

Graft Copolymer Modification of Polyethylene-Polystyrene Blends. II. Properties of Modified Blends

C. E. LOCKE* and D. R. PAUL, *Department of Chemical Engineering, The University of Texas at Austin, Austin, Texas 78712*

Synopsis

The use of graft copolymers of styrene onto polyethylene as additives to improve the mechanical properties of polyethylene-polystyrene blends is described. Blends containing equal proportions of low-density polyethylene and polystyrene were selected for this study since this composition represents the poorest balance of properties in this system. Graft addition generally increased both the yield strength and the elongation at break of the blend. Of the grafts employed, those prepared at an irradiation dose near 0.5 megarad appear optimal for this purpose. These conditions apparently balance the beneficial effects of grafting extent and the detrimental effects of crosslinking, both of which increase with irradiation dose.

INTRODUCTION

In the first paper of this series, the grafting of styrene to low-density polyethylene pellets was described. In this paper the use of these grafts as additives to improve the mechanical properties of polyethylene and polystyrene blends will be discussed. This work is part of a program to evaluate the potential value of reusing waste and scrap plastics as a blend of generic mixtures.²⁻⁴ Since such blends often have very poor mechanical properties, it is of interest to explore additives which can improve the properties of the blend.

The use of graft copolymers for impact modification of plastics with rubber is well known.⁵ Rubber simply blended with polystyrene will not produce the improved toughness that is sought,⁶ since it is generally believed that the adhesion at the polystyrene-rubber interface of the rubber domains is inadequate.⁵ Lundstedt and Bevilacqua⁶ showed that addition of a styrene-rubber graft gave impact strengths which were greater than that of either polystyrene or a polystyrene-rubber blend. It is believed that the graft provides adhesion at the interface since the two chain types can be expected to penetrate the phase of their own type in much the way a surfactant functions. This places chemical bonds across the interface.

* Present address: Department of Chemical Engineering, University of Oklahoma, Norman, Oklahoma.

From the above it is reasonable to expect that addition of polyethylene-styrene to blends of polyethylene and polystyrene should improve the adhesion at the domain interface of these very incompatible polymers.² This improved adhesion should in turn improve the mechanical properties of the blend. A single data point provided in an incidental way by Anderson et al.⁷ confirms this hypothesis. The effectiveness of the grafts described previously¹ as blend modifiers is discussed in detail here.

MATERIALS AND EXPERIMENTAL PROCEDURES

Most of the materials and procedures used here were described in the earlier paper,¹ but some points should be mentioned here. The polyethylene used in all blends was the same low-density material employed earlier for grafting, viz., DYNH from Union Carbide Corporation, with a density of 0.917 g/cc and 1.2 melt index. The polystyrene employed was the general purpose-grade Styron 685 from Dow Chemical Company.

Melt blends were prepared by introducing the desired proportions of polyethylene, polystyrene, and graft pellets into a Brabender Plasticorder with a Type 6 mixing head and mixing for 10 min at 170°C and 20 rpm. The mixed blend was transferred while still molten to a compression mold where a $4\frac{3}{4} \times 3\frac{1}{2} \times \frac{1}{8}$ in. sheet was formed at 180°C under a force of 15,000 pounds. All samples for testing were cut from these sheets. Instron and Rheovibron tests were executed as described earlier.¹ Instron results were obtained on at least four specimens. Parameters shown in tables are simple averages of these values. Graphs show both the average value and the range of all data by use of range markers. Occasionally, specimens which had been tested revealed visible defects in the cross section at the point of failure. In these cases additional samples were prepared and tested. The scatter in the data shown here is in part due to defects which were not apparent plus all of the associated difficulties of ultimate mechanical testing.

RESULTS

Effect of Graft Addition on Blend Stress-Strain Behavior

Figure 1 shows the ultimate mechanical properties of simple melt blends of polystyrene and polyethylene. The yield strength increases very slightly as polystyrene is added to pure polyethylene, but there is a slight minimum at about 45% to 50% polystyrene. After this, the yield strength increases steadily to the value for pure polystyrene. Low-density polyethylene is highly extensible since it readily necks and cold draws. Its elongation at break exceeds 700%, which was the maximum cross-head travel in the apparatus used here. Polystyrene, on the other hand, is very brittle, with an ultimate elongation of only 2% or so. As polystyrene is added to the low-density polyethylene, the elongation at break diminishes rapidly. This property goes through a minimum at 60% to 70% polystyrene and then increases slightly to the value for pure polystyrene.

