea). The commercial product, poly(lactic acid) (PLA, 2002D) was purchased from NatureWorks LLC. The various compatibilizers were employed such as ethylene propylene rubber (EPR-MAH, KEPA1130, Kumho Polychem, Korea), polycarbonate (PC, 3017IR, Samyang, Korea), epoxy terminated polyethylene (PE-epoxy, Elvaloy PTW, epoxy contents: 5 wt %, Samyang, Korea), maleic anhydride-grafted styrene acrylonitrile copolymer (SAN-MAH, Cheil Industries, Korea) and glycidyl methacrylate grafted styrene-acrylonitrile copolymer (SAN-GMA, Cheil Industries, Korea). The 2-(2'-hydroxy-3',5'-di-*t*-butylphenyl)-5-chlorobenzotriazole (Songsorb) (Songsorb-3270, Songwon Industries, Korea) and octadecyl-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate (Irganox), (Irganox-1076, Ciba, Swiss) were used as heat stabilizers.

Preparation of ABS/PLA composites

ABS, PLA, and G-ABS were dried in a vacuum oven at 60°C for 24 h. The polymer resins were mixed with appropriate ingredients by using a twin screw extruder (screw diameter = 19 mm, $L/D = 40$, Bau technology, Korea) at around $190\text{--}230^\circ\text{C}$. The extruded products were pelletized with an autocutter with about $2 \text{ mm}\phi \times 3 \text{ mmL}$ in shape and then were dried in the vacuum oven at 60°C for 24 h.

The pelletized resins were molded at 230°C by using an injection molder (screw diameter = 22 mm, clamping force = 50 t, Sunwoo heavy industry, Korea) to prepare the test specimens.

Characterization

The thermal properties of ABS/PLA composites were measured by thermo-gravimetric analysis

(TGA, TGA-Q50, TA instruments). The sample weight was 10–15 mg and scanned to 800°C under nitrogen atmosphere at 5, 10, 20, and $40^\circ\text{C min}^{-1}$.

The PLA fraction was retrieved from the ABS/PLA composites through the THF Soxhlet extraction for 1 week. Molecular weight of the extracted PLA was measured using a gel permeation chromatography (GPC, Pump: Waters 1515, detector: Waters 2414). Tetrahydrofuran (at a flow rate of 1 mL min^{-1}) was used as an eluent. Polystyrene (Shodex Standard SM-105 Lot No. 60502, Japan) was used for the calibration.

The mechanical properties of the composites were tested by using a universal testing machine (UTM, H10KS-0061, Hounsfield, UK). Tensile properties were measured following ASTM D638 at a crosshead speed of 50 mm min^{-1} . The dimension of the specimens for the tensile tests was 165 mm of total length, 115 mm of distance between grips, 13 mm of width and 3.2 mm of thickness. Flexural properties were obtained according to ASTM D790 at a crosshead speed of 2.8 mm min^{-1} . The dimension of the specimens for the flexural tests was 127 mm of length, 12.7 mm of width, and 6.4 mm of thickness. Impact strength was assessed with Izod impact tester (CEAST code 6545/000) according to ASTM D256 at room temperature. The dimension of the specimens for the impact tests was 64 mm of length, 12.7 mm of width, 3.2 mm of thickness, and 0.25 mm of notch length. The results of five measurements were averaged.

Scanning electron microscope (SEM) (S-4300, Hitachi, Japan) was used to observe the morphology of the fractured surface of the composites. The sample sheets were prepared by pressing at 230°C under 3 metric ton. The sheets were immersed in liquid nitrogen for 10 min and then fractured manually while holding them with tweezers. The fractured surface was coated with platinum to avoid electrostatic charging during the SEM examination.

RESULTS AND DISCUSSION

The mechanical properties of ABS depend strongly on its butadiene content, and ABS with the butadiene content of 25 wt % (ABS(BD25)) is most widely used for the automobile interior parts.

