

Cocrystallization and Polymer Miscibility

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Synopsis

Low-density polyethylene was blended in various proportions with an ethylene/propylene/1,4-hexadiene copolymer having an ethylene/propylene mole ratio of 4.5 and a low level of crystallinity. The DSC melting peak of polyethylene was decreased, the unit cell was expanded, and the spherulitic development was disturbed. The temperature of a dynamic mechanical loss peak varied smoothly with composition between the T_g of the copolymer and the β -relaxation of the polyethylene, but the glass temperature of the copolymer measured by DSC was unchanged. These effects were all diminished when the ethylene/propylene ratio of the copolymer was reduced. Blends with high-density polyethylene showed little depression of the melting point or change in crystal structure and much less effect on the dynamic mechanical behavior. However, the behavior of copolymers of ethylene with low levels of vinyl acetate or methyl methacrylate was similar to that of low-density polyethylene. Therefore, the ability to cocrystallize is an important factor for limiting the tendency of nonpolar polymers to separate, thereby facilitating the preparation of blends with desirable combinations of properties.

INTRODUCTION

Most pairs of polymers are not miscible on a molecular level, largely because the entropy of mixing is very small. Exceptions generally involve either a very close match in cohesive energy density or specific polar interactions which produce a favorable enthalpy of mixing.¹⁻⁵ It has been considered that the best evidence for molecularly intimate mixing is a dynamic mechanical relaxation at a temperature intermediate between those of the components.¹⁻⁵ Immiscible pairs will show the relaxations of both components at their original temperatures. When one component is crystallizable, the depression of the melting point provides additional evidence of miscibility. If the second component is not crystallizable, an interaction parameter may be calculated from the depression of the melting point.³

We have found that the ability to cocrystallize can provide an additional factor for promoting polymer miscibility. This is particularly useful in hydrocarbon systems where other approaches may not be available.

BLENDS OF POLYETHYLENE AND ETHYLENE/PROPYLENE COPOLYMERS

Crystalline Interactions

Copolymers of ethylene, propylene, and a diene monomer, commonly known as EPDM, play an important role as hydrocarbon elastomers. As the ethylene content is increased, they vary from tacky, amorphous elastomers to semiplastics

having low levels of crystallinity. The relationship between copolymer composition and crystallinity has been reviewed by Baldwin and Ver Strate.⁶ The copolymer designated EPDM-1 contained 72% ethylene, 24% propylene, and 4% 1,4-hexadiene by weight, corresponding to an ethylene/propylene mole ratio of 4.5. Differential scanning calorimetry (DSC) revealed a broad melting endotherm near 50°C which sometimes exhibited multiple peaks. The heat of fusion of 8 cal/g corresponds to about 11% polyethylene-type crystallinity.

Blends were made in the melt in various proportions from EPDM-1 and a low-density, branched polyethylene (LDPE) having a density of 0.919 g/cc after a standard cooling cycle. Blending was done on a roll mill at 180°C for 10 min after the addition of all ingredients. Melting peaks observed using a du Pont DSC are summarized in Table I. The heating rate was 10°C/min following cooling from the melt at less than 5°C/min.

DSC scans for EPDM-1, LDPE, and a 50/50 blend are shown in Figure 1. The baselines used for the calculation of the heats of fusion are shown as dashed lines. These scans are compatible with those published by Lindsay and co-workers⁷ for similar blends. The peak temperature for the melting of LDPE is reduced gradually from 115.5 to 108.5°C as the concentration of EPDM-1 is increased from 0 to 80% with little change in the temperature for the upper end of the melting range. These changes in the melting peak are taken to be evidence of partial cocrystallization. The temperature of the EPDM melting peak near 50°C remained within the range for the pure polymer, indicating that there are two populations of crystals as revealed by DSC although only one was seen by x-ray diffraction. However, this peak was absent in blends containing 40–50% EPDM-1 which had been melted and quenched in liquid nitrogen while remaining at higher levels of EPDM-1. This effect, which is shown in Figure 2, suggests that separate crystals of EPDM-1 are formed very slowly in these compositions. The total heat of fusion varied linearly with composition. Because of the large overlap of the two broad melting peaks, it was not possible to calculate reliable separate heats of fusion.

Blends were also made from LDPE and EPDM-2 or EPDM-3 at the 50% level.

