

Shear Flow Behavior and Oil Distribution between Phases in Thermoplastic Vulcanizates

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ABSTRACT: The high rate shear flow behavior and the morphology of five different oil-extended polypropylene (PP)/ethylene-propylene-diene monomer (EPDM) thermoplastic vulcanizate blends were investigated with the melt flow rate (MFR) of the PP varying from 0.7 to 20. The ratio of rubber to PP is 70 : 30 in three of the thermoplastic vulcanizates (TPVs) and 50 : 50 in the other two TPVs. The distribution of the high-temperature oil between the PP melt and the rubber is a key parameter because this will affect the viscosity of the PP/oil medium. The object of this study was to estimate the matrix composition in each of the TPVs at processing temperatures and to compare the shear viscosity of the effective matrix with that of the TPV. To this end, several PP/oil mixtures were prepared and their viscosity curves were correlated with the neat PP melt viscosity

curves by means of shift factors varying with oil concentration. The oil distribution between the PP and rubber phases was estimated from TEM micrographs of the TPV blends. The results show that the PPs are mixed with oil to different proportions in the different TPVs and the viscosity curves of these mixtures exhibit the same trends in magnitude as the corresponding TPV viscosity curves. Hence, the shear flow of TPVs can be understood more readily in terms of the effective PP/oil medium flow behavior than in terms of the neat PP melt flow. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 113–121, 2004

Key words: elastomers; swelling; polypropylene; rheology; morphology

INTRODUCTION

Thermoplastic vulcanizates (TPVs) consist of finely dispersed, micron-sized, crosslinked rubber particles in a thermoplastic matrix.^{1,2} These blends are produced by crosslinking of large proportions of rubber *in situ* during the mixing step with thermoplastic melt in the presence of extender oil. The oil partitions between the rubber and the thermoplastic phases and swells both phases. In effect, the TPVs are two-phase blends of oil-soaked rubber particles in a thermoplastic–oil matrix. TPVs with a variety of properties can be produced by varying the matrix characteristics (such as molecular weight and polydispersity), the disperse phase characteristics (such as loading and cure level), and the type of extender oil added.^{1–3}

The rheology of polypropylene (PP)/ethylene-propylene-diene monomer (EPDM) TPVs without any oil extender was evaluated by several researchers.^{4–7} They report that the TPV has a yield stress that increases with the rubber loading and that the shear viscosity curve for the TPV is more strongly shear

thinning than for the neat PP melt. A few studies have evaluated the rheology of oil-extended TPVs with varying hardnesses due to rubber fraction or to the cure state of the rubber. Steeman and Zoeteliff⁸ found that the yield stress increased with decreasing TPV hardness, but at high shear rates, the shear viscosities were lower with decreasing hardness. The effect of EPDM cure state on the rheology of TPVs was investigated with PP/EPDM blends⁵ as well as with PP/EPDM/oil blends,⁹ by varying the amount of crosslinker added during dynamic vulcanization. The storage modulus and dynamic viscosity values at low-strain rates were found to be higher in blends with the rubber of a higher degree of cure.

The medium or matrix in flowing TPVs is a homogeneous mixture of a high-temperature oil and molten PP that must be identified carefully and characterized; this was not done in previous studies and was the object of the present study. The distribution of the oil between the PP melt and the rubber is a key parameter because this will affect the viscosity of the PP/oil medium. This study was carried out with five oil-extended TPV blends containing PP grades of different average molecular weights. New experimental data are presented on viscosity of PP/oil mixtures with varying oil concentrations. Results presented in the following sections show that the shear flow of

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TABLE I
Composition of TPV Blends

TPV	PP	Composition ^a EPDM/PP/oil	MFR (dg/min) of PP	M_w (g/mol) of PP	M_w/M_n of PP
A1	PP1	100/41/130	0.7	331,000	3.05
A2	PP2	100/41/130	20	159,000	3.2
A3	PP3	100/41/130	2.2	309,000	12.3
B1	PP4	100/100/130	1.6	302,000	4.14
B2	PP5	100/100/130	3.8	270,000	3.8

^a All TPVs contain 10 parts clay per 100 parts of EPDM.

TPVs can be understood more readily in terms of the effective PP/oil medium flow behavior than in terms of the neat PP melt flow.

