

Graft Copolymer Modification of Polyethylene-Polystyrene Blends. I. Graft Preparation and Characterization

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Synopsis

The preparation and characterization of styrene-low-density polyethylene graft copolymers for addition to blends of polyethylene and polystyrene to improve blend mechanical properties is described. The direct method of grafting with ^{60}Co radiation was employed using the polyethylene in pellet form. This approach gave good grafting efficiency with maximum yields limited to about 1 g of styrene reacted per gram of polyethylene. Excessive crosslinking at radiation doses beyond about 1 mrad was detrimental to the melt processibility of the graft. Crystallinity, dynamic mechanical properties, morphology, and stress-strain behavior of the grafts were examined and compared with melt blends of similar composition in order to better characterize the material produced.

INTRODUCTION

In a recent paper,¹ the problems associated with reusing waste and scrap plastics without generic segregation were reviewed. A major problem is the poor mechanical properties of blends of incompatible polymers. A potential approach to this problem is to incorporate additives into the blend which will bind together the incompatible polymers. Suitably chosen block or graft copolymers are attractive candidates for this role since they are likely to locate at domain boundaries and provide adhesion between the phases.² Certain types of chlorinated polyethylenes have been shown³ to be very effective additives for improving the mechanical properties of polyethylene/poly(vinyl chloride) melt blends. This ability has been attributed² to the block-like character of the slurry (solid state) chlorinated polyethylenes used for this purpose.

It was postulated that a similar improvement would be possible for melt blends of polystyrene and polyethylene if the additives were a graft copolymer of styrene onto a polyethylene backbone. Such grafts have been studied extensively but no commercial source exists, so to test this hypothesis it was necessary to prepare the graft. It is the purpose of this paper

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to report some of the results generated during the course of making and characterizing this material which add further insight to existing knowledge on this system. Results on the use of this graft as a blend additive will be reported in a subsequent paper.

The use of high-energy radiation for forming this graft was chosen because of the ease associated with this method and the considerable background available.⁴⁻⁶ Previous radiation grafting work in this system has included both the direct method where the polyethylene is irradiated while swollen in styrene and the trapped free-radical approach where the polyethylene is irradiated alone and then immersed in styrene.⁷⁻¹⁶ Most reports in the literature have been concerned with the kinetics of grafting and the influence of such factors as dose rate, total dose, temperature, polymer type and form, etc., on the reaction. Only in a few instances have the properties of the resulting grafts been reported.¹⁵

The grafts produced in most of the reports in the literature would not have been suitable for use as a melt blend additive for various reasons. This application demands that the graft be melt processible and available in sizable quantities. The first condition requires that the polymer not be extensively crosslinked which is likely to result from most conditions of preparation reported in the literature. Both requirements make the use of polyethylene film or powder unattractive. As a result, it was necessary to use the polyethylene in the form of pellets. This form increases the problem of diffusional limitations during the reaction and makes a heterogenous grafting level throughout the pellet a certainty. These drawbacks were accepted since they appear to be almost inseparable from the above requirements.

MATERIALS AND EXPERIMENTAL TECHNIQUES

Materials

The polyethylene used in the graft preparation was a low-density commercial product of Union Carbide designated as DYNH, with a density of 0.917 g/cc and melt index of 1.2. The polymer was supplied as cylindrical pellets approximately $\frac{1}{8}$ in. \times $\frac{1}{8}$ in. The polymer is stated to be free of additives and was used as received in the pellet form.

Styrene monomer was freed of inhibitor before use by repeated caustic and water washes.

Polystyrene used in melt blends described here was obtained from Dow Chemical and is designated as Styron 685.

Melt Blending

After grafting, the pellets were melt mixed in a Brabender Plasticorder and the torque required for the blending was recorded. All blending was done at 170°C and 20 rpm motor speed. The melt was transferred to a heated (180°C) compression mold where a sheet with dimensions of $3\frac{1}{2}$

$\times 4^{3/4} \times 1/8$ in. was formed. The samples for stress-strain measurements, dynamic mechanical testing, DTA and microscopy were obtained from these sheets.

Stress-Strain Behavior

The stress-strain properties were determined per ASTM D638-71 using dog-bone specimens cut to the size specified by ASTM D 412, Type C. An Instron cross-head speed of 0.2 in./min was used.

Dynamic Mechanical Properties

The dynamic mechanical properties of the graft copolymers were obtained at 110 Hz using the Model DDV II Rheovibron Viscoelastometer manufactured by Toyo Measuring Instruments Co., Ltd.¹⁷

The samples were 3- to 8-mil films pressed from the sheets described above. Samples were held at 120°C between glass slides for a few minutes to remove any residual stresses due to the pressing operation.

Differential Thermal Analysis

The DTA data were obtained with the R. L. Stone H-5 subambient and LB-202 recorder/controller. This subambient instrument has the capability of programmed heating and cooling over the temperature range of -150° to 300°C. The areas under the melting peaks were determined by a polar planimeter by averaging three traverses of the peak area.

Optical Microscopy

The photomicrographs were obtained by transmitted light through samples cut with a microtome set at 5 microns.

PREPARATION OF THE GRAFT

Grafting of styrene onto polyethylene was accomplished by the direct method using a cobalt 60 source of γ -rays. The polyethylene pellets were introduced into glass tubes and then covered with styrene monomer. The weight ratio of styrene to polyethylene was maintained at 1.3. The tubes were immersed in liquid nitrogen to freeze the styrene, and then a vacuum was applied. Subsequently, the tubes were sealed while evacuated and then placed in a refrigerator for two days to allow the styrene to swell the pellets. After this, the tubes were placed in a cobalt 60 source at a position where they received 47,000 rads/hr of γ -radiation at 18°C. Exposure times were varied as necessary to achieve a range of total dose from 0.14 to 4 megarads.

