Blends of Poly(ethylene terephthalate) Bottle Waste with Modified Styrene Butadiene Rubber Through Reactive Mixing

O. Moini Jazani, A. Aref Azar

Polymer Engineering Department, Amir Kabir University of Technology, Tehran, Iran

ABSTRACT: Styrene butadiene rubber (SBR) was modified by the grafting reaction of maleic anhydride (MAH) in the presence of the initiator benzoyl peroxide (BPO). This modified elastomer was then blended with poly(ethylene terephthalate) (PET) bottle waste, and the mechanical and morphological properties of the resulting blends were studied. The amount of grafted MAH was determined by chemical titration. The results revealed that the concentrations of MAH and BPO strongly affected the grafting process. The morphology of the dispersed phase for blends of PET waste and SBR-*g*-MAH was quite different from that of a simple blend of PET waste and SBR. Dynamic mechanical thermal analysis revealed suitable compatibility between PET waste and styrene butadiene rubber-*graft*-maleic anhydride (SBR-*g*-MAH). The enhanced compatibility resulted in better impact properties. The better compatibility was concluded to result from bond formation between the carbonyl group of SBR-*g*-MAH and the hydroxyl or carboxyl end groups of PET. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 1615–1623, 2006

Key words: adhesion; alloys; blending; blends; graft copolymers; morphology; reactive processing

INTRODUCTION

Poly(ethylene terephthalate) (PET) is an engineering plastic widely used as an engineering thermoplastic and in packaging, electronics, and other applications.[1] One drawback of this polymer is its sensitivity to notch formation, which causes brittle failure at room temperature.

One of the methods for overcoming this problem is blending this plastic with an elastomer.[2–6] However, this plastic is incompatible with most rubbers.[7,8] Therefore, a simple blend of PET with styrene butadiene rubber (SBR) possesses low mechanical properties. This is due to the phase separation of the two polymers, which is the result of their incompatibility. Therefore, an increase in the compatibility of the two polymers will result in better mechanical properties. The method followed here involves the grafting of rubber with maleic anhydride (MAH) to build chemical links between the rubber and PET waste. The modified rubber was blended with PET. Then morphological, thermal, and mechanical properties of these blends were studied.

EXPERIMENTAL

Materials

PET bottle waste was taken from general use [the melting point, determined by differential scanning calorimetry (DSC), was 248.2°C; its source granule was derived from TexPET, Korea]. SBR (a random copolymer), from Bandar–Imam Petrochemical Co. (Poliran 1502), had a density of 0.93 gr/cm³ (ASTM D 790; styrene concentration = 22.5–24.5 wt %). Commercial MAH (grade 800408; Merk Co., Darmstadt, Germany) and benzoyl peroxide (BPO; grade 801641; Merk, Darmstadt, Germany) with melting points of 53 and 105°C, respectively, were used. A solution of HCl in isopropyl alcohol (grade 109973) and a KOH solution in ethanol (grade 109115) were obtained from Merk. Irganox, with a melting point of 170°C (Ciba–Geigy), was used to prevent oxidation.

Equipment

A Rheomixer HBI SYS 90 internal mixer with a chamber capacity of 300 mL and a fill factor of 75% was used in the mixing process, and an injection-molding machine (Imen Machine Co.) was used to prepare the samples for tests.

A Zwick extensometer was employed for tensile tests according to ASTM D 638. Impact tests (Izod notched) were carried out on a Zwick device accord-

Correspondence to: A. A. Azar (arefazar@aut.ac.ir).

TABLE I
Formulations Used for Grafting

Formulation	SBR (phr)	MAH (phr)	BPO (phr)
a	100	1	0.06
b	100	1.5	0.06
c	100	2	0.06
d	100	2.5	0.06
e	100	2	0.01
f	100	2	0.14
g	100	2	0.2

ing to ASTM D 256. Scanning electron microscopy (SEM; JXA-840, JEOL, Tokyo, Japan) was used to study the morphology of the samples. Dynamic mechanical thermal analysis (DMTA) measurements were carried out on a Thermal Analysis 983 DMA instrument from TA Instruments (New Castle, DE). The IR spectrometry analysis of maleated SBR was performed with a Bomem (Canada) Fourier transform infrared (FTIR) apparatus. Thermal analysis was carried out with a differential scanning calorimeter (910, Dupont, Wilmington, DE). The temperature was raised from 20 to 300°C at a rate of 10°C/min.

Procedure

Grafting of SBR

SBR was dried at 80°C for 6 h and then was fed into an internal mixer at 160°C. After 4 min, MAH was added, and after 1 min more, BPO was added to the mixture. The roller speed was 50 rpm, and the total mixing time was 10 min. The different formulations used to obtain grafted SBR are shown in Table I.

