# **Blends of Acrylonitrile–Butadiene–Styrene/Waste Poly(ethylene terephthalate) Compatibilized by Styrene Maleic Anhydride**

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**ABSTRACT:** Waste poly(ethylene terephthalate) (PET) from thin bottles was blended with acrylonitrile–butadiene–styrene (ABS) copolymer in different proportions, up to 10 wt %. Styrene maleic anhydride (SMA) copolymer was used as a compatibilizer. The tensile strength and heat deflection temperature of the blend were higher than that of virgin ABS. Flexural modulus remained unaffected, although a slight decrease in impact property was observed. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 2593–2599, 2001

**Key words:** acrylonitrile–butadiene–styrene copolymer; poly(ethylene terephthalate); compatibilizer; flexural modulus; styrene maleic anhydride

# **INTRODUCTION**

Poly(ethylene terephthalate) (PET) finds wide applications in soft drink bottles or transparent films and has fairly good mechanical properties. Because of its hydrolytic instability, however, it degrades rapidly if reprocessed and, hence, cannot be recycled for the same end use from which the waste may have been generated. Because PET has good oil resistance and toughness compared to that of nonpolar acrylonitrile–butadiene–styrene (ABS), a blend of ABS/PET can offer a blend that is comparable to ABS and polycarbonate.

Cook et al.1,2 previously studied ABS/PET blends using maleic anhydride–functionalized styrene–ethylene–butylene–styrene (SEBS) copolymer as a compatibilizer. They observed four domains in noncompatibilized ABS/PET blend

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and also noticed that properties of the blend depended on processing conditions resulting from degradation of  $PET<sup>1</sup>$ . They also observed that impurities in ABS affected the degradation of PET and hence properties of the blends.

Basu and Banerjee<sup>3</sup> showed that styrene maleic anhydride (SMA) copolymer can be used as a compatibilizer for the blend ABS/poly(butylene terephthalate) (PBT), the other type of polyester. There are few patents on poly(ethylene terephthalate)/ABS blends. $4-6$  The compositions and grades of PET, ABS, and compatibilizers used in some of the commercially available blends of ABS with polyesters, PEST (PET or PBT), are closely guarded secrets and the information is patent $ed$ <sup>7–11</sup>

PET can improve the heat deflection temperature (HDT) of ABS. There is no reported work on ABS/waste PET blends. Use of small proportions of waste PET into ABS to improve gloss, HDT, and other properties of ABS can be academically very interesting. The possible increase in HDT as well as changes in mechanical properties have not previously been reported and these changes can-

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		Blend Composition (wt $\%$ )	Compatibilizer, SMA (parts per 100 parts of blend)		
Blend No.	ABS	Waste PET			
	100				
	95	5			
П	95	5			
Ш	90	10			
IV	90	10			

**Table I Blend Composition of ABS/Waste PET System**

not be predicted *a priori.* Therefore the present work looks at these aspects.

# **EXPERIMENTAL**

#### **Materials**

A commercial grade of ABS, KM911M (Rajasthan Petroleum and Refineries, Rajasthan, India), and recycled waste bottle–grade PET (from a local supplier, Mumbai, India) were used in the present work. The compatibilizer SMA was prepared in the laboratory according to methods described by Paul.<sup>12</sup> The number-average molecular weights  $(M_n)$  of SMA and waste PET were found to be 35,000 and 43,600, respectively.

#### **Blending**

The required quantities of ABS and waste PET were dried at 100–120°C for 6 h in an air-circulating oven before dry blending. The required amount of compatibilizer SMA was added before dry blending and the dry blend was immediately fed into the Haake Rheomix TW100, counterrotating twin-screw extruder for melt blending. The temperature profile was: zone 1, 200°C; zone 2, 220°C; zone 3, 240°C; and zone 4, 260°C.

All blend compositions were compounded at 50 rpm.

#### **Testing**

Table I shows the composition of the blends studied. The extrudate strand was pelletized and dried, and then injection-molded samples were prepared using a Windsor SP30 injection-molding machine. The test specimens pertained to ASTM standards [dumbbell-shaped for tensile test (ASTM D638M-91), notched Izod for impact strength (ASTM 256), and rectangular bar for flexural strength (ASTM 790M-92)]. The injection temperature profile was zone 1, 220°C; zone 2, 240°C; and zone 3, 260°C; injection pressure was at 120 kg/cm<sup>2</sup>; and mold temperature was between 35 and 40°C. The mechanical (tensile and flexural) properties were determined using a Lloyd LR 50K tensile-testing machine. The crosshead jaw speed was 50 mm/min for tensile measurements and 2.8 mm/min for flexural measurements and a load cell of 5-kN capacity was used. The elongation of samples was measured with a laser extensometer (Lloyd Laser Scan 200).

