

On the Compatibilization and Dynamic Vulcanization of Polyacetal/Ethylene Propylene Diene Terpolymer Blends

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SYNOPSIS

This study describes an attempt to improve the impact resistance of polyacetal (POM)/ethylene propylene diene terpolymer (EPDM) blends by means of compatibilization and dynamic vulcanization. A commercial copolymer, poly(acrylic acid)-grafted polypropylene (PGP), has been used as a compatibilizer to control the phase morphology of the blend system. Dicumyl peroxide is used to dynamically vulcanize the EPDM elastomer in the blend. At temperatures higher than 185°C, the compatibilizer decreases the viscosity of compatibilized and dynamically vulcanized (cdv) POM/EPDM blends. Impact strength of the cdv blend system increases considerably with a marginal decrease in tensile yield stress and heat deflection temperature as the PGP content increases. The significant increase in impact strength seems to be due to the role of PGP as a linking agent for the binary blends rather than as a third component. Though dynamic mechanical studies do not indicate any compatibility in cdv-POM/EPDM blends, scanning electron microscopy reveals the strong interpenetrating interphase in the compatibilized blend system. Dynamic vulcanization raises elastic recovery and tensile modulus of the blends. Hysteresis energies of the blends increase consistently with the addition of PGP. The crystalline structure of POM is not affected by compatibilization and vulcanization. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

From the standpoint of commercial applications and developments, polymer blending represents one of the fastest-growing segments of polymer technology. Few polymers form truly miscible blends characterized by a single T_g and homogeneity at a molecular level. The majority of blends are immiscible, i.e., possess a phase-separated morphology. Polymer compatibility may be enhanced by various methods^{1,2} and more commonly through the use of copolymer (e.g., block, graft) with segments capable of specific interactions and/or chemical reactions with the blend components. The copolymer is thought to concentrate at the interface and act as an emulsifier, reducing interfacial tension. In addition, it can augment compatibilization through interpenetration, entanglements, and cocrystalli-

zation. Furthermore, dynamic vulcanization^{3,4} may be carried out in the case of plastic/rubber blend systems to prevent the possible coalescence of rubber particles upon subsequent melt processing. The vulcanization also imparts high elastic recovery,⁵ tensile modulus, and low creeping tendency to the blends.

Polyacetal (polyoxymethylene, POM) is a semi-crystalline engineering thermoplastic of considerable commercial importance. It is somewhat brittle in nature, especially when defects are present. Hence, to improve its impact strength, it is blended with various elastomers. Several POM/elastomer blends have been studied and a few of them commercialized successfully, claiming enhanced impact strength and processability, viz., Delrin (DuPont), Celcon C-400 (Celanese), Duraloy (Hoechst-Celanese), Ultraform N2540X (BASF), and Hostaform (Hoechst AG). A detailed literature survey reveals that a good amount of work in this area has been patented in the middle and later 1980s. The survey on patents shows that several elastomers, viz., thermoplastic polyurethanes,⁶⁻⁸ modified and unmodified ethylene propylene diene terpolymers (EPDMs),^{9,10} buta-

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diene-methylmethacrylate copolymers,¹¹ and hydrogenated butadiene-styrene block copolymers,¹² have been used widely to toughen POM. The methods employed range from simple melt blending and reactive extrusion grafting to copolymerization in the reactors. Since these are patents, details are not known. However, the published literature in rubber toughening of POM is rather scarce. As regards POM/EPDM blends, almost no work has been reported in the open literature except the recent one by Chiang and Huang,¹³ who reported the physical, mechanical, dynamic mechanical, and morphological properties of POM/EPDM blends. They found that the blends exhibited poor mechanical properties owing to their incompatible nature.

In the present investigation, we made an attempt to improve the impact resistance of POM/EPDM blends through the use of a polymeric compatibilizer. A commercial graft copolymer, namely, poly(acrylic acid)-grafted polypropylene (PGP) was examined in this study as a potential compatibilizer between POM and EPDM. The concept of applying a block or graft copolymer having different backbone chain segments as a compatibilizing agent to polymers has been studied thoroughly.¹⁴⁻¹⁹ Jiang et al.²⁰ utilized polycarbonate-polystyrene block copolymers as compatibilizing agents for blends of poly(ethylene terephthalate)/poly(ethylene oxide). In the present article, we describe a method for compatibilization of POM/EPDM blends using PGP and dynamic vulcanization of that system making use of the pendant unsaturation present in the EPDM rubber, with particular emphasis on the mechanical properties, morphology, and crystalline structure of the blends.