The extent of the MAH–SBR reaction was determined by a titration method. This was done through the dissolution of 1 g of grafted rubber in 100 mL of toluene with refluxing at 65°C for 3 h. Subsequently, 50 mL of water was added, and three different phases were formed: (1) an organic phase containing SBR grafted with MAH, (2) an aqueous phase containing unreacted MAH, and (3) a gel consisting of

crosslinked rubber. The organic phase was separated and was titrated with a KOH solution in ethanol with $0.1N$ thymol blue as an indicator. An excess of 0.5 mL of KOH was added to the solution (the color changed from yellow to blue), and it was retitrated with HCl (until the color changed to yellow). The acid number and the percentage of MAH that reacted were calculated according to the following relations:

Acid number (mg of KOH/g of rubber)

$$= \frac{\text{mL of KOH} \times \text{NKOH} \times 56.1}{1 \text{ g of Rubber}}$$

Reacted MAH(%) Reacted MAH (%)

$$= \frac{(\text{Acid number}) \times 98 \times \text{g of Rubber}}{2 \times 561 \times \text{g of MAH}}$$

where rubber is the SBR used in the sample formulation. The measurements of the MAH grafting reaction efficiency through titration are well known.[9–12] Some of the extracted organic phase before titration was placed on a watch glass and then placed in an oven for 10 min at 100°C, and thin films were formed. These films were used for FTIR spectroscopy.

Blending procedure

PET bottle waste was collected, ground, washed, and then dried for 12 h at 110°C; then, according to the formulations shown in Table II, blends were prepared with an internal mixer at a speed of 50 rpm at 260°C. The component addition sequence was as follows. First, PET with Irganox was added, and then after 4 min, styrene butadiene rubber-*graft*-maleic anhydride (SBR-*g*-MAH) was added to the system. After 7 min, mixing was stopped. After the mixing, the ground samples were kept in an oven for 4 h at 120°C. The specimens for tensile and impact tests were injection-molded with a mold temperature of 7°C and a feed stage temperature of 260°C.

TABLE II
Formulations Used in Blending

Code	Formulation	PET (phr)	SBR-g-MAH (phr)	Irganox (phr)
K_0	PETRW[a]	100	—	—
K_1	PETW50	100	—	0.1
K_2	PETWSBRP	100	15	0.1
K_3	PETWSBRd$_1$	100	15 (1 phr MAH)	0.1
K_4	PETWSBRd$_2$	100	15 (1.5 phr MAH)	0.1
K_5	PETWSBRd$_3$	100	15 (2 phr MAH)	0.1
K_6	PETWSBRd$_4$	100	15 (2.5 phr MAH)	0.1
K_7	PETWSBRd$_5$-t$_2$	100	10 (1 phr MAH)	0.1
K_8	PETWSBRd$_7$-t$_2$	100	20 (1 phr MAH)	0.1

[a] PET as received.

TABLE III
Percentage of MAH Grafted onto SBR and Gel Content

Formulation	Reacted MAH (%)	Gel content (%)
a	66.11	73
b	39.2	81
c	46.6	74
d	40.2	76

The mold temperature was kept low to approach a quenching operation in which the mold was sufficiently cold and the cooling time was short. Under these conditions, it was possible to obtain a mostly amorphous material.

Tensile tests were carried out at a strain rate of 50 mm/min according to ASTM D 638. Impact Izod specimens were notched (2 mm deep) with an angle of 45°. Samples 1.5 mm thick were cut from the fracture surfaces of impact specimens and gold-coated for the SEM studies. Also, DMTA samples were heated from room temperature to 180°C at a rate of 5°C/min. DSC was used to study the thermal properties of the PET waste. The temperature was raised from 25 to 300°C at a rate of 10°C/min.

RESULTS AND DISCUSSION

MAH grafting onto SBR

Effect of the MAH concentration

The results for the percentage of MAH-grafted groups on SBR are shown in Table III. As the MAH concentration increases from 1 to 1.5 phr, the percentage of grafting decreases, and the gel content increases from 73 to 81%. As the MAH concentration increases from
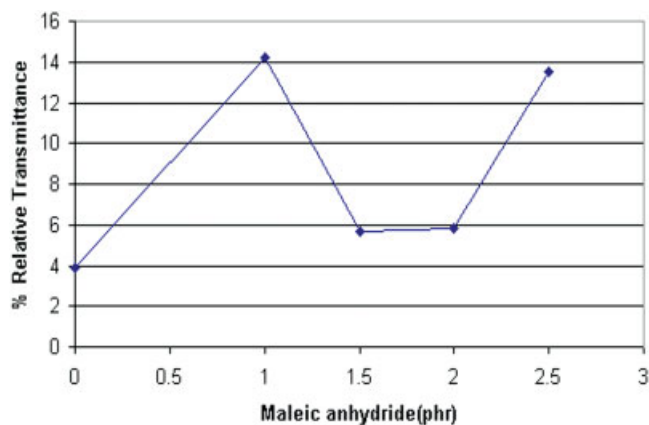

Figure 2 BPO concentration effect on the percentage of MAH grafted onto SBR (temperature = 160°C, N = 50 rpm).