When ABS(BD25) was compounded with PLA, the mechanical properties of (ABS(BD25)) were deteriorated significantly as shown in Table I, due to the lack of compatibility between the two polymers. For example, the impact strength of neat ABS(BD25) was 480 J m^{-1} , while that of ABS(BD25)50/PLA50 composite was as low as 22.0 J m^{-1} which is unacceptable to be used for the car console boxes. Therefore suitable compatibilizers and compounding techniques should be developed to raise especially the impact strength of the ABS(BD25)50/PLA50

TABLE I
Mechanical Properties of ABS/PLA Composites

Compatibilizers	Mechanical properties	
	Tensile strength (MPa)	Impact strength (J m^{-1})
ABS(BD25)	35.7	480
ABS(BD25)50/PLA50	43.8	22.0
ABS(BD25)40/PLA50/PC10	16.9 ± 0.31	30.3 ± 0.1
ABS(BD25)40/PLA50/PE-epoxy10	28.7 ± 0.86	28.2 ± 1.7
ABS(BD25)40/PLA50/EPR-MAH10	10.6 ± 0.26	25.1 ± 1.2
ABS(BD25)40/PLA50/SAN-MAH10	7.1 ± 1.20	14.6 ± 1.7
ABS(BD25)40/PLA50/SAN-GMA10	12.0 ± 1.74	29.3 ± 2.9

composite up to 80 J m^{-1} or above. The substances displayed in Figure 1 may increase the compatibility between ABS and PLA, because most of them have functional groups which are reactive toward PLA. The low-molecular-weight polycarbonate (PC) is whispered in industrial sectors as a potential compatibilizer for ABS/polyester blends.

ABS(BD25)50/PLA50 composites were prepared by using a twin screw extruder with L/D of 40 at $190\text{--}210\text{--}230^\circ\text{C}$ and 200 rpm. However, PC, PE-epoxy, EPR-MAH, SAN-MAH, and SAN-GMA were not effective at all for the ABS(BD25)50/PLA50 composites in that the incorporation of 10 phr of the five substances rather reduced the tensile strength. Moreover, the impact strength was also far inferior

to 80 J m^{-1} , the target value required for the car console boxes. Here the term “phr” means “hundred per resin.” For example, 10 phr of SAN-GMA corresponds to 10 g of SAN-GMA per 100 g of ABS(BD25)50/PLA50.

To raise the impact strength of the ABS/PLA composites, ABS with the BD content of 58 wt % (G-ABS) was added and thereby the BD content of ABS was increased from 25 to 28 wt % to prepare ABS(BD28)50/PLA50 composites. It can be seen in Table II that the tensile strength of ABS(BD28)50/PLA50 was lower than that of ABS(BD25)50/PLA50 because ABS(BD28) was more flexible than ABS(BD25). However, the impact strength of ABS(BD28)50/PLA50 was far superior to that of ABS(BD25)50/PLA50, indicating that a small increase in the BD content of ABS was very effective for the impact strength of ABS/PLA composites.

The tensile and impact strength of ABS(BD28)50/PLA50 composite are compiled in Table II as a function of the content of PC, PE-epoxy, EPR-MAH, SAN-MAH, and SAN-GMA. It can be realized that incorporation of SAN-GMA alone lowered the tensile strength of the ABS(BD25)50/PLA50, while the same compound raised the tensile strength of ABS(BD28)50/PLA50. SAN-GMA was more effective than the other substances for the enhancement of the mechanical properties. The ABS(BD28)50/PLA50 composite with 5phr of SAN-GMA exhibited the

