

Mechanical Properties of Blends Containing HDPE and PP

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Synopsis

The mechanical properties of binary blends of high-density polyethylene and polypropylene are quite good compared to those for blends of some other immiscible pairs. The property relationships observed depend strongly on the process used to fabricate the blends as shown by comparisons of specimens made by injection and compression molding with widely varied cooling rates in the latter. Strength and modulus may show additive behavior or have positive or negative deviations, depending on the process conditions; however, measures of ductility like impact strength or elongation at break always show negative departures from additivity and exhibit minima in some cases. Addition of an appropriate ethylene-propylene elastomer greatly improves the ductility of these blends but with a corresponding decrease in strength and modulus. The presence of weld lines has a serious detrimental effect on mechanical properties of these blends.

INTRODUCTION

A number of recent papers have reported on the behavior of the blends which can be formed from combinations of high-density polyethylene (HDPE), polypropylene (PP), and various ethylene-propylene elastomers.¹⁻¹⁵ A part of this interest stems from the need to improve the impact resistance of polypropylene, especially at low temperature, through rubber toughening,⁶ which may also employ combinations including HDPE.¹¹ Blends richer in the rubbery copolymer component have become important because of the need for thermoplastic materials with the characteristics of vulcanized rubber.¹⁵ A more general motivation stems, however, from the fundamental interest in the possibilities offered by physical blending for achieving tailored or unique behavior.

Several papers have demonstrated that binary blends of PP and HDPE may exhibit synergistic behavior with respect to strength and modulus.^{4,7,8} It has been further demonstrated that the presence of one component affects the crystallization kinetics and morphology of the other,^{8,10,16} which has been proposed as an explanation for this interesting mechanical behavior for blends that are essentially immiscible. This suggests that the mechanical behavior of such blends should be extremely sensitive to processing techniques and parameters. Despite the synergistic response mentioned, PP-HDPE binary blends seem to suffer some losses in ductility compared to the pure components. Based on previous experience, we felt that ductility could be restored to these blends by addition of a proper third component of which certain ethylene-propylene elastomers are prime candidates.^{2,17}

This paper addresses the two issues mentioned above. Blends were made using a broad range of processing techniques in order to determine the effect on properties. An ethylene-propylene elastomeric additive was employed as a

means to improve the ductility of PP—HDPE blends. The results obtained should be useful to attempts to derive useful products from scrap plastics composed of mixtures of polyolefins and contribute to better understanding of the property behavior of immiscible polymer blends.

MATERIALS

The polypropylene used is a commercial product of Shell Chemical Co., designated by the code 5520, and has a nominal melt flow value of 5.0 g/10 min. The high-density polyethylene was supplied by the Union Carbide Corp., and is their product designated as DGDA 6084 with a melt index of 0.3 g/10 min. Since the relative rheological characteristics of the components are an issue in determining phase morphology in blends, Figure 1 shows the torque vs. temperature relationship for each of these polymers determined by a Brabender Plasticorder at a rotor speed of 120 rpm. Over the entire range of temperatures accessible for processing, the HDPE is more viscous than the PP.

The ethylene-propylene elastomer is a terpolymer containing about 72% ethylene provided by the B. F. Goodrich Co. with the designation Epcar® 847. It has some ethylene crystallinity owing to rather long ethylene sequences in the polymer.

INJECTION-MOLDED BLENDS

Sample Preparation and Testing

Blends of the desired composition were compounded in a single screw extruder ($D = 1$ in., $L/D = 25$, compression ratio = 3). The extruder was passed through a water cooling trough, dried, and subsequently pelletized. The pelletized blend was fed to the hopper of a ram type injection molding machine (Van Dorn), where test specimens were formed. The mold was cooled by tap water, and the parts were formed into both dog bone (ASTM D-638 Type I) and Izod type bars. The mold runner could be gated so that the test bars did or did not have a weld line. The extrusion and molding temperatures were set at 232°C and 240°C, respectively, in most cases; however, these temperatures were varied to assess their effect on blend properties.

