

Effects of Blend Composition and Dynamic Vulcanization on the Morphology and Dynamic Viscoelastic Properties of PP/EPDM Blends

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ABSTRACT: The morphology and dynamic viscoelastic properties of isotactic polypropylene (PP) blended with oil-free/oil-extended ethylene-propylene-diene (EPDM) rubbers were studied. Unvulcanized and dynamically vulcanized blends with the compositions PP/EPDM = 50/50 and = 30/70 were investigated. The morphology was observed by phase contrasted atomic force microscopy. The dynamic viscoelastic properties were determined with a rheometer of plate-plate configuration. It was shown that the rheological behavior was strongly affected by both the composition and the morphology of the blends. Significant improvement in the flowability of the dynamically vulcanized blends was observed when oil-extended EPDM was used instead of the oil-free version. It was demon-

strated that the rheological properties are mostly controlled by the elastomer phase at low frequencies, while in the high-frequency range the influence of PP becomes dominant. The peculiarities in the rheological behavior of the thermoplastic elastomers (uncured blends, TPE) and thermoplastic dynamic vulcanizates (TPV, dynamically cured blends) containing oil-extended EPDMs were traced to a limited compatibility between the PP and EPDM components in the melt. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 1212–1220, 2008

Key words: ethylene-propylene-diene rubber; poly(propylene); rheology; thermoplastic elastomer; dynamic vulcanization; morphology

INTRODUCTION

The production of multicomponent materials such as blends and composites manufactured from the most inexpensive large-tonnage polyolefins (polyethylene, polypropylene, and their copolymers) still have an important role in the modern materials science. Thus, owing to the unique combination of mechanical and rheological behaviors of the components in a final product, thermoplastic elastomers (TPE), based on PP and various elastomers, are among the most widely used industrial materials (e.g., Ref. 1–3). TPE combines the advantageous mechanical properties of conventional rubbers with an easy processability inherently belonging to linear thermoplastic polymers above their melting temperatures.

The properties of TPEs can be substantially improved using the method of dynamic vulcanization.⁴ In this technique, the elastomer vulcanization and its mixing with thermoplastic component occur simultaneously at elevated temperature (i.e., beyond the melting of the thermoplastic component). TPEs

prepared by dynamic vulcanization are identified as thermoplastic vulcanizates (TPVs). TPV is a material in which crosslinked rubber particles are present in a relative high amount (50–70 wt %) and finely dispersed form (1–3 μm in diameter) in the continuous thermoplastic matrix. TPVs based on PP and ethylene-propylene-diene rubber (EPDM) are the most important materials from the commercial and scientific points of view. Although these TPVs are extensively used in the industry, only few papers addressed their rheological behavior.^{5–8}

The first investigation on the rheological properties of TPVs was performed by Goettler et al.⁵ Chung et al. studied the effect of dynamic vulcanization on the viscoelastic properties of PP/EPDM and PP/nitrile rubber systems with rubber concentration 20 and 60 wt %, respectively, using plate-plate and capillary rheometers.⁶ Han and White devoted a comparative study using different devices, viz. sandwich, cone-plate, and capillary rheometers, to three materials: PP, a blend of PP and ethylene-propylene copolymer (EPR), and a commercial available dynamically vulcanized PP/EPR blend.⁷ Medintseva et al. investigated the rheological properties of uncured and dynamically cured PP/EPDM blends with different component ratios varying from 75/25

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to 25/75 using a capillary rheometer.⁸ Thus, steady shear flow, uniaxial extensions, and oscillatory flows were studied.

It was demonstrated that with increasing of the elastomer crosslinking degree owing to dynamic vulcanization the overall viscosity of the TPVs increases markedly. TPVs exhibit not only non-Newtonian viscosity, but a yield value in shear flow. A yield stress of TPVs virtually does not depend on the crosslinking degree of the rubber. It was shown that TPVs in molten conditions behave like to particle filled polymer melts.

The main goal of the current study was to investigate how the composition affects the morphology and the rheological behavior of TPEs and TPVs containing PP and oil-free or oil-extended EPDM rubbers. The oscillatory shear flow properties and morphological features of both families of materials, viz. TPEs and TPVs, were determined and discussed.

EXPERIMENTAL

Materials

Commercial available PP and EPDM were used in this study. The basic characteristics of the materials are listed in Table I.

Blend preparation

Blends with different PP/EPDM ratio were prepared by mixing of components in Brabender-like internal

mixer at 190°C, 100 rpm for 10 min. Blending procedure was stopped when the maximum torque of mixing elements was achieved. The blends' compositions and curing recipes are disclosed in Table II. For further investigations, sheets were produced from the blends by hot pressing (190°C, 10 min).

Morphology investigation

Structural measurements of molded samples were performed at ambient conditions with scanning probe microscope (MultiMode™ Nanoscope IIIA, Veeco Instruments Inc., CA).⁹ Etched silicium tipped cantilever with a stiffness ~ 40 N/m were used. Imaging was performed in tapping mode at different tip-sample forces by varying ratio between free oscillation amplitude of the probe and set-point amplitude. This procedure allows us to obtain compositional maps from complex, multicomponent materials and to ensure a high phase contrast when visualizing submicron-scaled structural features.¹⁰ To study the bulk morphology the samples were cut at -130°C using cryo-ultramicrotome (MicroStar 01, Micro Star Technologies, TX).

