Macromolecules 1991, *24*, 561-566

Graft Copolymer Compatibilizers for Blends of Polypropylene and Ethylene-Propylene Copolymers

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Received April 12, 1990; Revised Manuscript Received June 27, 1990

ABSTRACT: A graft polymer with isotactic polypropylene (iPP) arms pendant from an ethylene-propylene (EP) copolymer backbone has been made and shown to effectively compatibilize EP/iPP blends. The synthesis is a two-stage process. In the first step, an ethylene-propylene-diene terpolymer (EPDM) is made, using a diene such as vinylnorbornene so that there are unreacted double bonds well removed from the backbone. These are important for the second step, during which iPP chains are grown through these double bonds to form the graft polymer. This grafting has been demonstrated by infrared spectroscopy, fractionation, and thermal analysis. The addition of a small (<10%) amount of this graft polymer to an iPP/EP blend has a large effect on its morphology and properties. The size of phase domains shrinks by a factor of 4, and low-temperature impact strength doubles. Thus, such graft polymers work well as interfacial agents or compatibilizers to improve blend properties.

Introduction

The field of polymer blends is developing rapidly, both in terms of scientific understanding and in terms of commercial utility. The long-chain nature of polymers leads to two factors that make the micron-scale structure of these mixtures important. First, the entropy of mixing for macromolecules is very small, so that most pairs of polymers are immiscible or insoluble in each other. However, their chain structure also makes the dynamics of these mixtures very slow, so that complete phase separation takes a very long time. The combination of these two factors means that most polymer blends have a morphology of phase domains separated on the scale of 0.1-10 μm. The physical properties (mechanical, transport, and optical) of these materials depend crucially on this structure, and the synergistic benefits of blending derive from blend morphology.

Among the largest classes of polymer blends in use today are the mixtures of isotactic polypropylene (iPP) and ethylene-propylene copolymer (EP). Useful materials are obtained from blends over nearly the whole range of composition.[1-4] Blends with a small percentage of EP rubber are a toughened version of iPP, while those with a majority of EP are thermoplastic elastomers. In between a wide variety of stiffness, toughness, and other physical properties can be obtained by choosing the proper composition. Thus it is easy to see why these blends have become so important.

As stated above, the physical properties are not just a function of the blend composition but also depend on the morphology of the blend and how it was made. This is because these blends are immiscible, at least below the crystallization temperature of iPP[5] and generally in the melt as well.[6-8] They therefore exhibit a two-phase morphology, and the sizes, shapes, and continuity of the phase domains determine the properties of the blend. Control of morphology is therefore control of properties.

One of the ways to obtain such control is through the use of "compatibilizers", block or graft polymers that act as interfacial agents in polymer blends.[9-11] These molecules are found at the interface[10,12] because part of the compatibilizer is miscible with one component, and part with the other; usually, but not always, the blocks of the compatibilizer are identical with the components. There are two effects of the presence of the compatibilizer at the interface: the adhesion between the phases increases,[12] and the interfacial tension, γ, between them decreases. At some level of compatibilizer incorporation γ drops to zero, so there is some finite, equilibrium size of the domains. Even when γ is nonzero, the fact that it is lower means that a finer dispersion of the phases can be achieved during intensive mixing.[13-15] The smaller phase size plus the increased phase adhesion results in improved physical properties such as impact strength[10,16,17] and tensile strength.[18]

The difficulty in making such compatibilizers for iPP/EP blends lies in the different natures of the two polymers and the ways by which they are polymerized. iPP is a semicrystalline thermoplastic because it is made with a heterogeneous catalyst that produces stereoregular incorporation of propylene monomer. The EP copolymers are made with homogeneous catalysts that produce no stereoregularity, thus making them amorphous elastomers. Moreover, the Ziegler-Natta catalysts used to make these polyolefins do not exhibit polymerization kinetics that facilitate block polymer synthesis. Even the so-called "reactor block copolymer" polypropylenes are actually blends of iPP, EP, and sometimes polyethylene.[19] Thus, even though compatibilization of EP/iPP blends would give materials with improved properties, it has not been possible previously to practice this.

In this paper the synthesis of an EP-*graft*-iPP polymer is demonstrated. This is a two-step process in which the EP part is made first and then the iPP is grown from it in the second step. Several methods are used to prove that a graft polymer has been made, and finally its utility as a compatibilizer for EP/iPP blends is shown.

