Morphology–Property Relationships in ABS/PET Blends. II. Influence of Processing Conditions on Structure and Properties

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SYNOPSIS

The effect of processing temperature on the low-speed tensile and high-speed impact properties of novel ABS/PET blends was investigated. In agreement with the conclusions from related studies of ABS/PC blends, it appears that catalytic impurities in the ABS accentuate the propensity of PET for chain scission. Due to the cocontinuous structure of the blend, the hydrolytic or thermomechanical degradation of the PET results in a dramatic loss in mechanical properties which can be explained by the entanglement theory for fracture and the Orowan brittle–ductile hypothesis. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Blends of acrylonitrile–butadiene–styrene copolymers (ABS) with bisphenol-A polycarbonate (PC) have been studied and commercially used for nearly three decades,[1,2] because ABS provides the blend with high-impact energy while the PC contributes to the blend's high heat-distortion temperature and solvent resistance. While there are several patents (e.g., see refs. 3–5) on the related blend of ABS with poly(ethylene terephthalate) (PET), there do not appear to be any articles on this material in the open literature. In part I of this series,[6] we reported on the morphology and properties of ABS/PET blends. In the early stages of this work, we noticed a strong dependence of the blend properties on the processing conditions which are similar to related unfavorable chemical interactions between blend components in ABS/PC blends.[7,8] In the present work, the effect of processing conditions on the mechanical properties in ABS/PET blends are reported and related to the reduction in PET molecular weight during processing.

EXPERIMENTAL

The ABS was supplied by Huntsman Chemical Co., Australia, and contained 19 wt % acrylonitrile, 36 wt % butadiene, and 45 wt % styrene monomer. Approximately 31 wt % of the SAN copolymer was ungrafted and had a number-average molecular weight (M_n) of 35,000 g/mol; the remaining 59 wt % was grafted to the polybutadiene. The PET (code 9921W), manufactured by Eastman Chemical Products Inc., was an approximately equimolar copolymer of terephthalic acid and ethylene glycol copolymerized with a few percent of cyclohexane dimethanol and included trace levels of a diethylene glycol degradation product. As received, the PET had an M_n of 24,500 g/mol and had a crystallinity of ca. 30% (ref. 6) with a peak melting point of approximately 240°C. As discussed in Part I, the level of crystallinity of the PET in the blends was much lower than in the virgin material. Further analytical details of the PET are given elsewhere.[9] Due to initial indications that a "compatibilizer" was required for optimum processing ease and blend properties, a styrene–ethylene/butylene–styrene triblock copolymer functionalized by maleic anhydride (supplied by Shell as Kraton FG1900X) and designated

MAKG was also incorporated into the blend. All blends in the present work were prepared in the weight ratio ABS/PET/MAKG = 47.5/47.5/5.0.

The PET, ABS, and MAKG were dried at 177°C/4 h, 80°C/16 h, and 50°C/12 h, respectively, prior to processing. All blending was performed on a PL2000 Brabender single-screw extruder with a 17 mm-diameter screw, barrel length of 0.46 m, length/diameter ratio of 24, and a 6 mm die. The external heating of the melt was controlled by three heating zones on the barrel and die. Since the differences between zone temperatures was kept constant, the average barrel temperature is used in this article as an indication of processing temperature. The ABS/PET/MAKG blends were prepared in a two-stage process. The PET and MAKG were first preblended at 40 rpm and pelletized. The PET/MAKG blend was dried and back-blended with the ABS with a screw speed of 100 rpm and at average processing temperatures ranging from 246 to 292°C and then pelletized. After redrying at 100°C/12 h, all specimens were prepared on an Engel SE600-125 120 tonne reciprocating screw injection molder operated at a screw speed of 40 rpm, a barrel temperature of 250°C, a mold temperature of 60°C, and a molding time of 33 s.