1.5 to 2 phr, the percentage of grafting increases, and the gel content decreases from 81 to 74%. Again, as the concentration increases from 2 to 2.5 phr, the grafting percentage decreases, and the gel content increases from 74 to 76%. This occurs because at a low concentration of MAH, the decomposition of peroxide mol-

Figure 1 Relative transmittance percentage (consumption of vinyl groups) as a function of the MAH content. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
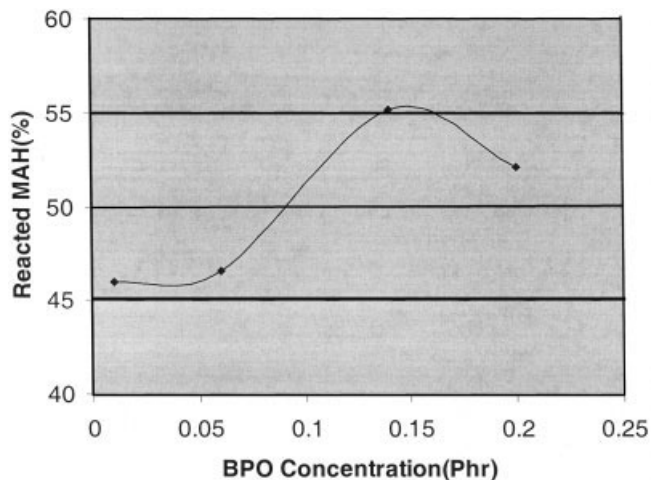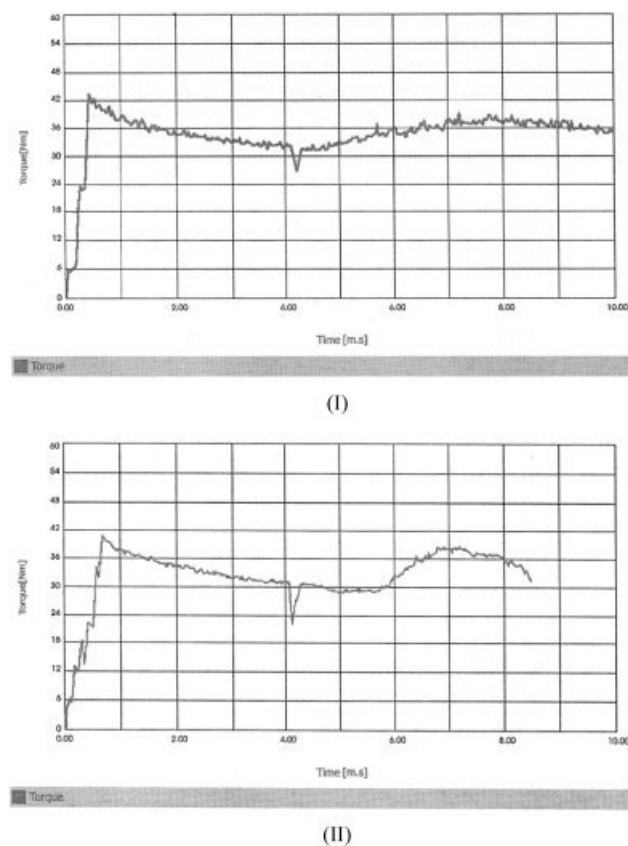

Figure 3 Torque–time curves for formulation c at different temperatures (N = 50 rpm): (I) 160 and (II) 190°C.
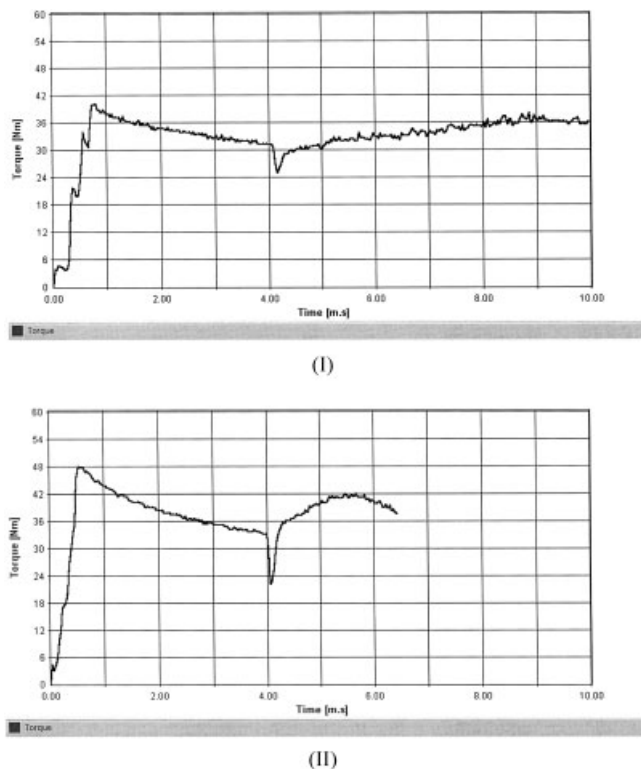
Figure 4 Torque–time curves for formulation d (temperature = 160°C, N = 50 rpm): (I) separate addition of materials and (II) simultaneous addition of materials.