Experimental Section

Materials. The polymers used in the blends with the graft copolymer are commercial EP's and iPP's from Exxon Chemical Co. The EP is Vistalon 457, containing 43 wt % ethylene and having a Mooney viscosity (M_L 1+8 at 127 °C, ASTM D-1646) of 25. This corresponds to an M_n of ca. 54 000. The iPP's are PP5052, which has a melt flow rate (MFR) of 1.2 g/10 min (ASTM

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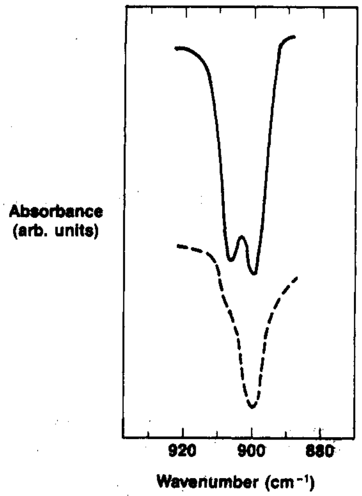

Figure 1. Infrared spectra (curves, arbitrary absorbance units): (a) iPP/VNB–EPDM blend (—); (b) EP-*graft*-iPP copolymer, VG (- - -).

D-1238) and a density of 0.90 g/cm^3, and E115 (MFR = 5.0 g/10 min and density = 0.90 g/cm^3). $TiCl_3$ was obtained as Stauffer AA from Stauffer Chemical Co., Westport, CT. Triethylaluminum and ethylaluminum sesquichloride were obtained from Texas Alkyls Co., Baton Rouge, LA. 5-Vinyl-2-norbornene (VNB), 1,5-hexadiene, and dicyclopentadiene were obtained from Aldrich Chemical Co., Milwaukee, WI.

Polymerizations. VNB–EPDM. A 1-L continuous-flow stirred tank reactor (CFSTR) was operated at 35 °C and 500 kPa with continuous agitation at 1200 rpm. A feed stream comprising 3.37 kg/h of hexane, 90.99 g/h of ethylene, 549 g/h of propylene, and 3.38 g/h of VNB was continuously fed to the CFSTR. The catalyst system was comprised of $VOCl_3$ and ethylaluminum sesquichloride (EASC) at an Al/V molar ratio of 5. $VOCl_3$ was added at 0.1348 g/h and EASC at 0.481 g/h. The average residence time in the CFSTR was ca. 9.5 min. Hydrogen (300 ppm) was added to act as a chain-transfer agent. An ethylene–propylene–diene terpolymer (EPDM) containing 44.52 wt % ethylene (as measured by IR), 52.68 wt % propylene, and 2.83 wt % VNB (by refractive index[20]) was produced. The product has a Mooney viscosity (M_L 1+8 at 100 °C) of 21.0 and M_n of ca. 30 000 as measured by GPC. IR film spectra of the polymer showed a band at 906 cm^{-1}, indicating the incorporation of VNB.

VNB–EPDM-*graft*-iPP (VG). The EPDM-containing effluent from the reaction described above was scavenged free of vanadium catalyst residues by passage through a column of activated silica before being fed into a second reactor, this time a batch reactor. About 30 g of the VNB–EPDM in hexane was introduced along with the second catalyst system, with heat being added to increase the temperature to ca. 50 °C. The catalyst was $TiCl_3$, Stauffer AA, and the cocatalyst was triethylaluminum (TEA). About 2 g of Stauffer AA was added; the molar ratio of Al to Ti was ca. 2. Gaseous propylene monomer was then added continuously over a period of ca. 30 min until 30 g of propylene had been added. About 3–4 mol % of ethylene, based on the propylene amount, was introduced along with the VNB–EPDM, resulting in addition of 1 g of ethylene. The reaction mixture thus formed was stirred and allowed to react over a period of ca. 2 h. The final product had an ethylene content of 8.9%. Infrared analysis of the product showed evidence of grafting, in that the peak at 906 cm^{-1} greatly decreased. This can be seen in Figure 1, which compares the 880–930-cm^{-1} region of a blend of iPP and VNB–EPDM with that of VG. The ratio of that peak to the ethylene peak at 720 cm^{-1} decreased from 0.32 for the VNB–EPDM to 0.05 for VG.

