

Mechanical Properties of HDPE-PS-SEBS Blends

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Synopsis

Blends of high-density polyethylene (HDPE), polystyrene (PS), and an SEBS triblock copolymer were extruded, pelletized, and injection molded. The binary HDPE-PS blends exhibit very poor ductibility; however, addition of the SEBS block copolymer greatly improves this characteristic but with an accompanying loss in strength and modulus. The modified blends are very tough and have mechanical properties suitable for many end use applications. However, weld lines pose a problem and should be avoided with these blends.

INTRODUCTION

Blends of immiscible polymers frequently exhibit inferior mechanical properties which preclude their use for most commercial purposes. This problem has been especially evident in attempts to reclaim value from mixed scrap plastics through reprocessing.¹ A significant part of this problem is poor stress transfer between component phases owing to a lack of adhesion or wetting. An approach to this situation has been to employ additives which might be expected to improve adhesion between the phases by an interfacial mechanism, and beneficial results have been obtained using these so-called compatibilizers.² Quite clearly, the mechanical properties of immiscible blends should also be very sensitive to the phase morphology generated during processing. In line with this, it was recently shown that mechanical properties of immiscible blends fabricated by injection molding were far superior to those for the same compositions formed by compression molding.³

Gergen and Davison⁴ recently reported that the mechanical properties of immiscible blends, where the components varied widely in chemical type, could be significantly improved by addition of certain block copolymers when proper attention was paid to rheological characteristics and processing conditions. They suggest that the block copolymer acts to stabilize the blend morphology and to prevent the formation of grossly heterogeneous structures that would otherwise result. Of particular interest is their observation that frequently the ternary blends containing the block copolymers formed an interlocking, or interpenetrating, network of phases as shown by extraction studies. An interpenetrating network of phases is the ideal morphology for an immiscible blend since it allows for more equal sharing of imposed stresses by the components.⁵

The purpose of this article is to report on some very encouraging results that have been developed relative to improving the properties of immiscible blends that might be produced from mixed scrap plastic using the ideas outlined above. The system high-density polyethylene (HDPE)-polystyrene (PS) was chosen since it represents an example of extreme immiscibility and these commodity

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polymers frequently comprise a large fraction of plastics scrap. A commercially available triblock copolymer of the type mentioned by Gergen and Davison⁴ was used as an additive to this system.

MATERIALS

The HDPE used in this study was a general purpose grade supplied by Union Carbide Corp. as DGDA-6084. This material has a density of 0.960 g/cm³ and a melt index of 0.3 g/10 min. The PS used was Cosden Polystyrene 550, a general purpose injection-molding grade of crystal PS supplied by Cosden Oil and Chemical Co.

The triblock copolymer employed in this work was Kraton G-1652 supplied by Shell Chemical Co. It has polystyrene endblocks which comprise 30% of the mass and a hydrogenated polybutadiene midblock. The midblock is equivalent to an ethylene-butene-1 copolymer (EB). Interestingly, the SEBS copolymer might be expected to adhere or wet both components of the present system owing to the identity of the end blocks with the PS component and the expected affinity of the EB midblock with HDPE. This was confirmed by performing double-peel adhesion tests on polymer sheets laminated by compression molding according to the scheme shown in Figure 1. Laminations of HDPE to PS showed no measurable adhesion as expected. However, laminations formed at 200°C and 1500 psi for 5 min with Kraton G-1652 reinforced with a glass mat as polymer 1 and either HDPE, PS, or a 50/50 blend of the two exhibited peel strengths of 9.4, 4.4, and 2.5 lb/in. of interface, respectively.

BLEND PREPARATION

As stated earlier, mechanical properties of immiscible blends should be considerably affected by the morphology of the mixture. Blend morphology is determined by the imposed stress fields during mixing and shape-forming opera-

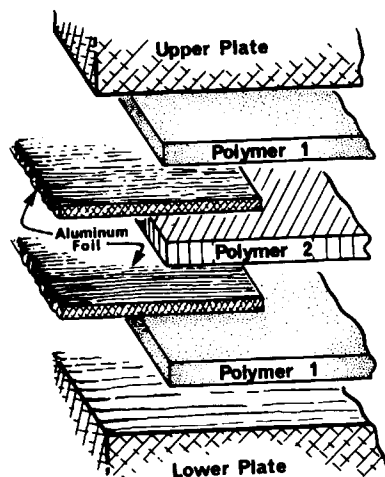


Fig. 1. Lamination scheme for double-peel adhesion test. The aluminum foil precludes bonding at the end of the laminate, thus, providing tabs on the two sheets of polymer 1 for insertion in the grip of an Instron. The upper and lower plates provide heat and pressure to form the laminate.

tions, by the component proportions, and by the relative rheological characteristics of the blend components.^{5,6} Various investigators⁷⁻¹⁸ have described the relationships between the relative proportions and viscosities of the components and the resultant morphology during mixing. Generally speaking, the mechanical performance of a blend may be improved by mixing the components in such a way that domain size of the minor phase is reduced and that some degree of interpenetration of the component phases is achieved.⁵ A general rule for obtaining this desired morphology appears to be to select conditions during mixing such that the viscosity of the major component is greater than that of the minor component or to match the viscosities when the two components are present in equal proportions.¹⁷ Obviously, the issue is more complex than this, but this simplification offers a useful point of departure for developing a process strategy. For fixed components, viscosities may be varied by processing temperature. To obtain a handle on this for the present system, torques were measured at 20 rpm in a Brabender Plasticorder for each component, with the results shown in Figure 2.