Rheological measurements

The rheological behavior of the TPE and TPV combinations was investigated with a plate-plate rheometer (Ares, Rheometric Scientific, NJ). The samples in

TABLE I
Characteristics of Blend Components

Material	Trade name	Producer	Property	Characteristic
PP	21030-16	Petrochemical Company, Tomsk (Russia)	M_n (g/mol)	7.7×10^4
			M_w (g/mol)	3.4×10^5
			Density (g/cm ³)	0.907
			Crystallinity (%)	55
			T_m (°C)	165
			MFI (190°C, 2.16 kg), dg/min	2.3
EPDM-4044	Dutral TER 4044	Polimeri Europa, Milan (Italy)	Propylene content (wt %)	35
			5-Ethylidene-2-norbornene content (wt %)	4.5
			Density (g/cm ³)	0.865
			Mooney viscosity, ML(1+4) at 100°C	44
EPDM-4535	Dutral TER 4535	Polimeri Europa, Milan (Italy)	Propylene content (wt %)	32
			5-Ethylidene-2-norbornene content (wt %)	4.5
			Oil content (wt %)	50
			Density (g/cm ³)	0.890
EPDM-6470	Buna [®] EPG 6470	Bayer AG, Leverkusen (Germany)	Mooney viscosity, ML(1+4) at 125°C	32
			Ethylene content (wt %)	71
			5-Ethylidene-2-norbornene content (wt %)	4.5
			Density (g/cm ³)	0.860
EPDM-3569	Buna [®] EPG 3569	Bayer AG, Leverkusen (Germany)	Mooney viscosity, ML(1+4) at 125°C	59
			Ethylene content (wt %)	66
			5-Ethylidene-2-norbornene content (wt %)	5.0
			Oil content (wt %)	50
			Density (g/cm ³)	0.870
			Mooney viscosity, ML(1+4) at 125°C	30

M_n , mean number-average molecular weight; M_w , mean weight-average molecular weight; T_m , melting point; MFI, melt flow index.

TABLE II
Composition of PP/EPDM Blends

Ingredient	Content of the ingredient (wt %)											
PP	50	50	50	50	50	50	30	30	50	50	30	30
EPDM-4044	50	50										
EPDM-4535			25	25								
EPDM-6470					50	50	70	70				
EPDM-3569									25	25	35	35
Paraffinic oil			25	25					25	25	35	35
ZnO	–	1.27	–	0.63	–	1.27	–	1.77	–	0.63	–	0.89
Stearic acid	–	0.50	–	0.25	–	0.50	–	0.70	–	0.25	–	0.35
TMTD	–	0.37	–	0.18	–	0.37	–	0.51	–	0.18	–	0.26
MBT	–	0.13	–	0.06	–	0.13	–	0.18	–	0.06	–	0.09
Sulfur	–	0.50	–	0.25	–	0.50	–	0.70	–	0.25	–	0.35

TMTD, Tetramethylthiuram disulphide; MBT, 2-Mercaptobenzothiazole.

form of circular discs (1 mm thickness and 25 mm in diameter) were punched from the compression-molded sheets and mounted in the gap between the plates of the rheometer. Dynamic frequency scan tests were conducted at 190°C at a strain sweep of 1% and strain amplitude (1%). These parameters were selected to stay within the linear viscoelastic region during the tests. The oscillatory flow properties, namely the storage modulus (G'), the loss modulus (G''), the loss tangent ($\tan \delta$) and the complex viscosity (η^*) (for their definitions cf. Ref. 11) were determined. G' and G'' were determined in an angular frequency range from ~ 0.1 to 100 rad/s.

RESULTS AND DISCUSSION

Morphology of PP/oil-free EPDM blends

The AFM phase images of the uncured TPEs and dynamically cured TPVs based on PP/EPDM = 50/50 with EPDM-6470 and EPDM-4044, respectively, are shown in Figure 1. In these images, lighter regions correspond to the crystalline PP and darker ones to the EPDM phase.

In Figures 1(a,b) one can see that the TPEs have a two-phase structure where EPDM forms discrete domains of irregular shape which are dispersed in the continuous PP matrix. A previous analysis of the

morphology of TPEs showed that in the PP/EPDM = 75/25 blend the EPDM was segregated in spherically shaped domains.¹² The dimension of the domains increased with increasing EPDM. Furthermore, the subsequent hot-pressing caused a similar enlargement of the dispersed domains.¹² For the uncured PP/EPDM-6470 blend, a transition toward a cocontinuous phase morphology can be noticed [cf. Fig. 1(a)].

Dynamic vulcanization of the same blends was accompanied with a size reduction of the rubber domains [Fig. 1(c,d)]. The EPDM appears in particles within a range of 0.2–2 μm . The irregular shape of the crosslinked rubber particles hints that they were produced by break-up of initially larger entities under the local stresses which evolved during melt mixing. It is noteworthy that the spatial distribution of rubber particles in the TPVs resembles to a three-dimensional network in the PP matrix [cf., Fig. 1(c,d)].