After removal from the source, the tubes were broken open and exposed to ambient conditions for several hours. The recovered pellets were heated at 60°C for 1 hr in a vacuum oven (~ 30 in. Hg vacuum) to remove the

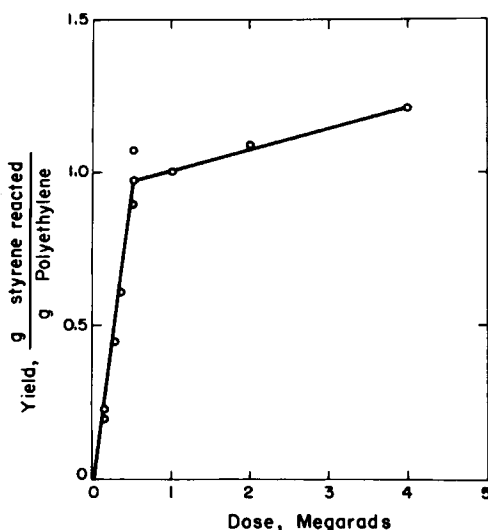


Fig. 1. Yield data.

unreacted styrene. The yield of styrene reacted in the polyethylene was determined gravimetrically as follows:

$$\text{yield} = \frac{W_g - W_{PE}}{W_{PE}}$$

where W_g = the weight of 100 pellets after grafting and W_{PE} = the weight of 100 pellets before grafting.

The yield data so obtained are shown in Figure 1. The yield increases linearly with radiation dose up to 0.5 megarad and then appears to plateau. The charge ratio of styrene to polyethylene here is 1.3, and this might be expected to cause the limit on yield. However, this is not entirely so since experiments at 0.5 mrad using a charge ratio 2.6 gave identical results to those shown in Figure 1. In part, the limit on yield is caused by the fact that the styrene outside the pellet is also polymerized due to free-radical initiation by the γ -rays. This external phase ranged from a viscous liquid at 1 mrad to a rigid material holding the pellets together at 2 and 4 megarads. Styrene monomer swells the polyethylene until a 13.6% by weight styrene content is reached in about one day. Higher yields than this may be attained on grafting since as the reaction uses up the liquid monomer more diffuses into the pellet. Furthermore, the monomer becomes more soluble as grafting proceeds. Kamel et al.¹⁶ cite experimental data which show that the solubility of styrene in low-density polyethylene increases from 15% to 30% by a 24% polystyrene graft. During grafting, styrene will diffuse into the polymer as needed; but as the monomer source outside the pellet is consumed by polymerization, the reaction inside the pellet must be drastically slowed down owing to partitioning of available monomer. A larger charge of styrene will not greatly alter this situation.

CHARACTERIZATION OF THE GRAFT

The pellets which were recovered from the grafting process described above are quite complex in character. The reactions involved do not occur uniformly throughout the pellets as one might expect on the basis of the diffusional limitations which are possible. Microscopic examination of sectioned pellets showed a gradation of change across the pellet diameter; however, these observations are not readily converted into quantitative information. In principle, the pellets may contain both polyethylene and polystyrene homopolymers in addition to polyethylene-*g*-styrene. It is the latter material which is of interest; however no technique has been devised to separate these individual components on a practical basis. In fact, there appears to be no unambiguous way to quantitatively identify the fraction of each component for analytical purposes. Beyond this information, it would be interesting to know the average length and number of styrene grafts attached to those polyethylene molecules which are grafted. This knowledge is also hard to obtain in terms of fundamental quantities. Further, the polyethylene present has undergone some cross-linking, and it would be of interest to characterize this feature. A number of characterization techniques have been employed to gain information of this type, and these results are described next. A complete description of the composite, however, has not been developed.

Extraction and Solubility

An external surface coating of polystyrene homopolymer was formed in the grafting process. To remove it, the pellets were washed in toluene at 40°C, then dried in a vacuum oven to remove residual solvent. The results of these experiments shown in Table I indicate that only a small amount of polystyrene was removed for high dose levels and none at the lower levels. This extraction procedure which uses the whole pellets probably did not remove any polystyrene homopolymer within the pellet.

Additional extraction experiments were performed to see if there was any homopolymer within the pellets that could be removed. Pellets were

TABLE I
Styrene Content of Grafted Pellets

Irradiation dose, mrad	Styrene content, g styrene/g polyethylene	
	Before extraction	After extraction with toluene at 40°C
2.0	1.11	1.02
1.0	1.0	0.9
0.50	0.91	0.83
0.25	0.50	0.50
0.14	0.23	0.23

TABLE II
Boiling Acetone Extraction of Ground Polymers

Sample	Styrene content, g styrene/g polyethylene	
	Before extraction	After extraction
Melt blend LDPE/PS	1.08	0.64
1 mrad graft	1.0	0.90
0.5 mrad graft	0.91	0.84

TABLE III
Tetralin Solubility of Graft

Irradiation dose, mrad	Fraction dissolved at 125°C, wt-%	Ratio of soluble to insoluble material at 25°C.
4.0	16%	—
2.0	60%	—
1.0	100%	26.8
0.50	100%	2.98
0.25	100%	0.75
0.14	100%	0.25

ground to 20 mesh in a Wiley Mill and placed in a porous bucket suspended above a heated flask containing boiling acetone. A water-cooled condenser was used to condense the acetone which then dripped onto the polymer, percolated through it, and then back into the flask. These extractions, lasting up to two weeks, had a distinct advantage in that the acetone contacting the sample was pure and thus avoided saturation effects. The results of these experiments are tabulated in Table II.

This procedure removed about 30% of the polystyrene contained in a polystyrene/polyethylene melt blend control. Therefore, this method cannot be expected to give the true amounts of polystyrene homopolymer in a graft. However, it can be seen that the level of homopolymer in the graft must be fairly low since so little was extracted. Furthermore, the amount of polystyrene removed in this manner was essentially the same as that removed by a toluene wash of the pellets. This suggests that most of the homopolymer is located on the surface.

The solubility of the pellets in tetralin was tested at 125°C and 25°C, with the results shown in Table III. The grafts prepared at dose levels of 1.0 mrad or less were completely soluble, while those made at 2.0 and 4.0 mrad were only partially soluble. This point will be discussed in more detail later.