Blends of the desired composition were mixed by simultaneously introducing pellets of all components into a laboratory extruder (Killion, $D = 1$ in., $L/D = 25$, compression ration 3) operated at temperatures selected according to the above criteria. The extrudate was passed through a water cooling trough, dried, and subsequently pelletized by a chopper. The blend pellets were fed to the hopper of a ram-type injection molding machine (Van Dorn) whose barrel temperature was set at 205°C. The latter temperature corresponds to the viscosity crossover point of HDPE and PS shown in Figure 1 and was selected for molding since equality of viscosity should minimize migration or lamination of components during laminar flow in the injection molding process. The mold was cooled by tap water and the parts were formed in the shape of a dog bone (ASTM D-638 Type I). The mold runner could be gated so that the dog bone did or did not have a weld line.

This process should create a good dispersion of components during mixing in the extruder with minimum phase migration occurring during subsequent molding. No morphological examination was performed to assess the effectiveness of this approach, however.

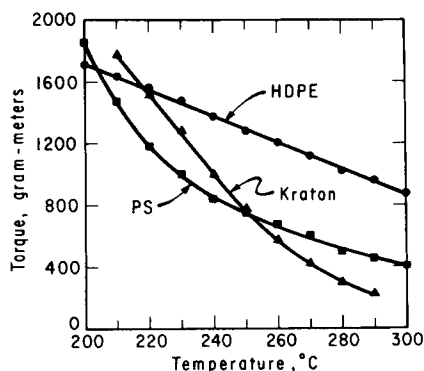


Fig. 2. Brabender torque vs. temperature responses for the polymers used in this study.

MECHANICAL PROPERTIES OF MOLDED BLENDS

The tensile properties of dog bone specimens, injection molded without weld lines as described above, were obtained with an Instron testing machine operated at a crosshead rate of 0.2 in./min. Ultimate and yield properties were obtained directly from machine measurements of force and deformation using the nominal gauge length and measured initial cross sectional areas of the specimens. Separate specimens were used to obtain the 0.5% secant modulus. The strains associated with calculation of this modulus, were calculated from measurements of crosshead deflections and an initial gauge length modified by "the method of constant force" to account for deformations outside the nominal gauge section of the specimen.

Figure 3 displays the modulus and yield strength (ultimate strength for brittle specimens) values observed for HDPE-PS blends and those containing 20% Kraton. Both modulus and strength fall just below the additive line connecting the values of the extreme compositions. As expected, addition of the Kraton block copolymer reduced both the modulus and the strength.

Figure 4 shows the elongation at break for these same compositions. Points are not shown for the compositions containing no PS since they were greater than the full traverse of the crosshead. The binary blends exhibit a minimum as expected for such incompatible mixtures.^{1,2} However, no minimum appears when 20% Kraton is present, and, in fact, these ternary blends are quite ductile. Figure 5 illustrates further the dramatic toughening which occurs by adding Kraton to a HDPE-PS blend. It converts a brittle and cheesy material into quite ductile and useful materials. Of course, the price for this improvement is loss of modulus and strength as further illustrated in Figure 6. Nevertheless, the ternary blends possess a dramatically improved balance of mechanical characteristics compared to the binary mixtures of HDPE and PS.

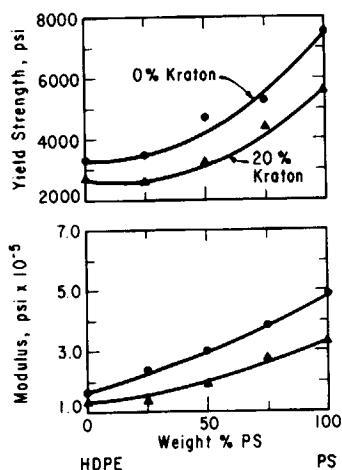


Fig. 3. Modulus and yield strength for HDPE-PS binary blends (●) and ternary blends containing 20% Kraton 1652 (▲).

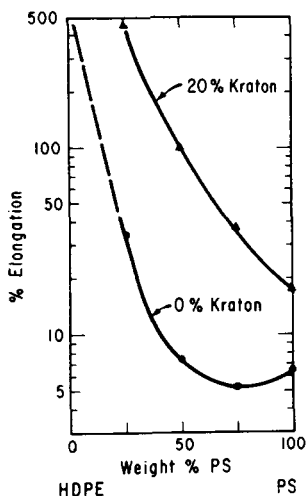


Fig. 4. Percent elongation at break for binary blends (●) and ternary blends containing 20% Kraton 1652 (▲).