ecules causes a high concentration of SBR radicals, which results in the formation of a crosslinked structure. With an increase in the concentration of MAH, the possibility of a grafting reaction rises. Because in the melt state MAH and SBR are incompatible, the rate of the grafting reaction depends on the diffusion of MAH into SBR and the concentration of MAH. On the other hand, at a high concentration of MAH (>2 phr), because of the high concentration of MAH free radicals, there is a possibility of competitive reactions occurring during MAH homopolymerization, and so the grafting percentage decreases. Also, at a high concentration of MAH, there is phase separation between MAH and SBR; consequently, side reactions can happen instead of grafting, and this results in the formation of a crosslinked structure.[13]

The results from FTIR spectrographs in the range of 4000–400 cm^{-1} are shown in Figure 1 for untreated SBR and maleated SBR in the form of the relative transmittance percentage versus the MAH concentration. These results belong to formulations a–d in Table I. In the pure SBR spectrograph, there is a strong peak at 962 cm^{-1} that belongs to vinyl groups. Because SBR is a mixture of linear and branched molecules (1,4- and 1,2-addition), the grafting of MAH can occur on the main chain or on the vinyl groups.[11] The spectrograph of formulation a (1 phr MAH), compared with that of

pure SBR, shows a decrease in the intensity of this peak. The aforementioned decrease is equivalent to an increase in the relative transmittance, which is indicative of a reaction of MAH with vinyl groups on SBR, which is shown in Figure 1. Because of the consumption of these vinyl groups, which have a tendency to crosslink, the gel content is reduced. At the concentration of 1.5 phr MAH (formulation b), the consumption of vinyl groups is reduced, and this means that MAH mainly reacts with cis and trans sites on the SBR backbone, so vinyl groups are free to form a crosslinked structure. In formulation c (2 phr MAH), vinyl group consumption is reduced, as found in formulation b, but because of a higher concentration of MAH and its higher diffusion rate, the grafting percentage is increased. The relative transmittance of formulation d (2.5 phr MAH) shows that, although the consumption of vinyl groups is increased, the grafting percentage is reduced because of side reactions such as the homopolymerization of MAH.

Effect of the BPO concentration

Figure 2 shows the effect of the BPO concentration on the grafting at a constant concentration of MAH for formulations e, c, f, and g. An increase in the BPO concentration to 0.14 phr results in the grafting percentage increasing; this is due to the increase in the formation of MAH free radicals.[13]

However, a further increase in the BPO concentration to 0.2 phr results in a decrease in the grafting percentage because of the occurrence of crosslinking reactions and the formation of a network (due to the high concentration of SBR free radicals).

Effect of temperature

Formulation c has been examined at 160 and 190°C to study this effect. Figure 3 shows that when the temperature is 190°C, because of the complete and quick decomposition of the initiator, the rate of torque increase until 7 min is higher than that at 160°C. This is due to an increase in the radical concentration in the mixture and an eventual increase in the percentage of grafted MAH. Also, the quicker decomposition of BPO