EXPERIMENTAL

Materials

POM, Celcon M 140, used in this study is of commercial type and was supplied by Hoechst Celanese, USA. It is a polyoxymethylene-based copolymer with a melt-flow index (MFI) value of 14.0 g/10 min. ¹³C-NMR reveals that this polymer contains 2-3% oxyethylene repeat units, the remainder being oxymethylene. The EPDM, Nordel 2722 (DuPont, USA), is a terpolymer containing ethylene, propylene, and 1,4-hexadiene. These monomers have been polymerized in such a manner as to produce an elastomer with a completely saturated backbone and pendant unsaturation for vulcanization. The compatibilizer, PGP, Polybond 1000 (melting point 161°C; density 0.91 g/cc), is a graft copolymer in

which polyacrylic acid (6%) has been grafted onto polypropylene; it was provided by BP Performance Polymers Inc., USA. The chemical structure of PGP is essentially a long nonpolar crystallizable stereoregular polypropylene (—PP—) chain linked to a short-chain acrylic acid (—AA—) containing polar carboxylic acid end groups.²¹

Preparation of Blends

Based on the optimization of mechanical properties, in all the compatibilized and dynamically vulcanized (cdv) POM/EPDM blends (cdv-POM/EPDM) under investigation, the ratio of plastic to rubber was held constant (80/20) while the PGP compatibilizer levels were 0, 2, 4, and 8% of the total blend. The preparation of blends was done in two consecutive steps: In the first step, EPDM, PGP, and a vulcanization agent, dicumyl peroxide (DCP, 0.1% of EPDM), were all premixed in a two-roll mill at 65°C for about 10 min to disperse the DCP thoroughly in the EPDM/PGP system and the resultant material was shredded into small and uniform pellets manually. In the second step, the dried pellets of the premix were blended with POM in a single-screw extruder ($L/D = 20$), equipped with a mixing head at the screw end, in the temperature range 165–200°C. The extruded products were subsequently pelletized, dried, and injection-molded into different test samples. The cdv-POM/EPDM blends thus prepared with 0, 2, 4, and 8% of the PGP were designated as AEDC0, AEDC2, AEDC4, and AEDC8, respectively. Similarly, a blend having 8% of PGP without dynamic vulcanization was also prepared and designated as AEC8.

In addition, a series of binary POM/EPDM blends with 10, 20, and 30% EPDM (designated as AE91, AE82, and AE73, respectively) was also prepared without any compatibilization and dynamic vulcanization, and their tensile and impact properties determined for comparison with cdv-POM/EPDM blends.

Characterization of Blends

An advanced autostart and autocalculate MFR system (Rosand Precision Ltd., UK) was used to measure the volumetric flow rate (VFR, ml/10 min) of the blends with the aid of a piston-following lever (tracer). The diameter of the die is 2.095 ± 0.005 mm and its length 8.2 mm. The cross-sectional area of the piston is 0.7163 cm^2 . VFR values were determined for the blends at four different temperatures for various loads. In the VFR measurement, an av-

erage of 10 values was taken and standard deviation was found to be in the range 0.10–0.30. The experimental data on the VFR vs. load were converted to viscosity vs. shear rate using the known relationships.²² Rabinowitsch corrections were applied to the viscosity values; Bagley end corrections, however, could not be applied as the MFR system that we used does not have dies with different L/D ratios. The die swell was measured directly and the die-swell ratio was computed for the blends.