Synthesis of 5-(3-Butenyl)-2-norbornene (BNB). The dicyclopentadiene was slowly cracked to cyclopentadiene in a distillation column packed with glass beads at 140 °C. The cracked cyclopentadiene was kept under an atmosphere of N_2 at −40 °C until used. The 1,5-hexadiene was distilled from sodium before use. The Diels–Alder addition of 1,5-hexadiene and cyclopentadiene was carried out in a 1:1 molar ratio in a 330-mL Hoke bomb. The bomb was equipped with an internal thermocouple, which controlled the external heating rate, and a pressure gauge. Before introduction of the reactants, the bomb was dried and purged with N_2 gas. Cyclopentadiene (102.5 mL, 82 g, 1.24 mol), 1,5-hexadiene (147.5 mL, 102.1 g, 1.24 mol), and *tert*-butylcatechol (0.1 g) as an antioxidant were added to the bomb, which was sealed and heated in an isothermal oil bath at 200 °C for 10 h. At the end of this period, the internal bomb pressure had dropped to 60% of its original value. The products of the reaction were distilled to yield 100 mL of a liquid mixture distilling at 180–190 °C and 760 mmHg. Gas chromatographic analysis indicated that this was ~72% BNB, ~2% cyclopentadiene, ~15% dicyclopentadiene, and ~7% 1,5-hexadiene. This product was redistilled at 175–180 °C and 760 mmHg to yield a liquid fraction that by gas chromatography contained >95% BNB. The yield in this entire synthesis was 54%. The product was identified by ^{1}H NMR, which showed the appropriate olefinic proton resonances, and by IR, which indicated a strong band at 915 cm^{-1} characteristic of α-olefins. The exo/endo ratio by GC of the isomers of BNB was near 4:1.

BNB–EPDM. The procedures for the polymerization using the BNB diene monomer were essentially the same. Into a 1-L CFSTR operated at 35 °C and 500 kPa and agitated at 1200 rpm were continually introduced 3.37 kg/h of hexane, 75.8 g/h of ethylene, 472 g/h of propylene, and 3.77 g/h of BNB as monomer feeds and diluent. The catalyst system used was an in situ mixture of $VOCl_3$ and EASC at an Al/V molar ratio of 10; $VOCl_3$ was added at 0.1887 g/h, and EASC was added at 0.676 g/h. In addition, NH_3 was also added to the reactor to act as a cationic branching suppressor at the rate of 2 mol of ammonia per mol of vanadium; also, 350 ppm of H_2 was added to act as a chain-transfer agent. The reactor produced 139 g of EPDM per hour, and an analysis indicated that it was 45.8 wt % ethylene (by IR), 51.5 wt % propylene, and 2.7 wt % BNB (by refractive index[20]). The film IR spectrum showed a band at 910 cm^{-1}, indicating the incorporation of BNB.

BNB–EPDM-*graft*-iPP (BG). The effluent from the above reaction was introduced into a 3.785-L CFSTR to which 200 g of propylene was added per hour. The catalyst system was Stauffer AA/TEA, and 2 g/h of Stauffer AA suspended in hexane was added. The Ti/Al ratio was maintained at 1/10 by the continuous addition of 11.5 g/h of TEA. The temperature of the reactor was maintained at 40 °C, and 217 g of polymer was collected from this reactor per hour. Analysis of the polymer indicated that 38.0 wt % was ethylene. The film IR indicated (i) the presnce of iPP and (ii) diminished intensity for the 910-cm^{-1} terminal α-olefin band, indicating successful incorporation of the BNB double bonds.

Equipment and Analysis. Solution Blending. The blends used in the fractionation and microscopy parts of this study were prepared from solution. The compositions of the blends are shown in Table III. All of the components (iPP, EP, and VG) were dissolved in 1,2,4-trichlorobenzene at 200 °C to form a 1% solution. After ca. 2 h of mixing, the solution was added to an excess of methanol at 2 °, and the precipitated polymer was recovered.