EXPERIMENTAL

Materials

Experiments were conducted on five PP/EPDM/oil TPV blends, containing the same EPDM (Vistalon 3666 from Exxon Mobil, Baton Rouge, LA) but different grades of PP. The composition of the blends and the PP grades are summarized in Table I. The PPs are of different average molecular weights with melt flow rate indices (MFR) ranging from 0.7 to 20 (advanced Elastomer Systems, Akron, OH). Three of the blends (A1–A3) contain a 70 : 30 proportion by weight of crosslinked EPDM and PP, whereas the other two (B1–B2) contain equal proportions by weight of the rubber and PP. The cure level of the EPDM rubber is similar in all blends as the amount of curative added is the same. The total oil content is the same in all five blends: 130 parts of oil per 100 parts of EPDM. The oil is a paraffinic oil (SUNPAR 150M) from Sunoco (Tulsa, OK) with low volatility. It has an open cup flash point (ASTM D92) of 245°C and a boiling point of 384°C. The oil is absorbed by the PP melt in large proportions as reported by Ellul.³ In the melt state, the oil is partitioned between the PP and the EPDM phases. Upon cooling, the PP does not contain as much oil because the crystallized domains, which constitute roughly 45 to 50% of the PP, release the oil. Presumably, the oil released by the PP is absorbed by

the rubber, which has a large capacity for oil even at room temperature^{1,2} and no oil is exuded from the blends. The individual weight fraction and corresponding volume fraction for each component is listed in Table II. All TPVs contain 10 parts of clay per 100 parts by weight of EPDM. In addition to the TPVs and the neat PPs, PP/oil mixtures were prepared with each of the PPs at two different oil concentrations—16.6 and 30 vol % oil for determining the effect of oil on the viscosity of these mixtures.

Rheometry

The shear viscosity of all the materials used in this study was measured at 190°C over apparent shear rates up to 5600 s⁻¹ in a Gottfert Capillary Rheometer with a die that is 1 mm in diameter and 20 mm long. A die of this length was chosen because the data obtained with longer dies displayed significant viscous heating effects. Slip effects were not evident on Mooney plots¹⁰ of data obtained on dies of different diameters with fixed L/D.

Microscopy

Samples for inspection of the microstructure were prepared from 3-mm-thick rectangular plaques injection molded with an injection temperature of 190°C. Thin sections (70- to 100-nm-thick) were cryomicrotomed at -130°C from the plaques, stained by ruthenium tetroxide,¹¹ and then observed by transmission electron microscopy (TEM) at 25°C.

TABLE II
Component Volume Fractions in TPV Blends

Component	Volume fractions of components					
	Density (g/cm ³)		25°C		190°C	
	25°C	190°C	A1–A3 blends	B1–B2 blends	A1–A3 blends	B1–B2 blends
EPDM	0.86	0.83	0.37	0.30	0.34	0.28
PP	0.905	0.757	0.14	0.29	0.15	0.31
Oil	0.875	0.765	0.47	0.39	0.49	0.40

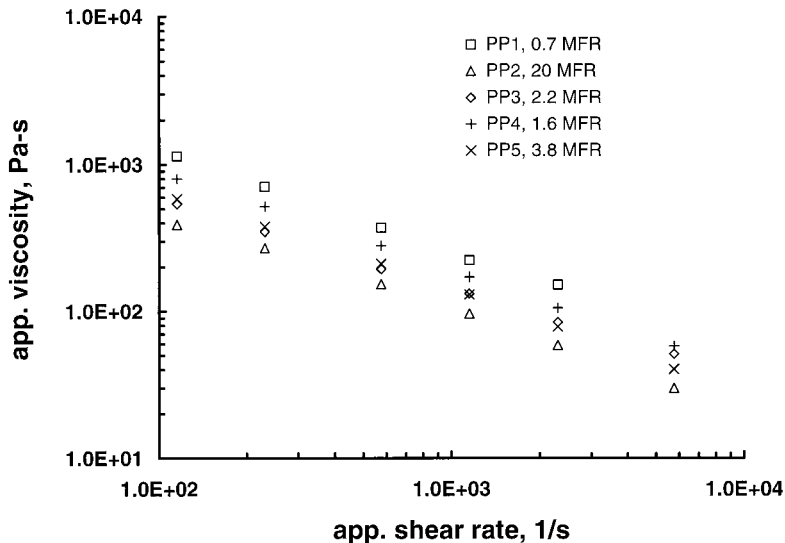


Figure 1 Shear viscosity curves at 190°C for five neat PP melts.