The notched impact strength was measured using an Avery Denison impact tester. A 5-J striker was used and the striking velocity was 3.46 m/s.

**Table II Variation of Mechanical Properties for ABS/Waste PET**

Blend No.	Maximum Load (N)	Extension at Maximum Load (mm)	Extension at Break $(\%)$	Tensile Strength (MPa)	Flexural Modulus (MPa)	Flexural Strength (MPa)	Izod Impact Strength $(kg-cm/cm)$	Heat Deflection Temperature $\rm ^{\circ}C)$
ABS	547.98	2.026	54.59	36.12	2236	58.3	30.6	92
	551.07	2.04	14.46	42.6	2243	57.03	16.83	94
п	586.0	2.02	15.39	45.44	2252	56.75	25.09	94
Ш IV	553.0 597.0	2.0 2.18	11.6 13.47	42.75 46.41	2240 2280	56.12 52.08	12.24 16.83	97 97



**Figure 1** Variation of shear viscosity of compatibilized blends: virgin ABS  $(-\triangle -)$ ; waste PET  $(-\times -)$ ; blend no. **II**  $(-\Diamond -)$ ; blend no. **IV**  $(-\Diamond -)$ .

The specimens for measuring flexural strength were used to determine HDT using a Davenport HDT vicat softening-point apparatus according to ASTM D648. All the above-mentioned results were the average of at least 10 measurements.



**Figure 2** Variation of storage moduli of compatibilized blends: virgin ABS  $(-\Diamond -)$ ; blend no.  $\mathbf{II}$  (— $\triangle$ —); blend no.  $\mathbf{IV}$  (— $\odot$ —).



**Figure 3** DSC thermograms (second heating) of waste PET (bottle grade).

The melting behavior of ABS/waste PET blends was studied using a Perkin–Elmer DSC 7 instrument (Perkin–Elmer, Foster City, CA). The scanning rate was 10°C/min and the sample weight varied between 7 and 9 mg. The DSC for virgin polymer was run using commercially available granules; extruded granules were used for blends.

For rheological studies, thin discs were compression molded under the following conditions: preheated for 2 min at low pressure, compressed for 2 min at 180 kg/cm<sup>2</sup> and 260 $^{\circ}$ C, and then demolded at 60°C and 180 kg/cm<sup>2</sup>. The viscous behavior at 260°C was studied using a rotational parallel plate viscometer (Haake RT 10). The shear rate range varied from  $0.001$  to  $100 \text{ s}^{-1}$ . The dynamic viscous properties, that is, storage modulus  $(G'$  in Pa) and loss modulus  $(G''$  in Pa) as functions of angular velocity ( $\omega$  in rad/s), were measured. Similarly the frequency of oscillation varied from 0.1 to 40 Hz.

Phase morphology was studied using a scanning electron microscope (Philips XL 30) for cryofractured samples. Other experimental details were previously documented by Paul.<sup>12</sup>

## **RESULTS AND DISCUSSION**

#### **Mechanical Properties**

Table II shows the variation of mechanical properties as well as HDT with composition. As PET content increased, the tensile strength as well as flexural modulus increased. Addition of SMA significantly improved the mechanical properties of ABS. Because the maleic anhydride moiety is likely to have compatibility with the poly(ester terephthalate) part, SMA has a compatibilizing effect. The role of SMA for the ABS/PBT system was previously reported.<sup>1-3</sup> The Izod impact, however, seems to decrease.

It is interesting to note that by adding even 10% waste PET, the HDT increased from 92 to 97°C. The HDT of PET is around 200°C. The increase in HDT of the ABS/PET blend is thus



**Figure 4** DSC thermograms (second heating) of ABS/waste PET blends.

much less than the predictions based on the linear additivity rule. Using waste PET to improve the tensile strength, flexural strength, and HDT of ABS was not previously reported.

The HDT of ABS/waste PET blend appears to be considerably higher than that of virgin ABS. The addition of SMA does not affect the HDT of the blend. Thus SMA seems to be an effective compatibilizer in improving mechanical properties. Properties of PET/SMA blends were previously reported by Utracki.<sup>13</sup> Accordingly, if SMA is added to PET in amounts of more than 10%, the HDT of PET increases. Because SMA added in the present work was only 1%, it did not influence the HDT to any extent. Because the impact properties of ABS appeared to decrease considerably (at 10% waste PET loading), blends with a higher content of PET (i.e., higher than 10%) were not prepared.

#### **Rheological Properties**

Figure 1 compares the viscous behavior of ABS, waste PET, and compatibilized blends containing 5 and 10% PET. The difference in viscosities of virgin ABS and waste PET is quite large. The viscosity of blend containing 5% PET is much higher than that of PET. Surprisingly, the viscosity of blend containing 10% PET appears to be higher than that of ABS at low shear rates. The blends seem to be more shear thinning than is PET.

