

Effects of Accelerated Aging and Compatibilizers on the Mechanical and Morphological Properties of Polypropylene and Poly(acrylonitrile-butadiene-styrene) Blends

Yun Kyun Lee, Jae Bok Lee, Dong Hyup Park, Woo Nyon Kim

Department of Chemical and Biological Engineering, Korea University, Anam-dong, Seoul 136-713, Korea

Correspondence to: W. N. Kim (E-mail: kimwn@korea.ac.kr)

ABSTRACT: The effects of maleic anhydride-grafted styrene-ethylene-butylene-styrene copolymer (SEBS-*g*-MAH) on the mechanical and morphological properties of polypropylene (PP) and poly(acrylonitrile-butadiene-styrene) (ABS) blends were investigated. Based on mechanical properties, including impact and tensile strengths, the PP/ABS (70/30) blends containing SEBS-*g*-MAH showed improved impact strength with minimal loss of tensile strength. As determined from morphological studies of the PP/ABS blends, addition of SEBS-*g*-MAH decreased PP/ABS blend droplet size more than the addition of SEBS. Additionally, the effects of SEBS-*g*-MAH and SEBS on the mechanical and morphological properties of the PP/ABS (70/30) blends were investigated during accelerated aging in an oven at 90°C for 72 h (one cycle). The impact strength of the PP/ABS (70/30) blends with SEBS-*g*-MAH (7 phr) decreased less than 10% after five cycles, but blends with SEBS (7 phr) and blends without compatibilizer decreased as much as 37%. The tensile strengths of the PP/ABS (70/30) blends after accelerated aging indicated a trend similar to that of the impact strength. The morphological studies indicated no significant changes in the PP/ABS (70/30) blends with SEBS-*g*-MAH; however, many cavities and damages were observed in the blend with SEBS. The above results suggest that SEBS-*g*-MAH acts as an impact modifier and as a good compatibilizer in the PP/ABS (70/30) blends. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: polymer blends; compatibility; mechanical property; morphology; accelerated aging

Received 31 May 2011; accepted 17 February 2012; published online

DOI: 10.1002/app.37504

INTRODUCTION

Polymer blending is an alternative way to synthesize new polymeric materials. Properties of the polymer blends are influenced by the properties of each component and dispersion of the dispersed phase. Unfortunately, most polymer blends are mutually incompatible.^{1–17} Compatibilizers have been used widely to improve the compatibility and properties of the polymer blends. The blending of various polymers containing polypropylene (PP) or poly(acrylonitrile-butadiene-styrene) (ABS) with maleic anhydride (MAH)-grafted polymers as a compatibilizer has been studied.^{5–15} In the melt, MAH groups react with functional groups of blending polymers and form block or graft copolymers easily.

Chiu and Hsiao¹⁰ have used maleic anhydride (MAH) grafted polyethylene-octene elastomer as a compatibilizer to improve mechanical strength of the nylon 6/ABS blends. Maleic anhydride grafted ABS has been used as impact modifier for polycarbonate/ABS blends.^{11–13} George et al.¹⁴ and Nakason et al.¹⁵

have used maleic-modified PP on the PP/nitrile rubber blends and PP/maleated natural rubber blends, respectively.

PP is one of the most widely used commodity polymers. It has good elongation and a high heat distortion temperature; in contrast, ABS has poor elongation and good impact strength. Hence, the PP/ABS blend is desirable to achieve higher impact strength without losing additional positive properties of each polymer. PP/ABS blends have been investigated in recent years and several papers describe PP/ABS blending.^{16–22} Previously, we investigated the effects of maleic anhydride-grafted polypropylene (PP-*g*-MAH) and maleic anhydride-grafted poly(styrene-*co*-acrylonitrile) (PP-*g*-SAN) on the mechanical, morphological, and rheological properties of a PP/ABS blend.^{16,17} Markin and Williams¹⁸ examined mechanical properties and morphology of a PP/ABS blend and reported improved impact strength with the addition of dispersed ABS to a PP matrix. Gupta et al.¹⁹ and Patel et al.²⁰ reported improvement in the compatibility of PP/ABS blends with the addition of polyethylene (PE) and PP-*g*-hydroxyethyl methacrylate (HEMA) to the blends,

© 2012 Wiley Periodicals, Inc.

