Macromolecules **1998,** *31,* 5407−5414

Thermoplastic Vulcanizates from Isotactic Polypropylene and Ethylene−Propylene−Diene Terpolymer in Supercritical Propane: Synthesis and Morphology

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Received February 3, 1998; Revised Manuscript Received June 5, 1998

ABSTRACT: New thermoplastic vulcanizates (TPV's) have been synthesized from isotactic polypropylene and ethylene−propylene−diene terpolymer (EPDM) in a supercritical propane solution. The ternary solution of polypropylene and EPDM in supercritical propane exhibited less solubility than the corresponding binary solutions of polypropylene or EPDM separately in propane. Higher pressure in the supercritical polymer solution enhanced the mutual solubility of the two polymers. EPDM was cross-linked with *tert*-butyl peroxide while in supercritical solution. On lowering the pressure while remaining above the melting temperature of the polymers, the supercritical TPV gel phase separated in a manner consistent with spinodal decomposition. On isobaric cooling of the supercritical TPV gel, the polypropylene crystallized, freezing the morphology. The cross-linking of EPDM in the homogeneous supercritical propane solutions was found to be nearly complete. The final TPV's were phase separated, exhibiting two melting transitions. The morphology of the TPV's was a microporous, apparently closed-cell polymeric foam. Phase contrast optical microscopy showed micro-heterogeneous EPDM domains dispersed in the polypropylene matrix for the TPV's. The phase domain sizes were much smaller, by a factor of 5−10 or so, than those of the corresponding melt blends.

Introduction

Polypropylene is one of the major commodity polymers, having excellent physical properties such as high stiffness and tensile strength. However, it is known to have poor impact strength at low temperatures, which limits its applications. Commercially, rubbery elastomers such as EPM (ethylene−propylene copolymer) or EPDM (ethylene−propylene−diene terpolymer) are added to polypropylene as minor components for the improvement of impact strength.[1] When EPDM is cross-linked during its blending with polypropylene, the blends become a special type of thermoplastic elastomer known as thermoplastic vulcanizates (TPV's)[2] or dynamic vulcanized alloys (DVA's).[3] The double bonds in EPDM are curing sites for cross-linking with peroxides, sulfur, or radiation. These polymer blend systems are also referred to as a type of thermoplastic interpenetrating polymer network (IPN) on the basis of the definition of an IPN.[4−6]

Thermoplastic vulcanizates exhibit a hybrid behavior of thermoplastic and thermoset rubber, which can flow at elevated temperatures under shearing conditions, yet behave as an elastomer at ambient temperature. The best known commercially successful example of a TPV is made by melt blending semicrystalline polypropylene and EPDM while simultaneously vulcanizing the EPDM. Figure 1 illustrates the morphology of the blends over a wide range of temperatures. When the temperature is higher than the melting temperature of polypropylene, the system can flow while shearing because polypropylene melts. However, when the temperature is lower than the melting temperature of polypropylene, the development of crystallinity from polypropylene freezes the morphology, but the system is a true elastomer, due to the presence of cross-linked EPDM and the properties of the polypropylene matrix.

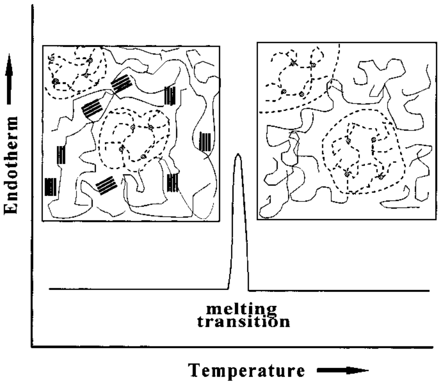

Figure 1. Morphological characteristics of thermoplastic vulcanizate from polypropylene and EPDM: solid line, polypropylene; thick solid line, crystalline region of polypropylene; dotted line, EPDM.

When polypropylene is blended with EPDM in the melt state in an extruder to produce a TPV, one of the major concerns is to achieve fine dispersion of EPDM into the polypropylene matrix because product proper-

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S0024-9297(98)00153-3 CCC: $15.00

Table 1. Characteristics of Polymers

polymer	M_w	M_w/M_n	T_g, °C	density at 23.0 °C
polypropylene	91 000	2.0	0.4	0.9065
EPDM	198 000	2.0	−38.0	0.8940

ties such as impact strength can be optimized by reducing the size of EPDM particles.[7,8] The melt viscosity of EPDM is usually higher than that of polypropylene with the same molecular weight, which makes it difficult to achieve a fine dispersion of EPDM by extrusion. Common practices to improve the mixing include application of high shear in the blender, addition of oil, and manipulation of the molecular weight of the components. For instance, Van der Wal et al. decreased the particle size of EPDM in polypropylene by lowering the intrinsic viscosity of EPDM.[8] However, most of the commercial EPDM polymers do not match polypropylene in melt viscosity; their difference in melt viscosity arises from the difference in the molecular structure of two polymers.[9,10]

To alleviate these problems, we investigate a method to process the polymer blends in a supercritical fluid to form a thermoplastic vulcanizate. Advantages of polymer blending in supercritical fluids, over conventional melt blending processes, are easy solvent recovery from the final product, easy recycling of the solvent, low viscosity during processing, little chain degradation, and high interspersion of components.[11] The main purposes of this work are to synthesize a thermoplastic vulcanizate from polypropylene and EPDM in supercritical propane and to study its morphology. The approach involves characterizing the phase behavior of polypropylene and EPDM in supercritical propane to determine processing conditions and then cross-linking the system via introduction of peroxide. The morphology of thermoplastic vulcanizate was investigated by phase contrast optical microscopy and scanning electron microscopy. The thermal properties were studied by differential scanning calorimetry.