Image analysis

The volume fraction and the morphology of the swollen rubber particles in representative TEM micrographs of each TPV blend were determined by using commercial image analysis software (SigmaScan Pro 5.0, SPSS Inc.). The boundary of each particle in the micrograph was manually outlined by using the software, which then returned the projected particle area, the lengths of major and minor axes, aspect ratio, and the shape factor. The accuracy of estimating projected area fraction from a representative image was evaluated by analyzing images of four different sections from a TPV. TEM micrographs of four different sections, containing a total of 290 swollen rubber

particles, were analyzed. The projected area fraction of the swollen rubber phase in each section was found to be within $\pm 4\%$ of the average value over all sections.

The true volume fraction is usually smaller than the projected area fraction estimated from TEM micrographs. The well-known correction factor for spherical particles^{12,13} can be modified for the prolate ellipsoidal rubber particles obtained here as

$$\phi_{vol} = \phi_A \left(1 + \frac{3t}{4b}\right)^{-1} \tag{1}$$

where t is the thickness of the TEM section and b represents the minor axis of the prolate ellipsoid. The

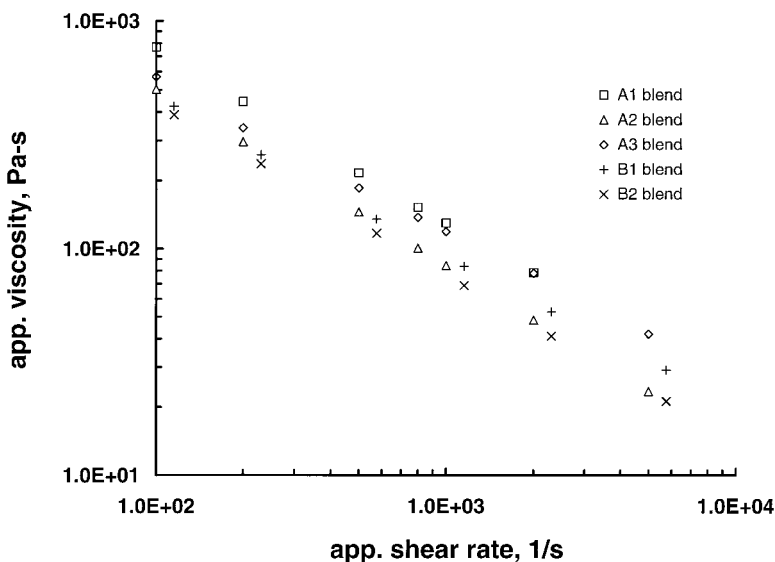


Figure 2 Shear viscosity curves at 190°C for three TPVs with 70 : 30 EPDM/PP ratio (A1–A3) and two TPVs with 50 : 50 EPDM/PP ratio (B1–B2).