The morphologies of the samples containing various types of the EPDM are very different (Fig. 1). For example, the size distribution of the cured EPDM particles is narrower and they are more uniformly dispersed when EPDM-6470 instead of EPDM-4044 was used as blending component [cf. Fig. 1(c,d)]. The agglomeration of the EPDM domains is more prominent for PP/EPDM = 50/50

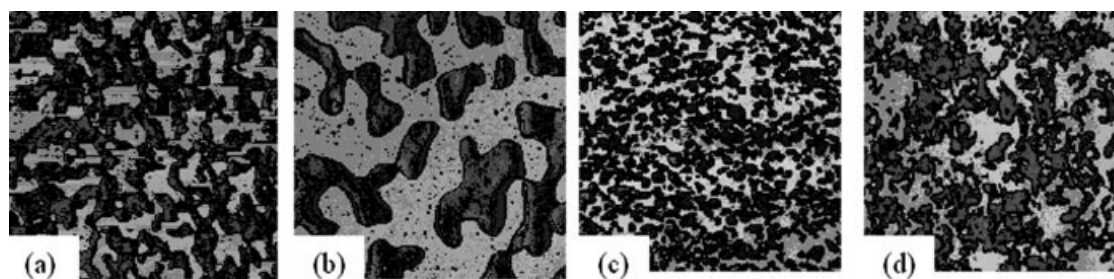


Figure 1 AFM phase images of TPEs (a, b) and TPVs (c, d) based on PP/EPDM = 50/50 with EPDM-6470 (a, c) and EPDM-4044 (b, d). The size of images: 50 \times 50 μm (a, b) and 15 \times 15 μm (c, d).

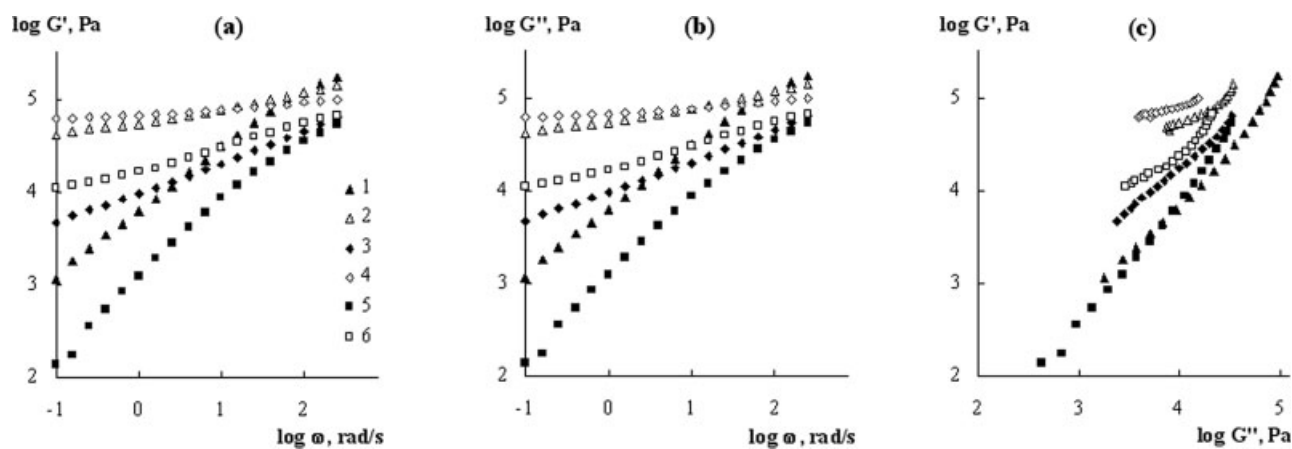


Figure 2 Plots of $\log G'$ (a), $\log G''$ (b) versus $\log \omega$ and $\log G'$ versus $\log G''$ (c) for the PP/EPDM blends containing EPDM-6470 (1–4) and EPDM-4044 (5, 6). The PP/EPDM ratio is 50/50 (1, 2, 5, 6) and 30/70 (3, 4), respectively. Uncured blends (TPEs)—1, 3, 5; dynamically vulcanized blends (TPVs)—2, 4, 6.

with EPDM-4044 than with EPDM-6470. So, phase-contrasted AFM is a very useful tool to clarify the morphology of PP/EPDM-based TPEs and TPVs.

Rheological behavior of PP/oil-free EPDM blends

It is well known that the structure definitely influences the rheological behavior of polymer blends. The viscoelastic properties of two-phase polymer blends depend on the size and deformability of the dispersed phase. It is worth of noting that the deformability of the domains is greatly affected also by their sizes.

The elastic and viscous characteristics of the polymer blends are well reflected by plots depicting the storage modulus, G' , versus the angular frequency, ω , and loss modulus G'' versus ω . In general, at low frequency the G' value provides information about the long-range relaxation (beyond entanglement distance), whereas the related value at high frequency is relied with short range relaxation (motion with entanglement).¹¹ One would expect to see strong dependences when plotting G' and G'' versus ω , as well as G' versus G'' . This expectation is based on the facts that the size and structuring of the domains of the disperse phase alter prominently with the blend composition.

The dependencies of $\log G'$ versus $\log \omega$ and $\log G''$ versus $\log \omega$ for the uncured and dynamically cured blends containing EPDM-6470 and EPDM-4044, respectively, are presented in Figure 2(a,b). It is seen that the values of G' and G'' increase monotonously with increasing ω for all blends.