The tensile yield stress, hysteresis, and tensile set tests were carried out with a Zwick 1465 universal testing machine. Test specimens for tensile strength, impact strength, and heat-deflection temperature (HDT) were prepared according to ASTM D 638, ASTM D 265, and ASTM D 648, respectively. A minimum of five samples was tested in each case, and the deviation of data around mean values was less than 5%. Hysteresis tests were carried out by loading to a predetermined load level and then returning at the same speed. A constant crosshead speed of 2 mm/min and different loading levels of 200, 175, 150, and 125 N were applied. Elastic recovery of the vulcanized and unvulcanized compositions was determined by measuring tensile set of the samples as per an ASTM D 142 procedure that had been modified as given in Ref. 5. The tensile set value was computed using the following formula:

$$\text{Tensile set} = \frac{L_2 - L_0}{L_1 - L_0} \times 100\%$$

L_0 = original length of gauge marks; L_1 = length between gauge marks at full extension, 100% strain;

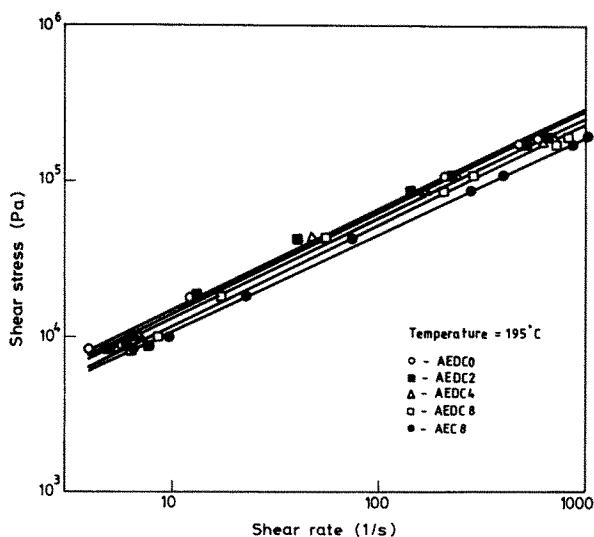


Figure 1 Flow curves for cdv-POM/EPDM blends.

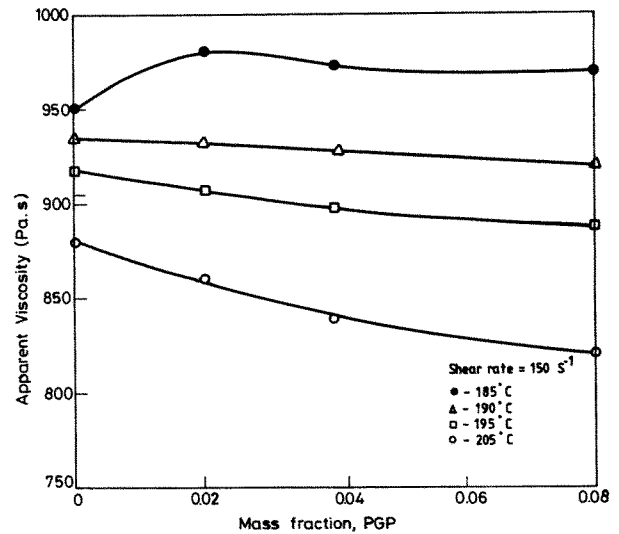


Figure 2 Apparent viscosity of the cdv-POM/EPDM blends as a function of mass fraction of PGP.

and L_2 = final length between gauge marks after recovery.

Dynamic viscoelasticity was measured with a Rheovibron DDV-II-C dynamic viscoelastometer at a heating rate of 1–2°C/min and a frequency of 11 Hz in temperatures ranging from –120 to 130°C. The phase morphology of the blends was investigated using scanning electron microscopy with a Cambridge Stereoscan S-180 instrument. The injection-molded tensile samples were first brittle-fractured in liquid nitrogen and then sputter-coated with gold–palladium using EMSCOPE AE 1231, UK. Wide-angle X-ray diffraction (WAXD) patterns of the blend samples were obtained using Rich-Seifert XRD 3000P X-ray diffractometer (CuK α radiation; Monochrome). The accelerating voltage and electric current used were 35 kV and 30 mA, respectively.