As discussed in more detail elsewhere,[9] the degradation of the PET in the blends was determined by GPC. Powdered blend samples were dispersed in hexafluoroisopropanol (which is a good solvent for PET) and then diluted with chloroform to a 2 vol % hexafluoropropanol/chloroform mixture. After filtration of the suspension to remove the ABS-grafted rubber particles, the samples were chromatographed using a Mixed-C (Waters) GPC column in line with a 100 A (Waters) GPC column. The PET elution was monitored by 254 nm UV detection—the absorption of the SAN at this wavelength was much lower than the PET and did not interfere in the analysis. The columns were calibrated with polystyrene standards and the polystyrene-equivalent molecular weights were converted to absolute molecular weight by use of the Mark–Houwink parameters for PET.

Tensile testing was performed according to ASTM 638-89 on type I dumbbell specimens with a thickness of 3.2 mm and width of 13 mm. Tensile testing was performed on an Instron 4505 tensile testing machine at 22°C using a crosshead speed of 5 mm/min. The gauge section of the tensile specimens was also used for three-point loading flexural testing (ASTM D790-86) at 1 mm/min using a span of 51 mm. Notched impact testing was performed with a Zwick (Model 7900) impact tester according

to ASTM D256-88 using the gauge section from the tensile specimen. Falling dart impact testing was performed using a Radmada instrumented impact tester operating at a dart speed of ca. 4 m/s. The specimens were 125 × 75 × 3.2 mm molded plaques and the test geometry was similar to the noninstrumented ASTM D3029-84 method and used a hemispherical impacting tup of 6.35 mm radius but utilized a 50 mm-diameter supporting ring (instead of a 38.1 mm diameter as specified for Geometry FB in the Standard).

Scanning electron micrographs of the blends were obtained with a JEOL JSM-840A SEM. Sample surfaces were obtained by freeze-fracture of molded plaques. The topological structure of the blends was exposed by two alternative selective etching techniques. To expose the ABS structure, the surface was etched with a 10 wt % solution of potassium hydroxide (KOH) in ethanol at room temperature for 20 h,[6] followed by careful washing of the surface with water. The corresponding PET microstructure was revealed by etching the ABS with methyl ethyl ketone. After room-temperature drying of the surface under vacuum, the specimens were coated with ca 0.1 μm layer of Au in a Dynavac sputter coater SC150 gold vacuum sputtering unit and were examined at ×1000 and ×4000 magnification.

RESULTS AND DISCUSSION

The nominal tensile stress–strain curves of ABS/PET blends prepared at various average extrusion temperatures are shown in Figure 1. The moduli and yield stresses do not vary significantly with extrusion
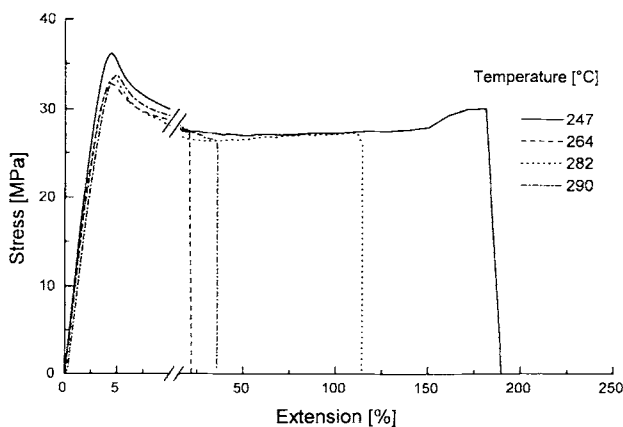
Figure 1 Nominal tensile stress–strain curves for ABS/PET/MAKG blends extruded at 247, 264, 282, and 290°C and having PET M_n of 19,000, 15,500, 13,900, and 12,900 g/mol.