The materials that were completely soluble at 125°C were allowed to cool to room temperature, whereupon a portion of the sample became in-

soluble. This insoluble fraction was separated from the soluble fraction at 25°C by vacuum filtration. The tetralin was removed from the soluble fraction in a vacuum oven (~30 in. Hg) at 100°C and the residue weighed. The insoluble fraction remaining on the filter paper was also weighed after a similar heat treatment. The weight ratio of the soluble to insoluble portions are presented in Table III.

Polystyrene is soluble in tetralin at 25°C, whereas polyethylene is not. Therefore, if only polyethylene and polystyrene homopolymers were present in the pellets, the ratios of soluble to insoluble material should be identical with the yield data given in Table I. The solubility ratios at all dose levels are larger than the yield ratios and the differences between these two increase with increasing dose level. These differences may be interpreted as evidence for the presence of a considerable amount of polyethylene-g-styrene if one makes the plausible assumption that polyethylene molecules with sizeable styrene grafts attached to them are soluble in tetralin at 25°C. Ideally, then, the soluble material would consist of polystyrene homopolymer plus polyethylene-g-styrene, while the insoluble material would consist of ungrafted polyethylene. However, several factors may be operative to make this test less than quantitative. First, there are degrees of grafting to be considered which would partition material between the two phases in an unknown way. Second, there may be some grafted chains which are also crosslinked to a degree to render them insoluble under these conditions. Finally, there is the possibility of the graft solubilizing some polyethylene homopolymer by a surfactant effect. However, the evidence for considerable grafting is indisputable.

To gain further insight into the composition of the soluble and insoluble phases, DTA thermograms were made of each. For the 0.14- and 0.25-mrad grafts, the insoluble phase showed the crystalline melting peak of polyethylene as was to be expected, whereas the soluble fraction showed little or no polyethylene by this test. For the 0.50- and 1.0-mrad grafts, the soluble material did have sizeable polyethylene melting peaks as did the insoluble material.

In summary, these observations give strong evidence for sizeable quantities of polyethylene-g-styrene in the materials prepared here.

Crosslinking

Crosslinking of polyethylene by means of γ -irradiation has been studied extensively⁴ and is used commercially to produce heat-shrinkable film, tubing, and insulation for certain types of power cables.¹⁸ Interestingly, the literature on grafting of styrene to polyethylene makes essentially no mention of this additional reaction. Generally, crosslinking studies employ higher dose levels than do grafting experiments; however, crosslinking is a definite side reaction of the grafting process. Crosslinking is an undesirable reaction for the present purposes since it affects the melt processibility of the resulting product. In this work, solubility or swelling

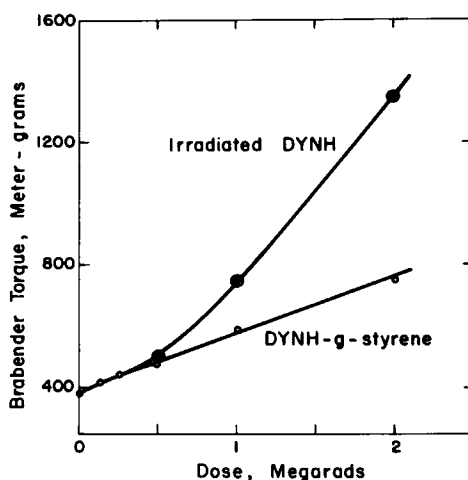


Fig. 2. Brabender torque required to melt mix irradiated materials at 170°C and 20 rpm. Upper curve for polyethylene irradiated with no styrene present. Lower curve is for grafts.

studies plus melt rheology observations were used to gain further insight into the extent of crosslinking.

In the solubility tests, the grafted pellets were immersed in hot tetralin (125°) for several hours. Pellets exposed to doses of 1 mrad or less dissolved completely, as shown in Table III, and it is therefore concluded that crosslinking was insufficient to form a gel network. At higher doses, the pellets became very highly swollen but would not dissolve completely. These swollen pellets were freed of tetralin in a vacuum oven, and the amount of polymer extracted by the tetralin was determined. The results are shown in Table III. These data confirm the presence of considerable crosslinking at the higher doses. Ideally, the extracted material, or sol fraction, may be composed of unattached polyethylene homopolymer and graft plus all of any polystyrene homopolymer that may be present. These figures, therefore, place an upper limit on the amount of the latter that may be present. From the rapidly declining sol fraction with dose, it may be concluded that the fraction of polystyrene homopolymer at lower dose levels must be fairly small since it is rather unlikely that further radiation would immobilize this material by crosslinking.

Melt rheological data for the grafts were obtained by observing the steady-state torque reading on the Brabender while mixing the graft at 20 rpm and 170°C. This reading is related to viscosity which would be dramatically increased by crosslinking. Formation of polystyrene as a graft or as homopolymer may affect this reading as well. Figure 2 shows such torque data for grafts prepared with up to a 2-mrad dose, along with similar data for polyethylene which had been exposed to γ -rays in the absence of styrene. The 4-mrad graft is not shown here since it was so highly crosslinked that the pellets retained their integrity in the Brabender and

did not flow. It was also impossible to form a molded sheet from this material.

The presence of styrene apparently reduces the amount of crosslinking as judged by the comparison in Figure 2. The torque steadily increases with dose when styrene is present, whereas the curve for polyethylene alone shows a dramatic increase above 0.5 mrad. A free-radical site on a polyethylene chain may add styrene or crosslink by reaction with another chain radical. Those that add styrene may or may not ultimately form crosslinks depending on the mechanism by which the growth of the styrene chain is ended. While the number of possibilities is great and cannot be adequately elucidated from the current data, it is clear that the presence of styrene seems to bias the reactions so that fewer crosslinks are formed.