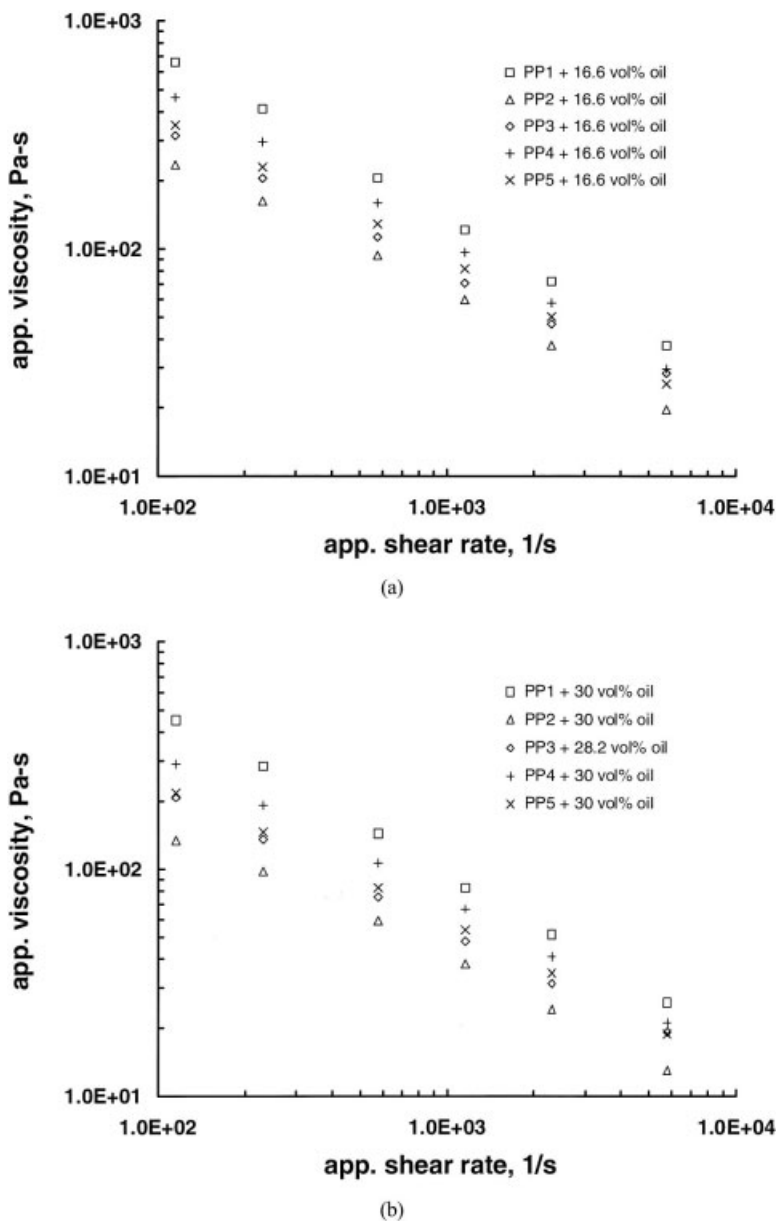


Figure 3 Shear viscosity curves at 190°C for PP/oil mixtures containing (a) 16.6 vol % oil, (b) 30 vol % oil.

number-average particle dimensions l and b were tabulated along with a shape factor, S_p , which was estimated as

$$S_p = \frac{1}{N} \sum \frac{P_i^2}{4\pi A_i} \quad (2)$$

where A_i and P_i are the projected area and perimeter, respectively, of individual particles. The shape factor $S_p = 1$ for a spherical particle and $S_p > 1$ for non-spherical particles. The shape factor was used here to quantify the extent of stretch of the swollen rubber phase, with a larger S_p value indicating a greater extent of stretch.

RESULTS AND DISCUSSION

Shear viscosity of TPVs, PPs, and PP/oil mixtures

The apparent shear viscosity is plotted against apparent shear rate for the five PP grades (with MFR ranging from 0.7 to 20) in Figure 1. The shear viscosity differs by a factor of 3 over these grades. The apparent shear viscosity curves for the five TPVs are presented in Figure 2. These curves are more shear thinning than the corresponding viscosity curves for neat PP melts; for example, the power law index $n = 0.23$ for A1 in contrast to $n = 0.34$ for the corresponding PP. Furthermore, the curves for the TPV blends are closer together, differing only by a factor of 1.7 or less. As

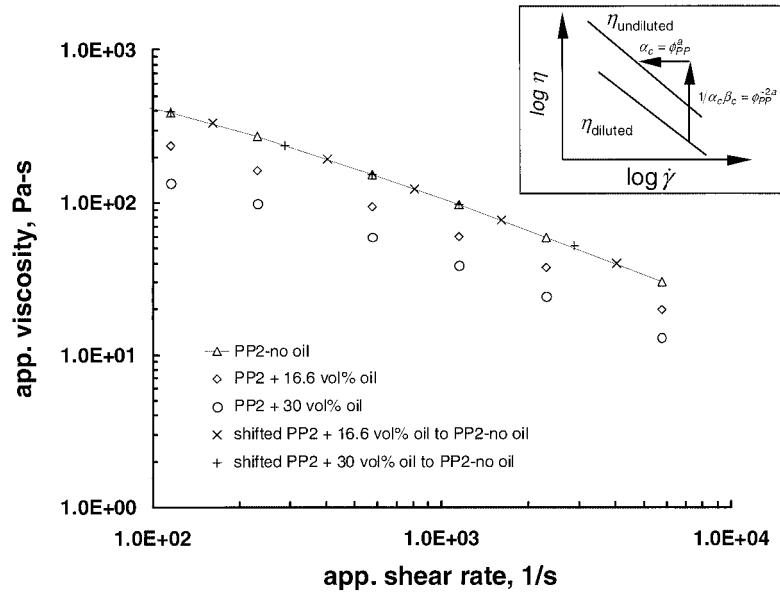


Figure 4 Demonstration of shifting procedure for viscosity curves at 190°C with oil concentration. The inset shows the vertical and horizontal shifts from the diluted polymer to the undiluted polymer.

noted above, the PP melt is mixed with oil to form the medium. The distribution of oil between the two phases at processing conditions must be analyzed to estimate the oil mixed in the medium; this will be done in a later section from image analysis of TEM micrographs.