The dog bone specimens were pulled at 2.0 in./min with a floor model Instron,

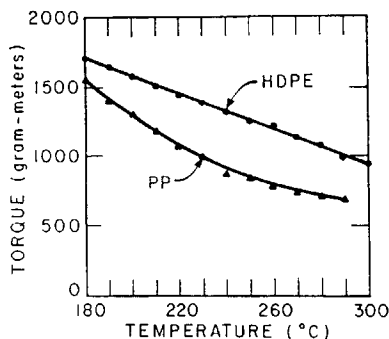


Fig. 1. Brabender torque-temperature relationships at rotor speed = 120 rpm.

and pertinent mechanical properties were computed from the recorded force-time traces. Tensile strengths reported are the stress at yield. Notched Izod strengths were determined using a TMI Impact Tester. The data shown are the average for approximately twelve specimens.

MECHANICAL PROPERTIES

This section presents mechanical properties of binary and ternary blends prepared at the standard processing conditions mentioned above for specimens formed without weld lines. Figure 2 shows the pertinent results from Instron testing as a function of the PP/HDPE proportions in the blends. The strength and modulus of the binary mixtures follow a simple additive relationship with no suggestion of synergism of the type mentioned earlier. The elongation at break on the other hand is not additive and, in fact, has a minimum at about 25% HDPE. Compared to other blend systems,^{18,19} this lack of additivity is not very serious since at the minimum the deformation at failure is nearly 100% corresponding to a high level of ductility.

Addition of 20% of the ethylene-propylene elastomer causes reductions in both strength and modulus as expected,¹⁷⁻¹⁹ and a substantial increase in the elongation at break. In fact, the dog bones containing Epcar did not fail during the test since the full traverse of the Instron crosshead (about 200%) was reached first. Figure 3 shows the effect of Epcar content on the strength and modulus of blends containing equal parts by weight of PP and HDPE. No elongation at break results are shown since the specimens containing as little as 10% Epcar did not fail prior to reaching the maximum travel of the crosshead.

Izod values for binary blends are plotted in Figure 4. The results fall well below the additive line but do not show a minimum in contrast to the deformation at failure. Blends containing 10% or more Epcar did not break but simply bent under the force of the striking hammer.

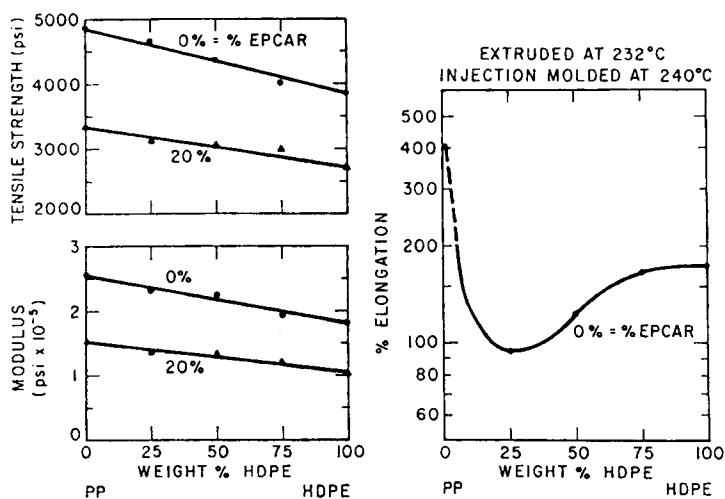


Fig. 2. Mechanical properties of injection-molded binary and ternary blends. Blends containing 20% Epcar have elongations at break greater than 200%—the full traverse of the crosshead.