**Table I   Effect of Extrusion Conditions on PET M_n and Impact Energy of ABS/PET/MAKG Blends**

| First Extrusion (90/10 Preblend of PET with MAKG)		Second Extrusion (Blend of ABS with PET/MAKG)		Properties of ABS/PET/ MAKG Molded Specimen	
Extrusion Temperature (°C)	M_n of PET (g/mol)	Extrusion Temperature (°C)	M_n of PET (g/mol)	Izod Strength (J/m)	M_n of PET (g/tool)
No processing[a]	24,500				
265[a]	21,550	—		—	
291	21,460	—		—	—
248		247	20,230	853	19,060
271		271	17,910	196	16,180
291	21,460	272	16,940	177	15,850
283		264	17,360	219	15,550
270	—	286	15,430	102	14,850
291	21,460	282	15,100	106	13,900
292		290	13,570	62	12,950

[a] No MAKG added.

temperature as was found also by 3-point flexural testing. However, blends prepared at the higher processing temperatures exhibit far lower ultimate extensions. It is well known that processing of ABS can result in oxidation of the polybutadiene unsaturation.[10] In addition, processing of PET may lead to a reduction in molecular weight as a result of hydrolytic and thermomechanical degradation.[11] To ascertain whether degradation of the ABS or the PET was involved in the changes in mechanical properties (Fig. 1), samples were prepared by first extruding PET at high or low temperatures and then blending with ABS at high or low temperatures. As shown in Table I, processing PET in the absence of ABS resulted in a ca. 12% reduction of M_n, irrespective of the extrusion temperature. In the second stage of the blending, only a small change (ca. 6%) in PET M_n was observed if the average processing temperature was low, but as the processing temperature was increased, the PET was increasingly degraded by up to 37%. Subsequent injection molding at a relatively low temperature (250°C) produced an average drop in M_n of only 7%. The observation that the loss of PET M_n and the reduction in properties occurred primarily when ABS and PET were processed together at high temperatures suggests that a residual polymerization catalyst or coagulant in the ABS is capable of catalyzing decomposition of the PET. Lee et al.[7] came to a similar conclusion in studies of the processing of ABS/PC blends. In this work, an ABS polymer with high residual levels of metal salt coagulant was found to produce brittle ABS/PC blends, whereas a low coagulant ABS gave tough blends. Although this suggestion of PC

degradation[7] was supported by variations in melt viscosity and glass transition temperature of the PC and ABS phases and by changes in the infrared spectrum of the blend, no quantitative correlation was reported between the impact energy and the M_n of the PC in the blend.

The variation in PET M_n in the ABS/PET blends is shown in Figure 2 as a function of the average processing temperature (during the second mixing stage). Processing at high temperatures resulted in a reduction in M_n; however, the polydispersity remained fairly constant at 2.3 ± 0.1.[9] Although it is not clear whether this loss in molecular weight is caused by hydrolytic or thermomechanical degradation, the effect of increased processing temperature on M_n is consistent with either process.
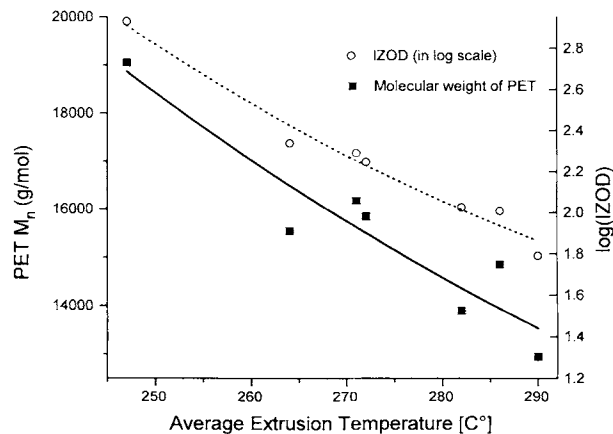
Figure 2   Variation of PET M_n and log(Izod strength) on average extrusion temperature in the second extrusion step.
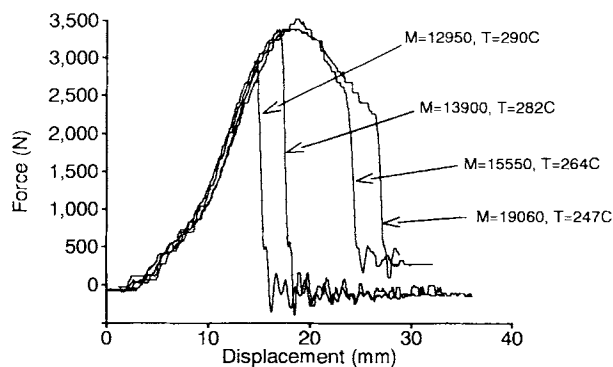
Figure 3 Falling dart traces of impacting force vs. penetration displacement for ABS/PET/MAKG blends extruded at 247, 264, 282, and 290°C.