RESULTS AND DISCUSSION

Rheological Properties

The flow curves (shear stress τ vs. shear rate $\dot{\gamma}$) plotted on log–log coordinates for the blends at a temperature of 195°C are given in Figure 1. It is observed that slopes of the lines are almost equal and are less than one, i.e., 0.628–0.643. This means that the blends exhibit non-Newtonian pseudoplastic behavior. The apparent viscosity values of the blends at a shear rate of 150 1/s at different temperatures are shown in Figure 2. It is noted that the addition of PGP to the blends decreases the viscosity

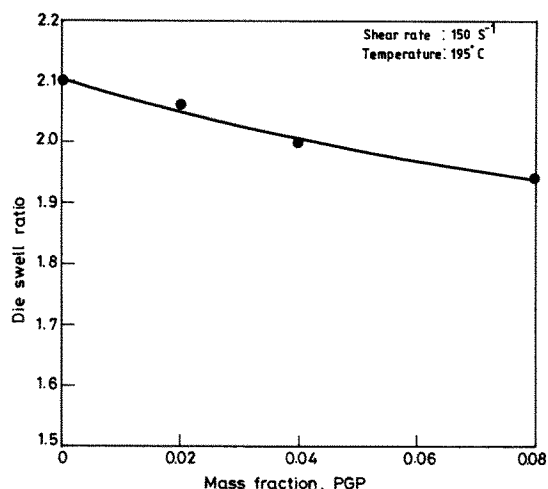


Figure 3 Die swell ratio vs. mass fraction of PGP for cdv-POM/EPDM blends.

in all temperatures except at 185°C, where the viscosity initially increases and then remains constant. This implies that the PGP added can, indeed, serve as a flow inducer at temperatures higher than 185°C. From Figure 3, it is noticed that the die-swell ratio keeps gradually decreasing as the PGP content increases.

Mechanical Properties

The binary blends of POM/EPDM show less than satisfactory properties, as one might expect for this pair on account of the gross incompatibility between POM and EPDM. As seen in Table I, both tensile and impact strength values decrease monotonically as the EPDM content increases. This observation is in accord with that of Chiang and Huang¹³ who noted a decrease in the tensile strength, modulus, and impact resistance, but a very modest increase of impact strength at 7.5% of EPDM. This incompatibility between the two phases of POM and

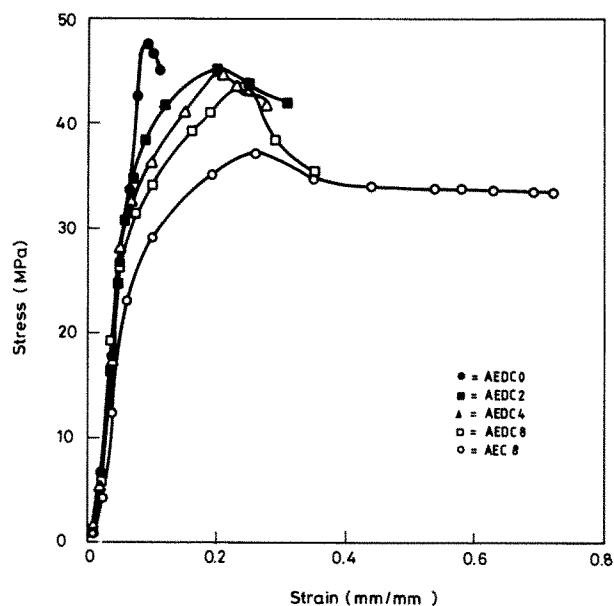


Figure 4 Tensile stress-strain behavior of cdv-POM/EPDM blends.

EPDM may be attributed to the high interfacial tension caused due to the absence of strong specific interactions between the polar POM and nonpolar EPDM polymers.

The 80/20 composition is chosen for cdv-POM/EPDM blends in keeping with the optimal mechanical properties, ease of extrusion processing, and the degradation of POM by DCP. Figure 4 depicts the tensile stress-strain behavior of the various blends. It is seen that the uncompatibilized dynamically vulcanized blend (AEDC0) displays behavior typical of brittle materials; on the other hand, the compatibilized unvulcanized blend (AEC8) exhibits behavior resembling that of ductile materials. However, one can note that the cdv blends behave in a manner intermediate to the two extremes. Even as the addition of PGP improves the ductility (high value of elongation at break), the dynamic vulcanization tends to limit the extent of ductility. The reduction in ductility is probably due to the mechanochemical degradation of POM by shear and DCP and the partial cross-linking of the rubber phase. Although the ductility is reduced, the impact strength of the blends is improved as an overall result of compatibilization and vulcanization.