The shear viscosity curves for PP/oil mixtures containing 16.6 and 30 vol % oil were obtained experimentally. These curves are presented in Figure 3(a, b). These curves can be related systematically to the corresponding neat PP melt viscosity curves by a shifting procedure patterned after the work of Nakajima and Harrel.¹⁴ They correlated the effect of oil concentration on the dynamic viscosity of elastomers in terms of two concentration-dependent shift factors α_c and β_c applied to the viscosity and shear rate as

$$\eta_{PP+oil} = \eta_{PP} \alpha_c \beta_c, \quad \dot{\gamma}_{PP+oil} = \dot{\gamma}_{PP} \alpha_c^{-1} \quad (3)$$

When the oil concentration is 0, $\alpha_c = \beta_c = 1$. Figure 4 demonstrates the success of this shifting procedure for mixtures of the 20 MFR grade PP with oil. The two shifts in eq. (3) are demonstrated graphically in the inset. Good fits were obtained by taking $\alpha_c = \beta_c$ in all cases. This is probably because the power law index and the extent of shear thinning of the PP/oil mixtures are very close to those of the corresponding neat PP melts in almost all cases. The values of the shift factors over oil concentrations up to 30% could be described by a power law relation of the form

$$\alpha_c = \beta_c \approx (\phi_{PP/PP+oil})^a \quad (4)$$

where $\phi_{PP/PP+oil}$ is the volume fraction of PP in the PP/oil mixture and the exponent a ranges from 1.9 to 2.1 (see Table III). A similar power law relation was found by Graessley and Edwards¹⁵ to correlate shift factors for the modulus of a polymer modified by a diluent.

Morphology analysis

TEM micrographs of representative sections from the three 70 : 30 blends are presented in Figure 5 and from the two 50 : 50 blends in Figure 6. The micrographs show densely packed swollen rubber particles in the 70 : 30 blends and relatively less packed swollen rubber particles in the 50 : 50 blends. The results of the image analysis of the TEM micrographs are presented in Table IV, along with the number of particles analyzed, the projected area fraction, the corrected volume fraction, the average particle dimensions, and the

TABLE III
Shift Parameter ($\alpha_c = \beta_c$) and Exponent a [see Eq. (4)]
for Various PPs

PP	MFR	Shift parameter ($\alpha_c = \beta_c$)		a
		16.6 vol % oil	30 vol % oil	
PP1	0.7	0.64	0.49	2.02
PP2	20	0.70	0.50	1.96
PP3	2.2	0.68	0.50 ^a	2.09
PP4	1.6	0.64	0.48	2.08
PP5	3.8	0.69	0.51	1.91

^a This mixture had 28.2 vol % oil.

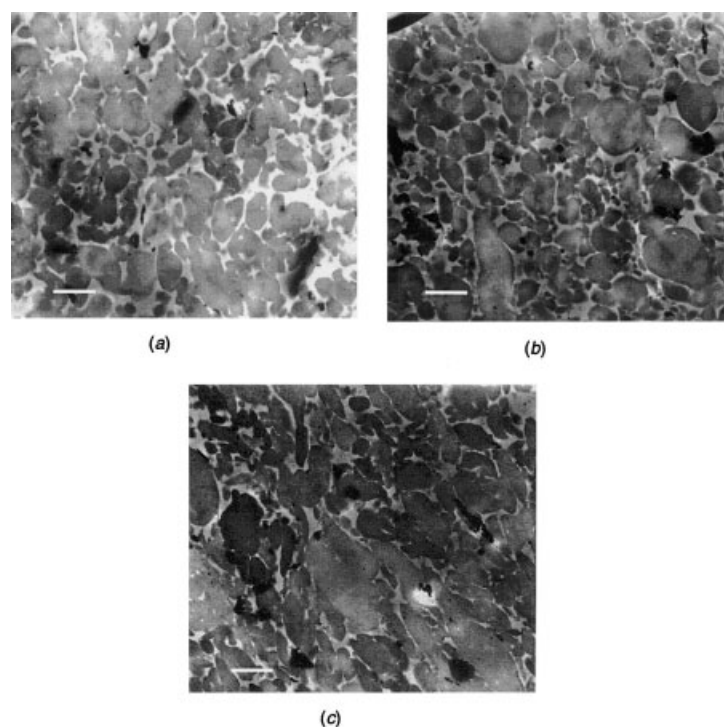


Figure 5 Transmission electron micrographs of three 70 : 30 TPV blends: (a) A1, (b) A2, and (c) A3. The dark regions represent the swollen rubber phase. The scale bar in each micrograph is 2 μm .

shape factor representing the extent of stretch—all at 25°C.