Blends that contain roughly equal proportions of polyethylene and polystyrene have the strength of polyethylene and the brittleness of poly-

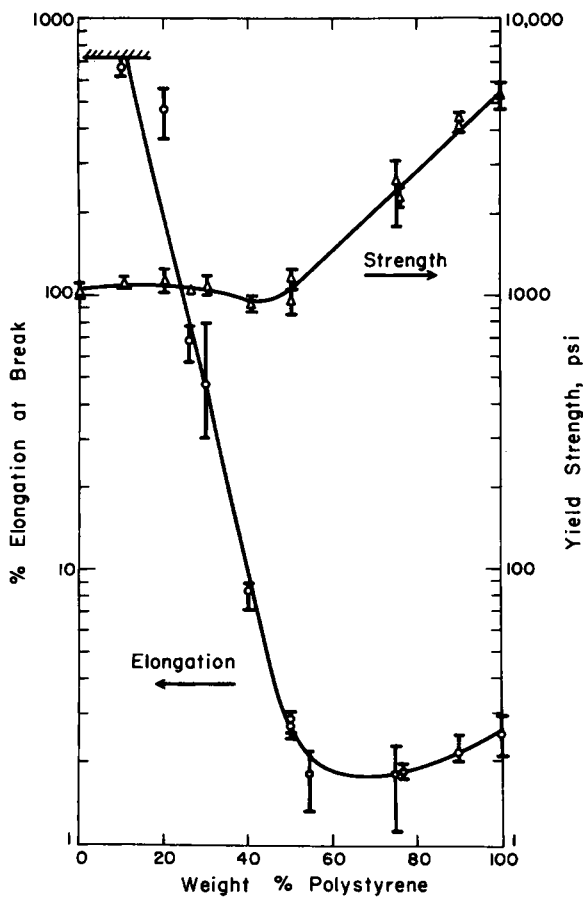


Fig. 1. Mechanical properties of low-density polyethylene (DYNH)-polystyrene (Styron 685) melt blends.

styrene. This combination of properties is very poor, and consequently such blends have little value as structural materials. Polyethylene and polystyrene are quite immiscible, and microscopic examination reveals rather large domain structures.^{1,2,4} In the midcomposition range, the morphology of the blend is very complex, and it is not always possible to describe the system in terms of continuous and discrete phases. This fact in itself probably contributes to the poor properties in this region.

The 50:50 blend composition was selected for studies of graft addition since it has about the poorest balance of properties of all blends. Because of its complex morphology, this composition may be more difficult to improve than any other. Table I summarizes the mechanical properties of all blends to which graft material has been added. In each case the polyethylene-to-polystyrene ratio is held at 1, while the amount of the graft material varies from 10% to 33 $\frac{1}{3}$ % of the total sample mass. At each level, different graft materials have been employed which are designated here by the radiation dose employed in generating that graft.

TABLE I
Effect of Graft Addition on the Mechanical Properties of
Polyethylene-Polystyrene (50:50) Melt Blends