TABLE IV
Percentage of Grafting of MAH onto SBR with Two Different Methods

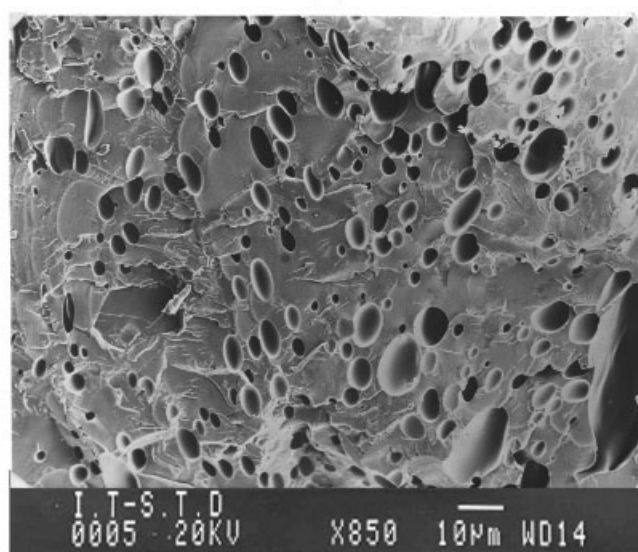| Formulation	Reacted MAH (%)	Gel content (wt %)
Simultaneous addition (d)	37.24	79.2
Separate addition (d)	40.2	76
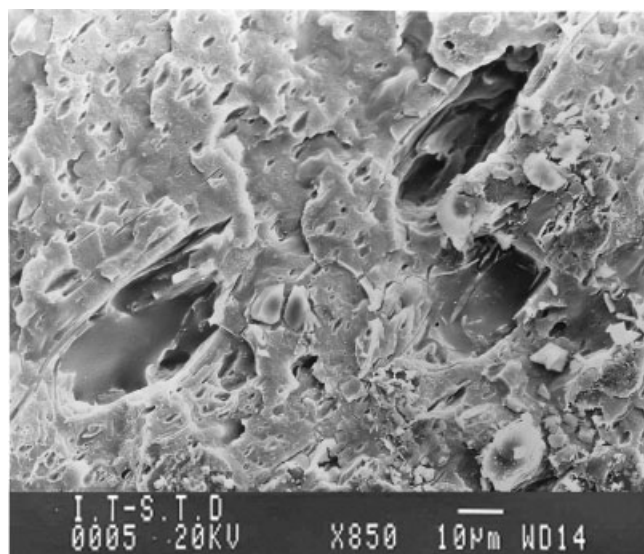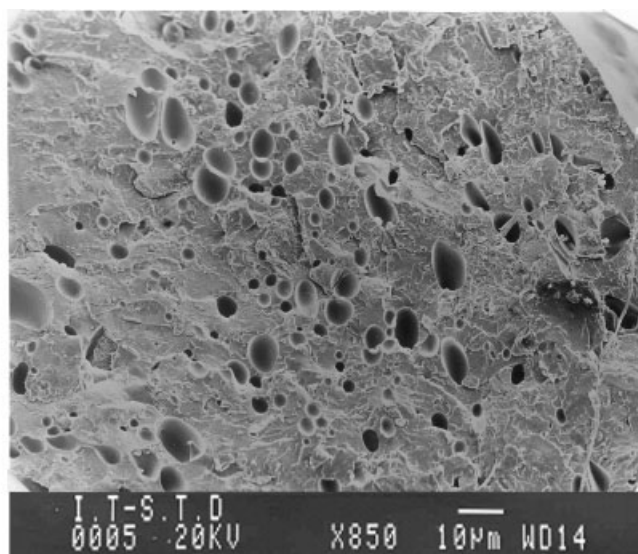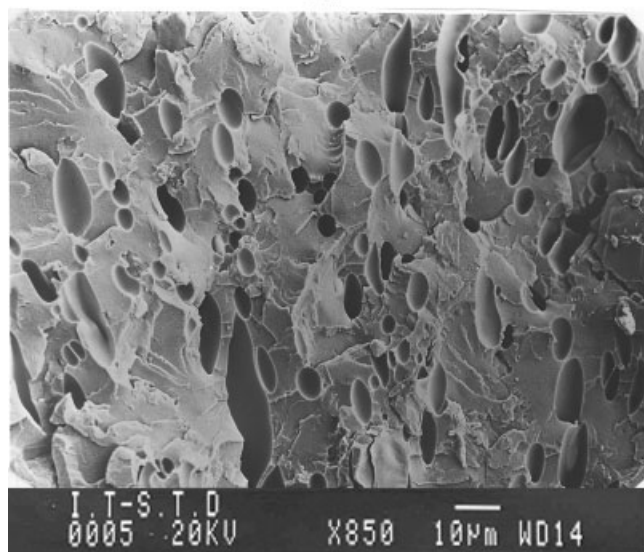
Figure 5 SEM illustrations for the K_2–K_6 formulations.

TABLE V
DMTA Results for Some Formulations

Code	Formulation	MAH used in rubber (phr)	T_g (°C)
K_0	PETRW[a]	—	79.7
K_1	PETW50	—	76
K_2	PETWSBRP	0	75
K_3	PETWSBRd$_1$	1	62
K_4	PETWSBRd$_2$	1.5	70
K_5	PETWSBRd$_3$	2	65
K_6	PETWSBRd$_4$	2.5	67

[a] PET as received.

leads to a higher concentration of SBR radicals and the formation of crosslinked SBR.

Effect of the feeding method

Formulation d was fed to the mixer with two different methods. In one case, MAH was added after 4 min, and BPO was added to the system after 5 min. In the second case, MAH and BPO were both added after 4 min. As can be seen in Figure 4, when both materials were added to the system after 4 min, the torque was reduced after 6 min [Fig. 4(I)]. However, when the materials were added separately, the torque was steady until 10 min [Fig. 4(II)].When the materials were added simultaneously, BPO was activated more quickly, and crosslinking reactions occurred more often than grafting. Also, there was a possibility of more MAH diffusion into SBR when the materials were added separately. Table IV shows the grafting percentages for these two cases.