Melt Blending. The impact strength measurements described below were made on blends prepared in the melt. In order to ensure good mixing, this was done in two stages. First, a small blend with a majority of elastomer (MB1 and MB2; see Table III for compositions) was prepared with the CSI-MAX screwless extruder (Custom Scientific, Whippany, NJ). This was then let down into more polypropylene in a Midget Banbury and mixed at 200 °C for 3 min (MB3 and MB4). Such a "master batch" scheme of mixing is well-known to give a good dispersion of rubber in plastic.

Graft Polymer Characterization. Fractionation. All of the extractions were performed in Kumagawa (Soxhlet) devices. A small amount (5–10 g) of the polymer was placed in a steel mesh bag hung over the refluxing solvent. The insoluble fraction was that which remained in the bag above, and the soluble fraction was recovered from the solution below. The fractionations were performed somewhat differently on VG than on BG. A sample of VG was first fractionated with heptane, and then a xylene fractionation was done on the heptane-insoluble fraction (subsequent fractionations). On the other hand, three separate

Table I
Composition of VG Fractions[a]

fraction	x_f	x_e	w_{EPDM}	y_{EPDM}	y_{PP}
original	100.0	8.9	20.0	100.0	100.0
heptane soluble	59.0	16.0	33.9	100.0	48.7
xylene soluble	99.6	8.9	20.0	100.0	100.0

[a] x_f = percentage of original sample in this fraction; x_e = ethylene content (weight percent) in fraction; w_{EPDM} = percentage of fraction that is EPDM; y_{EPDM} = percentage of EPDM that is in this fraction; y_{PP} = percentage of iPP is in this fraction.

Table II
Composition of BG Fractions[a]

fraction	x_f	x_e	w_{EPDM}	y_{EPDM}	y_{PP}
original	100.0	38.0	83.0	100.0	100.0
hexane soluble	27.5	45.8	100.0	36.7	0.0
heptane soluble	75.2	37.7	82.3	74.6	78.3
xylene soluble	85.7	37.2	81.2	83.9	94.7

[a] x_f = percentage of original sample in this fraction; x_e = ethylene content (weight percent) in fraction; w_{EPDM} = percentage of fraction that is EPDM; y_{EPDM} = percentage of EPDM that is in this fraction; y_{PP} = percentage of iPP that is in this fraction.

samples of BG were fractionationed in hexane, heptane, and xylene, and the results of these three fractionations were compared (separate fractionations).

Dynamic Mechanical Thermal Analysis. The thermal analysis of the polymers was performed on a Polymer Labs DMTA dynamic mechanical thermal analyzer at 3 Hz. Each sample was a bar of ca. 1 g with dimensions 1 cm × 4 cm × 0.25 cm. After mounting, the samples were quenched to -85 °C and then heated at 2 K/min to 200 °C during the measurement. The elastic modulus (E'), loss modulus (E''), and loss tangent (tan δ) were all measured once per K.

Electron Microscopy. The morphology of the blends was examined by scanning electron microscopy (SEM). The imaging contrast was provided by removing the EP with hexane. First the samples were compression molded, and then they were sectioned with a Reichert-Jung FC-4 ultramicrotome. The hexane-soluble EP was extracted at room temperature in a sonic bath. A JEOL 35C SEM was used to examine these prepared samples.

Impact Strength. The impact strength of the blends was measured by using ASTM D256, Method A. The blends were injection molded at a temperature of 200 °C, and five samples of each blend were tested at each of the temperatures shown in Table III. The low-temperature measurements were obtained by cooling the samples in a bath at the desired temperature, transferring them rapidly to the tester, and submitting them to the impact before time for any significant warming.

Results

Fractionation. Fractionation with several solvents, followed by characterization of the fractions by infrared spectroscopy and thermal analysis, was used to identify the presence of graft polymer. If no grafting takes place, all of the EPDM will be found in one fraction, and all the iPP in another. This has been confirmed many times in our laboratories by performing such fractionations on simple blends of EPDM and iPP. On the other hand, if some grafting does occur, some of the product will show up in intermediate fractions, and the more this occurs, the more complete the grafting is. The degree of grafting can be determined from the amount and composition of the various fractions.[21]