Table I. Characteristics of Polymers Used in This Study

Sample	M_w^a (g/mol)	T_g^b (°C)	T_m^b (°C)	Tensile strength ^c (kg _f /cm ²)	Impact strength ^d (kg _f cm/cm)
PP	230,000	-10	164	310	7.1
ABS	160,000	118	-	500	23.0

^aMeasured by GPC, ^bMeasured by DSC at a heating rate of 10°C/min, ^cMeasured by UTM according to ASTM D638, ^dMeasured by Izod notched impact tester according to ASTM D256.

respectively. Khare et al.,⁸ Hom et al.,²¹ and Sung et al.,²² studied morphology and electrical properties of the PP/ABS blends with fillers such as carbon nanotube, carbon black, and organo-clay, respectively.

Knowledge about the properties of recycled polymeric materials is necessary to find appropriate and useful applications and to increase the use of these materials. One appropriate investigation procedure for polymer materials is a simulated recycling method. Accelerated thermo-oxidative aging is a common method for estimating the service lifetime of polymeric materials. Effects of aging on various materials such as PP,^{23,24} ABS,²⁵ and a polystyrene and poly(lactic acid) blend²⁶ have been investigated.

In this work, effects of compatibilizers such as maleic anhydride-grafted styrene-ethylene-butylene-styrene copolymer (SEBS-g-MAH) and styrene-ethylene-butylene-styrene (SEBS) on the mechanical and morphological properties of PP/ABS (70/30, wt %) blends were investigated. The blends of PP with SEBS^{7,27} or SEBS-g-MAH²⁸ have been reported by several investigators. However, the blends of PP and ABS with SEBS or SEBS-g-MAH can hardly be observed. Further, the effects of aging on PP/ABS (70/30) blends with SEBS or SEBS-g-MAH were investigated by accelerated aging.

EXPERIMENTAL

Materials

The polymers used in this study were obtained from commercial sources. The PP was supplied by GS Caltex Co. under the

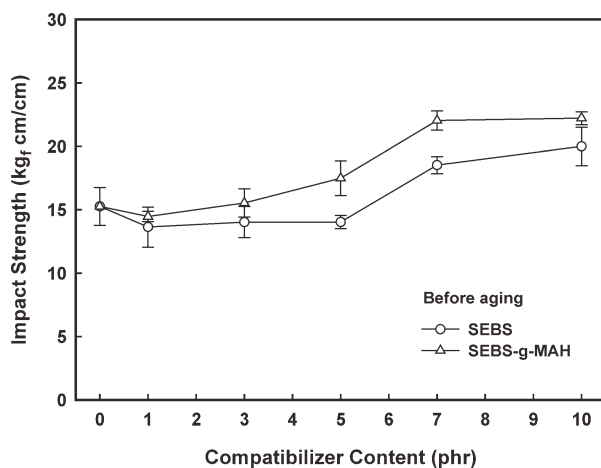


Figure 1. Impact strength of the PP/ABS (70/30) blends with compatibilizer: (○) SEBS; (Δ) SEBS-g-MAH.

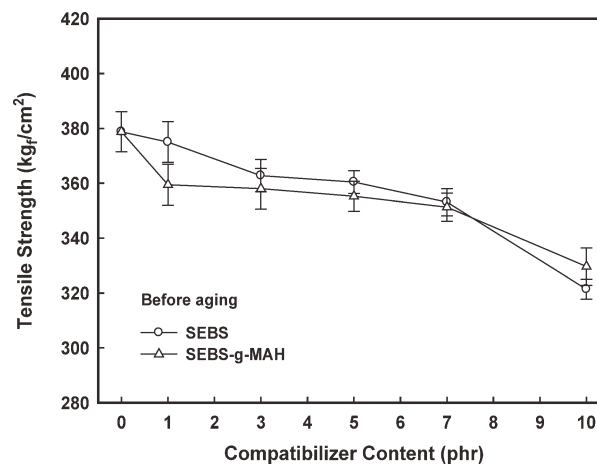


Figure 2. Tensile strength of the PP/ABS (70/30) blends with compatibilizer: (○) SEBS; (Δ) SEBS-g-MAH.

trade name H150. The ABS was supplied from LG Chem. Ltd. under the trade name XR-401. Both SEBS and SEBS-g-MAH were supplied from Shell Chemicals Co. under the trade names G1726M and FG1901X, respectively. The characteristics and sources of the polymer samples used in this study are shown in Table I

Blend Preparations

Blends of the PP/ABS were prepared in the ratio 70/30 by weight. Each compatibilizer was added to the PP/ABS (70/30) blends at 0, 1, 3, 5, 7, and 10 parts per hundred parts resin by weight (phr). The materials were dried in a vacuum oven (<1 mmHg) at 70°C for 24 h before use. The PP/ABS (70/30) blends were prepared via melt processing with a co-rotating, twin-screw extruder ($D = 11$ mm, $L/D = 40$) with six zones of temperatures, ranging from 200°C to 230°C along the barrel of the extruder. The screw speed of the extruder was set at 120 rpm.

