The effect of PP molecular weight on the complex viscosity of PP/EPDM blends

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Abstract. The effect of the molecular weight of isotactic polypropylene (PP) on the complex viscosity of unvulcanized and dynamically vulcanized blends of PP with ethylene-propylene-diene monomer (EPDM) was investigated. It was shown that individual PPs and PP/EPDM blends demonstrate a shear thinning behavior. The flow index varied with frequency and elastomer content for all blends. The dependences of complex viscosity versus PP molecular weight were observed for unvulcanized blends based on 25 wt% EPDM. The viscosity of composition with higher elastomer content was not practically affected by the variation of PP molecular weight. The complex viscosity of dynamically vulcanized blends depended on PP molecular weight, blend composition, and nature of crosslinking agents.

Keywords: rheology, isotactic polypropylene, ethylene-propylene-diene monomer, dynamic vulcanization, complex viscosity

1. Introduction

Thermoplastic elastomers (TPEs) based on PP and various elastomers are a large class of materials. They combine the elastic properties of thermoset rubbers with the advantages of the processability and recyclability of thermoplastic polymers [1, 2]. The properties of TPEs can be substantially improved using the method of dynamic vulcanization at which the curing process of elastomers occurs during their mixing with molten thermoplastic [3–6]. TPEs prepared by dynamic vulcanization are known as thermoplastic vulcanizates (TPVs). TPV is a material in which crosslinked rubber particles (1–3 μm) are finely dispersed in a continuous thermoplastic matrix. TPVs based on PP and EPDM are extensively studied and widely used as engineering polymeric materials [7]. Rheological studies are very important to access the processing characteristics of polymer blends, which depend on many variables, such as the nature of polymers, molecular weight, and its distribution,

blend composition etc. [8]. The effect of dynamic vulcanization on rheological properties of various rubber–plastic blends have been reported by several authors [9–13]. Thus, steady shear flow, uniaxial extensions, and oscillatory flows were studied. It was demonstrated that the overall viscosity of the TPVs increases markedly with increasing of the elastomer crosslinking degree owing to dynamic vulcanization. TPVs exhibit not only non-Newtonian viscosity but a yield value in shear flow. The 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 particle-filled polymer melts. The rheological behavior of PP/EPDM blends was strongly affected by both the composition and the morphology of the blends [14]. Significant improvement in the flowability of the dynamically vulcanized blends was observed when oil-extended EPDM was used instead of the oil-free one. It was demonstrated that rheological properties are mostly controlled by

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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 TPEs and TPVs containing oil-extended EPDMs were traced to limited compatibility between PP and EPDM components in the melt.

The type of curing agent plays a major role in determining the final performance of TPVs. So, the usage of a phenolic system and oil-extended EPDM allows producing softer materials with lower viscosity at higher rubber content in comparison with compositions containing oil-free EPDM [15].

The influence of the molecular weight of thermoplastic on the rheological behavior of TPVs is not practically reviewed in the literature. Early we investigated the melt flow properties of unvulcanized TPEs and dynamically vulcanized TPVs based on PPs with various molecular weight PP and EPDM using a capillary viscometry [16]. It was obtained that melt shear viscosity of uncured TPEs depends on PP molecular weight and elastomer content. At low shear stress, melt shear viscosity of dynamically vulcanized blends containing 25 wt% of oil-free EPDM is about 10 times higher than that of unvulcanized blends. An increase in elastomer content significantly inhibits the TPV melt flow, so it is almost impossible to study the rheological behavior of TPVs containing 50–60 wt% oil-free EPDM using a capillary rheometer.

The main goal of the current study was to investigate the effect of PP molecular weight on the complex viscosity of TPEs and TPVs based on oil-free EPDM by means of a rheometer of parallel plate geometry. The influence of two types of crosslinking agents (sulfur and phenolic resin systems) on the complex

viscosity of dynamically vulcanized TPVs also was studied.

2. Experimental

Commercial grades of PPs (Petrochemical Company, Russia) and oil-free EPDM Dutral TER 4044 (Polimeri Europa, Italy) with density 0.875 g/cm³, propylene contents 35%, Mooney viscosity 44 (125 °C), were used in this study. The molecular weight characteristics of PP samples (weight-average molecular weight (M_w), number-average molecular weight (M_n), polydispersity index (IP) = M_w/M_n), their melting temperature (T_m), crystallinity (K), melt flow rate (MFR) determined at 190 °C and a load of 2.16 kg) are listed in Table 1. Isotacticity of PP samples was about 95–96%.

Blends with PP/EPDM ratio 75/25, 50/50 and 40/60 were prepared by mixing of components in Plastograph[®] EC (Brabender[®], Germany) at 190 °C, 100 rpm for 10 min. Dynamic vulcanization was realized in one stage at the same conditions using two curing systems, which recipes are disclosed in Table 2. The amount of crosslinking agents was calculated on 100 wt% of elastomer.