Figure 5 illustrates the effect of PGP on the tensile yield stress, notched Izod impact strength, and heat deflection temperature (HDT) of cdv-POM/EPDM blends. As expected, the tensile stress and HDT are reduced by the addition of a compatibilizer that is somewhat elastomeric in nature; however,

Table I Tensile and Impact Properties of Binary POM/EPDM Blends

Blend Code	Tensile Yield Stress (MPa)	Notched Izod Impact Strength (J/m) ^a
POM	59.81	73.70
AE91	45.30	74.38
AE82	39.20	71.64
AE73	31.70	67.32

^a To convert J/m to ft-lb/in., divide by 53.39.

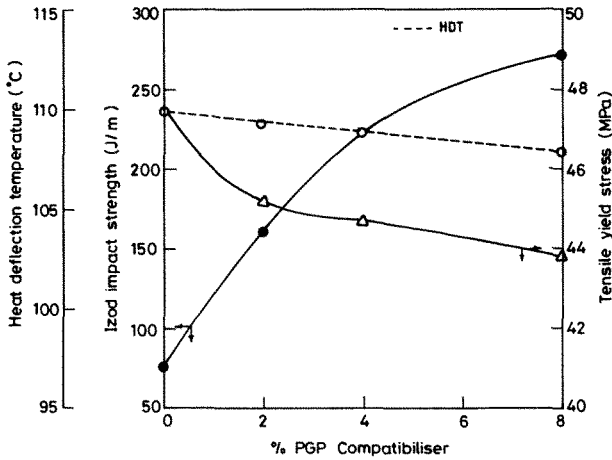


Figure 5 Effect of PGP content on the yield stress, impact strength, and HDT of cdv-POM/EPDM blends.

there is a dramatic increase in toughness upon adding modest amounts of this graft copolymer. The influence of this graft copolymer would appear to be primarily to control the phase morphology between POM and EPDM. The enhanced toughness may be owing to the surface activity and the anchoring ef-

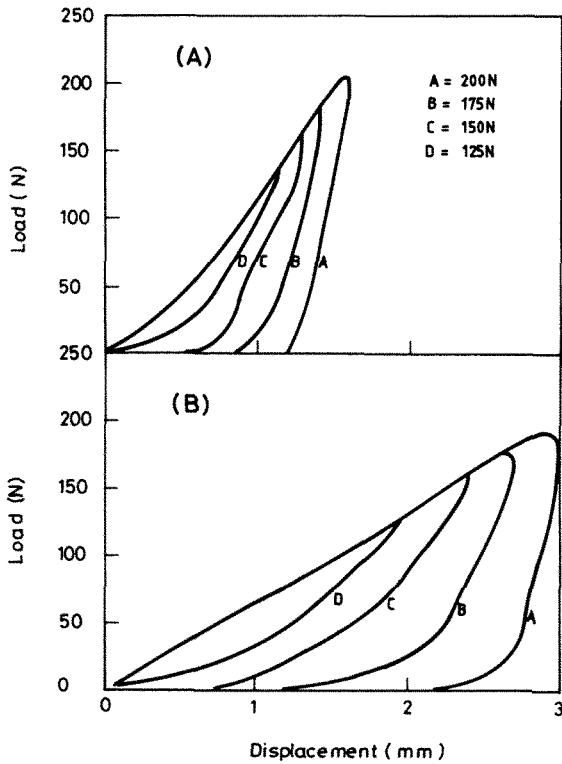


Figure 6 Hysteresis curves at different loading levels (A) AEDC2 and (B) AEDC8.

iciency of this polymeric emulsifier. This toughness improvement is due not only to the improvement of the interfacial adhesion but also predominantly to the interlocked-phase morphology (more discussion follows later).

Figure 6 shows the hysteresis curves of AEDC2 and AEDC8. Hysteresis studies reveal that higher load levels lead to higher percentage of hysteresis (loss) energy in POM and the blends. It is observed from Figure 7 that the hysteresis energy increases consistently with the addition of PGP compatibilizer in cdv-POM/EPDM blends, signifying toughness improvement. One may also note that this trend is almost synonymous with the impact strength, suggesting that the hysteresis energy can also be taken as an approximate measure of toughness/impact strength.