PET waste/SBR blends

Morphology studies

Figure 5 shows micrographs for formulations K_2–K_6. In the incompatible polymer blend, because of the high interfacial tension and polarity differences, a weak interface is formed, and therefore the addition of interfacial agents can improve the properties of immiscible polymer blends because these modifiers re-

duce the interfacial tension between the phases in contact.[14–16]

In this work, SBR droplets appeared as large holes; this is common in incompatible polymer blends. Therefore, SBR was maleated and compatibilized with MAH as a compatibilizer to achieve a more powerful interface, which led to a higher impact resistance. Well-dispersed SBR droplets were observed in the K_3 formulation, but with an increase in the compatibilizer concentration in the K_4 formulation, the droplets were stretched and became larger; therefore, the morphology was not as good as the previous one. Subsequently, in the K_5 formulation, a good dispersion of SBR droplets was considered. The results of the K_6 formulation were the same as those of the former one, but the droplets were a bit larger. The results showed the role of the compatibilizer in increasing the interfacial adhesion. On the other hand, the reaction of the carbonyl group grafted onto SBR and the hydroxyl (or carboxyl) groups on PET was key to improving the compatibility between PET and SBR. There is no doubt that chemical reactions between carbonyl groups of SBR and hydroxyl (or carboxyl) groups of PET occur during melt processing, which in turn generates graft copolymers at the interface. These newly formed graft copolymers can cause the interfacial tension to decrease, acting as compatibilizing agents.[1,17]

DMTA studies

To obtain an idea of their mutual interaction, the PET/SBR-g-MAH blends were investigated with DMTA. Table V shows the glass-transition temperature (T_g) of an incompatible blend (K_2) and T_g of compatibilized blends (K_3–K_6). In the case of the incompatible blend, T_g of the blend is not different from that of pure PET, but in the case of a compatibilized blend (K_3), because of interactions between the two phases and strong interface, T_g of the blend is reduced considerably. The results for formulations K_4–K_6 can be interpreted on the same basis, and these results are in good agreement with the SEM results shown previously. This effect is often observed when a strong interfacial interaction between the matrix and the dispersed phase

TABLE VI
Tensile Results for the Some Formulations

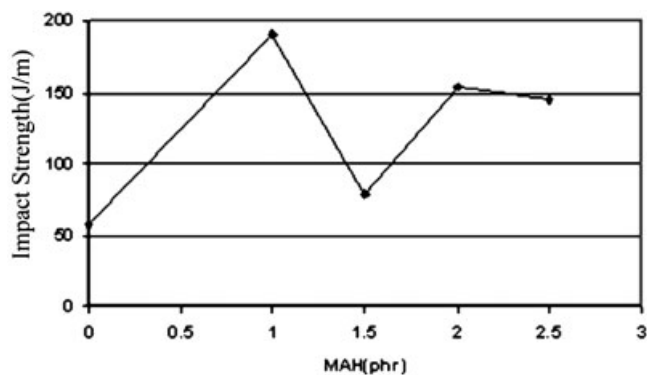| Code	Formulation	MAH used in rubber (phr)	Yield stress (MPa)	Elastic modulus (MPa)	Elongation at break (%)
K_2	PETWSBRP	0	44.2	5447	1.1
K_3	PETWSBRd$_1$	1	48.3	7468	1.51
K_4	PETWSBRd$_2$	1.5	35.47	4752	1.32
K_5	PETWSBRd$_3$	2	42.3	6752	1.43
K_6	PETWSBRd$_4$	2.5	39.16	4928	1.38

Figure 6 Impact strength of PET-*g*-SBR as a function of the MAH concentration. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley. com.]

is obtained and is attributed to a reduction of the interface mobility.[6,18]

Mechanical properties

Impact properties. Figure 6 shows the results of impact tests carried out on modified and unmodified blends (formulations K_2–K_6). As the compatibility of the blends increases, the impact strength increases from 57 to 190 J/m at the MAH concentration of 1 phr. When unmodified SBR is blended with PET, the dispersed SBR cannot act as an effective stress dispersant because of the large particle size and the lack of adhesion between the phases. However, when SBR-*g*-MAH is blended with PET, the dispersed SBR phase becomes small enough to act as a stress dispersant. Moreover, the particle adhesion between the phases transfers the stress field from the PET matrix to the dispersed elastomer effectively. All this is due to chemical bonding between PET and modified SBR. When the MAH concentration is increased from 1 to 1.5 phr, there is a decrease in the impact strength, which is in line with the FTIR spectrographs. As mentioned before, at a 1 phr MAH concentration, the highest consumption of vinyl groups takes place because of a grafting reaction with MAH. However, when the MAH concentration is increased to 1.5 phr, the consumption of vinyl groups goes through a minimum, which indicates that the grafting reaction now takes place on the main-chain double bonds and not on the vinyl branches. Better interfacial adhesion of the rubber to the PET matrix inhibits coalescence, resulting in an improved dispersion and hence improved impact strength. The results indicate that grafting on the vinyl groups leads to better adhesion and therefore better impact properties.