Accelerated Aging of PP/ABS Blends

Accelerated aging was performed in the oven. For the PP/ABS (70/30) blends with SEBS or SEBS-g-MAH, each aging cycle was 72 h at 90°C, which corresponds to thermo-oxidative degradation for 1 yr at room temperature.²⁹ Samples were extracted and analyzed after 1, 3, and 5 cycles of accelerated aging.

Mechanical Properties

The impact strength of the PP/ABS (70/30) blends before and after accelerated aging was measured using a notched Izod impact strength tester (Toyoseiki DG-IB2). The impact test was performed according to ASTM D-256. The tensile strength of the PP/ABS (70/30) blends before and after accelerated aging was conducted according to ASTM D-638 with a universal testing machine (Instron 4467) at a crosshead speed of 100 mm/min and ambient conditions. For all of the above mechanical tests, seven specimens were measured and averaged.

Morphology

The morphology of the cross-section of the extrudate was analyzed by scanning electron microscopy (SEM) in an Hitachi S-4300 microscope at 15 kV accelerating voltage after Pt coating.

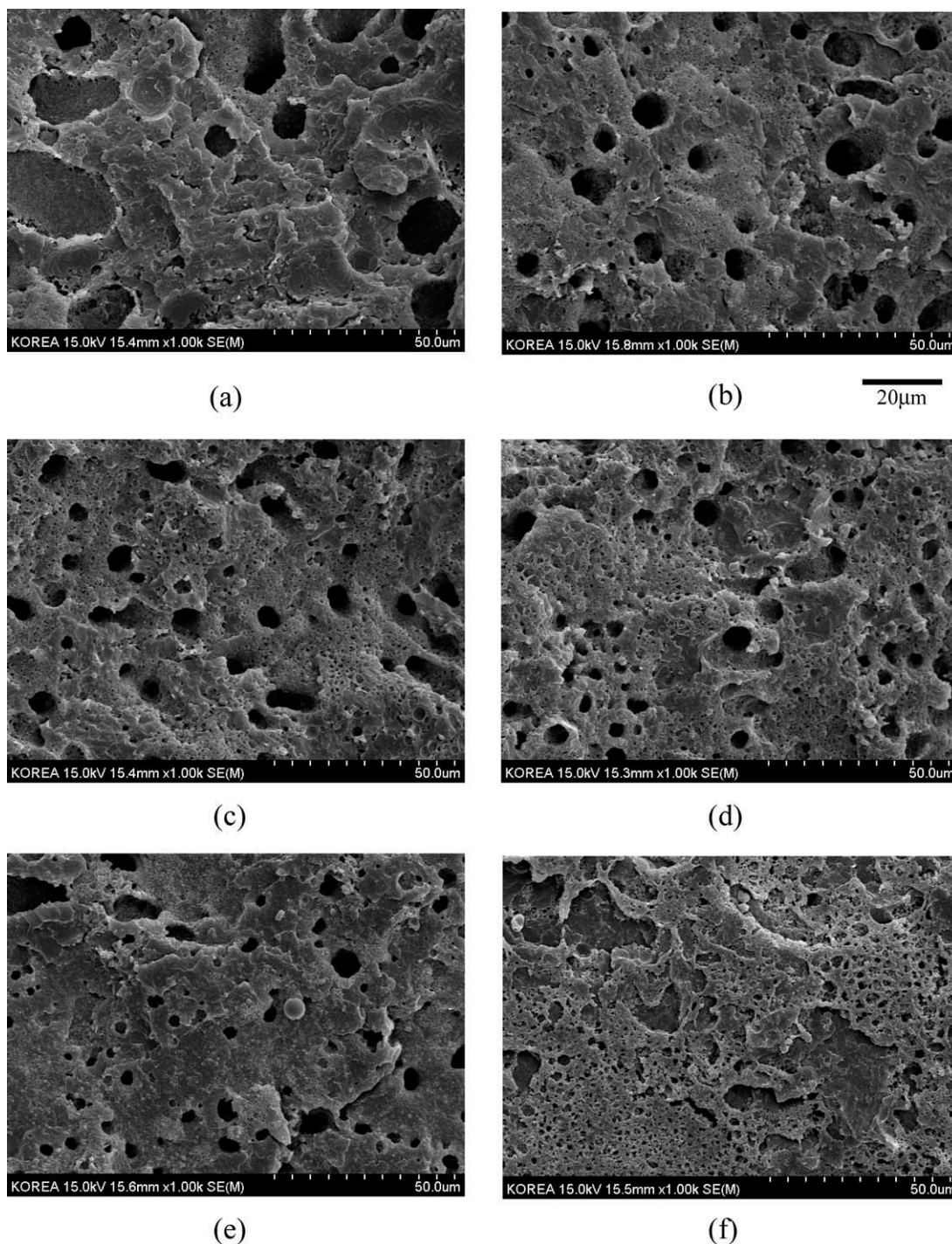


Figure 3. Scanning electron micrographs of the PP/ABS (70/30) blends with varying SEBS-g-MAH content: (a) 0 phr; (b) 1 phr; (c) 3 phr; (d) 5 phr; (e) 7 phr; (f) 10 phr.

The samples were fractured under cryogenic conditions and etched with methyl ethyl ketone (MEK) for ABS extraction.

RESULTS AND DISCUSSION

Mechanical Properties

Figure 1 shows the impact strength of the PP/ABS (70/30) blends according to SEBS or SEBS-g-MAH content (0, 1, 3, 5, 7, and 10 phr). Impact strength of the PP/ABS (70/30) blend

increases with increasing SEBS or SEBS-g-MAH content. For the PP/ABS (70/30) blend with SEBS-g-MAH (7 phr), the impact strength of the blends increases from 15.3 to 22.2 kg_f cm/cm, while the blends with SEBS increase from 15.3 to 19.1 kg_f cm/cm when the SEBS content is 7 phr. For concentrations of SEBS or SEBS-g-MAH greater than 7 phr, the impact strength of the blends does not change appreciably with further increase of SEBS or SEBS-g-MAH content.