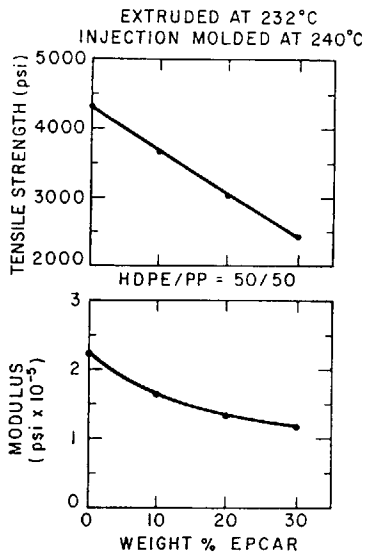


Fig. 3. Effect of Epcar level on strength and modulus of a 50/50 HDPE/PP blend. Blends with Epcar had elongations at break greater than 200%.

EFFECT OF PROCESSING TEMPERATURE

A matrix of extrusion and molding temperatures were used to fabricate specimens containing equal parts PP and HDPE in order to determine the influence of these processing parameters on properties. The strength and modulus results are shown in Figure 5 while elongation at break values for blends without Epcar are shown in Table I. Blends containing 10% or more of this additive did not break. Extrusion or blending temperature would primarily affect phase morphology. Strength and modulus were not greatly affected by this parameter. Molding temperature might be expected to have a significant effect on crystallization behavior. This parameter had a significant effect on mechanical

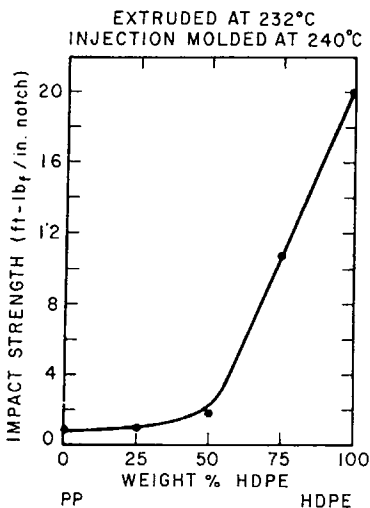


Fig. 4. Notched Izod impact strength for binary HDPE—PP blends. Blends containing Epcar did not fail.

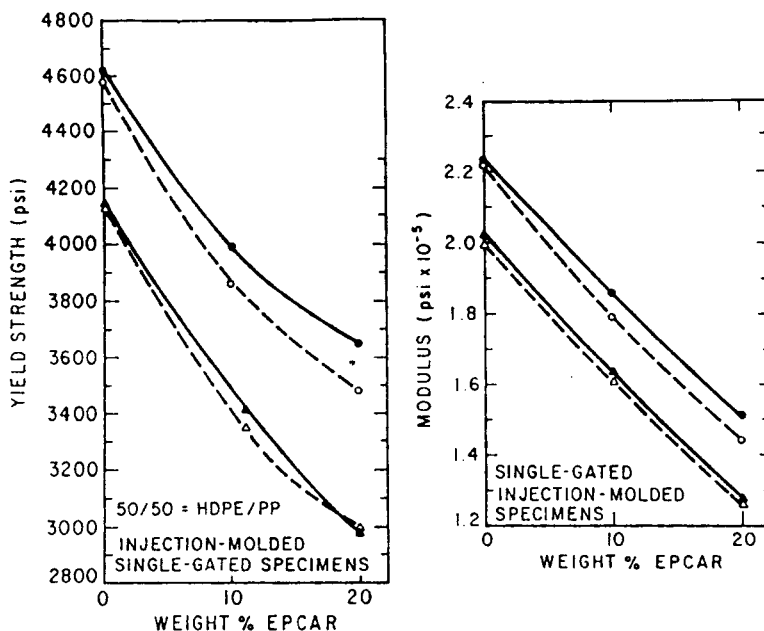


Fig. 5. Effect of processing temperatures on properties of blends containing equal parts HDPE and PP. See Table I for elongation at break data. (O) Blend. temp = mold. temp = 191°C; (Δ) blend. temp = 191°C; mold. temp = 274°C; (●) blend. temp = 274°C; mold. temp = 191°C; (▲) blend. temp. = mold. temp = 274°C.

properties. The higher melt temperature resulted in reduced modulus and strength and a corresponding increase in elongation at break, all of which are consistent with a lower level of crystallinity.