TABLE I
DSC Data for Blends of Polyethylene and EDPM

| EPDM | T_g , °C | T_m , °C | Polyethylene | T_m , °C, peak/end | Total ΔH_f , cal/g |
|-------------|------------|------------|--------------|-------------------------|-------------------------------|
| 100% EPDM-1 | -45 | 47-52 | — | — | 7.8 |
| 80% EPDM-1 | -44 | 45 | 20% LDPE | 108.5/128 | 13.3 |
| 70% EPDM-1 | -42 | 52 | 30% LDPE | 110/128 | 15.6 |
| 60% EPDM-1 | -44 | 52 | 40% LDPE | 111/128 | 17.7 |
| 50% EPDM-1 | -44 | 50 | 50% LDPE | 111/126 | 22.2 |
| 40% EPDM-1 | — | 50 | 60% LDPE | 113/129 | 23.9 |
| — | — | — | 100% LDPE | 115.5/126 | 34.6 |
| 100% EPDM-2 | -54 | — | — | — | — |
| 50% EPDM-2 | -53 | — | 50% LDPE | 113 | 17.2 |
| 100% EPDM-3 | -56 | — | — | — | — |
| 50% EPDM-3 | -56 | — | 50% LDPE | 114 | 16.4 |
| 50% EPDM-1 | — | 54 | 50% HDPE | 138 | 3.3 at 54° 32.2 at 138° |
| — | — | — | 100% HDPE | 137.5 | 63.4 |

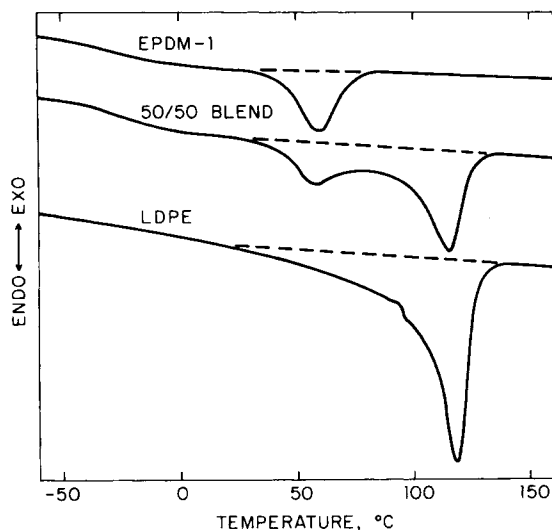


Fig. 1. DSC scans.

These copolymers have ethylene/propylene mole ratios of 2.9 and 1.8, respectively. The depression of the melting point of LDPE was only about half that observed for the corresponding blend with EPDM-1, and the latent heat for the EPDM peak at 45–46°C was less than 0.5 cal/g. Clearly, these materials are less able to cocrystallize with LDPE because they have fewer ethylene sequences of adequate length.

X-ray diffractometer scans were obtained for each of the blends by reflection, and the orthorhombic unit cell parameters were computed using a least-squares refinement. In most cases, 10 to 15 reflections were used, but the number decreased to seven for the blend containing 80% EPDM-1. For pure EPDM-1, only