The results from the fractionation of VG and BG (Tables I and II) clearly show that there was a significant amount of grafting in both cases. About 20% of VG came from the VNB–EPDM, and 80% was iPP made in the second reactor. All of the EPDM showed up in the heptane-soluble fraction of VG, but so did nearly half of the iPP. The IR spectrum for this fraction confirmed this by showing a strong signal (e.g., at 900 cm^{-1}) for iPP. Since <1% of the iPP by itself would be soluble in heptane,[19] this means that about half of the iPP was grafted onto the EPDM. Not all of the EPDM backbone chains necessarily had iPP grafts on them, but certainly the great majority did. The other 40% of VG was pure iPP, insoluble in heptane but soluble in xylene. This was the iPP grown in the second reactor which did not attach to the EPDM chains. The lack of any significant xylene-insoluble fraction indicates that there was no gelation in this synthesis. The presence of grafting in VG was also indicated by the decrease in the IR peak for the VNB unsaturation at 906 cm^{-1}. Thus, the majority of VG is an EPDM-*graft*-iPP copolymer.

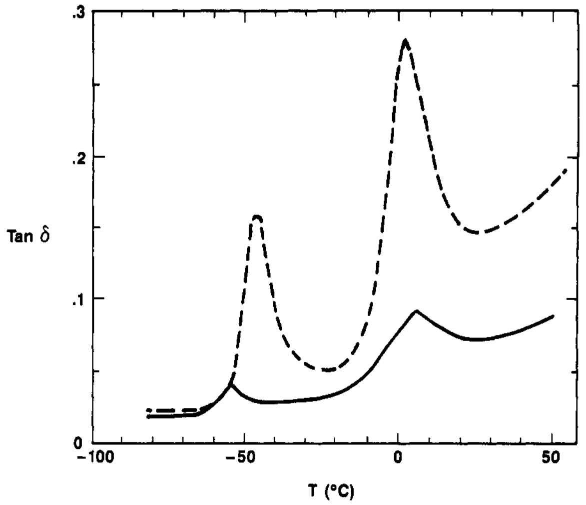

Figure 2. Loss tangent (tan δ) vs temperature by DMTA: (a) 80/20 iPP/EP blend (—); (b) EP-*graft*-iPP copolymer, VG (- - -).

BG also had a significant amount of grafting, albeit with some differences from VG. First of all, BG was mostly (83%) EPDM. The hexane-soluble fraction of BG was pure EPDM, having a little more than a third of the EPDM put into the second reactor. However, most of the EPDM was contained in the hexane–insoluble fraction, meaning that its solubility had been changed by the grafting of iPP arms. The most telling point is to look at the results in Table II for the fraction that was insoluble in hexane but soluble in heptane. If no grafting had occurred, there would have been little or none of this fraction. Instead, it contained ca. 40% of the EPDM and 80% of the iPP. Thus, most of the EPDM and nearly all of the iPP are found in graft copolymer. This was confirmed by the decrease in the IR peak for BNB unsaturation as well. The presence of a significant (14%) xylene-insoluble fraction shows that a sizable amount of gel was formed.

Dynamic Mechanical Thermal Analysis. More evidence for grafting can be found in the thermal behavior of VG and especially BG. Both theoretically[22] and experimentally,[23,24] it is well-known that block copolymers show more miscibility than blends; that is, a blend with components of a given molecular weight may be immiscible, while a block copolymer with arms of the same molecular weight and composition as the blend is homogeneous. The same should be true for graft polymers.[25] Thus any indication of miscibility or even enhanced compatibility in VG or BG would confirm their having a high degree of grafting.

Figures 2 and 3 show the comparison of the DMTA traces of VG and BG with PP/EP blends of the same or similar composition. The T_g's of EP and PP are clear in