EFFECT OF WELD LINES

Specimens prepared by double gating the flow to the mold were tested to ascertain the behavior at a weld line for these blends.¹⁷ The strength values are shown in Figure 6 while apparent deformations at failure are shown in Figure 7. All failures did occur at the weld line. Pure PP suffers no reduction in strength as a consequence of the weld line, whereas HDPE does. The blends experience a more serious reduction in strength as can be seen by comparing Figures 2 and 6. There is a minimum at about 75% HDPE which disappears on addition of Epcar. As may be seen by comparing Figure 7 with data in Figures 2 and 3, there is a serious loss in the total deformation experienced before failure for specimens with weld lines. For HDPE—PP blends, this situation is improved by addition of Epcar; however, addition of Epcar to pure HDPE or to pure PP worsens their response.

TABLE I
Effect of Processing Conditions on % Elongation at Break of 50/50 HDPE/PP Blends^a

Extrusion temperature	Molding temperature	
	191°C	274°C
191°C	81%	99%
274°C	88%	131%

^a Blends containing Epcar have elongation greater than 200%.

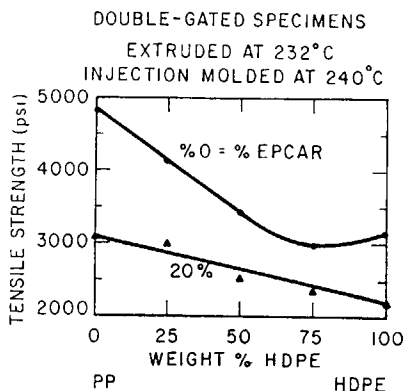


Fig. 6. Tensile strength of injection molded bars having a weld line.

COMPRESSION-MOLDED BLENDS

Sample Preparation and Testing

Blends of the appropriate compositions were batch-mixed in the melt state using a Brabender Plasticorder at 190°C for 8–10 min at a rotor speed of 20 rpm. After mixing, the molten mass was transferred to a compression mold with platens set at 190°C, where sheets were pressed. Sheets 1/8 in. thick were formed and stamped into specimens conforming to ASTM D-1882 Type L for tensile impact testing. Thinner sheets, 0.015 in., were pressed and stamped into dog bone specimens conforming to ASTM D-638-68 Type IV for Instron testing. These sheets were formed by either a Carver laboratory press or a larger Greenerd press. The sheets were cooled in the mold by either turning off the heat and slowly cooling to room temperature, which took about 2 hours for the Carver press, or by quenching by cooling water circulated through the platens of the Greenerd press. These different methods varied the time-temperature history for component crystallization. About 16 specimens of each composition were tested, and the results were averaged. Stress-strain diagrams were generated

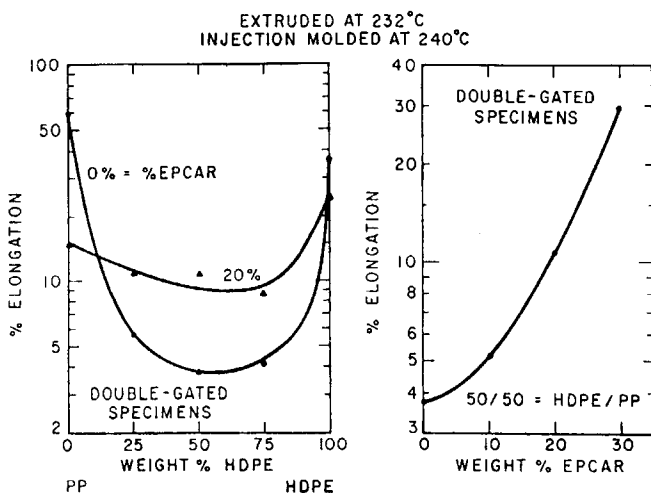


Fig. 7. Elongation at break for injection molded bars having a weld line.