Table II. Average Particle Radius (R_n) of the PP/ABS (70/30) Blends with Compatibilizer

Compatibilizer content (phr)	R_n^a	
	SEBS	SEBS-g-MAH
0	8.6	8.6
1	8.3	7.3
3	7.2	6.4
5	6.6	4.8
7	5.4	4.2
10	3.3	2.1

^a $R_n = \sum n_i R_i / \sum n_i$, where n_i is the number of particles and R_i is the radius of particles.

Figure 2 shows the tensile strength of the PP/ABS (70/30) blends with the SEBS or SEBS-g-MAH content (0, 1, 3, 5, 7, and 10 phr). Contrary to impact strength, tensile strength of the PP/ABS (70/30) blends decreases from 375 to 350 kg_f/cm² with increasing SEBS or SEBS-g-MAH content up to 7 phr. After this concentration, the tensile strength of the PP/ABS blends decreases suddenly with increasing SEBS or SEBS-g-MAH content from 7 to 10 phr. The sudden decrease in tensile strength with addition of 10 phr of SEBS may be because of behavior similar to that of a PP/ABS/SEBS ternary blend, which decreases tensile strength because of the plasticizer effect of SEBS in the PP/ABS blends. The above mechanical properties of the PP/ABS (70/30) blends with SEBS or SEBS-g-MAH suggest that SEBS-g-MAH acts more effectively as an impact modifier in the PP/ABS (70/30) blend than SEBS.

From Figure 2, the tensile strengths of the PP/ABS (70/30) blends with SEBS (3 phr) or SEBS-g-MAH (3 phr) are found to be 362.8 and 358.0 kg_f/cm², respectively. Standard deviations of the PP/ABS (70/30) blends with SEBS (3 phr) or SEBS-g-MAH (3 phr) are observed to be 5.8 and 7.4 kg_f/cm², respectively. From this result, it is suggested that the difference in tensile strength of the PP/ABS (70/30) blends with the compatibilizers of SEBS or SEBS-g-MAH is not significant, especially before aging the blends.

In the studies of PP/ABS (75/25) blends with PP-g-HEMA as a compatibilizer, Patel et al.,²⁰ reported that impact strength of the PP/ABS blends showed 0.6–4.3 kg_f cm/cm when the PP-g-HEMA content was 0 to 5 phr, respectively. For the tensile strength, the PP/ABS blends showed 294.9–308.2 kg_f/cm² when the PP-g-HEMA content was 0 to 5 phr, respectively. From this result, it is suggested that the PP-g-HEMA plays an important role as an impact modifier.