Experimental Section

Materials. Isotactic polypropylene (97.6% meso diad) was synthesized with a metallocene catalyst. The weight-average molecular weight of the polypropylene was 91 000, and its polydispersity index was 2.0. EPDM was a statistical terpolymer, which has 70 wt % of ethylene, 23−27 wt % of propylene, and 3−7 wt % of ethylidene norbornene. The weight-average molecular weight of EPDM was 198 000, and its polydispersity index was 2.0. The properties of polymers are summarized in Table 1. The solvent propane (99.9% purity) was obtained from Matheson Gas Co., and *tert*-butyl peroxide (99.4% purity) was obtained from Aldrich Chemical Co. Both were used without further purification.

Apparatus and Synthesis. The cloud-point pressure determination of polymer solutions and the TPV formation were performed in a high-pressure variable volume optical batch cell unit as shown in Figure 2. The design of this apparatus is described in detail elsewhere.[12,13] A brief description of the cloud-point experiment and TPV synthesis is as follows. The cell consists of three parts: window cap, cell body, and end cap. The total variable volume of the cell is 17 cm^3. The cell has four ports for charging a solvent and sampling: at the top, bottom, and each side of the cell. A sapphire window is attached to the cell body with a window cap. A movable piston controls the pressure of the system. For cloud-point experiments, a mixture of the polymer and propane of known composition was prepared and then the cloud-point transition of the polymer solution was observed visually through a sapphire window in the cell. The polymer solution was pressurized first to well above the cloud-point pressure to form a one-phase solution and equilibrated at a constant temperature with stirring. The pressure of the system was then lowered isothermally until the solution became hazy, indicating a liquid−liquid (cloud-point) phase transition. The cloud-point pressure was determined as the pressure at which the solution turns completely cloudy in the cell. For a solid−liquid transition, the homogeneous polymer solution was cooled isobarically until it turned hazy. For the TPV synthesis, polypropylene and EPDM were dissolved at certain concentrations to form a homogeneous solution. *tert*-Butyl peroxide was injected into the homogeneous supercritical propane solution through a feed line. The weight ratio of *tert*-butyl peroxide to EPDM was about 1 part to 100 parts. In a typical experiment, the amount of EPDM ranged approximately from 0.2 to 0.8 g, depending on the ratio to polypropylene and total polymer concentration. Initially, the liquid *tert*-butyl peroxide was injected with a microsyringe into a section of feed line, which was isolated by two two-way valves (High-Pressure Equipment Co. model 15-11AF1) before the sampling port in the cell. Then, the pressurized propane solvent flushes *tert*-butyl peroxide into the cell. The cross-linking reaction of EPDM was continued for 1 h at 175 °C and 650 bar with stirring. The polymers were precipitated by first reducing the pressure below the cloud-point pressure and then isobarically cooling to ambient temperature. The residual solvent was vented.

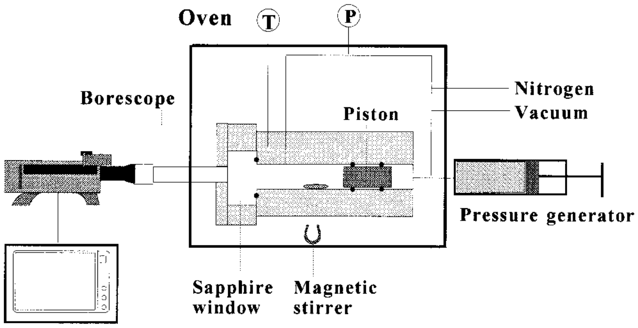

Figure 2. Schematic of a high-pressure optical batch cell.

Melt Blending. A Brabender plasticorder torque blender was employed to melt-process the blends of various compositions of polypropylene and EPDM. The plasticorder torque was recorded as a measure of the dynamic flow behavior. Typically, 53 g of sample was added to the preheated Brabender at 195 °C. After the polymer samples were melted, mixing continued for 5 min at 193 °C and 100 rpm. An equilibrium torque was recorded on the plasticorder.

Characterization. DSC was performed using a Seiko RDC220 to study melting transitions. The melting temperature was taken as the peak melting temperature of endotherms in the DSC thermograms. All the polymer sample weights were approximately 10 mg. The polymer samples were initially quenched to −110 °C and then heated at a rate of 10 °C/min up to 210 °C to measure thermal transitions. The glass transitions of the homopolymers were determined by modulated DSC (TA instruments). The heating rate was 1 °C/min, the modulation period was 100 s, and the modulation amplitude was ±0.5 °C. Dynamic mechanical spectroscopy was carried out to measure the melt viscosity of the homopolymers using a Rheometrics mechanical spectrometer 800 (Rheometrics, Inc.). The heating rate was 1 °C/min, and the frequency was 1 rad/s. The densities of polymers were determined using a density gradient column (Techne Inc.) at 23.0 °C. The specific volumes of the homopolymers at various temperatures and pressures were measured using a Gnomix P−V−T apparatus for solubility parameter determination. Scanning electron microscopy (SEM) (JEOL JSM35) was performed at 15 kV to examine the surface morphology. Before observation, all polymer samples were coated with a 10-nm thin layer of gold and palladium by a Hummer X plasma coater (Anatech Ltd.). Phase morphologies of thin samples from the thermoplastic vulcanizates and the melt blends were studied using a phase contrast optical microscope with polarizers (Leitz, Inc.)

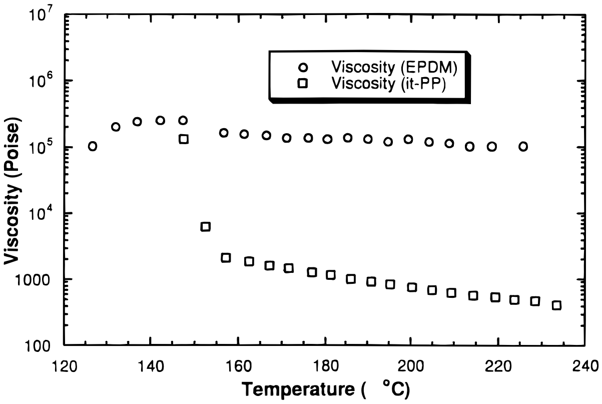

Figure 3. Shear viscosity of EPDM and polypropylene.