It was established that dynamic vulcanization increases G' when reading them at same value of ω (this holds especially at low frequencies), but G' is independent on both EPDM content and type. At low frequencies the $G'(\omega)$ traces approach to an

asymptotic value for the TPVs. At $\log \omega = 0$ and $\log \omega = 2$ the respective slopes of $G'(\omega)$ curves on a log–log scale are at about 0.04 and 0.24, respectively, (Table III). The slopes of $\log G'$ versus $\log \omega$ curves increase modestly with increasing ω for the TPVs. It is known that in the low-frequency zone of viscoelastic liquids the storage modulus, G' , is proportional to ω^2 , so the slope in $\log G'$ versus $\log \omega$ representation should be 2.¹¹ As this is by far not the case here, the viscoelasticity of PP/EPDM-based TPEs and TPVs blends can not be estimated by this rule of thumb.

The slopes of $\log G'$ versus $\log \omega$ curves for the TPVs are lower than for the TPEs (Table III). As the frequency increases, the $\log G'$ versus $\log \omega$ curves for these materials become close to each other. Assuming that G' is related to the stored energy, the above finding indicates that dynamically vulcanized samples have higher elasticity at low and medium frequencies. This behavior is typical for vulcanized rubbers or particulate-filled molten polymers.^{6,7} The higher G' values for TPEs compared with TPVs at high frequencies can be attributed to the formation of entanglements between the PP and EPDM. This may be the reason for the higher elasticity observed.

It is shown that at low frequencies the G' values of both uncured and dynamically cured PP/EPDM = 30/70 blends are higher than those for the 50/50 blends when containing EPDM-6470. But at higher frequencies one can observe an inversion in the G' values: the $\log G'$ versus $\log \omega$ curves of the different blends, i.e., PP/EPDM = 50/50 and = 30/70 are intersected at $\log \omega \sim 0.7$. Note that at low frequencies the blend elasticity is primarily controlled by the rubber whereas at higher ones the PP matrix gains in importance.^{13,14}

The difference between the G' values for is higher TPEs than for TPVs. As reported, the structure of the amorphous PP phase is altered by increasing

TABLE III
Slopes of the Curves for PP/EPDM Based TPEs and TPVs at Various Frequencies

Composition	log G' vs. log ω		log G'' vs. log ω		log η^* vs. log ω	
	log $\omega = 0$	log $\omega = 2$	log $\omega = 0$	log $\omega = 2$	log $\omega = 0$	log $\omega = 2$
Uncured blends (TPE)						
PP/EPDM-6470 (50/50)	0.68	0.42	0.64	0.17	-0.35	-0.65
PP/EPDM-6470 (30/70)	0.30	0.35	0.35	0.25	-0.69	-0.67
PP/EPDM-4044 (50/50)	0.90	0.45	0.70	0.23	-0.27	-0.62
PP/EPDM-3569 (50/50)	0.60	0.39	0.57	0.20	-0.42	-0.66
PP/EPDM-3569 (30/70)	0.37	0.39	0.42	0.28	-0.62	-0.64
PP/EPDM-4535 (50/50)	0.55	0.31	0.50	0.13	-0.48	-0.72
Dynamically vulcanized blends (TPV)						
PP/EPDM-6470 (50/50)	0.12	0.17	0.37	0.07	-0.87	-0.84
PP/EPDM-6470 (30/70)	0.04	0.10	0.25	0.13	-0.96	-0.90
PP/EPDM-4044 (50/50)	0.24	0.21	0.39	0.08	-0.75	-0.81
PP/EPDM-3569 (50/50)	0.43	0.35	0.55	0.15	-0.53	-0.70
PP/EPDM-3569 (30/70)	0.06	0.18	0.34	0.19	-0.94	-0.82
PP/EPDM-4535 (50/50)	0.46	0.29	0.49	0.11	-0.53	-0.74

EPDM content, presumably, owing to compatibility issues.¹⁵ This affects the molecular mobility and the formation of entanglements, as well. Dynamic vulcanization results in an apparent three-dimensional network built from dispersed rubber particles, and at the same time decreases the entanglement density. So the difference between the G' values of TPVs PP/EPDM = 30/70 and = 50/50 containing EPDM-6470 decreased in comparison with that of the TPE counterparts.

The G'' values of the dynamically vulcanized blends are higher than those of the TPEs at low frequencies [Fig. 2(b)]. At higher frequencies, an inversion may be noticed in respect with their G'' values. The frequency ω_{inv} at which log G'' versus log ω curves for the corresponding TPE and TPV materials are intersected depends on the type of EPDM: for PP/EPDM-6470 = 50/50 and 30/70 log $\omega_{inv} \sim 0$ and PP/EPDM-4044 = 50/50 log $\omega_{inv} \sim 1.0$. The dynamic vulcanization decreases also the slopes of log G'' versus log ω curves (cf., Table III). Taking into account that the dynamic loss modulus G'' represents the amount of the dissipated energy, one can conclude that vulcanization leads to materials with higher dissipated energy at low frequencies and with lower dissipated energy at high frequencies.

At very low frequencies (log $\omega \sim -1.0$), the TPEs containing EPDM-6470 at the compositions PP/EPDM = 50/50 and = 30/70 show almost the same G'' values [Fig. 2(b)]. With increasing frequency the slope of the log G'' versus log ω curves becomes higher for the TPE with the composition of PP/EPDM = 50/50 than for PP/EPDM = 30/70 (Table III). The G'' values of the TPV at PP/EPDM = 50/50 are much higher than those of the composition PP/EPDM = 30/70. These results indicate that blends with higher dissipated energy are produced.