| Graft added, % | Graft designation, mrad | Elongation, % | Yield strength, psi | Modulus, psi |
|--------------------------------|-------------------------|---------------|---------------------|-------------------|
| 0 | — | 2.7 | 1160 | 7.7×10^4 |
| 10 | 2.0 | 2.8 | 1313 | 7.90 |
| | 1.0 | 2.9 | 1350 | 7.49 |
| | 0.50 ^a | 2.5 | 1526 | 9.90 |
| | 0.50 ^a | 2.8 | 1479 | 7.09 |
| | 0.50 ^a | 3.1 | 1576 | 8.04 |
| | 0.28 | 2.5 | 1372 | 9.30 |
| | 0.25 | 3.4 | 1406 | 7.50 |
| | 0.14 ^a | 3.1 | 1448 | 7.88 |
| | 0.14 ^a | 3.1 | 1382 | 8.74 |
| | 20 | 2.0 | 4.1 | 1504 |
| 1.0 | | 3.9 | 1341 | 7.25 |
| 0.50 ^a | | 5.1 | 1637 | 7.06 |
| 0.50 ^a | | 4.6 | 1858 | 7.69 |
| 0.50 ^a | | 4.4 | 1533 | 8.30 |
| 0.28 | | 4.0 | 1580 | 7.91 |
| 0.25 | | 3.9 | 1396 | 6.87 |
| 0.14 ^a | | 5.6 | 1327 | 5.95 |
| 0.14 ^a | | 6.3 | 1475 | 6.63 |
| 33 ¹ / ₃ | | 2.0 | 3.8 | 1568 |
| | 1.0 | 5.1 | 1679 | 7.16 |
| | 0.50 ^a | 8.7 | 1800 | 6.67 |
| | 0.50 ^a | 5.6 | 1711 | 5.55 |
| | 0.50 ^a | 5.2 | 1546 | 7.45 |
| | 0.28 | 6.5 | 1573 | 7.17 |
| | 0.25 | 5.4 | 1502 | 5.77 |
| | 0.14 ^a | 9.2 | 1460 | 4.65 |
| | 0.14 ^a | 18.7 | 1401 | 5.69 |

^a Blends made with grafts produced in separate irradiations.

Data employing grafts prepared in separate experiments are shown to illustrate the consistency of the results obtained. The grafts in Table I may be identified in order of appearance with those described in Table V of the previous paper.¹ In general, the data in Table I show that blends to which graft material has been added have both higher strength and a larger elongation at break than the control blend which had no graft added. However, to understand fully the effect of adding a graft to this blend requires a more careful analysis. The grafts produced do not have the same ratio of polystyrene to polyethylene, and only in a few instances is this ratio near the value of 1 that exists in the blend. As a result, the materials that result from addition of grafts to the 50:50 blend do not have the same composition and some accounting of this by proper controls needs to be made.

To illustrate this point, Table I shows that the modified blends which have the largest elongation at break are those which employ grafts made

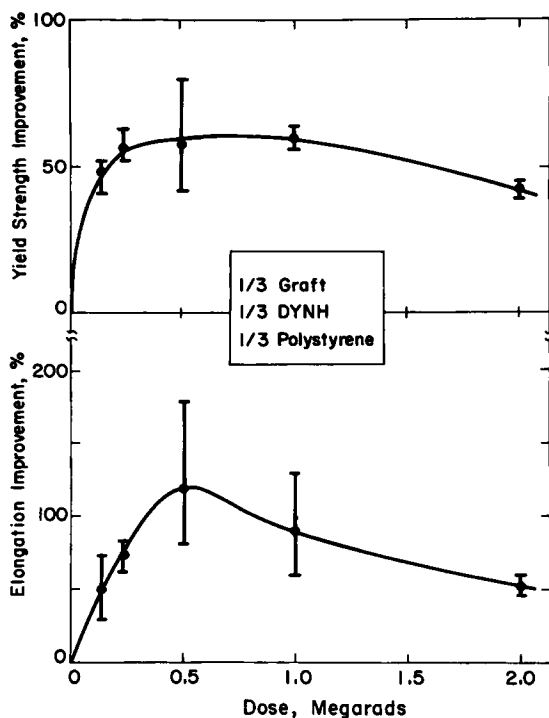


Fig. 2. Percentage improvement in strength and elongation of blends upon adding the indicated graft.

at the lowest radiation dose level. These grafts have the lowest polystyrene content.¹ Since they are rich in polyethylene, their addition to a 50:50 blend of polyethylene and polystyrene will raise the proportion of polyethylene above the 50% level. This action alone without the aid of any grafting benefit would raise the elongation at break, as can be seen in Figure 1. In other words, simply adding polyethylene to a 50:50 blend will improve its elongation at break. Therefore, to be interesting, a graft copolymer must improve properties in excess of what would occur by a simple composition change. Such improvements would result in data points that lie above the curves shown in Figure 1.

The following scheme has been used to evaluate the improvement produced by the presence of the graft copolymer in the blend. The polyethylene content of every modified blend in Table I was computed using the known graft composition.¹ The mechanical properties of a physical blend of this composition were taken from the curves in Figure 1. In all cases, the strength and elongation values for the modified blend were larger than these values. For a simple index, the amount they were larger was expressed as a percentage. This percentage would always be zero if pure polyethylene or a simple melt blend were added to the 50:50 blend. It thus serves as a guide to the advantage accrued by the presence of graft material.