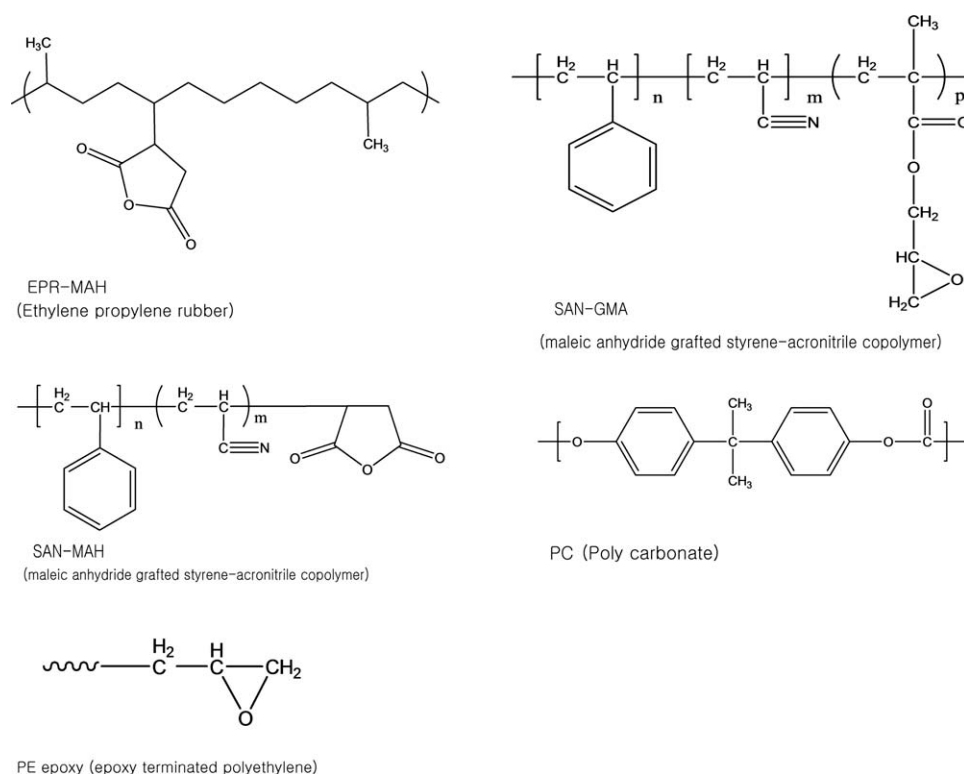


Figure 1 Compatibilizers for ABS(BD25)/PLA composites.

TABLE II
Tensile and Impact Strength of ABS(BD28)50/PLA50 Composite as a Function of the Content of PC, PE-epoxy, EPR-MAH, SAN-MAH, and SAN-GMA

Samples	Mechanical properties	
	Tensile strength (MPa)	Impact strength (J m^{-1})
ABS(BD28)50/PLA50	37.3	50.8
ABS(BD28)50/PLA50 PC 1 phr	33.6	21.0
ABS(BD28)50/PLA50 PC 2 phr	36.2	46.3
ABS(BD28)50/PLA50 PC 5 phr	35.3	63.6
ABS(BD28)50/PLA50 PE-Epoxy 1 phr	31.5	55.7
ABS(BD28)50/PLA50 PE-Epoxy 2 phr	23.7	50.2
ABS(BD28)50/PLA50 PE-Epoxy 5 phr	25.8	52.6
ABS(BD28)50/PLA50 EPR-MAH 1 phr	34.2	40.8
ABS(BD28)50/PLA50 EPR-MAH 3 phr	33.0	52.6
ABS(BD28)50/PLA50 EPR-MAH 5 phr	27.5	41.6
ABS(BD28)50/PLA50 SAN-MAH 1 phr	37.1	72.2
ABS(BD28)50/PLA50 SAN-MAH 3 phr	36.5	49.4
ABS(BD28)50/PLA50 SAN-MAH 5 phr	32.9	40.0
ABS(BD28)50/PLA50 SAN-GMA 1 phr	39.9	59.4
ABS(BD28)50/PLA50 SAN-GMA 3 phr	41.6	66.3
ABS(BD28)50/PLA50 SAN-GMA 5 phr	42.2	61.4

tensile strength higher than 40 MPa, the target value to be applied for the car console boxes. The impact strength also was increased due to the addition of SAN-GMA. However, the impact strength was below the target value. The mechanical properties of the ABS(BD28)50/PLA50 composites were examined in detail as a function of the content of SAN-GMA as summarized in Table III. Both tensile and flexural strength, flexural modulus and impact strength went up as the content of SAN-GMA increased, and thereby ABS(BD28)50/PLA50 incorporated with 20 phr of SAN-GMA met all the target properties to be used as car console boxes.

The mechanical properties of ABS(BD28)50/PLA50 composites in Table III were those prepared by compounding the ingredients with 0.1 phr of Irganox at 230°C. However, the thermally unstable PLA might be degraded considerably during the compounding process even in the presence of the

heat stabilizer to cause the lowering of the mechanical properties of the composites.