Morphology

Figure 3(a–f) shows SEM images of the cryogenically fractured surfaces of the PP/ABS (70/30) blends with SEBS-g-MAH concentrations of 0, 1, 3, 5, 7, and 10 phr, respectively. The ABS phase was dissolved selectively using MEK. From Figure 3, the particle size of ABS in the blends decreased with increasing SEBS-g-MAH content. As shown in Figure 3 and Table II, the size of the dispersed ABS is 8.6, 7.3, 6.4, 4.8, 4.2, and 2.1 μm with a SEBS-g-MAH content of 0, 1, 3, 5, 7, and 10 phr, respectively.

In Figure 4, panels (a) and (b) show the morphology of the PP/ABS (70/30) blends with SEBS and SEBS-g-MAH, respectively. The compatibilizer concentration is set at 7 phr. From Figure 4(a,b), the domain sizes of the dispersed phase (ABS) were 5.4 and 4.2 μm, respectively. Figure 5 shows the ABS domain sizes of the PP/ABS (70/30) blends with SEBS and SEBS-g-MAH. From Figures 4 and 5, the ABS domain sizes of the PP/ABS (70/30) blends with SEBS-g-MAH appear smaller than those of the blends with SEBS. For the PP/ABS (70/30) blends with SEBS-g-MAH, there may be dipolar interactions between the maleic anhydride group and the polar group in the ABS. Therefore, the size of the dispersed phase (ABS) decreased with addition of SEBS-g-MAH, which may act as a compatibilizer in the PP/ABS blends. These results suggest that SEBS-g-MAH is a more efficient compatibilizer than SEBS in the PP/ABS blends. This result is consistent with the impact strength results for the PP/ABS (70/30) blends.

Accelerated Aging of the PP/ABS Blends

Figure 6 shows impact strength of the PP/ABS (70/30) blends with accelerated aging cycle. Impact strength of the PP/ABS (70/30) blends decreases with an increase of aging cycles. For the PP/ABS (70/30) blend with SEBS-g-MAH (7 phr), impact

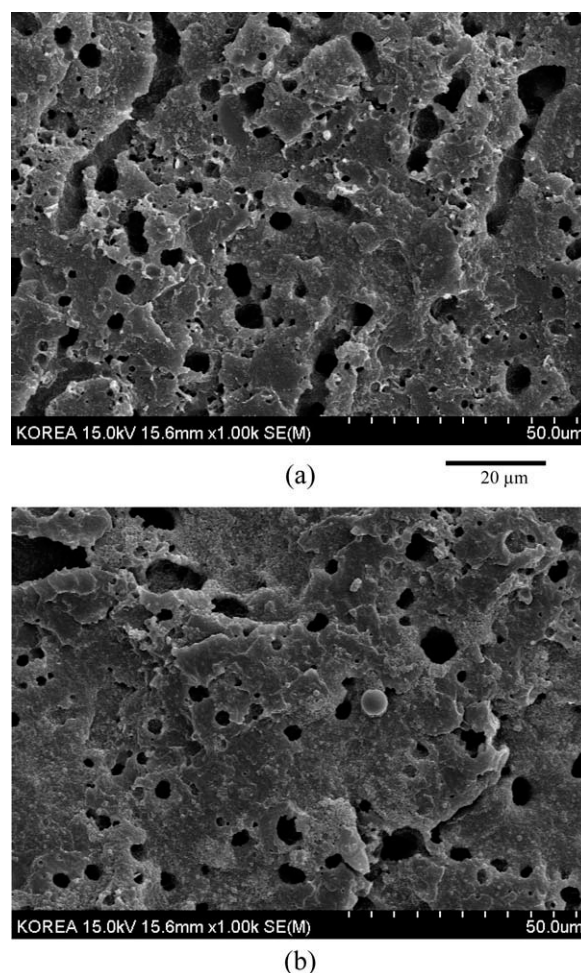


Figure 4. Scanning electron micrographs of the PP/ABS (70/30) blends with compatibilizer (7 phr): (a) SEBS; (b) SEBS-g-MAH.