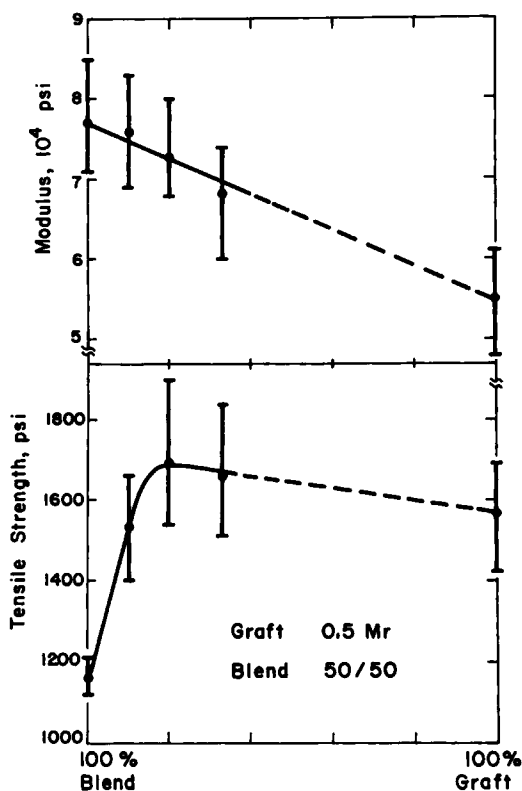


Fig. 3. Modulus and strength for blend containing various levels of a 0.50-mrad graft. (Note that this graft contains approximately 50% polyethylene.)

Figure 2 demonstrates the so-defined improvements in elongation and strength that result when equal parts of polyethylene, polystyrene, and graft are mixed together. Graft materials made using different radiation doses are represented here, and the improvements registered for each are plotted versus this dose. It is clear that grafts made with 0.50 mrad appear to be the optimum blend modifier. Improvements in excess of 50% for strength and 100% for elongation are noted here. The increase in effectiveness that occurs between 0 and 0.5 mrad is believed to be due to the increased amount of actual polyethylene-g-styrene in the graft composite that occurs in this region.¹ The decrease beyond this level is believed to be due to increased crosslinking¹ in the graft formed by radiation that prevents efficient blending of the graft with the blend. Crosslinked polyethylene-g-styrene will not be able to locate at the domain interface and provide the necessary bonding as it would if it were not crosslinked. These competing factors apparently vary in such a way as to produce an optimum at about 0.5 mrad. One other factor should be pointed out, however. The 0.5-mrad grafts have roughly equal proportions of polyethylene and polystyrene. Grafts made at doses less than this are polyethylene rich, while those at doses larger than this are polystyrene rich. One might reason

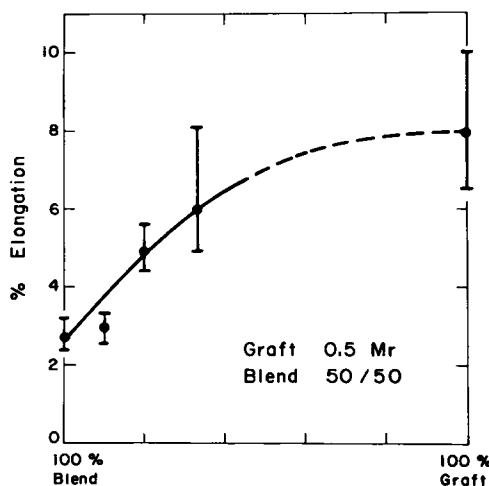


Fig. 4. Elongation at break for system shown in Fig. 3.

that the optimum graft to modify a 50:50 blend should have this same composition, other factors being the same. This may have some influence, but we feel that the balance of actual graft content versus crosslinking is the major factor in Figure 2.