To distinguish among homogeneous and heterogeneous blends, Han et al.^{16,17} introduced a criterion

based on the representation of G'' versus G' (Cole – Cole plot). In this representation a single curve holds for miscible blends and a series of curves (shifted as a function of the composition) represent immiscible ones. Figure 2(c) gives plots of log G' versus log G'' for uncured and dynamically cured PP/EPDM blends. As seen, the G' values increase with increasing G'' . But the range in which the G'' changes depends on the PP/EPDM ratio and whether or not dynamic vulcanization was applied. This range is wider for TPEs compared with TPVs, and it is narrowed with increasing EPDM content. Note that the log G' versus log G'' curves are shifted with respect to one another for both TPEs and TPVs when their composition is varied. Consequently, these systems are immiscible blends. This is in line with the AFM results (cf. Fig. 1).

Figure 3 gives the plots of the loss tangent $\tan \delta$ and the complex viscosity η^* versus log ω for uncured and dynamically cured PP/EPDM blends. The values of $\tan \delta$ are defined as the ratio of G''/G' . Ideally viscous fluids have a $\tan \delta$ value of infinity, whereas ideally elastic solids would show a $\tan \delta$ value of zero.

The traces of $\tan \delta$ versus log ω for the uncrosslinked PP/EPDM = 50/50 blend containing EPDM-6470 tend to decrease with increasing ω . On the other hand, the values of $\tan \delta$ for the uncured PP/EPDM = 30/70 blend is practically independent on the frequency [cf. Fig. 3(a)]. As can be observed, an increase in the PP content produces a significant decrease of $\tan \delta$ for the TPEs, especially at low frequencies. The difference in the elasticity of the TPEs becomes smaller with increasing frequency.

Dynamic vulcanization decreases the $\tan \delta$ values. It is well resolved in the plots of $\tan \delta$ versus ω that the $\tan \delta$ values of the TPVs are almost independent on the frequency, i.e., the ratio of the energy dissipated (G'') to the stored one (G') is less sensitive to

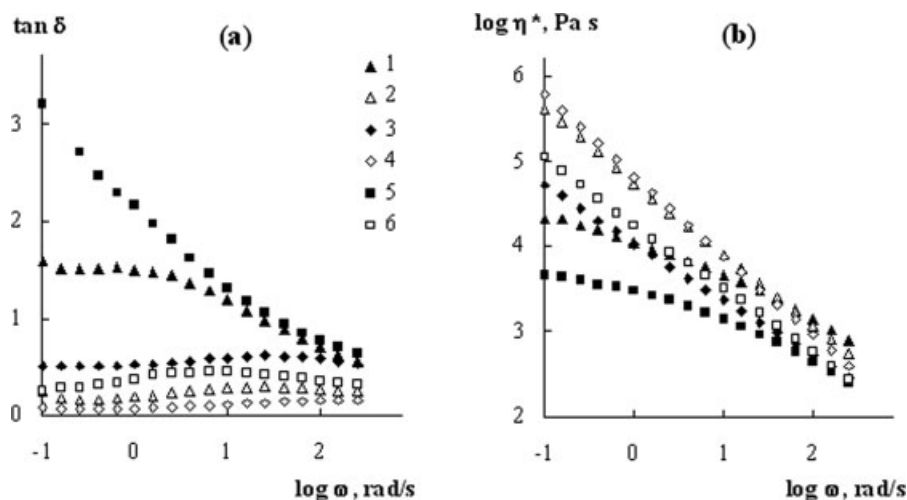


Figure 3 Plots of $\tan \delta$ (a) and $\log \eta^*$ (b) vs. $\log \omega$ for blends based on EPDM-6470 (1–4) and EPDM-4044 (5, 6). PP/EPDM ratio is 50/50 (1, 2, 5, 6) and 30/70 (3, 4). Uncured blends—1, 3, 5; dynamically vulcanized blends—2, 4, 6.

the frequency. Figure 3(a) shows that the dynamically vulcanized blends are much more elastic than the uncured ones. This note is valid especially at low frequencies and for the blend PP/EPDM = 50/50 with EPDM-6470. It is of interest to note that the elasticity of the uncured and dynamically cured PP/EPDM-6470 = 50/50 blends is higher than that of the PP/EPDM-4044 = 50/50 blends. With increasing EPDM content the $\tan \delta$ value of blend decreased independently whether or not dynamic vulcanization occurred.

Figure 3(b) displays the plots of $\log \eta^*$ versus $\log \omega$ for the TPE and TPV samples. It is well known that complex viscosity η^* implies the viscous and elastic characteristics of a viscoelastic fluid through the following relation: $\eta^* = \eta' - i\eta''$, where η' is in-phase or elastic (storage) and η'' is the out-of-phase or viscous (loss) component of the dynamic complex viscosity.¹¹ Moreover, these components are related to the energies stored/dissipated and the oscillatory frequency via the following formulae: $\eta' = G''/\omega$, $\eta'' = G'/\omega$. As shown, η^* of the uncured and dynamically cured materials decreases with increasing ω in the whole range of the studied frequency, so the related systems are of pseudoplastic nature. This arises from the randomly oriented and entangled polymer chains which, on application of high shear rates, become oriented and disentangled.¹⁸ Similar behavior for the storage η' and loss η'' viscosities with increasing ω can be noticed also.