Figure 2 also shows the dramatic dependence of the Izod impact energy on processing temperature. A related dramatic reduction in impact energy with increased processing temperature has also been reported in a patent by Jalbert and Cox[12] on ABS/polybutylene terephthalate blends.

As a comparison with the low strain rate results in Figure 1, the force-deformation traces obtained from the high-speed testing conditions of the falling dart impact test are illustrated in Figure 3. Blends processed at low temperatures are still partly ductile although the elongations at break are considerably smaller than those observed at lower testing rates. For samples blended above 280°C, the material is brittle and fails to yield before fracture under impact conditions. The dependence of M_n and impact energy on processing temperature automatically implies a correlation between the mechanical properties and M_n. This is shown in Figure 4, where the

low strain-rate ultimate extension and the high-speed notched Izod strength and falling dart energy to break all decrease as the molecular weight of the PET in the blend is reduced by chain scission.

There have been many studies of the effect of molecular weight on the brittle tensile strength,[13-15] impact energy,[16] and fracture energy[17-19] for single-component polymer glasses. In all cases, the fracture property increases to a plateau as the molecular weight is increased and several models[14,15,19] have been proposed to explain this behavior. Despite varying levels of refinement in these theories, the common origin is based on the concept of a physical entanglement network in the glassy polymer. The average mass of the polymer strands between entanglements (M_e) can be estimated from the rubbery modulus of the uncrosslinked polymer and can also be approximated as half the critical molecular weight identified in a plot of melt viscosity vs. molecular weight.[20] For high molecular weight polymers, the great majority of the chain segments are bordered by neighboring entanglement points and are therefore effective in bearing a stress. However, when the polymer molecular weight is reduced, a greater fraction of the chain is bordered by only one entanglement site and so cannot support a stress. Since the entanglement sites resist large-scale translational motion and slippage of the chain, the stress borne by the specimen is related to the number of polymer strands bridging the crack path and thus is a function of $1-2\ M_e/M_n$.[14,15,19] As the molecular weight of the polymer is reduced and M_n approaches $2\ M_e$, the number of effective strands capable of bearing the stress tends to zero and so the mechanical properties are predicted to be drastically reduced.
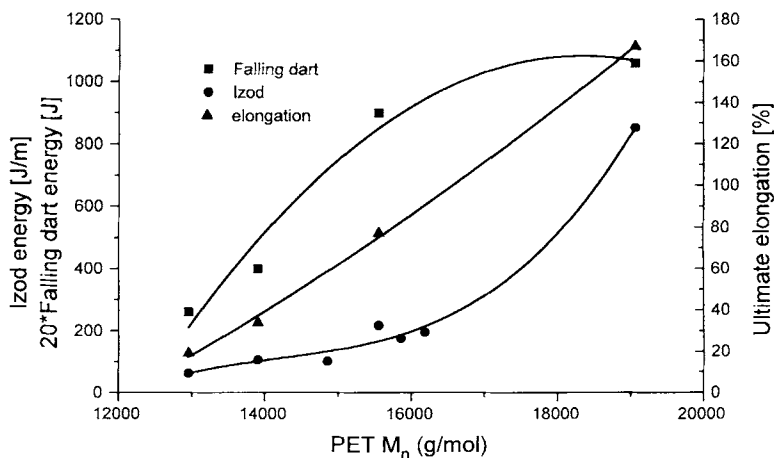

Figure 4 Dependence of Izod impact energy, falling dart energy to break, and low-speed ultimate elongation on PET M_n in ABS/PET/MAKG blends.