Molecular Weight of Graft Chains

The yield data in Figure 1 can be used to obtain a rough estimate of the length of the polystyrene grafts, provided some assumptions can be made. This calculation estimates the number of free radicals produced in the polyethylene by the radiation and then assumes that all of the styrene is equally reacted on these sites. Owing to the linearity of the yield with dose up to 0.5 mrad shown in Figure 1, this value is a constant independent of dose in this region. Using a G_R value of 7 free radicals per 100 electron volts of absorbed radiation,⁴ the number of radicals produced per 100 carbon atoms is 0.005 at 0.5 mrad. From the yield data, this gives 2700 styrene units per site for a molecular weight of 280,000. This calculation assumes that all radicals formed can react; however, owing to crystallinity and diffusional limitations to the pellet interior, this will not be so. These factors would reduce the number of available sites and raise the molecular weight estimate. Chain transfer, on the other hand, would lower this estimate. However, chain transfer to the polyethylene backbone, for example, appears to be of minor consequence since the chain transfer constant for a styrene radical and cyclohexane (a polyethylene analog) is about 3×10^{-6} at 60°C. If chain transfer is of any major consequence, it must occur with unidentified species or the monomer.

It appears, then, that the graft chains are rather long and have molecular weights of the order of 10^5 or higher. This is in agreement with some literature estimates. Yasukawa et al.¹⁴ measured the free-radical decay by ESR while grafting by the trapped free-radical method and estimated the branch molecular weight to be 360,000. Chen and Friedlander¹⁰ found that the molecular weight of polystyrene homopolymer formed as a by-product of grafting had a molecular weight of 178,000. Polystyrene produced under the same conditions but not in contact with the polyethylene had a molecular weight of 47,900. They concluded this increase in molecular weight was owing to a diffusional limitation of the termination reaction inside the swollen polyethylene. If the nature of the chain transfer reaction were changed because of reaction conditions in grafting, the polystyrene homopolymer should have had a lower molecular weight.

PROPERTIES OF THE GRAFT

The material referred to here as the graft is the composite of all species contained in the pellet. This material was subjected to a number of physical property determinations of interest for a variety of reasons. These results will be discussed here from the point of view of what additional insight they add to the nature of this composite. As described earlier, these tests were run on samples that had been melt processed after grafting.

Differential Thermal Analysis

The most dominant feature of thermograms of these grafts or corresponding blends of polyethylene and polystyrene is the melting endotherm for polyethylene. The glass transition of polystyrene at 100°C occurs in the same temperature range as the melting peak of the low-density polyethylene. There was no evidence of the polystyrene glass transition in any of the thermograms made with the grafts or blends. This is not surprising, since the energy associated with the heat of fusion is much greater than the heat effect due to the glass transition and, therefore, the glass transition is completely masked.

The area of the melting endotherm is potentially of value for grafts and blends since it might provide a useful analytical tool for the polyethylene content. To evaluate the quantitative accuracy of this technique, the areas were determined for a number of blends, A_B , and grafts, A_G , of known composition. These were compared with the area for pure low-density polyethylene, A_{PE} . All areas were expressed in terms of milligrams of total sample in each case for fixed instrument settings. Two thermal traces were made for each sample and are identified as first and second heatings. First heats may be biased by previous thermal histories, but second heats all have a common history. The ratios A_B/A_{PE} and A_G/A_{PE} were formed by always comparing first heat data with the first heat for PE and second heat data with PE second heat. Ideally, these ratios should be equal to the polyethylene fraction in the graft or blend. Figure 3 shows this is more nearly so for grafts than for blends but is of dubious quantitative value in either case.

These observations are interesting, however, since they strongly suggest that the presence of the polystyrene inhibits the crystallization of the polyethylene, since most points fall below the dashed diagonal. This is considerably more dramatic for the blends than for the grafts. This is puzzling, since it would be easier to see how a chain attached to a polyethylene molecule could retard its crystallization more than could the presence of a polystyrene domain which in the blend would be unattached to it. At least two differences between blends and grafts may contribute to this behavior. In blends and grafts, the polystyrene aggregates into domains,² and, as will be shown later, the domains in blends are much larger. It may be that these large domains hinder spherulite growth more than the smaller ones in grafts. Further, it may be argued that during grafting

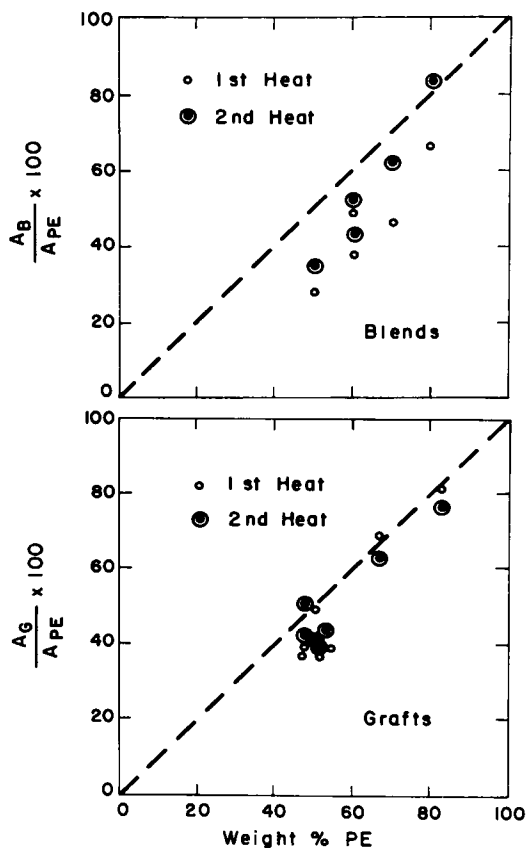


Fig. 3. Crystallinity comparisons for blends and grafts.

in the solid state, domains are only formed in the amorphous regions of the polyethylene. This may produce an ordering that can be remembered in subsequent melting and recrystallization so that full crystallinity is restored.