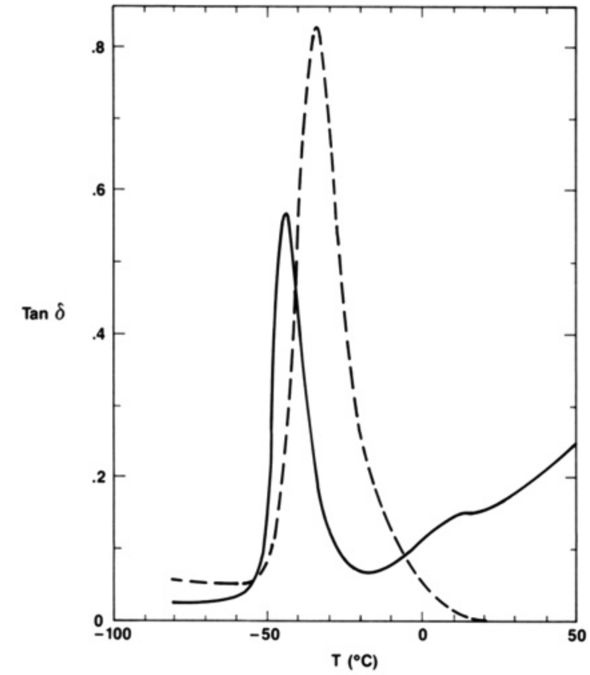

Figure 3. Loss tangent (tan δ) vs temperature by DMTA: (a) 30/70 iPP/EP blend (—); (b) EP-*graft*-iPP copolymer, BG (- - -).

the tan δ peaks near −50 and 0 °C, respectively. In Figure 2 it can be seen that the peaks for VG are sharper and somewhat closer together than are those for a blend of similar composition. Thus, it displays more compatibility than does the blend. Even more striking, Figure 3 shows that BG has only a single peak in between those of EP and iPP, near −35 °C, whereas the blend has two distinct transitions. By this measure BG seems to be single phase, at least down to the scale probed by the relaxations involved in the glass transition. This miscibility could occur without grafting if the iPP made in the second reactor were of a very low molecular weight, but this cannot be seen in GPC experiments. Thus, the DMTA data strongly suggest that VG and BG have a large amount of graft polymer.

Morphology. The structures of iPP/EP blends made with and without VG are shown in Figure 4. The blends were made in solution as described above, and the SEM micrographs shown were taken on the microtomed, extracted surfaces. The holes visible in Figure 4 are where the EP copolymer had been, and the remaining polymer was the hexane-insoluble iPP. Figure 4a shows the morphology of an 80/20 (by weight) blend of PP5052 and Vistalon 457. There is a wide range of sizes for the disperse EP domains, but the average size is ca. 2 μm. The blend in Figure 4b had a 72/18/10 composition of PP5052, Vistalon 457, and VG. The domains are clearly smaller than in the blend without VG, having an average size near 0.5 μm. Such a reduction in phase size can be attributed to the presence of the graft polymer at the interface of the blend.[10]

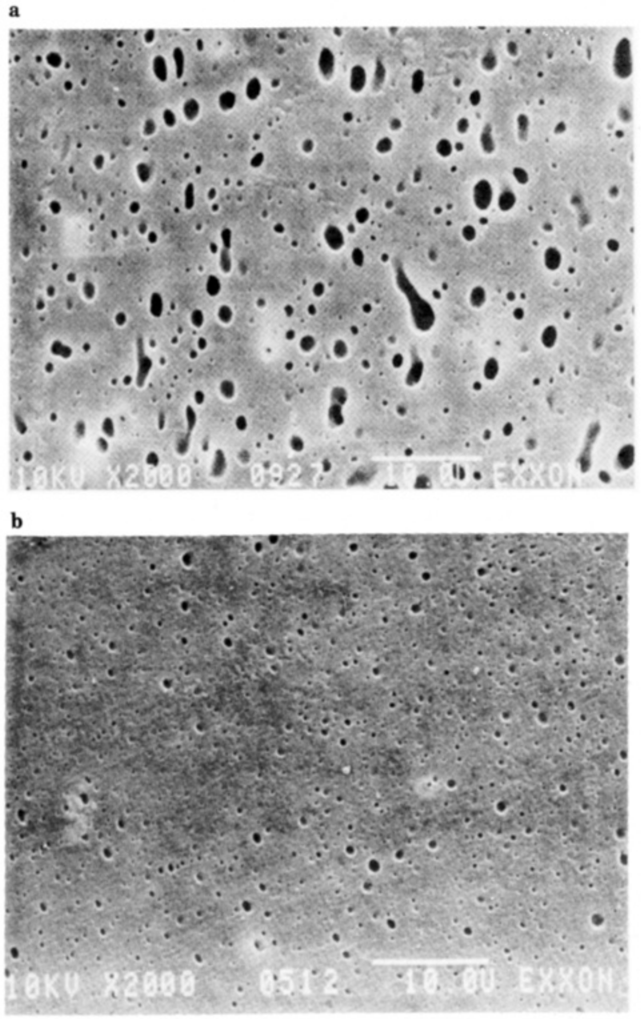

Figure 4. SEM micrographs of microtomed, hexane-extracted samples: (a) 80/20 iPP/EP blend; (b) 72/18/10 iPP/EP/VG blend.