The effect of amount of graft addition on blend improvement was explored using the optimum 0.5 mrad graft. The results are shown in Figures 3 and 4 by plots of modulus, strength, and elongation versus the proportion by weight that the graft contributes to the total sample. The data are expressed here on an absolute basis, not percentage improvement, because all across these diagrams the proportion of polyethylene is constant at 50%. The mechanical properties of the graft material itself are shown on the extreme right of these diagrams. In every case, an extrapolated dotted line is drawn to show how we expect the data for modified blends to connect with this point.

The modulus of the mixtures of the 50:50 blend and the graft fall on a straight line connecting these two extreme points. This response is more or less what one should expect.² The strength varies in a very interesting way in that it increases rapidly as graft is added to the blend. This property goes through an apparent maximum at about 20% graft. Modified blends in this region are slightly stronger than the graft itself. This would imply that the pure components in the blend are stronger than these components as they exist in the graft. The coupling provided by the graft allows these better properties to be realized in modified blends. The elongation at break of modified blends increase from the rather low value for the blend in a more or less additive way up to the value observed for the graft. The increases in strength and elongation caused by graft addition are quite significant but are still less than what might be hoped for to make a useful material. Figures 3 and 4 suggest, however, that these increases would be even larger if a graft of better properties could be produced. We have no assurance that the best graft made here for this purpose, i.e., the

0.50-mrad material, is the most optimum one possible. Further studies on graft optimization would thus appear to be a fruitful activity.

Effect of Graft Addition on Blend Morphology

Photomicrographs of microtomed sections of 50:50 polyethylene and polystyrene blends containing various amounts of the 0.50-mrad graft are shown in Figure 5. The unmodified blend in Figure 5a reveals rather large domains as discussed previously.¹ Addition of graft decreases the scale of heterogeneity in proportion to the amount of graft added as shown in Figures 5b, 5c, and 5d. A similar response was shown by Naimark et al.⁸ for the addition of cellulose acetate-g-acrylonitrile to CA/PAN blends. Wollrab et al.⁹ have shown evidence that domain regions and domain boundaries become less apparent when polyethylene-g-vinyl chloride is added to a 50:50 blend of poly(vinyl chloride) and polyethylene. Apparently the surfactant-like characteristics of graft copolymers decrease the interfacial energy at domain boundaries in blends which facilitates the generation of additional surface area during blending. The reduced scale of heterogeneity probably plays some role in the improved blend properties, although this alone is probably not adequate. This response, however, seems to be a corollary feature of adding an effective blend modifier.⁴

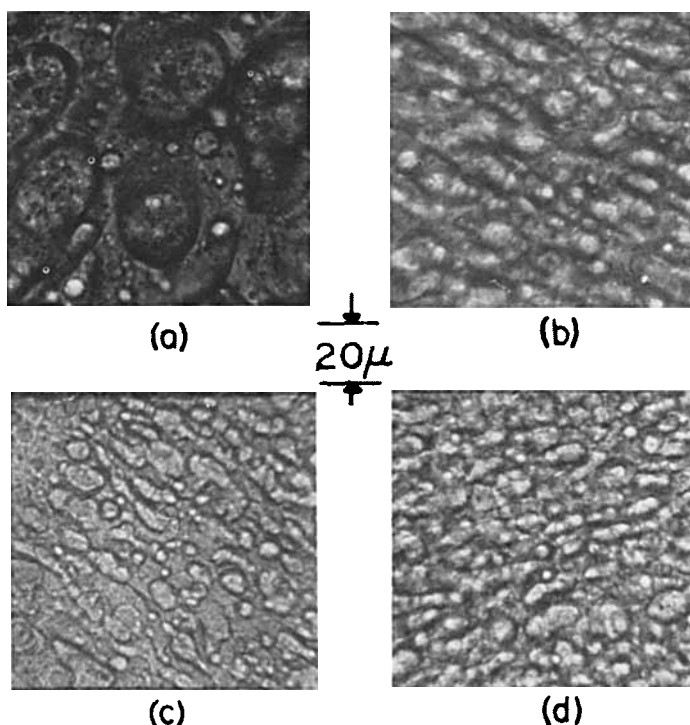


Fig. 5. Optical photomicrographs of microtomed sections of a 50:50 polyethylene-polystyrene blend containing various proportions of a graft prepared at 0.50 mrad. Percent graft: (a) 0%; (b) 10%; (c) 20%; (d) 33 $\frac{1}{3}$ %.