Dynamic Mechanical Properties

Figure 4 shows the storage modulus E' and loss modulus E'' for the graft copolymers made at 0.5, 1.0, and 2.0 mrad. Data for the low-density polyethylene, DYNH, is shown by a dashed line. The storage modulus for the graft copolymers does not drop as rapidly with temperature as it does for the DYNH, but the storage modulus at -150°C is lower for the grafts. This point will be discussed in greater detail later. The loss modulus of the graft copolymers indicates transitions in the region of -120°C and -10° to -20°C . DYNH also has these same transitions, but they are located at slightly different temperatures with different values of the modulus. The loss modulus has a relatively constant value over

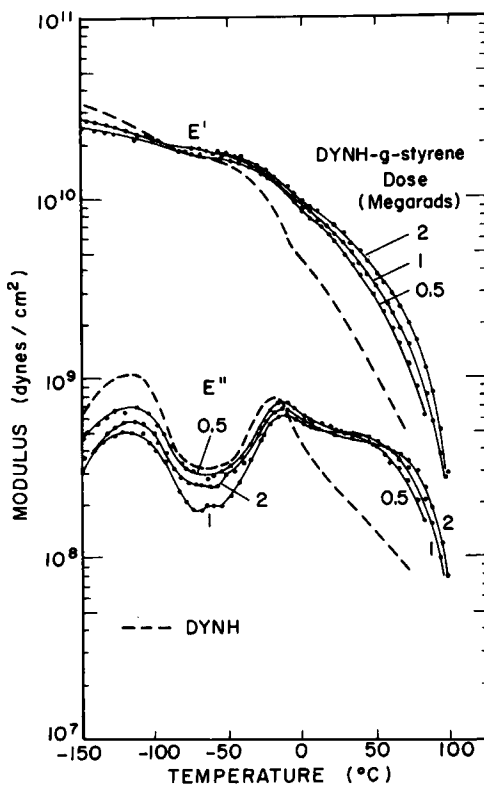


Fig. 4. Dynamic mechanical behavior of grafts. Dotted line is for DYNH.

the temperature range of 10° to 50°C for all the graft copolymers, and the temperature range of this "plateau" increases with increasing dose. DYNH has no indication of such a plateau. The value of the loss modulus between the two peaks is lower for the grafts than for the pure polyethylene.

Figure 5 contains data for the graft made with 0.25 megarad which has 33.3% polystyrene and data for a melt blend of 70% DYNH and 30% polystyrene. Data for DYNH is indicated by the dashed line. The storage modulus of the blend is lower than that of the graft at all temperatures but crosses the curve for pure DYNH, with the blend having the lower modulus at low temperature. The lower modulus of the blend is consistent with the lower polyethylene crystallinity observed for blends than grafts in Figure 3. The graft copolymer has the same general response as seen for the other grafts in Figure 4. The loss modulus for the blend and graft are similar in that the transitions at -120° and -20°C are indicated. The plateau region is clearly seen with the graft but is less prominent for the blend. The plateau is evidently caused by the stiffening effect of the polystyrene which is still rigid in this temperature region. It is interesting that this effect is greater for grafts than blends. This may be due to the direct coupling between the polystyrene and polyethyl-

ene chains which allows better stress transfer between phases. However, purely morphologic differences cannot be ruled out. The most significant difference in the $\tan \delta$ data is that the graft has consistently lower values over the entire temperature range. The minimum region for E'' between the -120° and -20°C transitions is lower for the graft than either DYNH or the blend.

Data for DYNH irradiated with 0.5 mrad are compared to DYNH in Figure 6. There was no styrene in this sample, so the data show the effect of irradiation alone on the polyethylene. There are very few points of

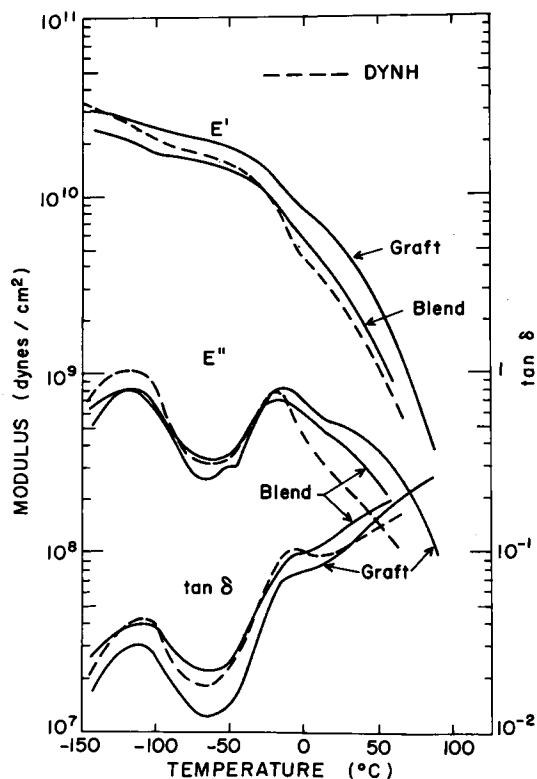


Fig. 5. Dynamic mechanical behavior of a 0.25-mrad graft and a melt blend containing a similar amount of polystyrene.

difference. Interestingly, irradiation reduces the storage modulus at temperatures below -120°C .

Figure 7 shows the variation of the storage modulus with polystyrene content for the grafts. The data at both -150°C and 25°C are nearly linear, suggesting that the properties of the graft are simple additive functions of the component properties. It is interesting that below all glass transition temperatures, polyethylene is more rigid than polystyrene. As a result, E' at -150°C decreases with polystyrene content.

The graft copolymers exhibit the β - and γ -transitions found in pure low-density polyethylenes. These transitions have been extensively studied¹⁹⁻²⁷ with tentative molecular motions assigned to each. It would be interesting to know whether grafting produces any changes in these well-known transitions. Each of these transitions are examined for such effects in the following discussion.