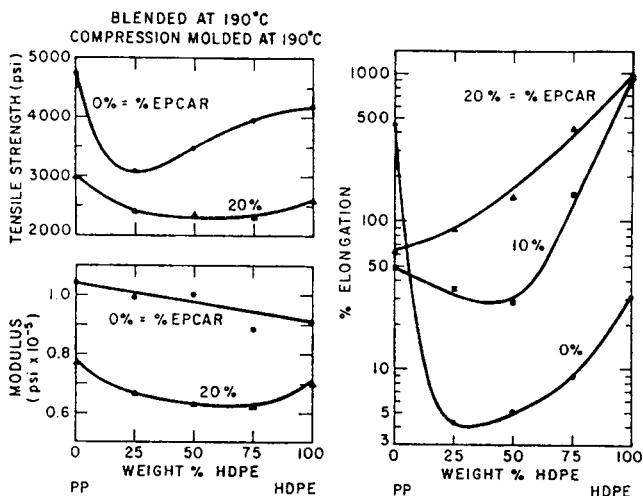


Fig. 8. Mechanical properties of batch mixed/compression molded specimens. Formed in a Carver press and slowly cooled.

via a table model Instron using a crosshead speed of 1 in./min while tensile impact measurements were made using a TMI tester.

Mechanical Properties

Figures 8 and 9 show the Instron results for blends molded and slowly cooled in the Carver press. Unlike the injection molded samples, the binary blends exhibit a minimum in yield stress at about 25% HDPE. A less pronounced minimum exists when Epcar is added. The moduli for all specimens made by compression molding are considerably lower than those seen in Figure 2 for injection-molded samples. This, no doubt, reflects the much higher degree of molecular orientation induced by injection molding. The differences in strength behavior is probably the result of a higher degree of parallelization of the phases

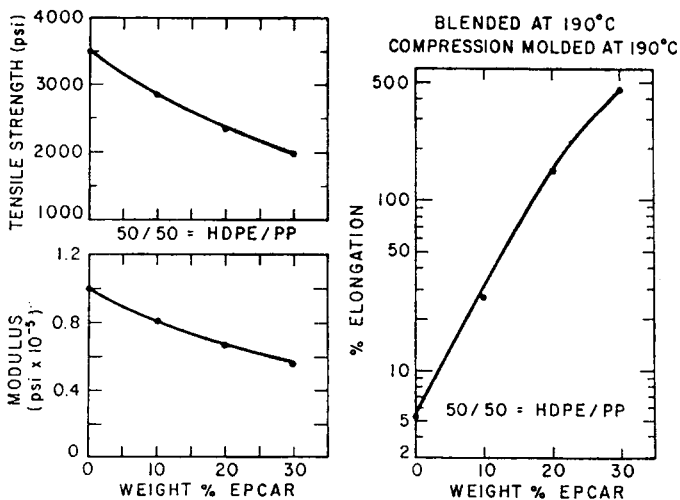


Fig. 9. Effect of Epcar level on blends containing equal parts HDPE and PP.

expected from injection molding, i.e., the latter would be expected to produce a fibrillar morphology of phases while compression molding most likely yields a more globular dispersion of the discrete phase in the matrix of a continuous phase.

As found in the past,¹⁷ lower values of elongation at break are found when compression molding is used. A very dramatic increase in elongation at break for blends is caused by addition of Epcar. The corresponding decreases in strength and modulus on adding Epcar parallel those seen for injection-molded specimens.

Tensile impact strengths are shown in Figure 10 for binary PP—HDPE and ternary blends containing 5% Epcar. The former exhibits a broad minimum paralleling the elongation at break values. However, the addition of as little as 5% Epcar eliminates the minimum and produces a dramatic increase in toughness. These results demonstrate very clearly the propensity of Epcar 847 to toughen PP—HDPE blends.