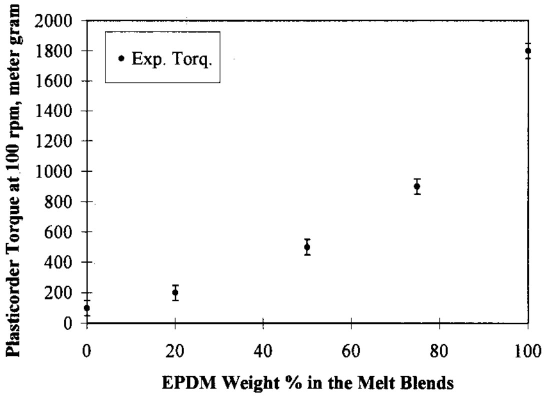

Figure 4. Comparison of experimental torque data for the melt blends.

to enhance the phase contrast image. Gel content tests were performed using solvent xylene and a Soxhlet extraction apparatus. A known amount of the thermoplastic vulcanizate sample was refluxed with boiling xylene at 140 °C for 3 h. The boiling xylene was a good solvent for polypropylene and linear or branched EPDM but ineffective for cross-linked EPDM. The amount of unreacted polymers was determined by taking an aliquot of the solution and determining the concentration of solute via evaporation of the solvent.

Results and Discussion

Figure 3 illustrates the complex viscosity of the polypropylene and EPDM determined by a Rheometrics dynamic spectrometer. The melt viscosity of EPDM was about 2 orders of magnitude higher than that of polypropylene at temperatures from 160 to 220 °C. Based on the ratio of their molecular weights raised to the 3.4 power, a factor of 14 only is predicted.[14] These large differences in viscosity can have a significant effect on the morphology of the melt blends particularly in regard to phase continuity. It is expected that EPDM will not disperse well in polypropylene during melt mixing.

To show the morphologies of the melt blends, the two polymers were blended in the Brabender at various compositions. Figure 4 illustrates the plasticorder torque at 100 rpm at 193 °C for the melt blends with various compositions. The plasticorder torque represents the shear viscosity of the system. As the EPDM content increased, the plasticorder torque increased, because EPDM had a higher shear viscosity than polypropylene as shown in Figure 3. The phase morphologies of the melt blends at various compositions are shown in Figure 5. EPDM was dispersed as spherical particles, with domain sizes of over 100 μm. Although the EPDM fraction increased above 50% in the melt blends, the EPDM domains remained discontinuous because of its high viscosity. Polypropylene with lower viscosity encapsulated the more viscous EPDM because this reduces the rate of energy dissipation.[15,16] The criterion for phase inversion can be expressed as follows. If ϕ_i is the volume fraction of phase i and η_i its viscosity and if $\phi_1\eta_2/\phi_2\eta_1 > 1$, then phase 1 is continuous, and if this ratio is less than 1, phase 2 is continuous. If this ratio is near unity, a co-continuous structure is expected.

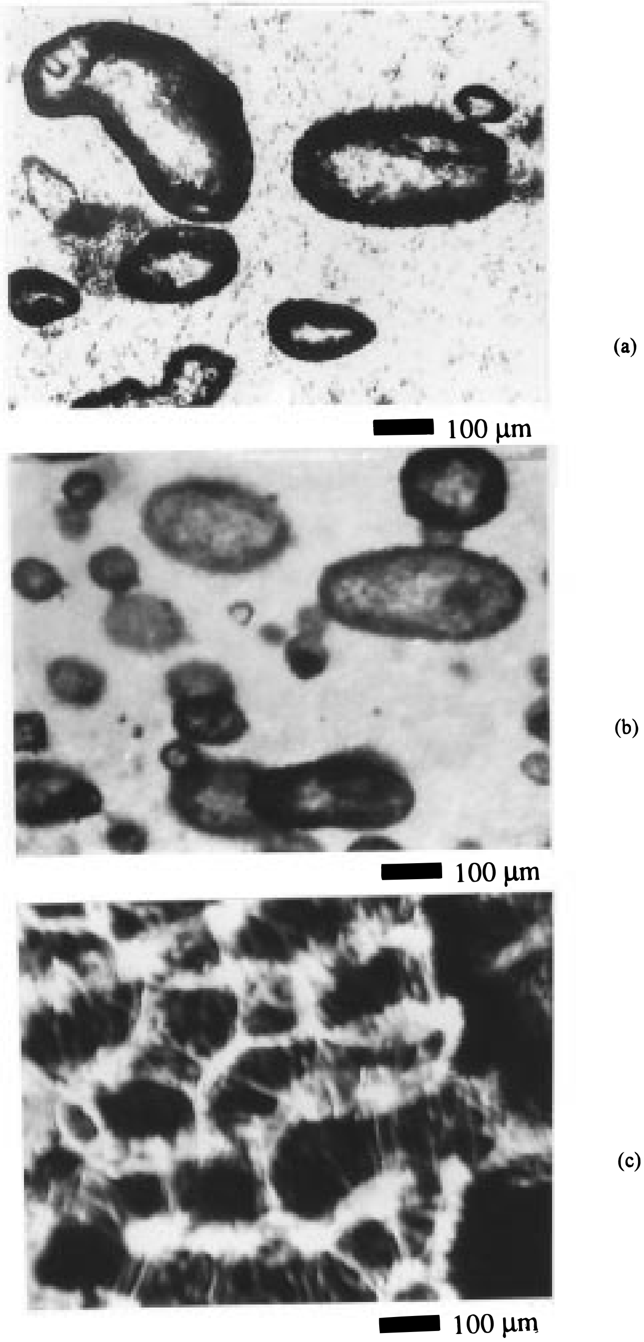

Figure 5. Phase morphologies of the melt blends: light phase, PP; dark phase, EPDM. (a) 20% EPDM, (b) 50% EPDM, (c) 75% EPDM (Phase contrast microscopy).