The loss modulus (or $\tan \delta$) peak in the region of -120°C has been labeled the γ -transition. Such a peak occurs at about the same temperature for all graft copolymers and the pure DYNH. The magnitude of the loss

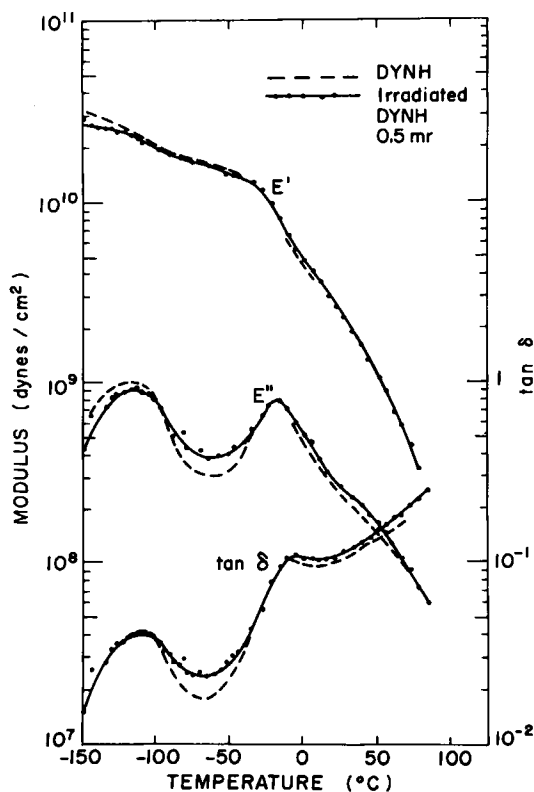


Fig. 6. Effect of radiation on DYNH dynamic mechanical properties.

modulus and $\tan \delta$ peaks do decrease with dose level and thus the polystyrene content. This decrease may be due simply to the decreased polyethylene content (there are no transitions for polystyrene in this temperature range^{22,23}) since the values of E'' at the peak are very nearly the same for the blend and the graft copolymer (Fig. 5). The γ -transition is thought to be due to the motion of a limited number of $-\text{CH}_2-$ groups in the polyethylene main chain.^{20,21,23,26,27} From this interpretation of this transition, it is reasonable that no change in it should be observed on grafting.

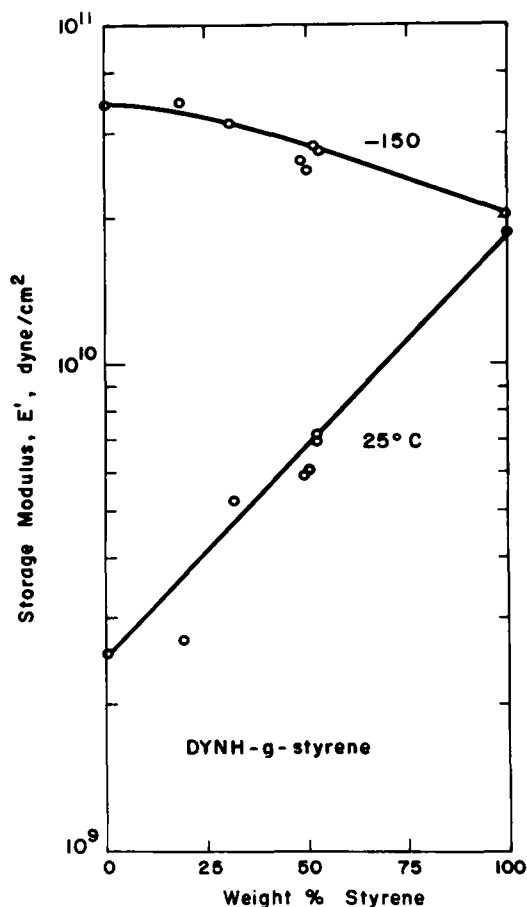


Fig. 7. Storage modulus of grafts as a function of polystyrene content.

The temperature, shape and magnitude of the β transition for the graft copolymers are somewhat different from those for DYNH as shown in Figure 4.

The slight shift in the peak temperature was selected for further analysis and is plotted versus radiation dose and polystyrene content in Figure 8. Increasing the radiation dose increases this transition temperature in an almost linear manner up to 0.5 megarad and then has no further effect, which is reminiscent of the yield data in Figure 1. The peak temperature is also shown plotted versus styrene content in the upper half of Figure 8. The more continuous nature of this curve suggests that dose per se may not be the real variable.

The preponderance of the literature claims that the β -transition is due to the movement of the polyethylene chain in the vicinity of branch points.¹⁹⁻²⁶ Several authors^{21,22} have stated that the nature of the moiety forming the branch point is unimportant. An analog of low-density

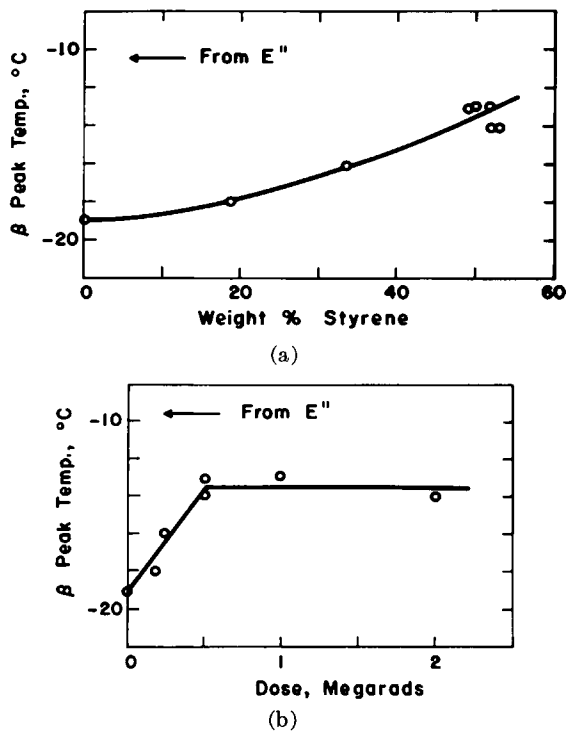


Fig. 8. Effect of grafting on the location of the polyethylene β -peak.

polyethylene on this basis is chlorinated polyethylene were chlorine atoms form the branch points. Increasing the branch points (chlorine or branch concentration) up to about 4 branch points per 100 carbon atoms decreases the β -transition temperature.^{22,29} Further increases in chlorine concentration cause an increase in this transition temperature.²² There are no data available for further increases in branch point concentration for low-density polyethylene.