In this context, the effects of the further addition of a heat stabilizer, Songsorb, to the ingredients were investigated on the mechanical properties of the composites as summarized in Table IV. Songsorb in Figure 2 has been developed for the thermal stabilization of many polyesters.

Incorporation of Songsorb in the range of 0.0–1.0 phr did not affected the tensile strength, flexural strength, and flexural modulus, but raised the impact strength up to 158 J m^{-1} , indicating Songsorb was effective for the enhancement of the impact strength.

Figures 3 and 4 exhibit the TGA thermograms of PLA and ABS(BD28), respectively before and after the addition of 0.5 phr of Songsorb. The weight loss rate profile of PLA was unimodal, while that of ABS(BD28) showed multiple maxima, indicating that ABS(BD28) was not homogeneous but was heterogeneously composed of BD-rich phase and SAN-rich phase. The onset degradation temperature of PLA rose slightly, while that of ABS(BD28) remained almost unchanged as a result of the addition of 0.5 phr of Songsorb, indicating that Songsorb was more effective for the stabilization of PLA than ABS(BD28).

The enhancement of thermal stability can be quantified by measuring the change in the activation energy of the degradation reaction, which can be obtained from the TGA thermograms by using, for example, the Kissinger's equation as expressed in eq. (1).

$$\ln \frac{\beta}{T_{\max}^2} = \left\{ \ln \frac{AR}{E} + \ln \left[n(1 - \alpha_{\max})^{n-1} \right] \right\} - \frac{E}{RT_{\max}} \quad (1)$$

From the maximum peak temperatures, T_{\max} , in the thermal degradation rate profile in Figure 5 at different scanning rate, β , the thermal degradation reaction activation energy can be determined from the linear relationship between $\ln \frac{\beta}{T_{\max}^2}$ and $\frac{1}{T_{\max}}$.

TABLE III
The Mechanical Properties of ABS(BD28)50/PLA50 Composites as a Function of the SAN-GMA Content

Samples	Tensile strength (MPa)	Flexural strength (MPa)	Flexural modulus (MPa)	Impact strength (J m^{-1})
Target properties	40	60	2000	80
ABS(BD28)50/PLA50 SAN-GMA 0 phr	37.3	45.6	1960	50.8
ABS(BD28)50/PLA50 SAN-GMA 5 phr	42.2	43.4	2180	61.4
ABS(BD28)50/PLA50 SAN-GMA 10 phr	44.8	46.1	2220	63.4
ABS(BD28)50/PLA50 SAN-GMA 15 phr	49.7	59.8	2210	91.6
ABS(BD28)50/PLA50 SAN-GMA 20 phr	50.9	62.9	2300	92.3

TABLE IV
Effect of the Incorporation of Songsorb-3270 on the Mechanical Properties of the ABS(BD28)50/PLA50 Composites

Samples	Tensile strength (MPa)	Flexural strength (MPa)	Flexural modulus (MPa)	Impact strength (J m^{-1})
Target properties	40	60	2000	80
ABS(BD28)50/PLA50/SAN-GMA20/Songsorb 0.0 phr	50.9	62.9	2300	92.3
ABS(BD28)50/PLA50/SAN-GMA20/Songsorb 0.3 phr	49.8	63.7	2110	97.8
ABS(BD28)50/PLA50/SAN-GMA20/Songsorb 0.5 phr	51.9	67.4	2270	99.2
ABS(BD28)50/PLA50/SAN-GMA20/Songsorb 0.7 phr	51.9	67.0	2120	151
ABS(BD28)50/PLA50/SAN-GMA20/Songsorb 1.0 phr	51.9	68.0	2120	158

Because Songsorb contributes to the stabilization of PLA rather than ABS(BD28), the lower peak temperatures in Figure 5(b) were employed for the determination of the thermal degradation reaction activation energy.

Figure 6 displays the results of the Kissinger's equation plot for the ABS(BD28)50/PLA50 composite as a function of the Songsorb loading. It can be realized that the relationship between $\ln \frac{\beta}{T_{\max}^2}$ and $\frac{1}{T_{\max}}$ is linear enough to determine reliably the thermal degradation reaction activation energy. The results in Table V reveal that the thermal degradation reaction activation energy increases with increase in the Songsorb loading.