Table III
Impact Strength

	MB1	MB2	MB3[a]	MB4[b]
composition, wt %				
PP E115	33.3	33.3	85.0	78.3
Vistalon 457	66.7	42.9	15.0	14.0
VG		23.8		7.7
overall % EPDM	66.7	47.7	15.0	15.5
Izod impact strength, J/m				
notched, 25 °C			75 ± 5	68 ± 7
notched, 0 °C			17 ± 3	30 ± 5
unnotched, −20 °C			285 ± 20	396 ± 24

[a] 77.5% PP E115, 22.5% MB1. [b] 67.5% PP E115, 32.5% MB2.

Impact Strength. Such a large reduction in the size of the disperse rubbery phase should cause a large change in physical properties, particularly the impact strength.[10,26] That this occurs with these graft polymers is shown in the data of Table III. All of the blends used in the Izod impact measurements were blended in the melt as described above. The first two blends, MB1 and MB2, were the master batches made on the small CSI-MAX screwless extruder. These blends were then mixed with more iPP in a Midget Banbury to arrive at the final blends, MB3 and MB4. This sort of two-step mixing scheme is known to result in a good dispersion of the rubber phase. As can be seen in Table III, the composition of MB4 was picked so that it would have about the same overall EP content as MB3; the only difference between the blends is the addition of VG to MB4. The impact strengths of the two blends are essentially the same at 25 °C, above the T_g of iPP. At this temperature iPP is still ductile, so compatibilization (i.e., smaller EP domain sizes and better phase adhesion) is not expected to have much effect on toughness.[16,17] Below its glass transition, however, MB4 has a much higher Izod impact strength than MB3; 76% larger at 0 °C and 39% larger at −20 °C. This improvement can be directly attributed to the presence of the graft polymer at the blend's interface, acting as a compatibilizer.

Discussion

The results described above show in several ways that graft polymers were made by this synthetic route:

(i) The decrease in diene unsaturation shown by IR shows that some of these bonds reacted during the second stage of the synthesis, presumably by being incorporated into the growing iPP chains.

(ii) The existence of fractions that had solubility intermediate between that of iPP and EP indicates that both EP and iPP were present in the fraction; this could only have happened if there were graft polymer molecules with EPDM covalently bound to iPP.

(iii) The DMTA results show an enhanced compatibility or even miscibility in the products of these reactions, which could only have come about by a linkage of the EPDM to iPP.

The differences in the results for VG and BG can be partly explained by the differences in the structures of the diene monomers and partly by the difference in how much iPP was made in relation to the EPDM feed. Since only a small amount of iPP was made in the case of BG, some EPDM was left without graft arms while essentially all of the iPP ended up in the graft polymer. On the other hand, since a large amount of iPP was made in VG, nearly all of the EPDM was grafted in this case but some homopolymer iPP remained. The formation of gel in BG, while it was absent for VG, could be due to the more accessible double bond from the BNB. The reason for using VNB and BNB as the dienes in the first step of this process was to make EPDM's with pendant double bonds as far removed from the backbone as possible. The unsaturation found in commercial EPDM, which is typically made by using dienes such as 1,4-hexadiene or ethylidenenorbornene, is much less accessible for further reaction than is that from the polymer described herein made with VNB and especially BNB. This also means that the BNB-EPDM should be more reactive than the VNB-EPDM, which is shown by the fact that more gel was present in BG than in VG (compare Tables I and II). Such an increase in reactivity, plus the higher concentration of EPDM in the second reactor, would increase the probability of the growth of an iPP chain through two or more pendant BNB double bonds, leading to some gelation.