A possible explanation for the small increase in the β -transition temperature shown in Figure 8 may be the additional branch points introduced into the polyethylene chain by styrene grafting. Based on literature sources,^{30,31} DYNH should have 2 to 3 butyl branches per 100 carbon atoms. An analysis of data given by Schmieder and Wolf²² using the assumption that the nature of the branch is immaterial shows that the number branches per 100 carbon atoms that would be required to produce the *increase* shown in Figure 8 is several orders of magnitude greater than the number of grafting sites possible according to our calculation discussed earlier. Therefore, increased branch points by grafting cannot produce this shift in the β -transition unless these long grafts restrict chain motion by orders of magnitude more than butyl or chlorine branches do.

An alternate explanation for the results shown in Figure 8 is that the plateau to the right of the β -peak observed in the graft and attributed to

TABLE IV
Activation Energies for β - and γ -Transitions

	Activation energy, kcal/mole	
	γ	β
0.5 mrad graft (this study)	11	35
Polyethylene		
Oakes and Robinson ³²	6	30
Starkweather ³³	12	34
Woodward and Sauer ²⁴	15	20-100

the polystyrene causes an apparent shift in the β -peak location to the right. In this case, Figure 8 would have no molecular meaning. This explanation lacks some strength from the fact that blends do not show the β -peak shift; however, blends do not show this plateau as prominently as grafts do. The exact meaning of Figure 8 is still uncertain.

Dynamic mechanical properties for the 0.50-mrad graft were determined at 11 Hz in addition to the 110 Hz data shown in Figure 4. The effect of frequency on the E'' peak temperatures in the γ - and β -regions were used to compute the activation energies for these transitions in the blend which are shown in Table IV. The current values are in good accord with similar data for pure polyethylene and thus suggest that the nature of the molecular motions in the polyethylene chain are not altered by grafting.

Graft Versus Blend Morphology

Photomicrographs of microtomed sections of melt blend and graft copolymer samples are shown in Figures 9 and 10. Resolution is not very good in either case, but dramatic differences can be discerned nevertheless. In the melt blends of Figure 9, there are rather large domains suspended in a continuous phase. The discrete domains are polystyrene, and they generally increase in size as the proportion of polystyrene is increased. Some of the smaller appearing domains in Figure 9 may be actually the tops of larger domains which were cut off in the sectioning process. The scale of heterogeneity for the grafts shown in Figure 10 is at least one to two orders of magnitude *smaller* than that shown in Figure 9 for corresponding blends. Identification of discrete and homogeneous phases is quite uncertain. It is quite clear that the polystyrene is distributed in a more homogeneous fashion in the graft than in the blend.

Stress-Strain Behavior

Average values for the elongation at break, the yield tensile strength, and the initial modulus for the graft materials are shown in Table V. In general, the elongation decreases while the strength and modulus increase with increased polystyrene level, although there are individual exceptions.

These trends are expected on the basis of the characteristics of pure polystyrene and low-density polyethylene.

Figure 11 displays the entire stress-strain diagrams for a 0.50-mrad graft and a 50/50 melt blend of DYNH and Styron 685 for the purpose of

TABLE V
Stress-Strain Behavior of Grafts

Irradiation dose, mrad	Polystyrene, %	Mechanical properties		
		Elong., %	Yield, psi	Modulus, $\text{psi} \times 10^{-4}$
4	55.0	n.t.*	n.t.	n.t.
2	52.5	13.2	1822	4.19
1	50.0	5.4	1521	6.70
0.5	47.5	6.1	1533	5.35
0.5	49.2	9.0	1600	6.86
0.5	52.1	8.0	1631	5.55
0.28	38.5	14.5	1238	4.80
0.25	33.3	17.0	1482	3.59
0.14	18.6	124	1382	2.03
0.14	16.5	349	1325	2.84

* n.t. = not tested.

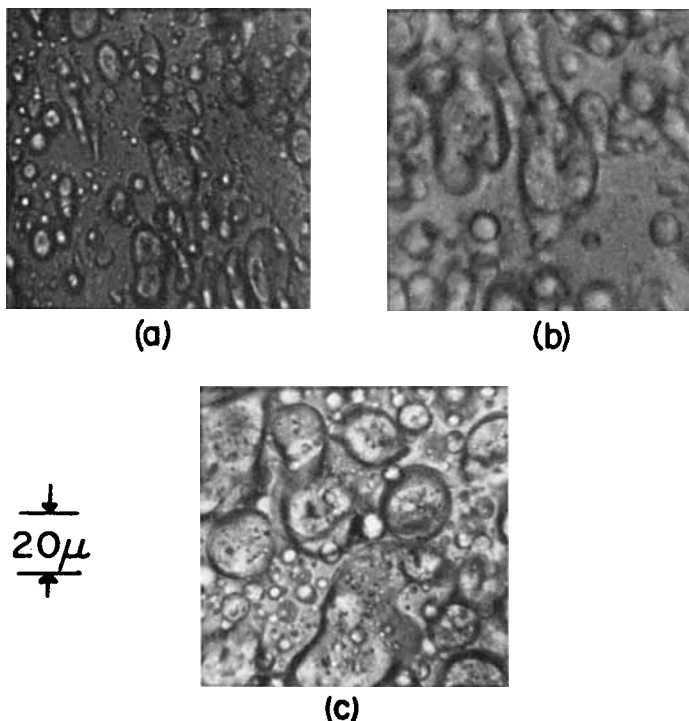


Fig. 9. Photomicrographs of microtomed sections of polyethylene-polystyrene melt blends: (a) 30%; (b) 40%; (c) 50% polystyrene.