Another index to assess the thermal stabilization is the integral procedural decomposition temperature (IPDT).^{23,24} The IPDT values determined from eq. (2) based on Figure 7 are summarized in Table VI.

$$\text{IPDT}(^{\circ}\text{C}) = A \cdot K \cdot (T_f - T_i) + T_i \quad (2)$$

where, $A = (S1 + S2)/(S1 + S2 + S3)$, $K = (S1 + S2)/S1$

In line with the results of the thermal degradation reaction activation energy determined by using the Kissinger's equation, the IPDT values of the ABS(BD28)50/PLA50 composites went up with increase in the Songsorb loading.

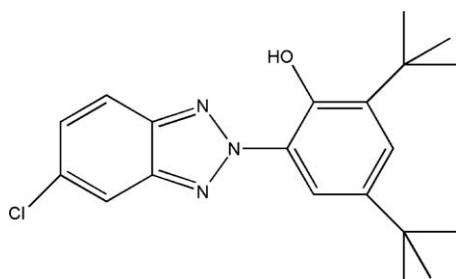


Figure 2 Molecular structure of Songsorb-3270.

To ascertain the stabilization effect of Songsorb more evidently, the ABS(BD28)50/PLA50 composite incorporated with 0–1 phr of Songsorb was subjected to the Soxhlet extraction for 1 week with THF. Because THF can dissolve selectively PLA from the ABS(BD28)50/PLA50 composite, the molecular weight of the extracted fraction in Table VII should be that of PLA.

It can be confirmed that Songsorb contributed to the stabilization of PLA and thereby decreased the

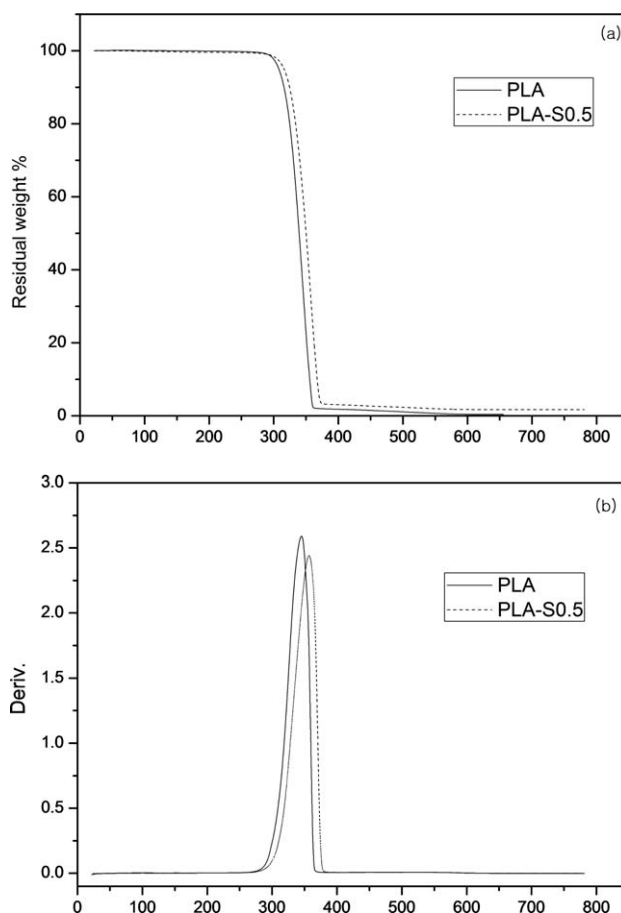


Figure 3 TGA (a) and DTG (b) thermograms of PLA before and after incorporation of 0.5 phr Songsorb.