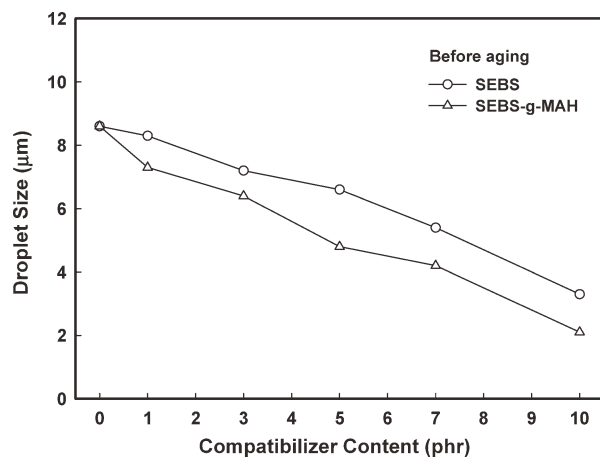


Figure 5. Droplet size of the dispersed phase (ABS) in the PP/ABS (70/30) blends with compatibilizer: (○) SEBS; (Δ) SEBS-g-MAH.

strength decreases from 22.1 to 20.0 kg_f cm/cm after five cycles. For the PP/ABS (70/30) blend without compatibilizer and the blend with SEBS (7 phr), impact strengths decrease steeply after the first cycle and decrease as much as 37% after five cycles of accelerated aging relative to the preaging values.

Tensile strength of the PP/ABS (70/30) blends with accelerated aging cycle is shown in Figure 7. For the PP/ABS (70/30) blend with SEBS-g-MAH (7 phr), the tensile strength reveals no significant change, but the tensile strength of the PP/ABS (70/30) blend with SEBS (7 phr) decreases steeply with the number of accelerated aging cycles. By investigating mechanical properties of the PP/ABS (70/30) blends after accelerated aging, similar tendencies were observed. After accelerated aging cycles, impact and tensile strengths of the PP/ABS blends with SEBS-g-MAH decrease slower than those with SEBS. Thermo-oxidative degradation, which was caused by accelerated aging of ABS, was expected for polybutadiene, since it is the most sensitive component of ABS.^{30,31} Decreases of mechanical properties are possibly caused by a deple-

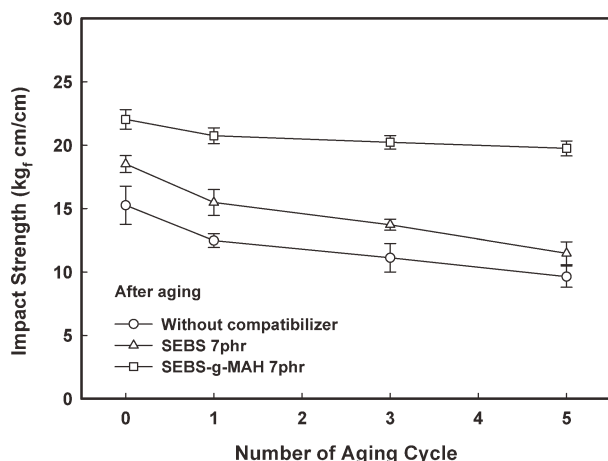


Figure 6. Impact strength after accelerated aging of the PP/ABS (70/30) blends: (○) without compatibilizer; (Δ) with SEBS (7phr); (□) with SEBS-g-MAH (7 phr).

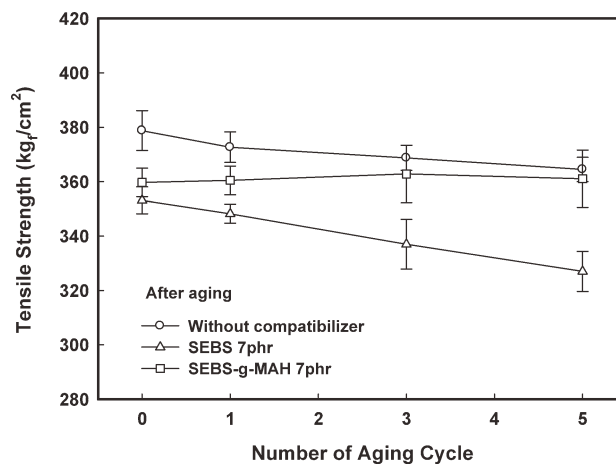


Figure 7. Tensile strength after accelerated aging of the PP/ABS (70/30) blends: (○) without compatibilizer; (Δ) with SEBS (7 phr); (□) with SEBS-g-MAH (7 phr).