As shown in Figure 5 and discussed in more detail in Part I of this series,[6] the morphology of 50/50 blends of ABS and PET are cocontinuous and the microstructure is only slightly dependent on the PET M_n. Thus, the stresses and strains imposed on the blend are shared by each domain and so the mechanical properties of the cocontinuous blend will be nearly as sensitive to chain scission of one of the components as would apply to the unblended polymer. Consequently, the entanglement theories for fracture properties are applicable to ABS/PET blends. The relevance of these theories to the impact results is based on the Orowan brittle–ductile transition.[21] In this hypothesis, the failure mode of a material is dependent on the relative values of the stresses required for plastic deformation or simple cleavage. If the yield stress is less than the stress required for cleavage, then the material is capable of large-scale deformation (and thus energy absorption) and will be ductile, whereas if the yield stress is higher than that required for fracture, the material will be brittle. As indicated by Figures 1 and 3, the PET M_n has little influence on the yield stress. This observation is in agreement with studies by Chang et al.[22] for PC and by Stearne and Ward[23] for PET and is also consistent with the independence of yield stress on PC molecular weight in ABS/PC blends.[24] As the PET M_n is reduced by chain scission, the decreased number of stress-bearing segments will lower the brittle stress below the yield stress. Therefore, the blend will lose ductility and ultimately become brittle, absorbing little energy during fracture. The value of M_e for PET was tabulated as lying between 3500 and 6000 g/mol,[25] which suggests that the minimum strength of the blend will occur at a PET M_n equal to 2 M_e or 7000–12,000 g/mol. This estimate is consistent with the data in Figure 4. Studies on cocontinuous blends of PC with methacrylate–butadiene–styrene[22] or ABS[24] also show that as the M_n of the PC component approaches 8000 the strength and toughness tend to zero, in general agreement with the data presented here for ABS/PET blends.

CONCLUSIONS

During the blending of ABS with PET, the molecular weight of the PET in the blend was found to be very sensitive to the processing temperature. This hydrolytic or thermomechanical degradation of the PET appeared to be due to catalytic impurities in the ABS. The reduction in PET molecular weight resulted in a decreased tensile strength and ultimate
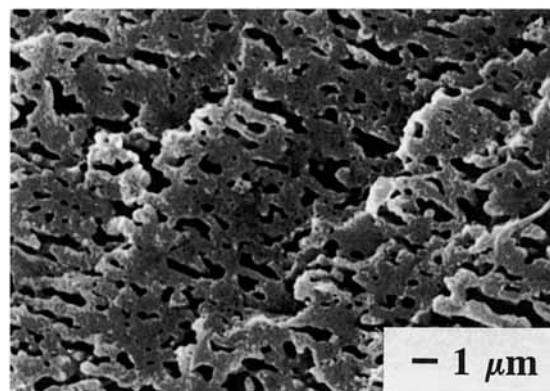
(a)
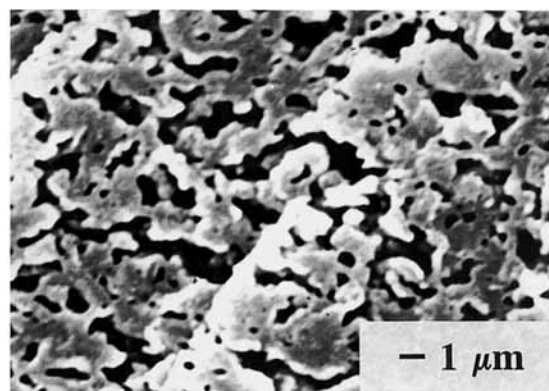
(b)

Figure 5   SEM of KOH etched freeze-fracture surfaces of ABS/PET/MAKG blends prepared at (a) 247°C (M_n = 19,000 g/mol) and (b) 290°C (M_n = 12,900 g/mol).

extension and a significant loss of impact energy, which are interpretable in terms of the entanglement theory and the brittle–ductile hypothesis. In contrast, the yield stress and modulus were virtually unaffected by the PET degradation.

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