Figure 2 depicts the variation of storage modulus  $G'$  with frequency. It seems that the blend containing 10% PET showed higher rigidity. The given grade of waste PET has extremely high rigidity  $(G' \sim 10^8 \text{ Pa at comparable frequencies of})$ 0.1–40 Hz) compared to that of ABS, as reported by Shertukde. $14$  The increase in rigidity of the blend with increasing amounts of PET can be explained in light of this. This behavior is interesting in that it may lead to some novel applications.

The changes in the mechanical properties of the blend are also in agreement with these findings.



 $\left( \mathrm{c}\right)$ 





 $(e)$ 

**Figure 5** SEM photographs of ABS/waste PET blends: (a) virgin ABS; (b) blend no. **I**; (c) blend no. **II**; (d) blend no. **III**; (e) blend no. **IV**. Magnification  $\times$  4000.

# **Thermal/Differential Calorimetric Properties**

Figure 3 shows the thermal characteristics of waste PET (bottle grade). Figure 4 shows the DSC thermograms for second heating of compatibilized and noncompatibilized blends of ABS/waste PET. Comparison of Figures 3 and 4 clearly indicates that the characteristics of waste PET are retained in the blends.

## **Morphology**

Figure 5 compares the morphological characteristics. The ABS and PET formed a noncompatible system, as shown by domain size and poor adhesion in Figure 5(b) and (d). The domain size in noncompatibilized blend containing 5% PET appears to be greater than that of compatibilized blends. The large difference in viscosities of ABS and PET could be one of the reasons for this, apart from the noncompatible nature of the two polymers. The domain size of compatibilized blend containing 10% PET seems to be slightly greater, although the distribution appears to be uniform. The presence of SMA seems to show interfacial interaction. The reduction in impact properties may be explained on the basis of larger domain size. By selecting either a proper variety of ABS of lower viscosity and/or altering process conditions, perhaps a smaller domain size of PET may be generated. The impact properties could then be improved.

## **Physical Appearance**

The blends containing waste PET seemed to have slightly better gloss and a less-yellow appearance, although no quantitative estimation was possible.

## **CONCLUSIONS**

Blends of waste PET with ABS can be attractive. A concentration of 10% or more of PET can yield product with improved tensile strength, flexural modulus, HDT, and rigidity, but of slightly lower impact strength. Using waste PET for such improvements was not previously reported. SMA is effective as a compatibilizer. Different grades of ABS and/or processing conditions may further improve the properties. Blends of higher PET contents with rubberlike components such as SEBS may also compensate for reduced impact strength, which should be the subject of further investigation.

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#### **REFERENCES**

- 1. Cook, W. D.; Moad, G.; Fox, B.; Van Deipan, G.; Zhang, T.; Cser, F.; O'Shea, M. J Appl Polym Sci 1996, 62, 1699.
- 2. Cook, W. D.; Moad, G.; Fox, B.; Van Deipan, G.; Zhang, T.; Cser, F.; McCarthy, L. J Appl Polym Sci 1996, 62, 1709.
- 3. Basu, D.; Banerjee, A. J Appl Polym Sci 1997, 64, 1485.
- 4. Udipi, K. (to Monsanto) Eur. Pat. 0,388,388, 1990.
- 5. Akkapeddi, M. K.; Kraft, T. J.; Vanbuskrik, B. (to Allied Signal Inc.) U.S. Pat. 5,115,018A, 1992.
- 6. Binsack, R.; Rempel, D.; Bier, P.; Linder, C. (to Bayer AG) Eur. Pat. 82,100,044, 1982.
- 7. Gergen, W. P.; Davison, S. (to Shell Oil Co.) U.S. Pat. 4,090,996, 1977; 4,088,711, 1978; 4,101,605, 1978.
- 8. Tanaka, C.; Nakajima, S.; Morikawa, M. (to Toray Industries Inc.) Jpn. Pat. 040,851, 1979.
- 9. Orikawa, Y.; Sakazume, S.; Nishimura, S.; Maki, Y. (to Nippon Petrochemicals Corp. Ltd.) Eur. Pat. 314,188, 1989.
- 10. Bier, P; Inder, C. (to Bayer AG) Eur. Pat. 063,263, 1982.
- 11. Deyrup, E. J. (to E. I. du Pont de Nemours & Co.) PCT Int. WO 8,503,718, 1985.
- 12. Paul, S. M.S. Dissertation, University of Mumbai, 1999.
- 13. Utracki, L. A. Commercial. Polymer Blends; Chapman & Hall: London, 1998, p. 356.
- 14. Shertukde, V. V. Ph.D. Dissertation, University of Mumbai, 1997.