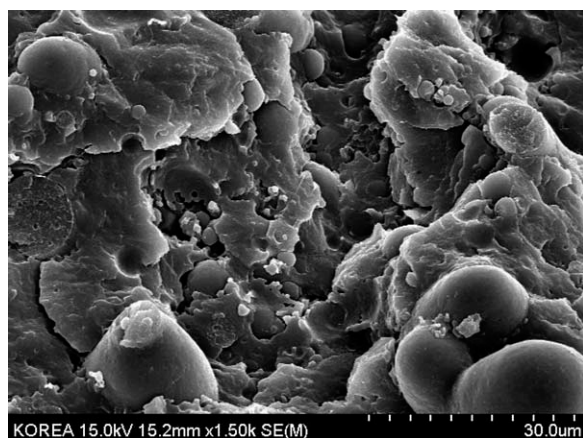
tion of polybutadiene unsaturation by oxidation. Such a decrease of unsaturation may produce a brittle surface layer that is more likely to initiate cracks in the bulk of the material and consequently to reduce adhesion.^{32,33} A possible explanation for the mechanical property differences of the PP/ABS (70/30) blend with SEBS and SEBS-g-MAH after accelerated aging may be related to improved compatibility between the two polymers (PP and ABS) by interaction of the MAH groups of SEBS-g-MAH and the polar groups of ABS, slowing unsaturation of polybutadiene.

Figure 8(a,b) show SEM images of the fractured surface of the PP/ABS (70/30) blends with SEBS (7 phr) and SEBS-g-MAH after accelerated aging for five cycles, respectively. No significant changes were observed in the PP/ABS blends with SEBS-g-MAH, but many cavities and damages of surface were observed in the blend with SEBS. These results suggest that SEBS-g-MAH improves compatibility between PP and ABS and slows oxidation as both an impact modifier and compatibilizer.

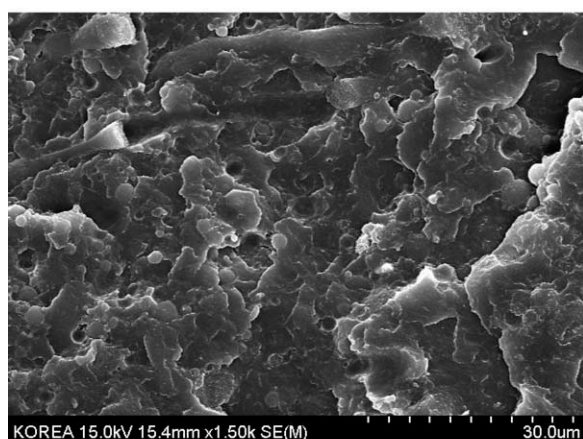
CONCLUSIONS

This study investigated the effects of SEBS-g-MAH and SEBS on the mechanical and morphological properties of the PP/ABS (70/30) blends during accelerated aging. The PP/ABS (70/30) blends containing SEBS-g-MAH showed improved impact strength with minimal tensile strength loss. This result suggests that MAH in SEBS-g-MAH plays an important role as an impact modifier and compatibilizer with the PP/ABS blend. Given the results of the morphological studies, PP/ABS (70/30) blends with SEBS-g-MAH have a smaller droplet size than the blends with SEBS.

Studying accelerated aging of the PP/ABS (70/30) blends in an oven at 90°C for 72 h (one cycle), the impact strength of blends with SEBS-g-MAH (7 phr) decreases less than 10% after five cycles and that for blends with SEBS (7 phr) and blends without compatibilizer decreases as much as 37%. The tensile strengths of the PP/ABS (70/30) blends after accelerated aging demonstrated a tendency similar to that of impact strength. From the morphological studies, there were no significant changes in the PP/ABS



(a) 15 μm



(b)

Figure 8. Scanning electron micrographs of the PP/ABS (70/30) blends with compatibilizer (7 phr) after accelerated aging for five cycles: (a) SEBS; (b) SEBS-g-MAH.

blends with SEBS-g-MAH; however, many cavities and extensive damage were observed after five cycles of accelerated aging in the blends with SEBS. The above results suggest that SEBS-g-MAH can improve compatibility between the PP and ABS and slow oxidation, thus acting as both an impact modifier and compatibilizer, possibly because of dipolar interactions between the MAH group and polar group in ABS.

ACKNOWLEDGMENTS

This research was supported by the National Research Foundation of Korea Grant funded by the Korean Government (MEST) (NRF-2010-0012831).

REFERENCES

- Paul, D. R.; Bucknall, C. B. *Polymer Blends*; Wiley: New York, 2000.
- Utracki, L. A. *Polymer Alloys and Blends*; Hanser: New York, 1989.