To synthesize the TPV in supercritical propane, we needed to determine the phase behavior of polymer solutions in supercritical propane. Figures 6 and 7 illustrate the ternary phase diagram of polypropylene,

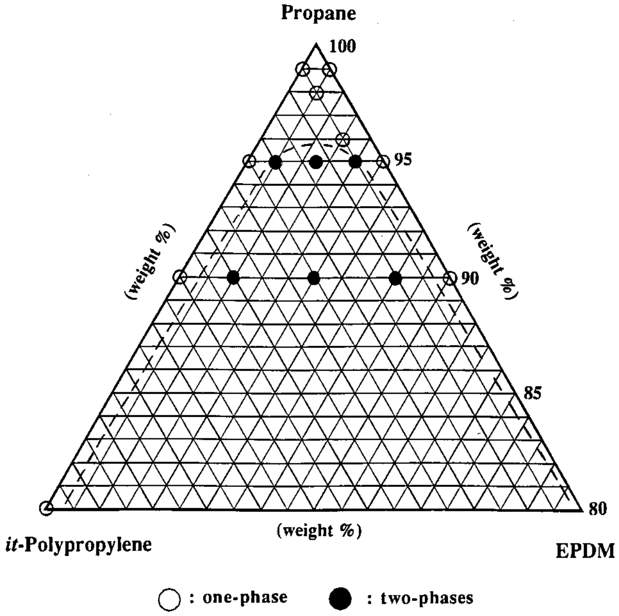

Figure 6. Ternary phase diagram at 175 °C and 600 bar.

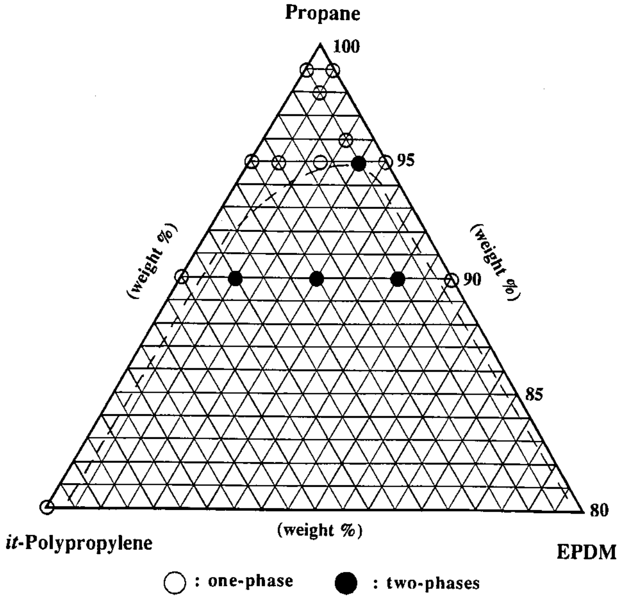

Figure 7. Ternary phase diagram at 175 °C and 700 bar.

EPDM, and propane at 175 °C. The dotted lines indicate approximate phase boundaries in the ternary system. The filled symbols indicate the two-phase region, while the open symbols represent the one-phase region. The miscible regions in the ternary systems were limited to the edges of the diagram and to the propane-rich corner. As the pressure increases, the miscible region in the phase diagram also increases. This type of phase behavior (miscibility increases with pressure) is commonly seen in these hydrocarbon polymer solutions. For instance, the upper critical solution temperature (UCST) generally decreases and the lower critical solution temperature (LCST) increases during pressurization. Thus, these ternary solution phase diagrams are consistent with previous work.[17]

Figure 8 shows the cloud-point pressures of binary and ternary solutions of polypropylene, EPDM, and propane, in a pressure−temperature phase diagram. The cloud-point pressures of the ternary solutions were higher than those of the binary solutions. The solid−liquid transition line of the polypropylene solution was steep and located well below the melting temperature of polypropylene at ambient pressure, due to the plasticization effect of supercritical propane. For the binary systems, the cloud-point pressures of the less branched EPDM solution were higher than those of polypropylene in propane because the cohesive energy density of EPDM is higher than that of polypropylene.[18] We have previously measured the short-chain branching effect on the cloud-point pressure of ethylene copolymers in propane.[17] It was found that, as the ethylene content increased, the solubility parameters and so the cloud-point pressures of the ethylene copolymers increased. Polypropylene was found to have cloud-point pressures lower than those of the ethylene copolymers.

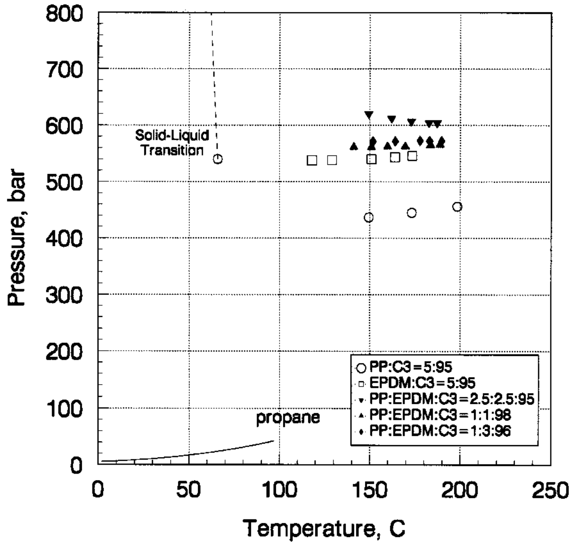

Figure 8. Pressure−temperature phase diagram of the binary and ternary solutions at various polymer compositions: one-phase, above symbol; two-phase, below symbol.