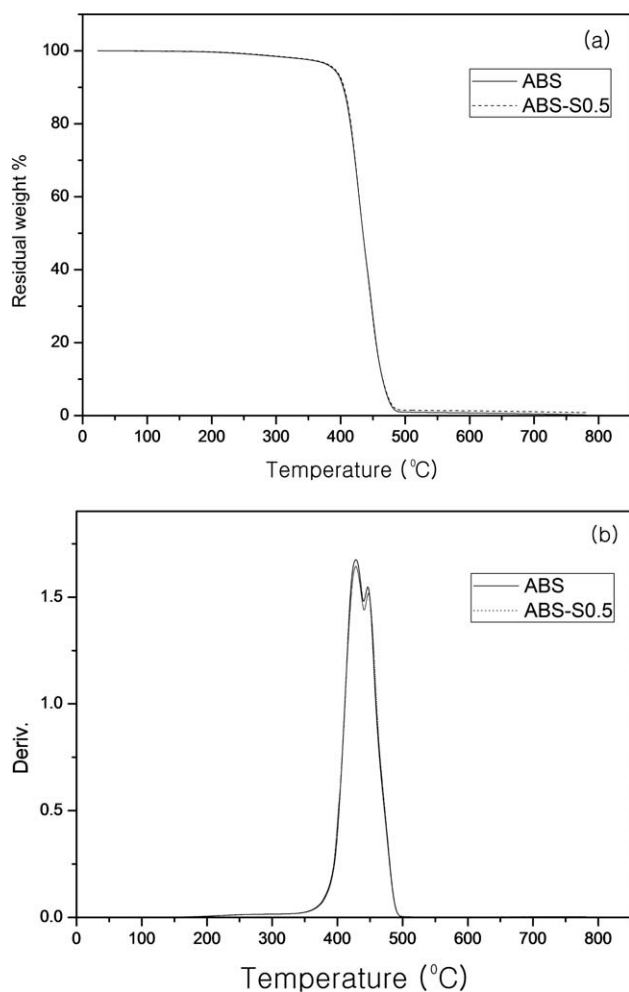


Figure 4 TGA (a) and DTG (b) thermograms of ABS(BD28) before and after incorporation of 0.5 phr Songsorb.

molecular weight reduction during the compounding process.

Figure 8 compares the cryofractured surface of the ABS(BD28)50/PLA50 composite sheet with and without 1.0 phr of Songsorb. The ABS(BD28)50/PLA50 composite without Songsorb exhibits dispersed islands with a well-defined boundary and even void interstices are seen between the continuous and dispersed phase. Composites with well-phase separated morphology usually originate from the lack of compatibility limiting the shear transfer between the constituents. However, the appearance of the void interstices at the boundaries in Figure 8(a) cannot be rationalized solely by the lack of compatibility.

PLA in the ABS(BD28)50/PLA50 composite without Songsorb may be degraded during the compounding process to produce substances such as L-lactide and other low molecular weight products which may be volatile at the compounding conditions. Those gaseous substances may accumulate

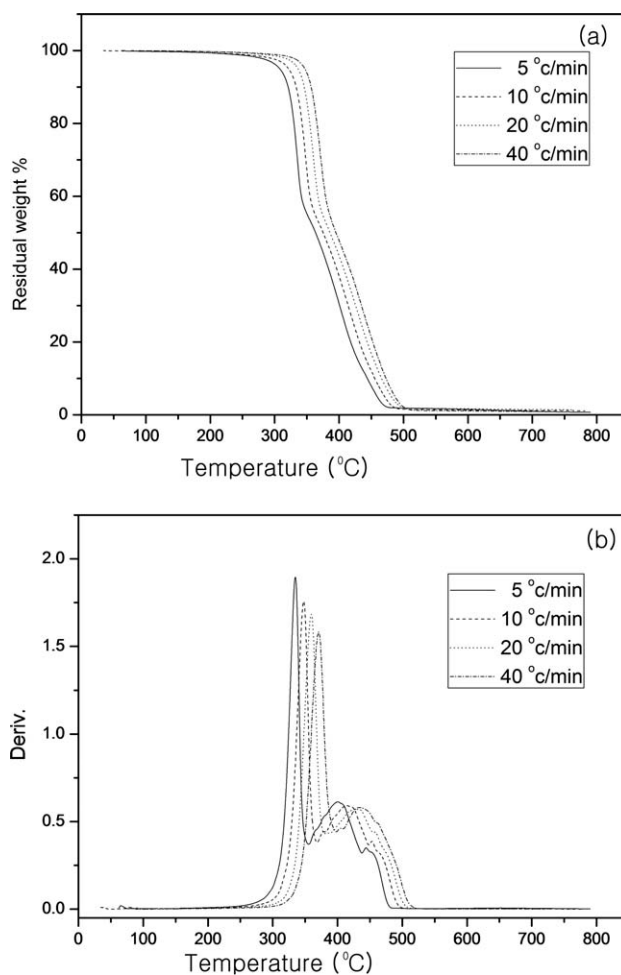


Figure 5 TGA and DTG thermograms of ABS(BD28)50/PLA50 composites as a function of heating rate.