Tensile properties. Table VI shows the results for the mechanical properties (the elastic modulus and yield stress as well as the elongation at break) of modified
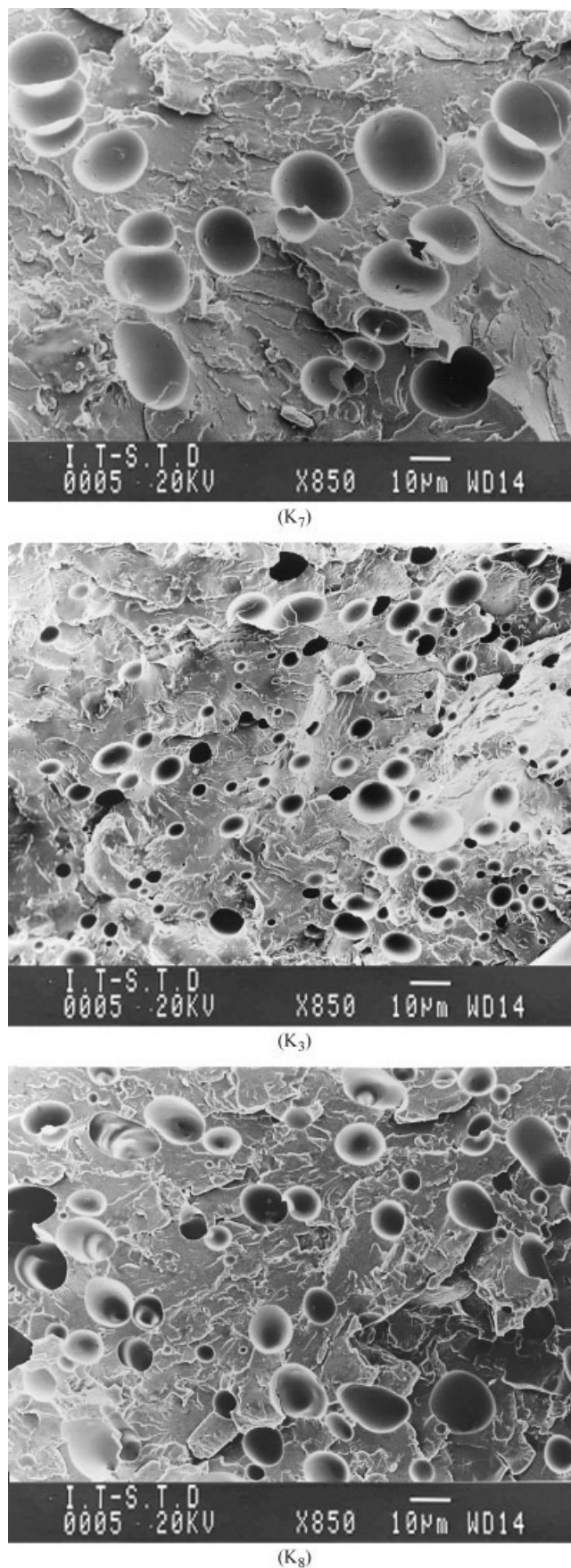

Figure 7 SEM illustrations for the K_7, K_3, and K_8 formulations.

and unmodified PET/SBR blends. In the unmodified blends, these properties are low because of a lack of compatibility. However, when the interfacial adhesion is increased between the phases, there is an increase in the modulus and yield stress. The change in the modulus and yield stress follows the same trend observed for the impact strength.

Effect of the rubber concentration

Morphology studies

To examine the effect of the rubber concentration, at an MAH concentration of 1 phr, three different rubber concentrations (10, 15, and 20 phr) are examined. Figure 7 shows micrographs for these blends. Increasing the rubber concentration from 10 to 15 phr causes a decrease in the size of the dispersed phase, which could be due to better adhesion of the phases and therefore less coalescence. Nevertheless, the reason for this decrease is still unknown but may be related to the matrix elasticity.[19] This reduction in the size of the dispersed phase results in a higher impact strength. However, there is also an increase in the particle size of the dispersed phase and hence a reduction in the impact strength at a rubber concentration of 20 phr, which is due to an increase in the coalescence, because of the larger number of particles and particle–particle collisions, which lead to the increase in the coalescence.

DMTA studies

According to Table VII, with an increase in the rubber concentration from 10 to 15 phr, T_g decreases, and this shows more compatibility between the phases. With a further increase in the rubber concentration, this increase can be explained by the weaker interface due to the excess volume fraction of the rubber. These results are in good agreement with the SEM results.

Mechanical properties

Impact properties. Table VIII shows the impact strengths for blends with different rubber concentrations. When the rubber concentration is increased from 10 to 15 phr, there is an increase in the impact strength of the blend that is due to high interfacial adhesion and better dispersion of the rubber droplets.

TABLE VIII
Impact Strength for Some Formulations

Code	Formulation	SBR (phr)	Impact strength (J/m)
K_1	PETW50	0	63.21
K_7	PETWSBRd$_5$-t$_2$	10	119.17
K_3	PETWSBRd$_1$	15	190.51
K_8	PETWSBRd$_7$-t$_2$	20	77.91

The decrease in the impact strength at 20 phr of SBR-*g*-MAH can be related to the overall increase in the rubber volume fraction that results in coalescence, which in turn may have a negative effect on the impact strength of the blends.