It is observed that at low frequencies the η^* values of the TPE of PP/EPDM = 30/70 with EPDM-6470 are higher than those of the TPE of PP/EPDM = 50/50. However, the related curves intersect when ω rises. The η^* values of the TPE of PP/EPDM = 50/50 based on EPDM-4044 are lower than those containing EPDM-6470. This can be traced to differences in their

morphologies: the domains of EPDM-4044 are more prone for deformation in the PP melt than those of EPDM-6470. The slopes of $\log \eta^*$ versus $\log \omega$ curves for all dynamically cured samples and uncured PP/EPDM = 30/70 blends are practically independent on the frequency. They increase, however, with increasing ω for the TPEs of PP/EPDM = 50/50 (cf. Table III). The slopes of $\log \eta^*$ versus $\log \omega$ curves for the TPVs are higher than for the TPEs. As the frequency increases, the $\log \eta^*$ versus $\log \omega$ traces of the TPEs and TPVs become closer to each other. At low frequencies the difference between η^* values is increasing. As shown in Figure 3(b), almost the same η^* values were obtained for dynamically vulcanized PP/EPDM-6470 = 50/50 and = 30/70 samples. This suggests that the structure of these materials is very similar.

As mentioned earlier, the morphologies of uncured TPEs and dynamically vulcanized TPVs are different. The formation of an apparent three-dimensional network composed of the dispersed rubber particles can be made responsible for the high initial values of complex viscosity. With increasing ω , this network is deformed and even destroyed at high frequencies. This is associated with a pronounced reduction in the η^* values. So, the rheological behavior of the blends under consideration strongly depended on both the composition and the morphology of the blends. At low frequencies the rheological properties are controlled by the EPDM phase, while at higher frequencies the influence of PP becomes more prominent.

Morphology of PP/oil-extended EPDM blends

The rheological properties of the PP blended with oil-extended EPDM were strongly influenced by the

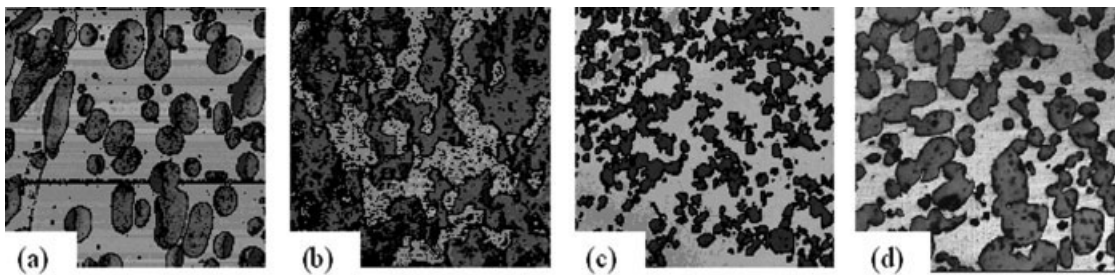


Figure 4 AFM phase images of TPEs (a, b) and TPVs (c, d) based on PP/EPDM = 50/50 with EPDM-4535 (a, c) and PP/EPDM = 30/70 with EPDM-3569 (b, d). The size of images: $50 \times 50 \mu\text{m}$ (a, b) and $15 \times 15 \mu\text{m}$ (c, d).

amount of oil and its distribution between the EPDM and PP phases.^{12,19–21} It was demonstrated that the incorporation of oil in PP/EPDM blends reduces their viscosity and physicomechanical characteristics.

The AFM phase images of TPEs and TPVs based on EPDM-3569 and EPDM-4535 are shown in Figure 4. One can see that these blends exhibit a two-phase structure, too. The particle size distribution of the EPDM is very coarse. The morphology of the related TPEs and TPVs depends on the amount and type of EPDM.

In case of the PP/EPDM = 50/50 TPE there are small spherically shaped particles with diameters of $0.5\text{--}4.0 \mu\text{m}$ and ellipsoidal shaped domains with sizes of about $5 \times 15 \mu\text{m}$ visible. For the PP/EPDM = 30/70 TPE a transition toward a cocontinuous phase morphology can be noticed. Recall that hot-pressing supports the coalescence of EPDM domains. The analysis of the morphology of PP/oil-extended EPDM blends has shown that the EPDM segregates in more spherically shaped domains in comparison with the PP/oil-free EPDM blends.

Dynamic vulcanization of the oil-extended EPDM containing blends also reduces the size of domains. The size of the rubber particles (in the range of

$\sim 0.2\text{--}6 \mu\text{m}$) is similar to that of the TPVs with oil-free EPDM [Fig. 4(c,d)]. But the structure of the oil-extended EPDM containing blends depends on the type of elastomer. Cured EPDM-3569 particles are agglomerated—so one can observe both small rubber particles as well as larger rubber domains. The structure of the PP/EPDM-4535 TPV is very similar to that one produced with oil-free EPDM-6740: the fine dispersed rubber particles form an apparent three-dimensional network [cf., Fig. 4(c) and 1(c)]. The presence of oil can be detected by AFM inspection at very high magnifications.¹² Nanometer-sized oil inclusions could be observed in both EPDM regions and PP matrix. This oil partition yielded a significant reduction of the melt viscosity and promoted the deformability of the rubber particles.

Rheological behavior of PP/oil-extended EPDM blends

Figure 5 gives plots of $\log G'$ and $\log G''$ versus $\log \omega$. The courses of the related traces are similar to those TPEs and TPVs which were produced with oil-free EPDMs (cf. Figs. 2 and 5). Figure 5 shows that both G' and G'' increase monotonously with increasing ω .