The specific volumes of the bulk homopolymers at various temperatures and pressures determined by the P−V−T apparatus are shown in Figure 9. As the pressure increases, the specific volumes decrease. The melting temperature of polypropylene obtained from the P−V−T apparatus was similar to the melting temperature from DSC. However, the melting transition of EPDM from the P−V−T apparatus was not obvious because of the temperature-scanning limit of the P−V−T apparatus and the low crystallinity. The melting transition is about 45 °C by DSC, but the melting starts at subambient temperatures, which are beyond the P−V−T apparatus range. Figure 10 illustrates the calculated solubility parameters of polypropylene and EPDM at temperatures from 170 to 200 °C. The solubility parameter of each polymer was calculated from internal pressure measurement, which was determined by the isobaric thermal expansion coefficient and isothermal compressibility from the P−V−T apparatus.[18] As the temperature increases, the solubility parameters of both polymers decrease because the molecular interaction between polymer molecules decreases. The solubility parameters of EPDM are also higher than those of polypropylene at the temperatures investigated, and the difference is greater than 1 MPa$^{1/2}$. According to the Flory−Huggins−Staverman expression[19−21] for the free energy of mixing two polymers and regular solution theory,[22] the miscibility limit for two high molecular weight polymers ($M_{\rm w} \sim 10^5$) is approximately 0.3

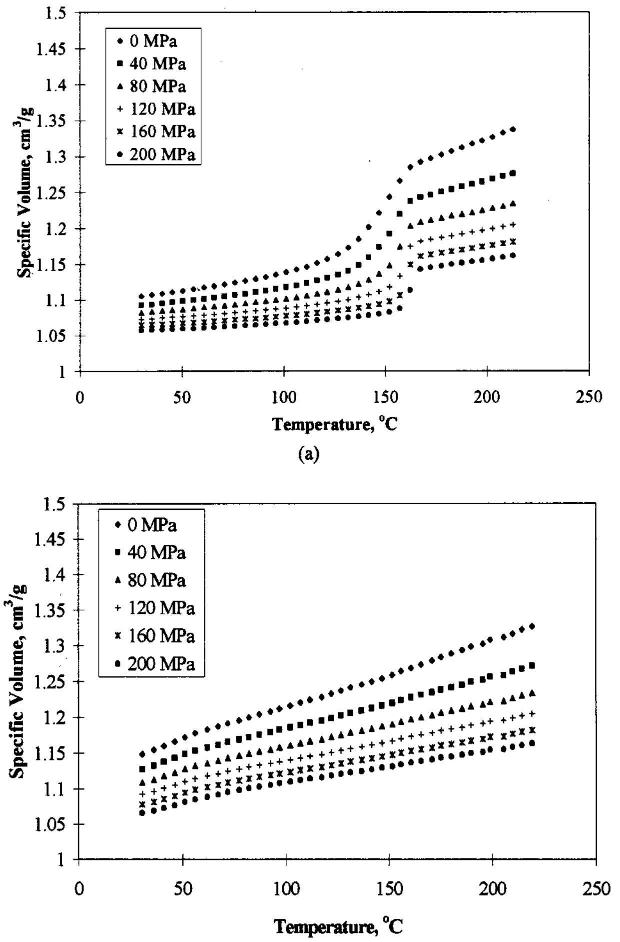

Figure 9. Experimental specific volumes of polymer plotted as a function of temperature at different pressures: (a) isotactic polypropylene; (b) EPDM.

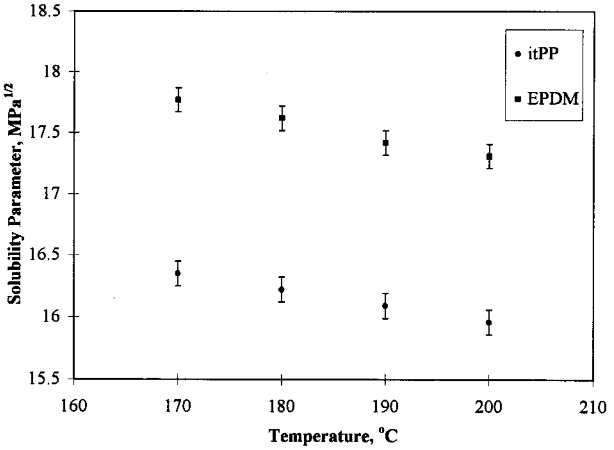

Figure 10. Solubility parameters of polymers.

MPa$^{1/2}$.[17] These data suggest that the ternary system should have two phases, which is borne out by Figures 6 and 7.

The reaction conditions to form the thermoplastic vulcanizates in supercritical propane are summarized in Table 2. The half-life of *tert*-butyl peroxide (due to thermal decomposition), which is strongly dependent on temperature, is expected to be about 12 min at 175 °C.[23] The concentration of peroxide for the cross-linking reaction was 1 part peroxide per 100 parts EPDM. After the peroxide was injected into a homogeneous solution with stirring, conditions were maintained for 1 h. The reaction time was substantially long enough for several half-lives of the peroxide, to nearly complete decomposition of the peroxide. During this period, the solution was transparent. The cross-linked EPDM could be swelled with supercritical propane, which has a refractive index very similar to that of the polymer solution. As a result, the solution did not show any obvious indication of phase separation. After the reaction was complete, the pressure of the solution was lowered to 200 bar, well below the cloud-point pressures of the solution. During this step, the solution demixes by liquid–liquid phase separation presumably in the spinodal region, followed by coarsening. Then, the solution was cooled isobarically to ambient temperature. The subsequent crystallization of the polypropylene froze the morphology of the thermoplastic vulcanizates, still in propane. Then, the propane was evaporated.