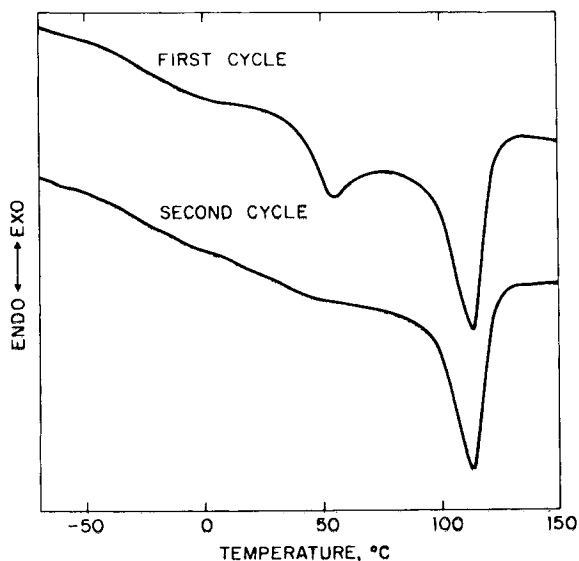


Fig. 2. DSC scans for a 50/50 blend of LDPE and EPDM-1

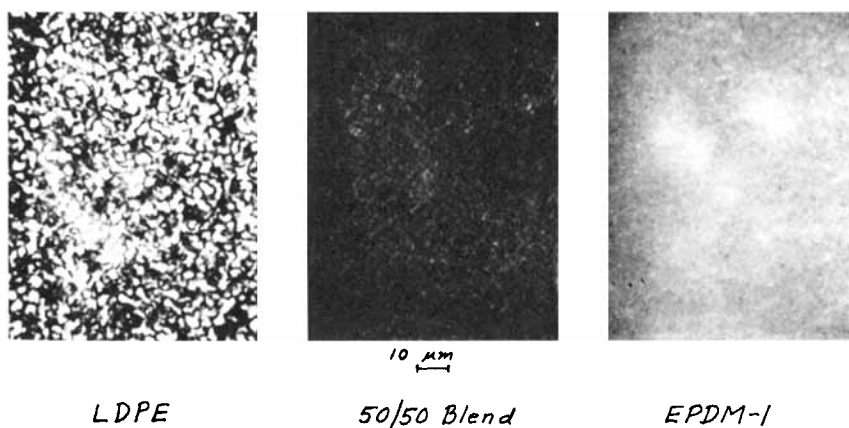


Fig. 3. Effect of blending with EPDM-1 on the spherulitic structure of LDPE.

the (110) and (020) reflections were resolved, making it impossible to calculate the c parameter. It is seen from the data in Table II that when LDPE is blended with EPDM-1, the unit cell is expanded substantially in the a direction while the b and c parameters are almost unchanged. This is in line with the effect of comonomers on the unit cell of polyethylene.⁸ For a given level of methyl branches in the total composition, the unit cell parameters of these blends are quite close to those reported for methyl-branched polyethylene.⁹⁻¹¹

In blends of LDPE with EPDM-2 or EPDM-3, the expansion of the a parameter is much less than in the comparable blend with EPDM-1, in parallel with the melting point data.

Optical microscopy reveals that EPDM-1 inhibits the spherulitic development of LDPE, especially after rapid cooling from the melt. This is shown in Figure 3. These micrographs were taken with crossed polarizers at a magnification of 900 \times . This effect is much less evident for blends of EPDM-2 or EPDM-3 with LDPE.

TABLE II
Unit Cell Parameters for Blends of Polyethylene and EPDM

| Composition | Parameters, Å | | |
|-------------|-------------------|-------------------|-------------------|
| | a | b | c |
| LDPE/EPDM-1 | | | |
| 100/0 | 7.515 \pm 0.007 | 4.989 \pm 0.004 | 2.559 \pm 0.002 |
| 60/40 | 7.640 \pm 0.041 | 5.015 \pm 0.014 | 2.572 \pm 0.009 |
| 50/50 | 7.581 \pm 0.025 | 4.991 \pm 0.009 | 2.555 \pm 0.005 |
| 30/70 | 7.635 \pm 0.013 | 4.992 \pm 0.006 | 2.570 \pm 0.004 |
| 20/80 | 7.873 \pm 0.098 | 4.987 \pm 0.018 | 2.548 \pm 0.010 |
| 0/100 | 8.35 | 4.98 | |
| LDPE/EPDM-2 | | | |
| 50/50 | 7.545 \pm 0.022 | 4.985 \pm 0.009 | 2.552 \pm 0.006 |
| LDPE/EPDM-3 | | | |
| 50/50 | 7.523 \pm 0.016 | 4.977 \pm 0.007 | 2.566 \pm 0.005 |
| HDPE/EPDM-1 | | | |
| 100/0 | 7.455 \pm 0.005 | 4.977 \pm 0.004 | 2.563 \pm 0.002 |
| 50/50 | 7.460 \pm 0.006 | 4.975 \pm 0.004 | 2.560 \pm 0.002 |

A 0.2- μm section of a 50/50 blend of LDPE and EPDM-1 was treated with OsO_4 to stain the EPDM which contains double bonds. A transmission electron micrograph at 92,000 \times showed that the components are blended very intimately, at least down to a scale of several hundred angstroms.

All of these observations pointed to at least partial cocrystallization of LDPE and EPDM having a relatively high level of ethylene. The interactions are diminished as the ethylene content of the EPDM is reduced.

With high-density polyethylene (HDPE), the situation is markedly different. The melting point and the unit cell parameters are unchanged in a 50/50 blend with EPDM-1 (Tables I and II). There is very little change in the spherulitic structure.

These combinations show that the interaction of polyethylene and EPDM is greatest when the polyethylene is branched (LDPE) and the ethylene content of the EPDM is relatively high. In these compositions, the melting and crystallization ranges are quite broad and overlap even though two peaks are still resolved in the DSC curves in most cases.

Amorphous Interactions

The logarithmic decrement for the blends of LDPE and EPDM-1 measured with a Plastech torsion pendulum is plotted against temperature in Figure 4. The frequency varied inversely with temperature between 3 and 37 Hz. The loss peak associated with the glass temperature in EPDM-1 occurs at -52°C . As the concentration of LDPE is increased, the peak shifts upward in temperature toward the β -relaxation of the polyethylene. This kind of effect is frequently taken to indicate that two polymers are miscible on a molecular scale. It also gives some support to the view that the glass temperature in polyethylene is associated with the β -relaxation.^{9,12,13} It is seen in Figure 5 that for each variety of EPDM the temperature of the β -dynamic mechanical relaxation is about 10°C higher in a 50/50 blend with LDPE than in the pure copolymer.