Vulcanization of the compatibilized blends with DCP leads to a substantial decrease in tensile set, which is a measure of the residual permanent deformation after elastic recovery. The tensile set (%) values of AEDC8 and AEC8 obtained are 11.2 and 28.7, respectively. The lower value of AEDC8 indicates that the ability of the entangled rubber molecules to slip past each other is minimized and, hence, the permanent plastic deformation is prevented.

Dynamic Mechanical Properties

Figure 8 shows plots of $\tan \delta$ vs. temperature for POM and selected blends obtained here. The relax-

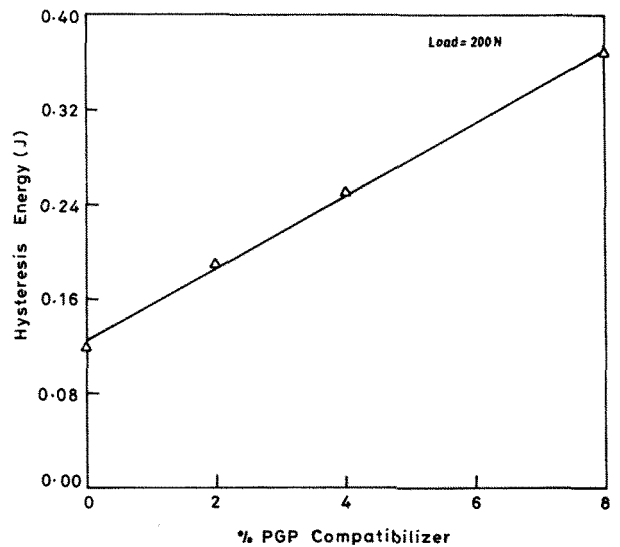


Figure 7 Effect of PGP content on the hysteresis energy of cdv-POM/EPDM blends.

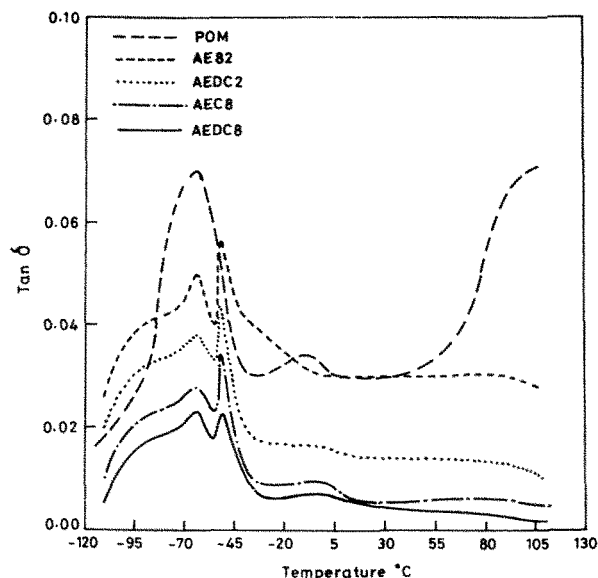


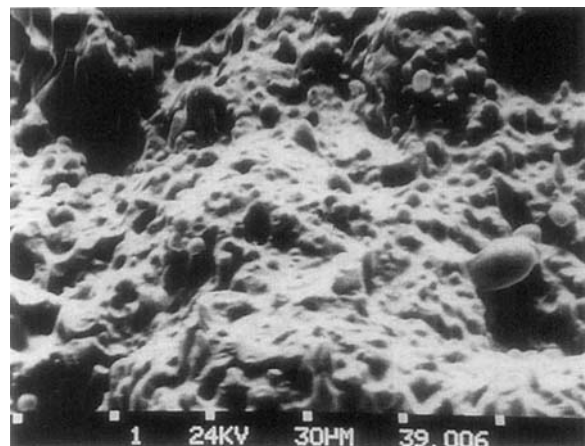
Figure 8 Plots of loss tangent vs. temperature for POM and selected blends.

ations of POM have been reported extensively.^{23–25} For pure POM, three thermal transitions, i.e., 125°C (α), -6°C (β), and -64°C (γ), below the melting point (T_m) are observed. The α transition at 125°C has been clearly associated with molecular motion within the crystalline phase. There exists some controversy as to whether the transition at β or γ corresponds to the T_g of the POM amorphous phase.²⁶ In our study here, we consider the γ transition observed at -64°C to be the T_g of POM. In general, when the binary blends show only one T_g , it is inferred that the system is compatible. In the case of cdv-POM/EPDM blends (Fig. 8), two peaks were present, one at -64°C and another at -52°C, representing the T_g 's of POM and EPDM, respectively. The T_g 's of pure components have not shifted from their respective original positions after compatibilization/vulcanization, indicating lack of miscibility. This is because the interaction between the segments of PGP vs. POM and EPDM is not strong enough to influence the T_g and T_m . This seems to show that the role of PGP has been essentially to bring about interpenetration of the polymer phases.