- Leite, P. R. S.; Soares, B. G.; Siqueira, A. S. *J. Appl. Polym. Sci.* **2011**, *120*, 981.
- Razavi-Nouri, M.; Naderi, G.; Parvin, A.; Ghoreishy, H. R. *J. Appl. Polym. Sci.* **2011**, *120*, 1365.
- Elmaghor, F.; Zhang, L.; Fan, R.; Li, H. *Polymer* **2004**, *45*, 6719.
- Zhidan, L.; Juncai, S.; Chao, C.; Xiuju, Z. *J. Appl. Polym. Sci.* **2011**, *121*, 1972.
- Su, F.-H.; Huang, H.-X. *J. Appl. Polym. Sci.* **2009**, *112*, 3016.
- Khare, R. A.; Bhattacharyya, A. R.; Kulkarni, A. R. *J. Appl. Polym. Sci.* **2011**, *120*, 2663.
- Brostow, W.; Datashvili, T.; Geodakyan, J.; Lou, J. *J. Mater. Sci.* **2011**, *46*, 2445.
- Chiu, H. T.; Hsiao, Y. K. *Polym. Eng. Sci.* **2004**, *44*, 2340.
- Balakrisnan, S.; Neelakantan, N. R.; Saheb, D. N.; Jog, J. P. *Polymer* **1998**, *39*, 5765.
- Zhang, X.; Chen, Y.; Zhang, Y.; Peng, Z.; Zhang, Y.; Zhou, W. *J. Appl. Polym. Sci.* **2001**, *81*, 831.
- Elmaghor, F.; Zhang, L.; Fan, R.; Li, H. *Polymer* **2004**, *45*, 6719.
- George, S.; Varughese, K. T.; Thomas, S. *Polymer* **2000**, *41*, 5485.
- Nakason, C.; Saiwari, S.; Kaesaman, A. *Polym. Test* **2006**, *25*, 413.
- Kum, C. K.; Sung, Y. T.; Kim, Y. S.; Lee, H. G.; Kim, W. N.; Lee, H. S.; Yoon, H. G. *Macromol. Res.* **2007**, *15*, 308.
- Lee, H. G.; Sung, Y. T.; Lee, Y. K.; Kim, W. N.; Yoon, H. G.; Lee, H. S. *Macromol. Res.* **2009**, *17*, 417.
- Markin, C.; Williams, H. C. *J. Appl. Polym. Sci.* **1980**, *25*, 2451.
- Gupta, A. K.; Jain, A. K.; Maiti, S. N. *J. Appl. Polym. Sci.* **1990**, *39*, 515.
- Patel, A. C.; Brahmabhatt, R. B.; Devi, S. *J. Appl. Polym. Sci.* **2003**, *88*, 72.
- Hom, S.; Bhattacharyya, A. R.; Khare, R. A.; Kulkarni, A. R.; Saroop, M.; Biswas, A. *J. Appl. Polym. Sci.* **2009**, *112*, 998.
- Sung, Y. T.; Kim, Y. S.; Lee, Y. K.; Kim, W. N.; Lee, H. S.; Sung, J. Y.; Yoon, H. G. *Polym. Eng. Sci.* **2007**, *47*, 1671.
- Jansson, A.; Moller, K.; Gevert, T. *Polym. Degrad. Stab.* **2003**, *82*, 37.
- Wang, X.; Yu, W.; Nie, Q.; Guo, Y.; Du, J. *J. Appl. Polym. Sci.* **2011**, *121*, 1220.
- Boldizar, A.; Moller, K. *Polym. Degrad. Stab.* **2003**, *81*, 359.
- Hamad, K.; Kaseem, M.; Deri, F. *J. Mater. Sci.* **2011**, *46*, 3013.
- Setz, S.; Stricker, F.; Kressler, J.; Duschek, T.; Mulhaupt, R. *J. Appl. Polym. Sci.* **1996**, *59*, 1117.
- Ao, Y.-H.; Tang, K.; Xu, N.; Yang, H.-D.; Zhang, H.-X. *Polym. Bull.* **2007**, *59*, 279.
- Kelen, T. *Polymer Degradation*. Van Nostrand Reinhold: New York, 1983.
- Wyzgoski, M. G. *Polym. Eng. Sci.* **1976**, *16*, 265.
- Suzuki, M.; Wiklie, C. A. *Polym. Degrad. Stab.* **1995**, *47*, 217.
- Carter, R. O.; McCullum, J. B. *Polym. Degrad. Stab.* **1994**, *45*, 1.
- Bair, H. E.; Boyle, J. D.; Kelleher, P. G. *Polym. Eng. Sci.* **1980**, *20*, 995.