Tensile properties. Table IX shows the results of tensile tests of the blends. Both the modulus and yield stress decrease as the rubber content increases. This result is expected because the dispersed phase creates stress concentrations and forces the material to yield at small strain values.

CONCLUSIONS

SBR was modified via melt grafting with MAH and BPO as the reaction initiator. This process not only depended on the MAH and BPO concentrations but also on the processing parameters, such as the temperature and mixing sequence of the materials. Optimum grafting results were obtained at an MAH concentration of 1 phr at 160°C and 50 rpm. Modified SBR was blended with PET bottle waste and compared with a simple blend of PET/SBR. In view of the blend morphology, the dispersed particle sizes of PET/SBR-*g*-MAH were finer than those of the PET/SBR blends, and the PET/SBR-*g*-MAH blends showed homogeneous dispersions and better adhesion between the dispersed and matrix phases. This indicated that the PET-*g*-SBR graft copolymers were generated during the melt processing and acted as compatibilizers. As for the mechanical properties, the PET/SBR-*g*-MAH blends showed improved notched Izod impact strengths over the PET/SBR blends. A maximum of

TABLE VII
DMTA Results for Some Formulations

Code	Formulation	SBR (phr)	T_g (°C)
K_7	PETWSBRd$_5$-t$_2$	10	66
K_3	PETWSBRd$_1$	15	62
K_8	PETWSBRd$_7$-t$_2$	20	69

TABLE IX
Tensile Results for the Following Formulations

Code	Formulation	SBR Concentration (phr)	σ_y (Mpa)	E (Mpa)	%ε_b
K_0	PETRW*	0	59.39	8813	0.88
K_1	PETW50	0	57.45	8283	0.91
K_7	PETWSBRd$_5$-t$_2$	10	49.42	7609	1.38
K_3	PETWSBRd$_1$	15	48.3	7468	1.5
K_8	PETWSBRd$_7$-t$_2$	20	44.04	5859	1.58

the impact strength of PET/SBR-*g*-MAH was observed when the modified rubber concentration in the blend was 15 phr. At this concentration, the impact resistance was approximately 3.1 times that of pure PET. The particle size and interparticle distance of the dispersed rubber phase had a strong effect on the interparticle impact strength, but the modulus and yield stress of the PET/SBR-*g*-MAH blend depended only on the rubber concentration in the blend.

References

1. Park, J.-G.; Kim, D.-H.; Sub, K.-D. Appl Polym Sci 2000, 78, 2227.
2. Wu, S. Polym Int 1992, 29, 229.
3. Gaymans, R. J. In Polymer Blends; Paul, D. R.; Bucknall, C. B., Eds.; Wiley: New York, 2000; Vol. 2, Chapter 25.
4. Groeninckx, G.; Dompas, D. In Structure and Properties of Multiphase Polymeric Materials; Araki, T.; Tran-Cong, Q.; Shibayama, M., Eds.; Marcel Dekker: New York, 1998; Chapter 12.
5. Bucknall, C. B. Toughened Polymers; Applied Science: Essex, England, 1997.
6. Loyens, W.; Groeninckx, G. Macromol Chem Phys 2002, 203, 1702.
7. Sanchez-Solis, A.; Estrada, M. R.; Cruz, J.; Manero, O. Polym Eng Sci 2000, 40, 1916.
8. Sanchez-Solis, A.; Calderas, F.; Manero, O. Polymer 2001, 42, 7335.
9. Gaylor, N. G.; Metha, R.; Kumar, V.; Tazi, M. J Appl Polym Sci 1989, 38, 359.
10. Countinho, F.; Ferreira, M. Eur Polym J 1994, 30, 911.
11. Sanchez-Solis, A.; Estrada, M. R.; Cruz, M. J.; Manero, O. Adv Polym Technol 2000, 19, 34.
12. Sheng, J.; Lu, X.; Yao, K. J Macromol Sci Chem 1990, 27, 167.
13. Grioryeva, O. P.; Karger-Kocsis, J. Eur Polym J 2000, 36, 1419.
14. Gonzalez-Nanez, O. R.; Chan, C. F.; Favis, B. D. J Appl Polym Sci 1996, 62, 1627.
15. Bardollet, P.; Bousmina, M.; Muller, R. Polym Adv Technol 1995, 6, 301.
16. Gonzalez, R.; Kee, D.; Favis, B. D. Polymer 1996, 37, 4689.
17. Chen, C. C.; White, L. L. Polym Eng Sci 1993, 33, 923.
18. Willis, Y. M.; Caldas, V.; Favis, B. B. Mater Sci 1991, 26, 4742.
19. Utracki, L. A.; Shi, Z. H. Polym Eng Sci 1992, 23, 24.