The degree of grafting in VG and BG is difficult to determine directly. Molecular weight determinations, such as GPC, that have been useful to show that block copolymers have been formed are generally inconclusive for graft polymers. This is because molecular volume does not greatly increase when branches are grafted on, whereas it does for the addition of blocks to a linear polymer. However, a good estimate can be obtained from the fractionation data. The amounts of each fraction (Tables I and II) can be used to provide upper and lower bounds on the grafting efficiency, but the possibility that any of the fractions might contain ungrafted materials must always be kept in mind. Thus for VG an upper bound on the amount of graft polymer is 60%, since the heptane-insoluble fraction is all iPP. Since whatever iPP is in the heptane-soluble fraction must be grafted, 40% is a lower bound. Most likely between 50 and 55% of VG is graft polymer.

Similarly, the hexane-soluble fraction of BG contains only EPDM and so no graft polymer. The xylene-insoluble fraction is gel, so that even though this is most likely covalently bound EPDM and iPP, this cannot be counted as graft polymer either. This puts an upper limit of 59% on the grafting efficiency in BG. Since nearly all of the upgrafted EPDM would be soluble in hexane, and the ungrafted iPP insoluble in heptane, the lower limit in nearly the same. So again ca. 50–55% of BG is probably graft polymer.

The presence of a large amount of graft polymer in VG is also supported by the demonstration of its effectiveness as a compatibilizer. The fact that a small (<10%) amount of it could dramatically affect the morphology and toughness of a blend strongly indicates that there is an interfacial agent or compatibilizer in VG. The amount of graft polymer in VG is hard to estimate from its compatibilizing efficiency, because so little compatibilizer is needed to have such large effects.[10] Given the estimates of grafting efficiency above, however, it is not unreasonable to expect the effects seen in Table III from the presence of 3.5–4% of graft polymer.

The synthetic schemes described in this paper have not been optimized for the highest level of grafting efficiency. There are several parameters here that could be adjusted to increase the amount of graft polymer made beyond the 50% level in these two examples. The type of diene used in the production of the EPDM in the first reactor, especially the structure of the secondary double bond, could be changed, as well its level of incorporation into the polymer. The relative amounts of EPDM and iPP made in the two reactors could also be varied to control the degree of grafting. Beyond these there are also the usual reactor conditions of temperature, concentration, residence time, etc., which could also be adjusted to optimize the grafting efficiency. However, it should also be recognized that it is not crucial for application of the graft as a compatibilizer to have complete or nearly complete graft formation. Since the product of this reaction will be mixed with an EP/iPP blend for use as a compatibilizer, the presence of ungrafted iPP or EPDM will not worsen the properties of the compatibilized blend. Thus, the consideration of the best conditions for conducting such a synthesis is not just the efficiency of the grafting alone, but rather the efficiency of the whole compatibilization process.

Conclusions

The synthesis of graft polymers with iPP arms pendant from an EPDM backbone and their use as compatibilizers in EP/iPP blends have been described in this paper. This is a two-step process, where EPDM is made in one reactor and is then fed to a second in which iPP grows through the unreacted double bonds of the diene, forming the graft polymer. The formation of a significant (>50%) amount of graft polymer in this way was shown by spectroscopy, fractionation, and thermal analysis. The synthesis was further confirmed by the demonstration of its utility as a compatibilizer. The addition of the graft polymer as a minor component to an EP/iPP blend reduced the sizes of phase domains by more than 4 times and double low-temperature impact strength. Thus, the synthetic procedure outlined herein has been shown to produce EP-*graft*-iPP polymers that are effective compatibilizers for EP/iPP blends.

Acknowledgment. This work could not have been performed without the help of a number of people at Exxon. F. T. Morrar is thanked for his work on the synthesis of the EPDM's and the graft polymers, as are E. Janiec and H. Morcos for the analysis of the graft polymers and their fractions. L. Ban and J. Oskam provided the microscopy analysis of the blends. Finally, discussions with M. J. Doyle and G. R. Smith were important in the development and execution of this work.

References and Notes

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Registry No. iPP, 25085-53-4; BNB, 5235-56-3; EASC, 12075-68-2; EPDM (copolymer), 27155-45-9; TEA, 97-93-8; $VOCl_3$, 7727-18-6; $TiCl_3$, 7705-07-9; (ethylene)(propylene)(VNB) (graft copolymer), 130548-42-4; (ethylene)(propylene)(BNB) (copolymer), 7705-07-9; 1,5-hexadiene, 592-42-7; cyclopentadiene, 542-92-7; (ethylene)(propylene)(BNB) (graft copolymer), 130434-97-8.