EFFECT OF WELD LINES

Weld lines in molded parts pose serious problems for most polymer systems but are especially severe for two phase blends.³ Dog bone specimens with a weld line in the gauge section were prepared using identical processing conditions as for the samples mentioned in the previous section except that the runners were gated so that the mold was filled from both ends. Figures 7 and 8 show the strength and elongation characteristics for these specimens. Even specimens of pure HDPE and PS were weakened considerably by the presence of the weld line (compared with Figs. 3 and 4). The binary blends elongated approximately 1% and failed; however, the specimens containing Kraton deformed measurably before failing as shown in Figure 8. The lines drawn in Figure 7 were calculated from a simplistic model³ that includes the effect of mismatch of nonadhering phases at the weld line. In general, the observed strengths are higher than those

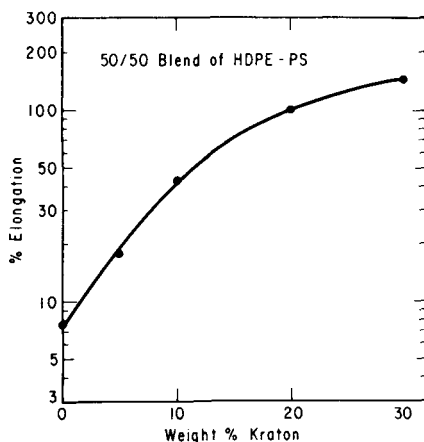


Fig. 5. Effect of Kraton level on percent elongation at failure for blends containing equal parts of HDPE and PS.

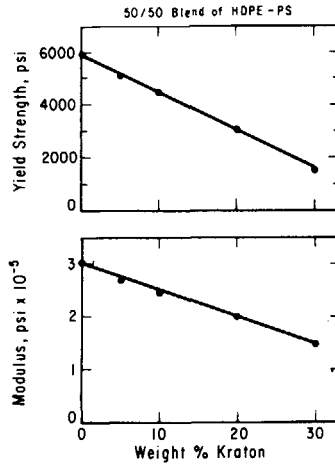


Fig. 6. Effect of Kraton level on modulus and yield strength.

predicted by this model. Certainly, weld lines pose serious problems for this system and should be avoided; however, incorporation of Kraton does help the situation.

SUMMARY

As expected for most immiscible polymer blends, the mechanical properties of binary blends of polystyrene and high-density polyethylene are quite poor. This is especially true of the ductility of these mixtures. However, addition of an SEBS block copolymer dramatically increases the ductility of these blends which is accompanied by some reduction in yield strength and modulus. To illustrate the increase in ductility, a 50/50 blend has an elongation at break of

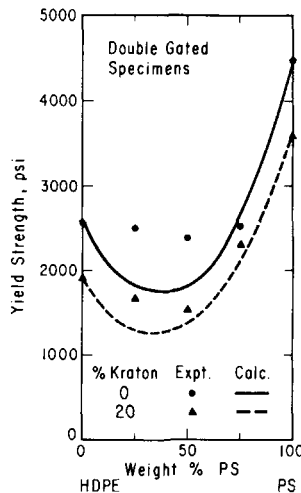


Fig. 7. Yield strength for specimens containing a weld line. The lines drawn were calculated (ref. 4) from $\sigma = \sigma_{11}\phi_1^2 + \sigma_{22}\phi_2^2$, where ϕ_i is the volume fraction and σ_{ii} is the strength of weld line for pure i . For 0% Kraton: (●) experimental, (—) calculated; for 20% Kraton: (▲) experimental, (---) calculated.

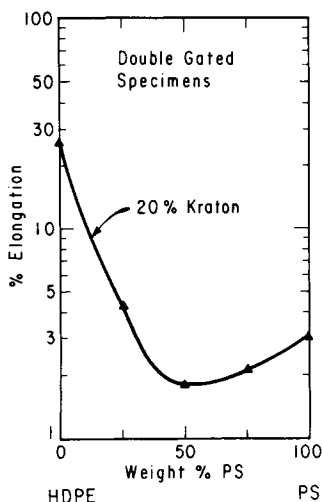


Fig. 8. Apparent elongation at break for Kraton containing blends with a weld line. The binary blends without Kraton broke at elongations of the order of 1% and are not shown here.

less than 8%, but addition of 20% of the block copolymer to this blend raises this to approximately 100%. Thus, this brittle and rather useless blend can be converted into a quite ductile material that is not precluded from useful applications because of deficient mechanical properties.

An important question which remains for future work is to develop an understanding of the mechanism by which the block copolymer is able to improve the mechanical performance of these and other blend systems. Among other things, this will require determination of any changes in phase morphology which its addition induces. However, an especially interesting question is whether the previously mentioned mutual ability of the SEBS block copolymer to adhere to each of the primary blend components (when they in fact do not adhere to each other) plays any role in this mechanism or not.

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