The T_g was taken to be the point of departure from the low-temperature baseline in a DSC scan. It should be noted in Table I, however, that the glass

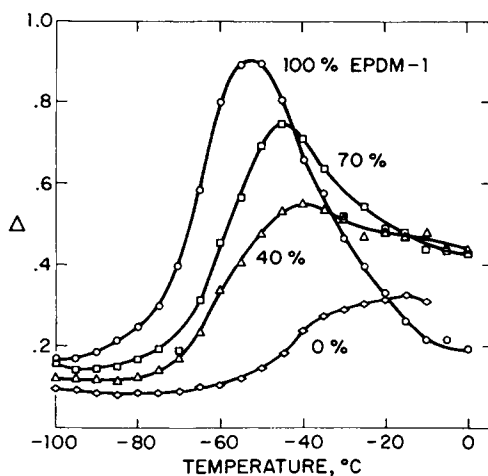


Fig. 4. Logarithmic decrement for blends of low-density polyethylene and EPDM-1.

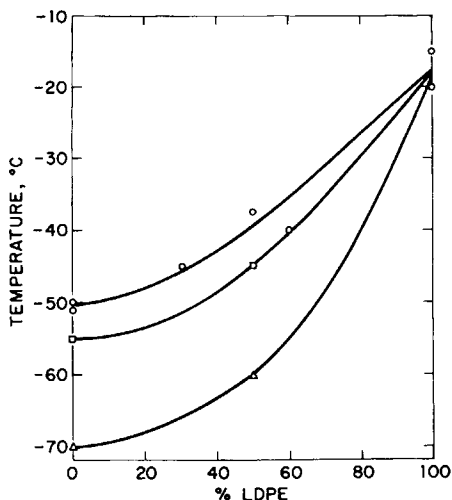


Fig. 5. Dependence of the temperature of the beta dynamic mechanical loss peak on composition in blends of EPDM and LDPE: (O) EPDM-1; (□) EPDM-2; (Δ) EPDM-3.

temperatures of EPDM polymers measured by DSC, using a heating rate of 20°C/min, unlike the dynamic mechanical loss peak, did not shift to significantly higher temperatures in blends with LDPE. This raises a serious question about the degree of mixing in the amorphous regions. A possible explanation is that the DSC is sensitive to nearest-neighbor interactions while the dynamic mechanical properties reflect the composition on a somewhat larger scale. Limited short-range mixing would also be consistent with the two-peak melting curve from the DSC.

The amorphous interactions like the crystalline ones are much smaller when HDPE is used in blends with EPDM. In a 50/50 blend of high-density polyethylene (HDPE) with EPDM-1, the dynamic mechanical loss peak only increased to -45°C, in contrast to -35°C in the comparable blend with LDPE. When a copolymer similar to EPDM-2 was blended with HDPE, the temperature of its loss peak was unchanged.

BLENDS OF EPDM WITH COPOLYMERS OF ETHYLENE AND POLAR MONOMERS

Ethylene/propylene copolymers and low-density polyethylene have similar cohesive energy densities in the amorphous phase. It is therefore not surprising that there should be evidence for molecularly intimate mixing. However, the incorporation of polar monomers such as vinyl acetate or methyl methacrylate in copolymers with ethylene produces significant increases in the cohesive energy density.

Blends were prepared from equal weights of EPDM-1 and various copolymers of ethylene with vinyl acetate or methyl methacrylate. The thermal properties are summarized in Table III. For the copolymers containing more than 90% ethylene by weight, the DSC melting peaks were lowered by 3–4°C in blends with EPDM-1. This did not occur when the level of the polar comonomer was 15–20% by weight. Apparently, there is a significant amount of cocrystallization when