For further investigations, sheets were prepared by molding the melt mixed blends in a hot hydraulic laboratory press (Carver[®] Inc., USA) at 190 °C for 10 min.

Table 1. Characteristics of PPs.

PP	M_w [g/mol]	M_n [g/mol]	IP	T_m [°C]	K [%]	MFR [g/10 min]
PP-1	150 000	40 000	3.8	166.0	57.0	10.0
PP-2	210 000	58 000	3.6	163.8	53.5	2.6
PP-3	280 000	95 000	2.9	162.4	55.0	0.3

Table 2. The composition of PP/EPDM blends.

Ingredient	Content of the ingredient [wt%]					
PP	75	75	50	50	40	40
EPDM	25	25	50	50	60	60
Sulfur-containing accelerating system (SAS)						
Sulfur	0.25	–	0.50	–	0.60	–
Zinc oxide	0.64	–	1.27	–	1.52	–
Stearic acid	0.25	–	0.50	–	0.60	–
Tetramethylthiuram disulphide	0.19	–	0.37	–	0.44	–
2-Mercaptobenzothiazole	0.07	–	0.13	–	0.15	–
Phenolic resin system (PRS)						
n-Tert-butylphenol-formaldehyde resin (PR)	–	1.50	–	3.00	–	3.60
Zinc dichloride	–	0.75	–	1.50	–	1.80

Dynamic rheological measurements of PPs, EPDM and their unvulcanized and dynamically vulcanized blends were carried out using parallel-plate rheometer ARES (Rheometric Scientific Inc., NJ) at the same temperature (190 °C) at which the blends were prepared [14]. The samples in the form of a circular disc (1 mm thickness and 25 mm in diameter) were punched from compression-molded sheets and mounted in the gap between the plates of the rheometer. The complex viscosity η^* was determined in an angular frequency range ω from 0.1 to 100 rad/s. Averages of three measurements were reported in every case. The deviation in the measurements was around 5%.

Structural studies of molded samples were performed at ambient conditions by atomic force microscopy (AFM) using a scanning probe microscope (MultiMode™ Nanoscope IIIa, Bruker, USA) [17]. The samples were sectioned by means of low-temperature microtomy at –100 °C with a Microstar instrument (Microstar Technology, USA). The surface images of a specimen were taken in the intermittent contact or tapping mode. Silicon probes with a spring constant of ~40 N/m and a resonance frequency of 150–20 kHz were used. To enhance phase contrast, the scanning amplitude was selected to be 0.4–0.5 of the free-oscillation amplitude of the probe. Under these conditions, the brightest places on the phase image correspond to the most rigid component and vice versa.

3. Results and discussion

3.1. Rheological properties of neat PPs and EPDM

The dependencies of $\log \eta^*$ vs. $\log \omega$ for thermoplastics and elastomer are presented in Figure 1. As it was expected, the η^* value increases with the rising of PP molecular weight. It is seen that PP-1 is the least viscous and elastic polymer, while PP-3 is the most viscous and elastic. At low-frequency region ($\log \omega < 0$) the complex viscosity of PP-1 and PP-2 attains a value independent of ω within the limits of experimental error and exhibits a short Newtonian plateau but PP-3 and EPDM does not reach a viscosity plateau. At low frequencies the difference between $\log \eta^*$ values of all polymers is larger than at high frequencies. EPDM viscosity is significantly exceeded that of PPs at low frequencies. As ω values increases, all curves become close to one another;

Figure 1. Plots of $\log \eta^*$ vs. $\log \omega$ for neat PPs and EPDM.

moreover, the viscosity of PP-3 and EPDM are coinciding at high frequencies.

As frequency increases, the complex viscosity gradually decreases. This behavior shows the pseudo-plastic or shear-thinning behavior of all samples. EPDM shows more shear-thinning than PP. Pseudo-plasticity of the neat polymers is due to the random orientation and highly entangled state of the macromolecules, which under high frequency get disentangled and become oriented, resulting in a reduction of viscosity [8, 18].

The complex viscosity at a given shear rate can be calculated as $\eta^* = K\omega^{n-1}$, where K is a pre-exponential sample factor, and n is the flow index. The magnitude of n can be determined from the slope of straight-line drawing to the $\log \eta^*$ vs. $\log \omega$ plot at a given shear rate. A greater slope indicates a higher degree of shear thinning. The values of flow index n for neat PPs and EPDM determined at three zones are listed in Table 3. It is seen that n for neat PPs decreases with their molecular weight. It is interesting to note that the value of n for EPDM is substantially lower than those of neat PPs, especially at low frequencies. When the ω value increases, the magnitudes of n for PP-3 and EPDM are practically identical.