The projected area fractions of the swollen rubber phase were identical ($=0.75$) for the A1 and A2 blends, where the polydispersity of the corresponding PPs were similar. In the A3 blend where the PP polydispersity is much higher, the projected particle area fraction of the swollen rubber is noticeably higher at 0.80. The shape factor is highest in the A3 blend, followed by A1 and A2. The 70 : 30 TPV with the broad molecular weight distribution PP (MFR = 2.2) contains the most swollen rubber; hence, it is the most readily stretched. The 70 : 30 TPV with the lowest molecular weight PP (MFR = 20) contains the least swollen rubber with the least stretched particles. This

indicates that the more viscoelastic medium combined with the greater particle volume leads to the greatest stretching of the particles. The swollen rubber area fractions in B1 and B2 are identical (projected area fraction = 0.61). Once again, the particles in B1 with the high molecular weight PP are larger and more stretched than in B2 with the lower molecular weight PP. After correcting for the projection error, the swollen rubber volume fractions range from 0.70 to 0.75 for 70 : 30 blends and from 0.56 to 0.57 for 50 : 50 blends. In general, the TPV containing a PP grade that is more viscous and/or more viscoelastic was found to contain swollen rubber particles that are larger in size and more stretched during the dynamic vulcanization process.

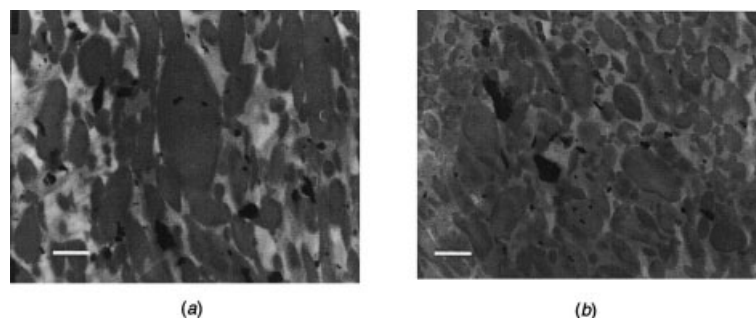


Figure 6 Transmission electron micrographs of two 50 : 50 TPV blends: (a) B1 and (b) B2. The scale bar in each micrograph is 2 μm .

TABLE IV
Results of Image Analysis on Swollen Rubber Morphology in TPVs at 25°C

TPV	No. of particles N	Area fraction of swollen rubber ϕ_A	No. avg. major axis length l	No. avg. minor axis length b	Shape factor S_p	Volume fraction [see Eq. (1)] $\phi_{EPDM+oil}$	Swell ratio $\frac{\phi_{EPDM+oil}}{\phi_{EPDM}}$
A1	71	0.75	2.50	1.44	2.5	0.72	2.05
A2	122	0.75	1.89	1.03	2.2	0.70	1.99
A3	71	0.80	2.91	1.34	2.9	0.75	2.16
B1	100	0.61	2.35	0.89	2.1	0.56	1.94
B2	263	0.61	1.23	0.67	1.5	0.57	1.95

Estimated oil distribution

Once the volume fraction of swollen rubber is known, it is straightforward to calculate the oil distribution between the two phases in the blend from the known amounts of the blend components and the component densities. These results are presented in Table V for two different temperatures: 25°C and the processing temperature of 190°C. The oil content of the rubber varies among the 70 : 30 TPVs from 104.3 phr for A3, the TPV with the very broad molecular weight distribution PP (MFR = 2.2) to 88.6 phr for A2, and the TPV with the lowest molecular weight PP (MFR = 20). The oil fraction in the PP/oil medium varies from 0.39 for A3 to 0.50 for A2 in the 70 : 30 blends and is about 0.33 in the PP/oil medium of the two 50 : 50 blends. Because more PP by weight is contained in the 50 : 50 blends, the effective oil fraction in the medium is lower in these blends than in the 70 : 30 blends. At the processing temperature, besides taking changes in density into account, the oil distribution must be adjusted further because PP is fully amorphous at processing temperatures but 45% crystalline in the solid state. The oil is soluble only in the amorphous portion and not in the crystalline domains of the PP network.³ Consequently, it can absorb $1/(1 - 0.45)$ times the weight of oil that it would have absorbed at room temperature. The reestimated oil distribution between

the PP and EPDM phases at processing temperatures is tabulated for the various blends in Table V.