between the phases at which the shear force is minimum, limiting the transfer of the shear force during the compounding. That is why the ABS(BD28)50/

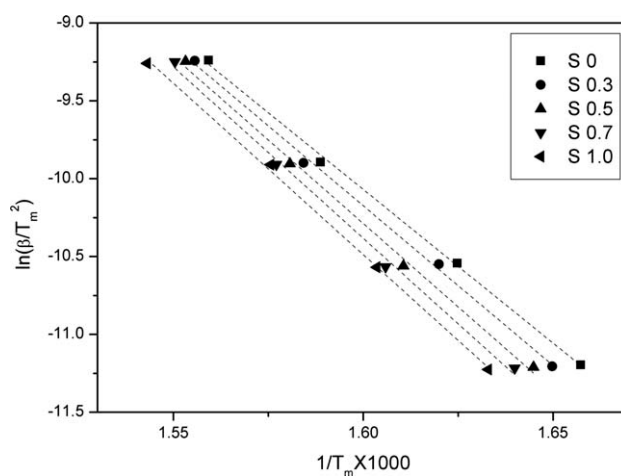


Figure 6 Representation of the TGA data of ABS(BD28)50/PLA50 composites by using the Kissinger's equation. The numbers of the legend correspond to the content of Songsorb in phr.

TABLE V
The Thermal Degradation Reaction Activation Energy as a Function of the Songsorb Loading

Songsorb content (phr)	0	0.3	0.5	0.7	1.0
Activation energy (kJ mol ⁻¹)	164 ± 0.02	171 ± 0.47	178 ± 0.15	183 ± 0.18	183 ± 0.03

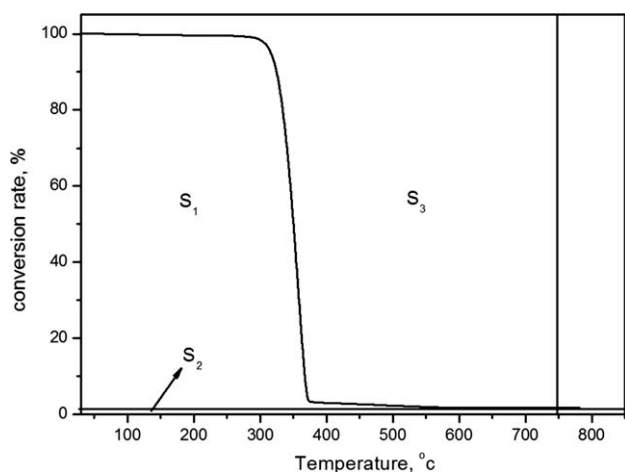


Figure 7 Schematic representation of S1, S2, and S3 for the calculation of A and K in eq. (2).

PLA50 composite without Songsorb demonstrates huge-sized dispersed islands with void interstices at the boundaries. In sharp contrast, ABS(BD28)50/PLA50 composite with 1.0 phr of Songsorb in Figure 8(b) shows a morphology with tightly adhered boundaries devoid of void interstices. Moreover the size of the dispersed phases in the ABS(BD28)50/PLA50 composite added with Songsorb is much smaller than that in the absence of Songsorb as compared in Figure 8(a,b).

Therefore it can be concluded that the mechanical properties of the ABS50/PLA50 composites can be improved significantly with increase in the BD content by the incorporation of G-ABS. The thermal stabilizer, Songsorb, was effective for the heat stabilization of PLA in the ABS50/PLA50 composites.

CONCLUSION

ABS50/PLA50 composites were prepared to raise the content of renewable substance in the ABS-based automobile interior parts. Incorporation of PLA into ABS deteriorated the mechanical properties of ABS significantly as was expected.