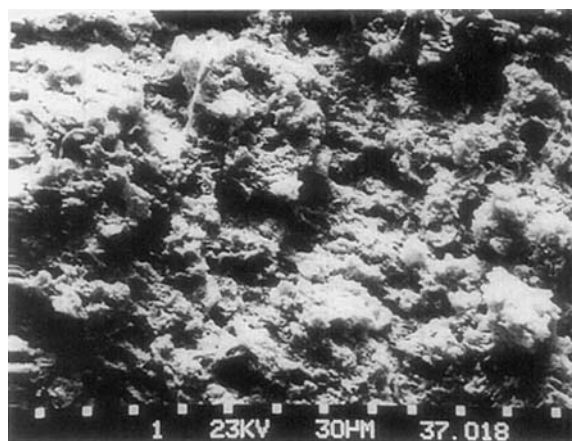
Morphology

The morphology of AE82 blend is shown in Figure 9(a). The major phase (POM) forms the matrix and the minor phase (EPDM) has been segregated into spheroidal domains. No morphological evidence of good adhesion¹³ at the interface between the ma-

trix and the dispersed phase can be seen. The spheres have almost completely smooth surfaces, and during the fracture process, many domains have pulled away from their previous positions, which remain partly as empty holes and partly as spheres, as in Figure 9(a). A significant difference in morphology of the cdv blend (AEDC8) is expected and can be seen in Figure 9(b). As the addition of the PGP graft copolymer has drastically reduced the size of the dispersed phase, separate domains could not be distinguished at the magnification used. Also, there may be cocontinuity of phases, i.e., an interpenetrating network of phases, such as that described by Gergen and Davison.²⁷ From these observations, we conclude that one of the major functions of the graft copolymer additive is to reorganize the blend morphology into an interpenetrating network of phases that is beneficial for mechanical properties.



(a)



(b)

Figure 9 SEM micrographs of fracture of blends: (a) AE82; (b) AEDC8.

Chen et al.¹⁷ studied the mechanism of polymeric compatibilizers (block/random/graft copolymers) and proposed three models to explain their behavior. As per their first model, the compatibilizer may be concentrated along the interface and act as an emulsifier in reducing interfacial tension. In the second model, the compatibilizer distributes itself between the polymer phases, and the resulting interface between EPDM/PGP and POM/PGP could have a lower interfacial tension. The mechanism by which the PGP graft copolymer compatibilized the present blend system can better be explained by their third model, which is a combined model of the above