Table 2. Reaction Conditions for the Thermoplastic Vulcanizate Syntheses

reaction composition, (weight ratio)	cross-linking reaction condition: 1 part peroxide per 100 parts EPDM	reaction time (h)
PP:EPDM:propane = 4:1:95	170 °C, 700 bar	1
PP:EPDM:propane = 2.5:2.5:95	175 °C, 650 bar	1
PP:EPDM:propane = 1:3:96	175 °C, 650 bar	1
EPDM:propane = 10:90	175 °C, 650 bar	1

Gutowski et al.[24] explained liquid–liquid separation of polybutadiene in a hexane solution in terms of gravity separation, which would be very similar case to our system. The dilute phase, either polymer or solvent, is expected to be separated by nucleation and growth when the system pressure is just below the cloud-point pressure (i.e., near the lower critical solution temperature). However, the system was entered relatively deep into the spinodal decomposition region of the phase diagram during a pressure lowering step (i.e., pressure-induced phase separation), in the typical cloud-point experiments. In this region, an interconnected cylinder type of each phase tended to form due to phase separation, which would be stable in a solid (e.g., polymer blends). However, such a network in a liquid would be highly unstable to surface tension and gravity, allowing a drainage path for the dilute phase and resulting in a faster settlement of a solvent-rich phase and a polymer-rich phase.

Figure 11 shows scanning electron micrographs of the surface morphologies of the pure components and a TPV precipitated from supercritical propane. The EPDM solution was cooled to room temperature isobarically at 600 bar from a homogeneous solution, resulting in a microporous open-cell foam structure. Typical pore sizes of EPDM were about 10 μm. Polypropylene was also directly cooled isobarically at 600 bar from a homogeneous solution to the temperature below the solid–liquid transition of the solution. In contrast to the open-cell-type EPDM morphology, the morphology of polypropylene from direct crystallization in a propane solution was a microporous closed-cell foam structure, which resulted from accumulation of polypropylene microspheres. Pradhan and Ehrlich reported similar structures of polypropylene precipitated from supercritical propane.[25] They explained that the morphology of nearly uniform size microspheres was formed by a rapid nucleation step in comparison to crystal growth. The surface morphology of the microsphere was suggested as a radial orientation of lamellaes, somewhat

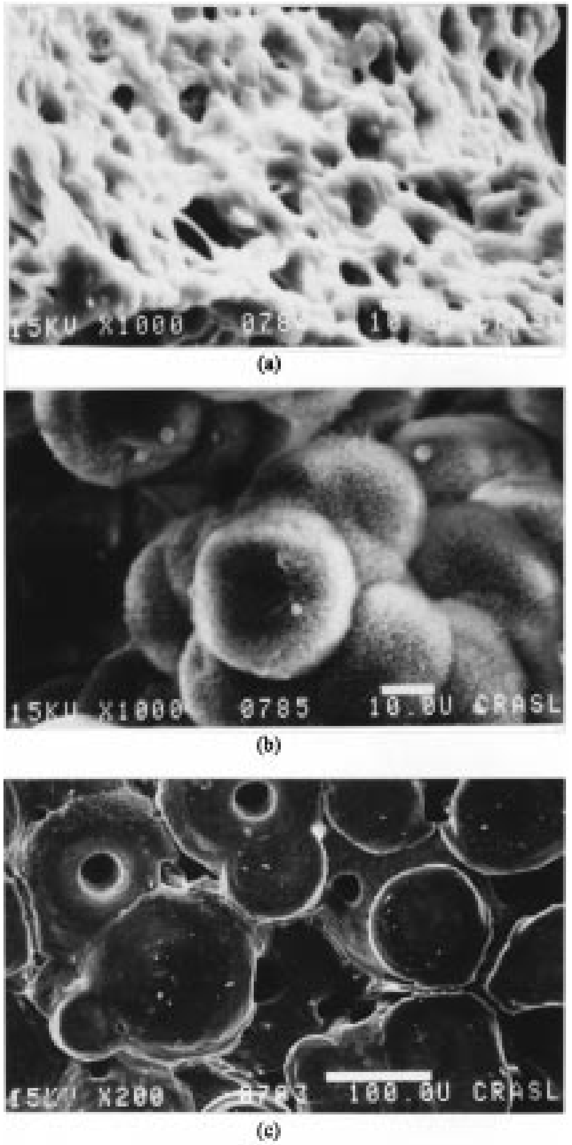

Figure 11. Scanning electron micrographs of the surface of polymers: (a) EPDM; (b) isotactic polypropylene; (c) thermoplastic vulcanizate (20% EPDM).

reminiscent of a prespherulitic structure. The TPV with 20 wt % EPDM showed apparently closed-cell foam structures, but the cell sizes were much larger than those of the polypropylene homopolymer precipitated from supercritical propane. The rapid phase separation and isobaric cooling steps of the thermoplastic vulcanizates are expected to avoid any fractionation of polymers by crystallization during the isobaric cooling step. However, it is thought that the phase-separated solution coarsened. Figure 12 shows the phase morphologies of the TPV's at different compositions, characterized by optical phase microscopy. The higher viscosity EPDM particles were dispersed in the lower viscosity polypropylene matrix, the same as in the melt blends. However, the sizes of the EPDM domains in the TPV's were much less than 100 μm, which are about 5−10 times smaller than those from the melt blends, and were relatively uniform because the solution mixing in supercritical propane provided a better interspersion of two components than melt-mixing in bulk. At 75% EPDM (Figure 12c), the condition of dual-phase continuity may exist.