Instron results for binary blends molded and quenched in the large Greenerd press are shown in Figure 11, and there are some dramatic differences compared with those for samples slowly cooled in the Carver press. The tensile strength does not develop a minimum but instead deviates positively from additive behavior. The modulus displays a distinct maximum much like that reported by others. The elongation at break is somewhat larger for the quenched specimen than those slowly cooled. Thermal analysis of pure HDPE and PP revealed that slowly cooled specimens had melting endotherms with about 15% more area than quenched ones. This difference in crystallinity would explain the tendency for the pure components to be stronger and stiffer but less ductile when slowly cooled than when quenched but does not explain the synergistic behavior for blends. The proposal advanced by Lovinger and Williams concerning crystalline texture of the blends and supported by the crystallization kinetics data of Martuscelli et al.¹⁰ appears to be the best rationalization for this behavior. Furthermore, the latter work also demonstrates that the influence on crystallization behavior by the presence of other polyolefin components is very temperature-sensitive, which might allow one to hypothesize about why such behavior is not seen for slowly cooled compression molded blends. In addition, the immense differences

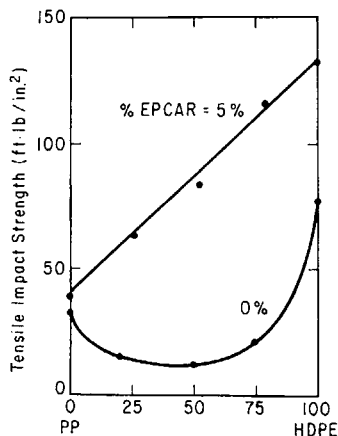


Fig. 10. Tensile impact strength of compression-molded blends.

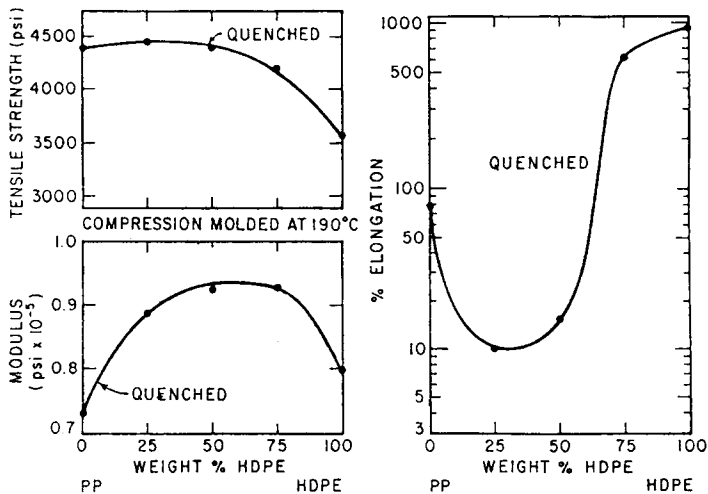


Fig. 11. Properties of binary blends pressed into film in Greenerd press and quenched.

in crystallization and phase orientation attending injection molding might be reasonable factors in precluding this synergism from developing when this fabrication method is used.

SUMMARY

Fabrication technique plays a very large role in the mechanical property responses observed for binary PP—HDPE blends which range from the display of minimum, additive, and maximum behavior. In any case, the properties of these blends are quite outstanding compared to many other immiscible blends. It appears that synergistic behavior in strength or modulus may occur under certain thermal conditions for fabrication processes like compression molding or roll milling used in previous studies,^{4,7,8} which do not involve large stresses during solidification. Evidently in these cases, properties are highly influenced by alterations in the crystalline texture of each component caused by the presence of the other component.^{8,10} However, these issues appear to be swamped by the greater effects of stress on crystalline texture and on phase morphology in processes like injection molding. At the present time, of course, this rationalization of observed behavior involves a high degree of speculation, but it is clear that the synergisms reported previously are not innate to the HDPE—PP system.

For all fabrication techniques, PP—HDPE binary blends show less than additive ductility. Addition of a semicrystalline ethylene—propylene elastomer, Epcar 847, dramatically improves the ductility of these blends which may be desired for certain applications.

As seen for other blend systems, the presence of weld lines in molded parts causes a serious diminution in mechanical behavior.^{17,19}

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