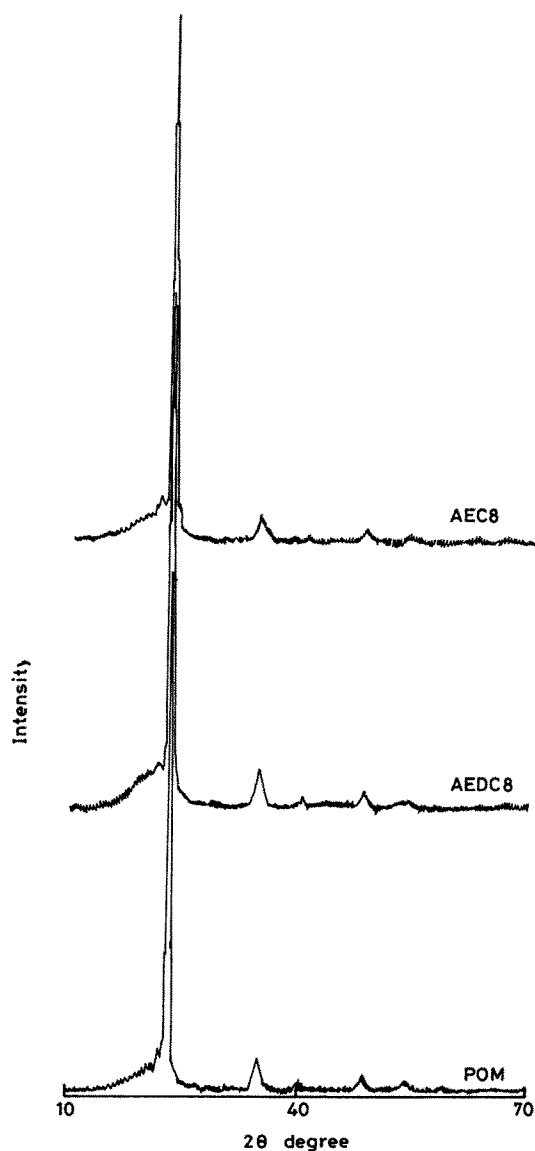


Figure 10 X-ray diffractogram of POM, AEDC8, and AEC8.

Table II WAXD Analysis of POM, AEDC8, and AEC8

Sample Code	fwhm	2θ	d Spacings of POM Crystal Planes (Å)	ACS (Å)
POM	0.524	23.280	3.8179	2.7016
AEDC8	0.616	23.162	3.8371	2.2976
AEC8	0.527	22.798	3.8975	2.5389

two. The third model obtained by combining the previous two will be more suitable in this case, considering the higher quantity of compatibilizer used in the work. The possible specific interactions, such as (i) hydrogen bonding between the —AA— segment of PGP and ether linkage of POM and (ii) cocrystallization between the —PP— segments of PGP and EPDM, might account for the first part of the combined model. The mechanical entanglement of PGP between POM and EPDM phases leading to interpenetration network of phases might explain another part the combined model.

Crystalline Structure

The X-ray diffraction of POM, AEDC8, and AEC8 are shown in Figure 10. POM and the blends give a sharp crystalline peak and about three small and broad peaks in the region of the Bragg angle (2θ) between 10° and 70° , indicating their semicrystalline nature. It is noticed that the incorporation of EPDM or PGP does not alter the crystal structure of the POM at all, judging from the fact that the four intensity peaks of POM in the blends are observed in the same Bragg angles in all the cases. It is also exemplified from the fact that the d -spacings of POM crystal planes do not vary much with EPDM/PGP as seen in Table II. Various process steps such as compatibilization and dynamic vulcanization also have not changed the crystal structure of POM.

The apparent crystallite size (ACS), which is a measure of both the size of the crystallites and the degree of crystalline imperfection, is determined from the full-width at half-maximum $\Delta_{(2\theta)}$ (fwhm) of the crystalline peaks using the Scherrer equation²⁸

$$\text{ACS} = 0.9\lambda[\Delta_{(2\theta)}\cos\theta]^{-1} \quad (1)$$

where λ is the wavelength (1.542 Å) and 2θ is the position of the peak maximum. As seen from Table II, the crystallite size of AEDC8 and AEC8 is lower than that of the pure POM. This suggests that the

growth of the crystallites is inhibited in the blends compared to that in pure POM. Such lower crystallinity and smaller or imperfect crystallites might contribute toward improved fracture toughness of the blends. This is in addition to the beneficial role of the PGP graft copolymer in enhancing the interfacial strength between the semicrystalline domains of POM and EPDM. Furthermore, it may be speculated that the cocrystallization of the PP in PGP with the PP segment of EPDM may take place, leading to excellent interfacial contact between the PGP and EPDM.

CONCLUDING REMARKS

The incompatible POM/EPDM blends exhibiting poor impact strength have been converted into a material with improved properties by compatibilization and dynamic vulcanization. The compatibilizing effect is achieved by incorporating a commercial polymeric compatibilizer (PGP), having segments different from those of the POM and EPDM polymers; partial vulcanization of the rubber phase is effected by a peroxide (DCP). The resultant blends possess higher impact strength and elastic recovery and at the same time decreased yield strength and HDT. The significant increase in toughness is due not only to the improvement of the interfacial adhesion but also predominantly to the interlocked phase morphology. Further studies are required to deduce the accurate mechanism for the mechanical properties as a function of morphology.

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