Dynamic Mechanical Properties

The dynamic mechanical behavior of a blend containing one third each of polyethylene, polystyrene, and a 0.50-mrad graft is shown as a function of temperature in Figure 6. The storage modulus drops slightly at about -120°C and then falls gradually from about 10^{10} to 10^8 dynes/cm² over the range of -20° to 100°C . The loss modulus, E'' , has peaks in the vicinity of -120° and -20° which coincide with the changes in E' . These peaks are the polyethylene γ - and β -transitions.¹ The E'' curve has a "plateau" in the 0° to 50°C region. This feature was observed earlier in grafts¹ but is not so apparent in unmodified blends of polyethylene and polystyrene. The $\tan \delta$ curve shows these transitions plus the beginning of the polystyrene T_g .

The loss modulus and $\tan \delta$ values for the blend in Figure 6 at the γ -transition peak are about one half the values for the 0.5-mrad graft and about one third the values for polyethylene. Similar comparisons prevail over the range of -150° to -40°C . Polystyrene has very low values of these quantities ($\tan \delta \sim 10^{-3}$ from -150° to $+50^{\circ}\text{C}$), and evidently the reductions seen here reflect the component properties in a more or less additive fashion.

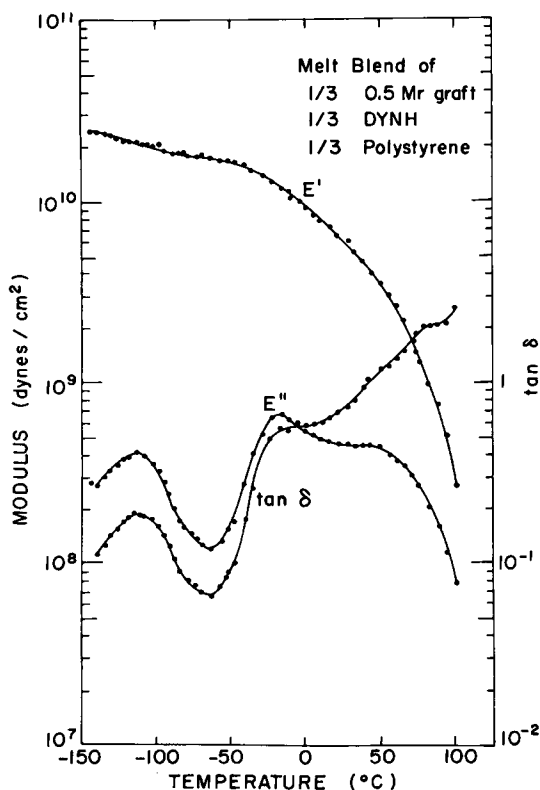


Fig. 6. Dynamic mechanical behavior of a graft-modified blend.

The peak values of E'' and $\tan \delta$ for this blend at the β -transition are approximately the same as those for the graft and polystyrene. The plateau region of E'' coincides closely with that for the grafts shown in Figure 4 of the previous paper.¹

CONCLUSIONS

The results of this work show that graft copolymers of styrene onto polyethylene are effective additives to improve the mechanical properties of polyethylene and polystyrene melt blends. For the grafts used here, those prepared at an irradiation dose of 0.50 mrad were most effective for this purpose. Apparently the competition between extent of grafting and crosslinking, both of which increase with radiation dose, is responsible for this optimum. The mechanism of blend improvement is believed to involve increased interfacial adhesion that the graft copolymer can provide. The graft also decreases the domain size in the blend.

The property improvements shown here are significant; however, larger changes using less additive would be desirable. It is reasonably assured that the grafts used here do not represent the ideal molecular structure for this purpose. The ideal process would produce a uniform grafting of styrene to all polyethylene chains without the occurrence of crosslinking. Actually, a diblock copolymer containing one polyethylene block and one polystyrene block with properly optimized molecular weights might be even better. The shorter the blocks, the less additive would be required on a weight basis; however, adequate block lengths to anchor them securely in their respective phases would be needed. The extent of blend improvement that could be realized by the "best" additive is unknown. Development of such additives for the current system appears to be limited by the available techniques for preparation and characterization; however, this is not necessarily true for other systems. Further optimization of known techniques for grafting styrene onto polyethylene would likely improve on the present situation.

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