TABLE III
Blends of EPDM-1 and Copolymers of Ethylene with Polar Monomers

| Material | Ethylene/ comonomer mole ratio | Temp. of β - relaxation, $^{\circ}\text{C}$ | T_g , $^{\circ}\text{C}$, by DSC | DSC melting peaks, $^{\circ}\text{C}$ | Unit cell parameter a , \AA |
|----------------------------|--------------------------------------|--|--|---|--|
| EPDM-1 | | -52 | -45 | 53 | 8.35 |
| E/8.5% Vinyl acetate | 33 | -32 | -34 | 102 | 7.590 ± 0.027 |
| 50/50 Blend with EPDM-1 | | -35 | -43 | 52, 99 | 7.638 ± 0.040 |
| E/15% Vinyl acetate | 17 | | | 92 | |
| 50/50 Blend with EPDM-1 | | | | 53, 93 | |
| E/5.7% Methyl methacrylate | 59 | -25 | -27 | 108 | 7.538 ± 0.009 |
| 50/50 Blend with EPDM-1 | | -45 | -47 | 50, 104 | 7.585 ± 0.025 |
| E/20% Methyl methacrylate | 14 | | | 93 | |
| 50/50 Blend with EPDM-1 | | | | 53, 93 | |

the mole ratio of ethylene to polar comonomer is greater than 30, but not when it is less than 20. The a parameter of the unit cell was also found to increase in the blends of the former group. Interest is therefore focused on the lower levels of polar comonomers.

The logarithmic decrement in the region of the β -relaxation for a copolymer of ethylene with 8.5% vinyl acetate is shown in Figure 6. In the 50/50 blend with EPDM-1, the damping is very similar to that of the ethylene/vinyl acetate copolymer. The peak at -52°C in EPDM-1 is largely suppressed, and the damping at the lower temperatures is significantly less than would be expected from a proportionate combination of the properties of the components.

Similar data for a copolymer of ethylene with 5.7% methyl methacrylate by weight are presented in Figure 7. In this case, the temperature of the damping peak in the 50/50 blend is between the T_g of EPDM-1 and the β -relaxation of the ethylene/methyl methacrylate copolymer. Again, the damping on the

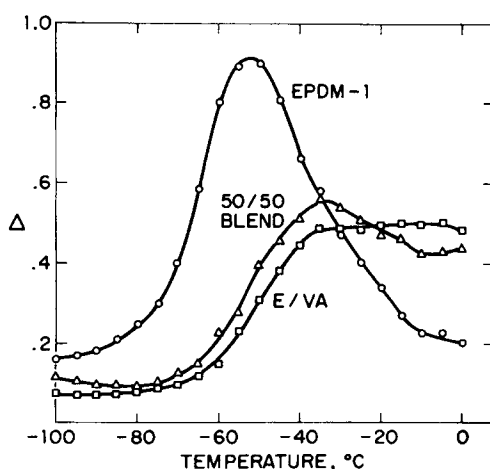


Fig. 6. Logarithmic decrement for EPDM-1 and a copolymer of ethylene with 8.5% vinyl acetate.

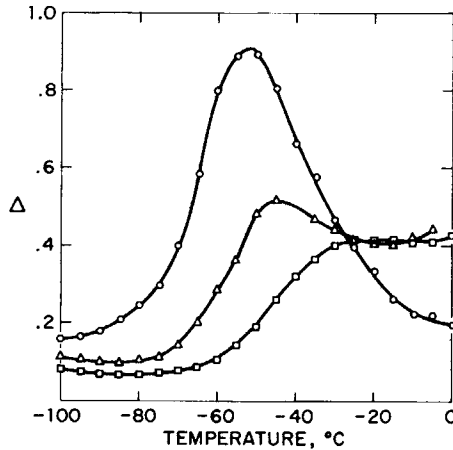


Fig. 7. Logarithmic decrement for EPDM-1 and a copolymer of ethylene with 5.7% methyl methacrylate: (○) EPDM-1; (□) E/MMA; (△) 50/50 blend.

low-temperature side of the peak in the blend is significantly less than would be expected from the properties of the components.

In these blends, as in those with LDPE, the glass temperature of EPDM-1 as measured by DSC was not changed significantly.

CONCLUSIONS

There is evidence for miscibility of EPDM with LDPE or ethylene copolymers in both the amorphous and crystalline regions. However, the extent of mixing depends on the size range to which each experimental technique is sensitive. DSC is sensitive to very short-range effects, and we see no shift in the T_g of EPDM, the retention of the separate melting endotherms of the components, and shifts of melting points of only a few degrees.

Dynamic mechanical measurements and optical microscopy are sensitive to composition on a larger scale. They show a single amorphous relaxation at a temperature intermediate between those for the components, a modification of spherulitic development, and an expansion of the unit cell in the a direction.

Lindsay and co-workers⁷ reported that similar blends have unexpectedly high tensile strengths and that the crystallization temperature is lower than in pure LDPE. They also recognized the probable role of cocrystallization.

Thanks are due to Robert P. Schatz for optical and electron microscopy.

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Received July 9, 1979

Revised September 17, 1979