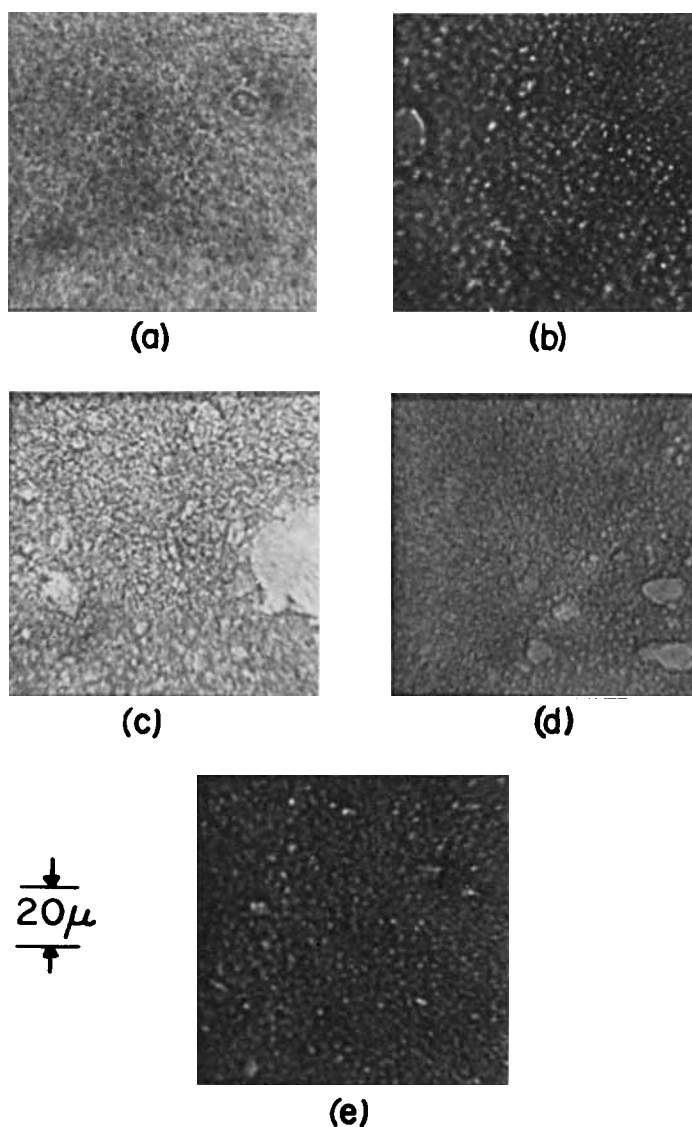


Fig. 10. Photomicrographs of microtomed sections of graft copolymers: (a) 0.14 mrad; (b) 0.25 mrad; (c) 0.50 mrad; (d) 1.0 mrad; (e) 2.0 mrad.

comparing a graft to a blend with comparable compositions. The crosses illustrate the variation in the failure location for replicate specimens. The graft is somewhat stronger and has a significantly higher elongation at break than the blend. This superior mechanical behavior is believed to be owing to the better adhesion between the phases in the graft which improves the ability to transfer stress from one phase to another. The effect of the much smaller phase sizes in the graft compared to the blend undoubtedly contributes in some way to this mechanical behavior.

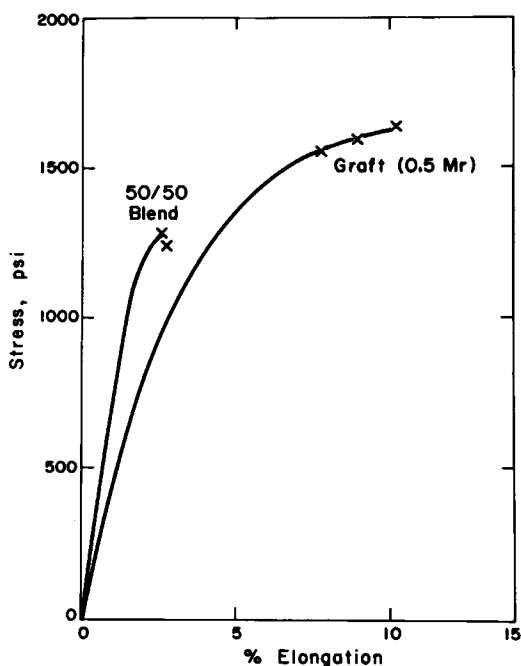


Fig. 11. Stress-strain diagrams for a blend and a graft.

It is interesting that in Figure 11 the blend has a higher modulus than the graft, since in Figure 5 the graft has the higher modulus. These comparisons involve two factors that may contribute to this reversal. The materials in Figure 5 contain about 30% polystyrene and were tested at very low strains oscillating at a high frequency (110 Hz). The materials in Figure 11 contain about 50% polystyrene and were tested at rather large strains at a low rate of constant straining.

CONCLUSIONS

The results of this study show that it is possible to graft styrene to low-density polyethylene in pellet form with a relatively high content of grafted chains using the direct method with ^{60}Co radiation. The yield is limited to about 1 g reacted styrene per gram of polyethylene because of polymerization of the monomer outside the pellet. Crosslinking is a side reaction that severely limits the melt processibility of the pellets at radiation doses beyond about 1 megarad. The styrene grafts appear to have a molecular weight of the order of 10^5 .

DTA results suggest that the presence of polystyrene in grafts and blends seems to retard the crystallization of the polyethylene, but more so for blends than grafts. Dynamic mechanical testing revealed that the polyethylene solid-state transitions were unaltered by grafting, with the possible exception a slight shift of the β -relaxation to a higher temperature.

This change may or may not reflect molecular processes. Microscopy has shown that the scale of heterogeneity in the graft is one to two orders of magnitude smaller than the domains observed in melt blends of equal compositions. The graft is stronger and considerably more ductile than the corresponding melt blend.

This research was sponsored by a grant from the Environmental Protection Agency. Various materials were supplied by the Dow Chemical Company, Union Carbide Corporation, and the Monsanto Company. The authors express their appreciation to each of these organizations and the individuals involved for this invaluable assistance.

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Received January 22, 1973