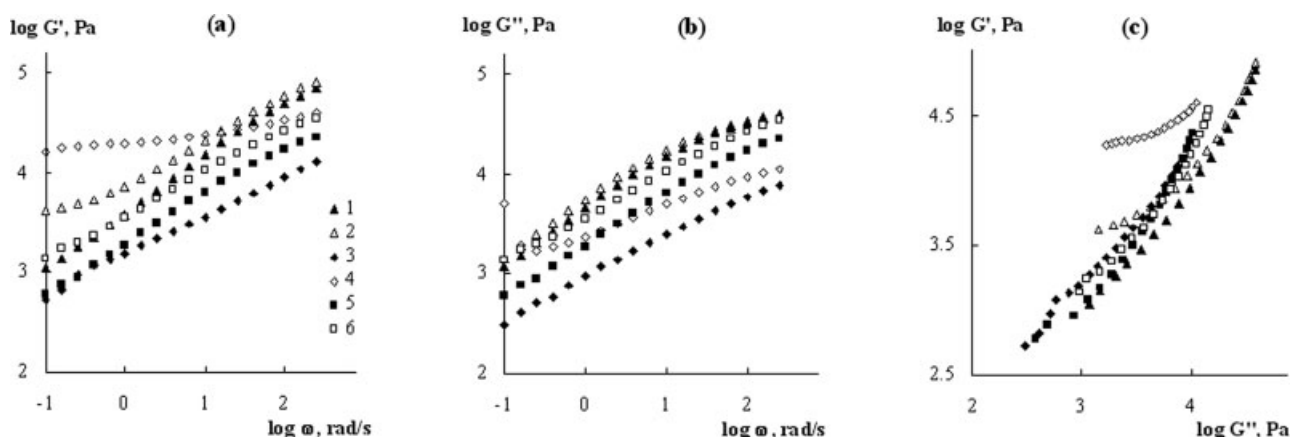


Figure 5 Plots of $\log G'$ (a), $\log G''$ (b) versus $\log \omega$ and $\log G'$ versus $\log G''$ (c) for blends based on EPDM-3569 (1–4) and EPDM-4535 (5, 6). PP/EPDM ratio is 50/50 (1, 2, 5, 6) and 30/70 (3, 4). Uncured blends—1, 3, 5; dynamically vulcanized blends—2, 4, 6.

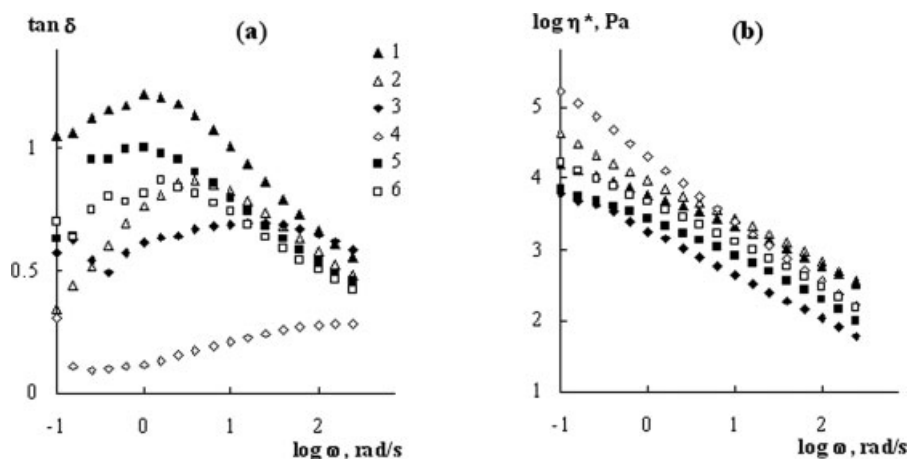


Figure 6 Plots of $\tan \delta$ (a) and $\log \eta^*$ (b) vs. $\log \omega$ for the blends based on EPDM-3569 (1–4) and EPDM-4535 (5, 6). PP/EPDM ratio is 50/50 (1, 2, 5, 6) and 30/70 (3, 4). Uncured blends—1, 3, 5; dynamically vulcanized blends—2, 4, 6.

The dynamic vulcanization is found to increase G' independently on the content and type of the EPDM. As shown, at low frequencies, G' values of samples of TPV PP/EPDM = 30/70 with EPDM-3569 are higher than those of samples of TPV PP/EPDM = 50/50 with the same EPDM. At higher frequencies G' values of samples of TPV PP/EPDM = 50/50 with EPDM-3569 are higher than those of samples of TPV PP/EPDM = 30/70 with the same EPDM. Thus, there is the inversion of G' values. The intersection of the $\log G'$ versus $\log \omega$ traces occurs at $\log \omega \sim 1.0$.

At high frequencies the $\log G'$ versus $\log \omega$ curves of the TPEs and TPVs become close to each other. As expected, the slopes of $\log G'$ versus $\log \omega$ curves for the uncured and dynamically cured PP/EPDM blends depend on the EPDM content. The slope of the TPE PP/EPDM = 50/50 with EPDM-3569 is higher than the value of the PP/EPDM = 30/70 with the same EPDM at low frequencies (Table III).

Further, the slopes of the $\log G'$ versus $\log \omega$ curves for TPEs are higher than for the TPVs. The slopes increase with increasing ω for PP/EPDM-3569 = 30/70 but decrease for the corresponding 50/50 blends (Table III). Thus, at low frequencies the blend elasticity is likely controlled by that of the rubber. With rising frequency the influence of PP on the blend elasticity becomes more important. All these findings are in line with those deduced for the PP/oil-free EPDM systems.