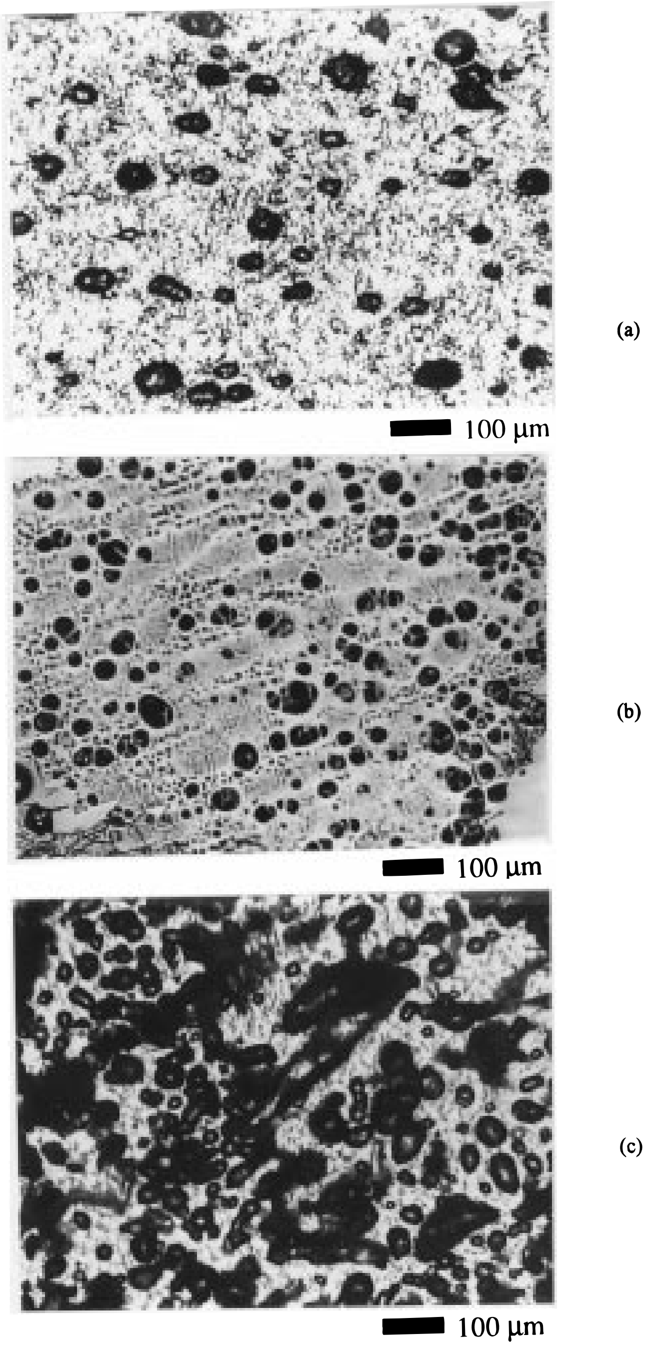

Figure 12. Phase contrast optical micrographs of the thermoplastic vulcanizates: light phase, PP; dark phase, EPDM. (a) 20% EPDM, (b) 50% EPDM, (c) 75% EPDM.

The gel contents in the different TPV's are illustrated in Figure 13. The gel content correlates well with the weight percent of EPDM in the TPV, indicating the nearly complete network formation of EPDM. The high conversion of EPDM with *tert*-butyl peroxide is probably due to cross-linking reactions in the homogeneous supercritical propane solution.

Figures 14−16 illustrate the DSC thermograms for the pure components, the TPV's, and the melt blends with different compositions. The melting temperatures are summarized in Table 3. All the DSC thermograms for the blends showed two distinctive melting peaks. There is little effect of cross-linking on the melting transitions of EPDM in the TPV's because the cross-linking reaction occurred in the ethylidene norbornene side groups in EPDM. The melting transitions of

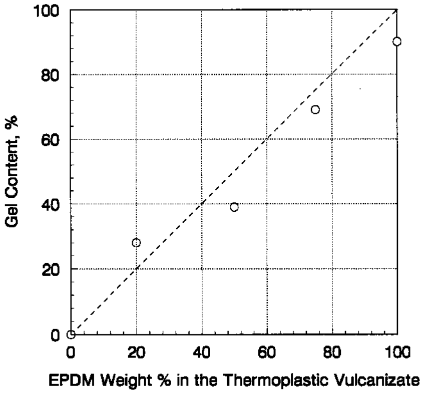

Figure 13. Gel contents of the thermoplastic vulcanizates.

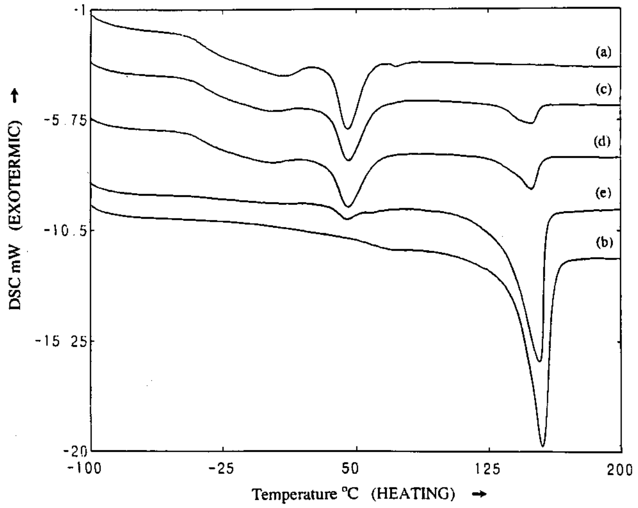

Figure 14. DSC thermograms of the thermoplastic vulcanizates on heating at 10 °C/min: (a) EPDM; (b) isotactic polypropylene; (c) 75% EPDM; (d) 50% EPDM; (e) 20% EPDM.