However, incorporation of G-ABS enhanced the impact strength of ABS/PLA composites astonishingly. The mechanical properties of the ABS/PLA composites were further improved by the addition of SAN-GMA, which was more effective than either PC, PE-epoxy, EPR-MAH, or SANMAH. The ABS50/PLA50 added with G-ABS and 5phr of SAN-GMA exhibited the tensile and impact strength higher than 40 MPa and 80 J m⁻¹, respectively, the target values to be applied for the car console boxes.

Incorporation of Songsorb in the range of 0.0–1.0 phr did not affect the tensile strength, flexural strength, and flexural modulus, but raised the impact strength significantly. Songsorb contributed

TABLE VI
The IPD Values of the ABS(BD28)50/PLA50 Composites as a Function of the Songsorb Loading

Songsorb content (phr)	0	0.3	0.5	0.7	1.0
A	0.45	0.45	0.46	0.46	0.46
K	1.01	1.015	1.022	1.033	1.041
IPDT (°C)	397 ± 0.23	399 ± 0.48	406 ± 0.14	409 ± 0.13	410 ± 0.35

TABLE VII
Molecular Weight of the Fraction Soxhlet Extracted from the ABS(BD28)50/PLA50 Composite at Different Loading of Songsorb

Songsorb content (phr)	0	0.3	0.5	0.7	1.0
M_n	56,900	61,100	60,600	63,900	65,600
M_w	117,200	117,300	115,900	124,300	128,100

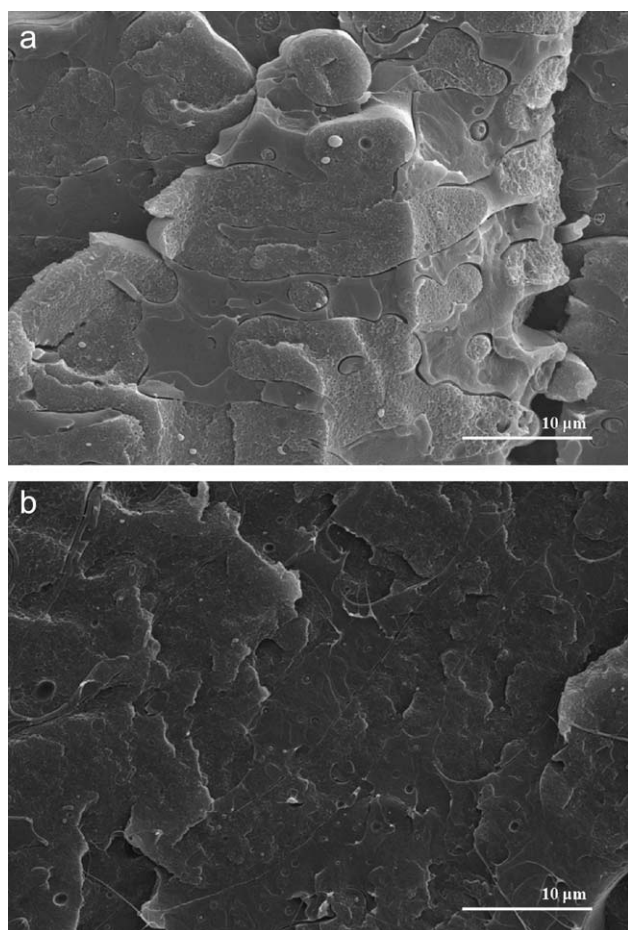


Figure 8 Cryofractured surface of the ABS(BD28)50/PLA50 composite with and without Songsorb (a) Songsorb 0.0 phr, (b) Songsorb 1.0 phr.

especially to the stabilization of PLA during the compounding process. Addition of Songsorb during the compounding process increased the activation energy of the thermal degradation of the ABS/PLA composites. It minimized the decrease in the molecular weight of PLA and reduced the production of volatile low molecular weight substances which should cause the formation of the void interstices

between the dispersed phase and the matrix of the composites.

The improved mechanical properties of the ABS50/PLA50 composites were attributed to the thermal stabilization effect of Songsorb toward PLA and to the increase in the BD content of ABS by the incorporation of G-ABS.

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