The dependencies G'' versus ω are similar to G' versus ω ones [Fig. 5(b)]. The slopes of these curves decrease with increasing ω practically for all blends. The curves for uncured and dynamically cured PP/EPDM-3569 = 50/50 become close to each other at high frequencies and coincide at $\log \omega \sim 2$ (Table III). The G'' values of the PP/EPDM = 50/50 TPE

based on EPDM-3569 are higher than those of the PP/EPDM = 30/70 counterpart.

Dynamic vulcanization increases G'' independently on the EPDM content and the type of EPDM at a fixed ω . The G'' values of the PP/EPDM = 50/50 and = 30/70 TPVs based on EPDM-3569 coincide at low frequencies, but they are higher for the 50/50 composition at high frequencies as compared with the 30/70 TPV. The slopes of $\log G''$ versus $\log \omega$ curves of the PP/EPDM-4535 blends do not change, their run parallel. This indicates that blends containing 50 parts EPDM are characterized by higher dissipated energy.

Figure 5(c) shows plots of $\log G'$ versus $\log G''$ for the TPEs and TPVs. One can observe that G' values of TPE and TPV containing 50 parts EPDM-3569 are coincided at high G'' values. At low G'' for TPV G' containing 50 parts EPDM-3569 is higher than those of TPE with the same content of EPDM-3569. Dynamic vulcanization increases the G' values for blends PP/EPDM = 30/70 with EPDM-3569 at a fixed value G'' . The variation range of G'' for TPEs is wider than for TPVs. It can also be noticed that the $\log G'$ versus $\log G''$ curves for uncured and dynamically cured PP/EPDM = 30/70 blends are higher than those for PP/EPDM = 50/50 systems. This finding can be traced again to a limited compatibility of PP and oil-extended EPDM in the melt.⁸

Figure 6(a) gives plots of $\tan \delta$ versus $\log \omega$ for the TPEs and TPVs. Note that dynamic vulcanization leads to a reduction of the $\tan \delta$ values at a fixed ω value. It is seen that for unvulcanized and dynamically vulcanized PP/EPDM = 50/50 blends the $\tan \delta$ values pass through a maximum within the $\log \omega$ range from 0 to 0.5. At high frequencies the difference between the $\tan \delta$ values for these materials are markedly reduced. For the PP/EPDM = 30/70 blends $\tan \delta$ first drops sharply and then increases

modestly with increasing ω at low frequencies. In this range the difference between TPEs and TPVs is larger than at higher frequencies. For TPEs based on EPDM-3569 the $\tan \delta$ versus $\log \omega$ curves coincide at $\log \omega \sim 2$. The $\tan \delta$ values for the PP/EPDM = 50/50 TPVs are higher than those for the 30/70 TPVs in the whole frequency range studied. The partition of the paraffinic oil is probably the reason for the different behaviors of the PP/EPDM = 50/50 and = 30/70 blends.

Figure 6(b) depicts plots of $\log \eta^*$ versus $\log \omega$. As shown, the complex viscosity of both unvulcanized and dynamically vulcanized PP/EPDMs decreases with increasing ω . So, the related blends are pseudo-plastic melts in the whole frequency range. The $\log \eta^*$ values for TPVs are higher than for the TPEs. The $\log \eta^*$ versus $\log \omega$ curves for the PP/EPDM = 50/50 blends with EPDM-3569 are coinciding at $\log \omega \sim 2$. The slopes of the $\log \eta^*$ versus $\log \omega$ curves for the uncured and dynamically cured PP/EPDM-4535 blends are the same as they run parallel to each other.

For TPEs the $\log \eta^*$ values are reduced in the whole frequency range when the EPDM content in the blend is increasing. At low frequency the viscosity of the PP/EPDM = 30/70 TPV is higher than for the 50/50 TPV counterpart. However, at high frequencies one can observe an inversion as the related curves are intersecting at $\log \omega \sim 0.7$.

As obvious by comparing Figures 3 and 6, the TPVs with oil-extended EPDM possess a better melt flowability than the corresponding TPVs produced with oil-free EPDMs. These data indicate that complex rheological behavior of the blends with oil-extended EPDMs is due to the limited compatibility between the EPDM and PP in the molten state.

CONCLUSIONS

The morphology and rheological properties of PP-EPDM blends (PP/EPDM = 50/50 and 30/70, respectively) using oil-free and oil-extended rubbers with (TPV) and without additional dynamic vulcanization (TPE) were studied.

It was shown that both TPEs and TPVs exhibited a two-phase structure: the EPDM particles and domains were dispersed in the continuous PP matrix. The size and distribution of the elastomer depended on the amount and the type of EPDM.

The process of dynamic vulcanization leads to a reduction of the particles size prominently. The cross-linked rubber particles formed an apparent three-dimensional network which was obviously the reason of higher viscosity of dynamically cured TPVs.

The amount and the type of EPDM are strongly affected on the rheological properties of TPEs and TPVs. Significant improvement in the flowability was observed for oil-extended TPVs. The rheological properties are mostly controlled by the elastomer phase at low frequencies, while in the high frequency range the influence of PP becomes dominant. The peculiarities in the rheological behavior of the TPE and TPV based on oil-extended EPDM were traced to a limited compatibility between the PP and EPDM components in the melt.

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