Table 3. Melting Temperatures of the Homopolymers, Thermoplastic Vulcanizates, and Melt Blends

sample code	samples	T_m of EPDM, °C	T_m of PP, °C
	Homopolymers		
a	EPDM	45.4	
b	PP		154.2
	Thermoplastic Vulcanizates		
c	PP:EPDM = 1:3	45.4	149.9
d	PP:EPDM = 1:1	46.1	149.2
e	PP:EPDM = 4:1	45.4	149.2
	Melt Blends		
f	PP:EPDM = 1:3	44.7	150.6
g	PP:EPDM = 1:1	45.4	152.0
h	PP:EPDM = 4:1	46.1	153.5

polypropylene in both blends were also little affected by the presence of EPDM, because polypropylene and EPDM are thermodynamically immiscible. The heats of melting transition for each component in the TPV's and the melt blends increased as the fraction of each component increased. The glass transition temperatures of the homopolymers and polymers in the blends were not observed clearly in DSC because of the crystallinity of each polymer. A plot of reversing heat flow and temperature from modulated DSC revealed that the glass transition temperatures of polypropylene and EPDM homopolymers were at 0.4 and −38.0 °C, respectively. The reversing heat flow was determined by multiplying the heat capacity of the polymer by the average heating rate. The heat capacity was calculated from the ratio of the modulated heat flow amplitude divided by the modulated heating rate amplitude. However, no clear glass transition temperature of either polymer in the blends was observed in the modulated DSC, possibly because the glass transition of polypropylene overlapped with the melting transition of EPDM.

Conclusions

Thermoplastic vulcanizates have been synthesized from isotactic polypropylene and EPDM in supercritical propane solution. The ternary solutions of polypropylene and EPDM in supercritical propane exhibited lower solubility than the corresponding binary solutions of polypropylene or EPDM in propane. The thermoplastic vulcanizates were phase-separated, exhibiting

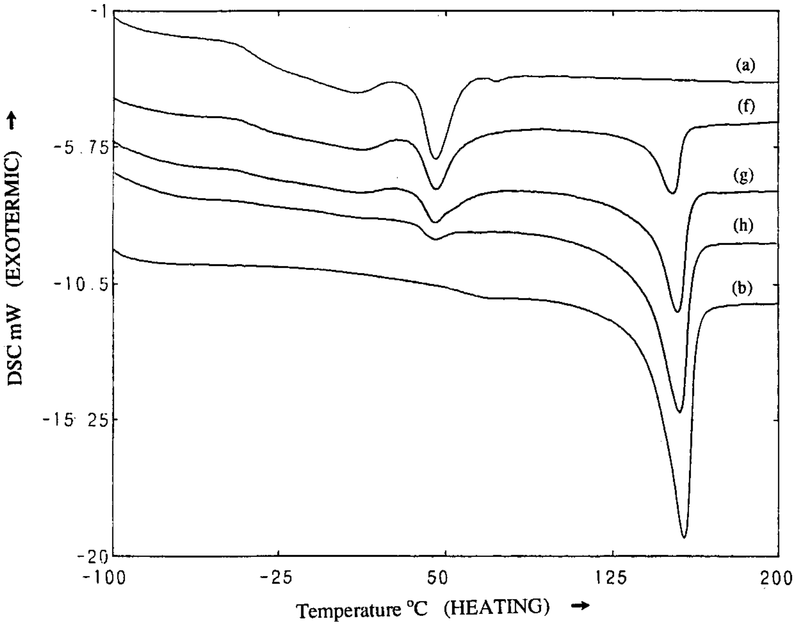

Figure 15. DSC thermograms of the melt blends on heating at 10 °C/min: (a) EPDM; (b) isotactic polypropylene; (f) 75% EPDM; (g) 50% EPDM; (h) 20% EPDM.

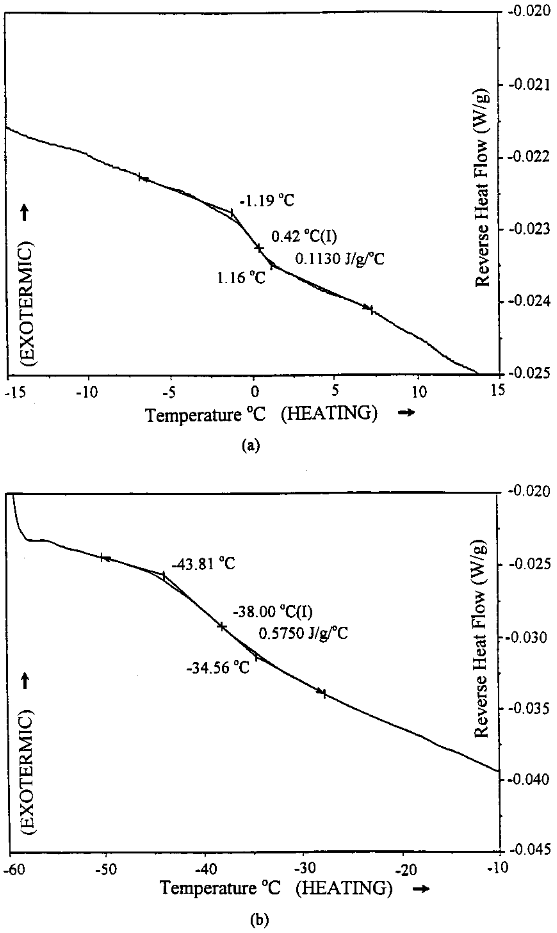

Figure 16. DSC thermograms of the pure components: (a) isotactic polypropylene; (b) EPDM.

two melting transitions because of the thermodynamic immiscibility of two polymers. The morphology of the TPV's was a microporous, apparently closed-cell polymeric foam. Phase contrast optical microscopy showed that the micro-heterogeneous EPDM domains in the polypropylene matrix from the thermoplastic vulcanizates prepared in supercritical propane were much smaller than those of the corresponding melt blends. This should result in improved physical properties for these materials (e.g., tensile strength), which we plan to investigate soon.

Acknowledgment. M.R. acknowledges U.S. Department of Energy Grant No. DE-FG 02-96ER12201.

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MA980153V