Medium viscosity curves

The oil concentrations in Table V are used to estimate shift factors and obtain the shear viscosity curves for the PP/oil medium in the various TPVs. These are presented in Figure 7(a) for the mediums in the 70 : 30 TPVs and in Figure 7(b) for the mediums in the 50 : 50 TPVs. For comparison, these figures include the corresponding TPV viscosity curves. The comparison among the PP/oil medium viscosity curves is different from that among the neat PP melt viscosity curves. The curves for the PP/oil mixtures with the lowest molecular weight PP (MFR = 20) and the highest molecular weight PP (MFR = 0.7) are much closer than the curves for the corresponding neat PP melts because the latter PP contains more oil. Even in the 50 : 50 TPVs, where the oil fractions in the mediums are about equal, the separation between the medium viscosity curves is less compared to the separation between neat PP curves; this is a result of the different shift factors. The oil fraction in the mediums of the 50 : 50 TPVs is less, causing their viscosity curves to be higher than the viscosity curves of the mediums in the 70 : 30 blends. Hence, the PPs are mixed with oil to

TABLE V
Oil Distribution Between EPDM and PP Phases in TPV Blends at Room Temperature and at Processing Temperature

	TPV	Wt. of oil in swollen EPDM (phr EPDM)	Wt. of oil in swollen PP (phr EPDM)	Vol. fraction of oil in swollen PP $\phi_{oil/PP+oil}$
at 25°C	A1	94.0	36.0	0.47
	A2	88.6	41.4	0.50
	A3	104.3	25.7	0.39
	B1	82.6	47.5	0.33
	B2	83.5	46.5	0.33
	at 190°C	A1	64.5	65.5
A2		54.7	75.3	0.65
A3		64.5	65.5	0.53
B1		43.7	86.3	0.46
B2		45.5	84.5	0.46

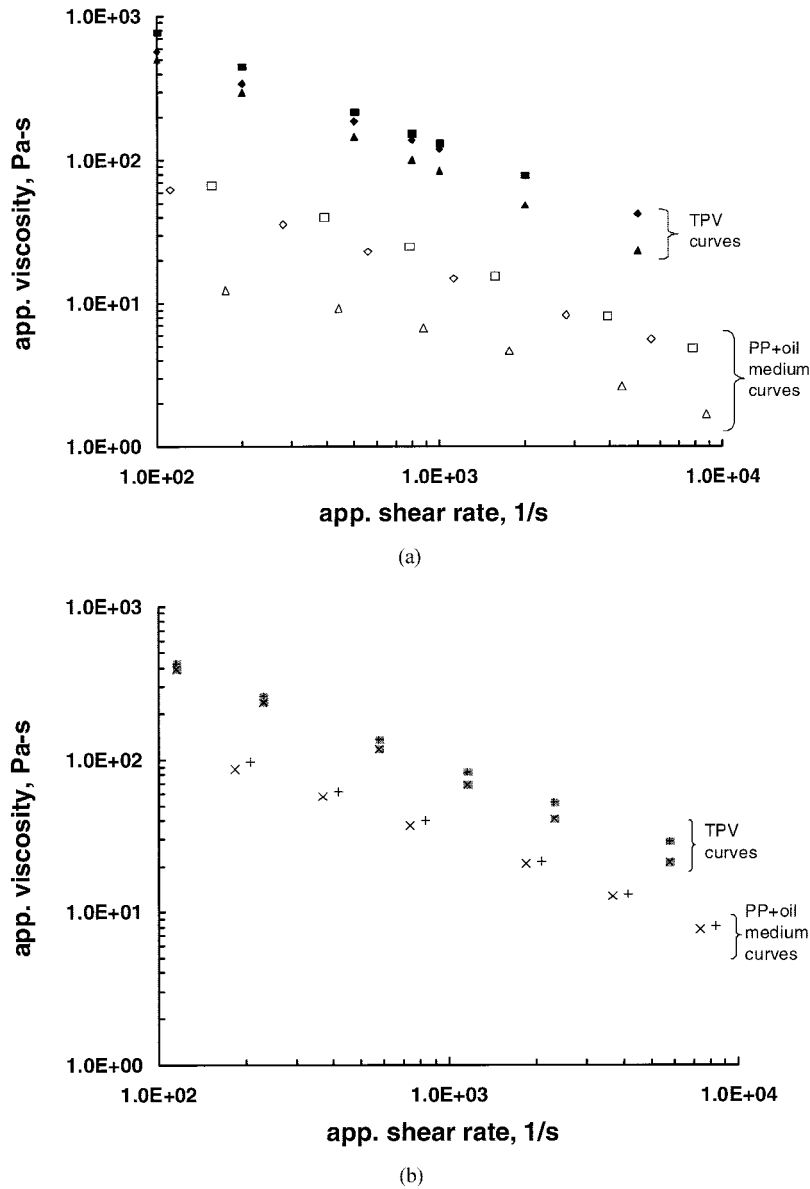


Figure 7 Shear viscosity curves at 190°C for the effective PP/oil medium in the TPVs determined using the shifting procedure: (a) medium viscosity curves for 70 : 30 TPVs, (b) medium viscosity curves for 50 : 50 TPVs. The TPV viscosity curves are also replotted for comparison.

different proportions in the different TPVs and these mixtures have viscosity curves that exhibit the trends in the TPV viscosity curves.

Relative viscosity of TPVs

The relative viscosity is defined as a ratio of blend viscosity to the medium viscosity at matching shear rates. This is estimated by interpolating along the medium shear viscosity curves, using a power-law model in most cases, and the Ellis model for the medium with the PP of MFR = 20, because the power-law model does not capture the low shear rate plateau of the viscosity. The relative viscosity curves are pre-

sented in Figure 8. The relative viscosity curves are higher in the 70 : 30 TPVs (by at least a factor of 2.5) than in the 50 : 50 TPVs showing the effect of higher particle volume fraction. Most of these curves are flat, showing no dependence on shear rate; this is consistent with the point made earlier that the PP/oil medium viscosity curves follow the same trend as the TPV viscosity curves. However, the relative viscosity for the 70 : 30 TPV with the PP of MFR = 20 becomes flat only toward the high end of the shear rate range. This may be explained by the observation that the lower viscosity medium can deform and repack the less swollen particles significantly only at the highest shear rates. It is established for concentrated suspen-

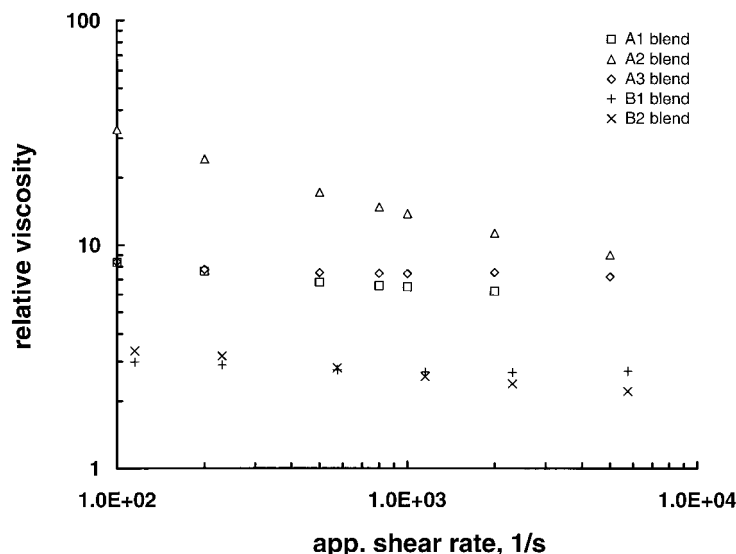


Figure 8 Relative viscosity curves evaluated at matching shear rates for (a) 70 : 30 TPV blends and (b) 50 : 50 TPV blends.

sions of rigid particles that the maximum packing fraction increases at higher shear rates, leading to decreases in relative viscosity with increasing shear rate.^{16,17} Although the particles in TPVs are deformable, smaller extents of particle deformation in the TPV made with the PP of MFR = 20 leads to more gradual changes in packing with shear rate.

CONCLUSION

The composition of the matrix or medium in five different thermoplastic vulcanizates was identified in terms of the oil fraction mixed with PP by analyzing TEM images of the TPVs. All five TPVs have the same vulcanized EPDM rubber cured to the same extent and the same total content of a high-temperature paraffinic oil. It was found that the PPs were mixed with oil to different proportions in the different TPVs; this was influenced by the proportion of rubber as well as the PP grade. The PP/oil mediums in TPVs with a 50 : 50 ratio of rubber to PP had a lower volume fraction of oil than the mediums in TPVs with a 70 : 30 ratio of rubber to PP. Among the 70 : 30 blends, the PP/oil mixture with the broad molecular weight distribution PP (MFR = 2.2) had the lowest volume fraction of oil. The viscosity curves of several PP/oil mixtures were found to correlate well with the neat PP melt viscosity curves at 190°C when shift factors were employed. The shift factors followed a power-law function of the polymer volume fraction with exponents between 1.9 and 2.1. The medium viscosity curves derived with the appropriate oil content then displayed the same trends in magnitude as the corre-

sponding TPV viscosity curves. Hence, the shear flow of TPVs can be understood more readily in terms of the effective PP/oil medium flow behavior than in terms of the neat PP melt flow.

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