The molecular structure of neat polymers is mainly composed of physical crosslinks created by trapped entanglements. The difference in rheological behavior of neat PP and elastomer observed at low frequencies may be due to a change in the initial entanglement density of polymer macromolecules [19].

Table 3. The flow index for PPs, EPDM and unvulcanized PP/EPDM blends.

Sample	n		
	$\log \omega = 0$	$\log \omega = 1$	$\log \omega = 2$
PP-1	0.82	0.65	0.44
PP-2	0.78	0.59	0.39
PP-3	0.55	0.37	0.22
EPDM	0.29	0.28	0.23
PP-1/EPDM = 75/25	0.80	0.65	0.45
PP-2/EPDM = 75/25	0.75	0.59	0.39
PP-3/EPDM = 75/25	0.75	0.56	0.36
PP-1/EPDM = 50/50	0.74	0.62	0.43
PP-2/EPDM = 50/50	0.72	0.60	0.41
PP-3/EPDM = 50/50	0.71	0.57	0.40
PP-1/EPDM = 40/60	0.70	0.60	0.43
PP-2/EPDM = 40/60	0.70	0.57	0.37
PP-3/EPDM = 40/60	0.66	0.57	0.42

3.2. Rheological properties of unvulcanized TPEs

Figure 2 shows the plots of $\log \eta^*$ vs. $\log \omega$ for unvulcanized PP/EPDM blends. The complex viscosity decreases monotonously with the increase of frequency. All TPEs exhibit the rheological behavior of non-Newtonian fluids and shear thinning behavior similar to PPs. Shear-thinning starts early at very low frequencies. Therefore, the unvulcanized blends are pseudoplastic melts in the whole frequency range. The complex viscosity of PP-1/EPDM and PP-2/EPDM blends are higher than those of neat PP-1 and PP-2, but lower than those of EPDM (cf. Figure 1 and Figure 2). At the same time, the values $\log \eta^*$ of PP-3/EPDM blends are lower than those of individual PP-3 and EPDM. The viscosity of unvulcanized blends slightly increases with elastomer content. This effect is most pronounced at low frequencies. The

Figure 2. Plots of $\log \eta^*$ vs. $\log \omega$ for unvulcanized PP/EPDM blends. PP/EPDM ratio is (a) 75/25, (b) 50/50, and (c) 40/60.

complex viscosity of unvulcanized blends with low EPDM content (25 wt%) increases with PP molecular weight (Figure 2a). However, the viscosity of TPEs with higher elastomer content (50–60 wt%) is not practically affected by the variation of PP molecular weight (Figure 2b and Figure 2c).

The magnitudes of flow index n for unvulcanized blends determined at three zones are summarized in Table 3. One can observe the change of n with ω and with the elastomer content for all blends. The value of n noticeably varies with PP molecular weight for the compositions based on 25 wt% EPDM, but it is

practically independent of PP type for other TPEs at a given PP/EPDM ratio.

Obviously, the structure of the studied TPEs determines the peculiarities of their rheological behavior. Our investigations show that the morphological structure of unvulcanized blends is practically independent of PP molecular weight. So, we discuss below the comparison of morphological features of TPEs on the example of PP-2/EPDM blends.

The AFM phase images of the unvulcanized TPEs are shown in Figure 3. In these images, lighter regions correspond to the crystalline PP and darker ones to

Figure 3. AFM phase images of unvulcanized PP-2/EPDM blends. PP/EPDM ratio is (a) 75/25, (b) 50/50, and (c) 40/60. The size of images is 50×50 μm .

the EPDM phase. One can see that the morphology of the sample containing 25 wt% elastomer has matrix-type morphology, where elastomer particles with sizes less than 3 μm are dispersed in the PP matrix fairly uniformly (Figure 3a). Therefore, it can be assumed that the rheological behavior of such material is substantially determined by PP characteristics. So one can observe a growth of complex viscosity of these blends with PP molecular weight (Figure 2a). With increasing of EPDM content, its domains enlarge, most likely due to their coalescence/aggregation as a process competitive to the dispersion one. Furthermore, the hot-pressing of a sample caused a similar enlargement of the dispersed domains [17]. It is evident that the elastomer phase remained as dispersed phase in continuous PP matrix up to 50 wt% EPDM content. In the blend, PP/EPDM = 50/50, both small rubber particles of $\sim 0.5\text{--}4.0\ \mu\text{m}$ in diameter and larger domains of an average size of $10\text{--}20\ \mu\text{m}$ distributed in the continuous PP matrix are present (Figure 3b). Finally, a transition towards a co-continuous phase morphology can be noticed for the unvulcanized PP-2/EPDM = 40/60 blend (Figure 3c). With an increase of elastomer content and an enlargement of its domains, a contribution of EPDM to the complex viscosity of TPEs begins to grow. The higher its content, the more significant its effect on the viscosity of TPE. The viscosity of the elastomer is much higher than one of the PP matrix, especially at low frequencies (Figure 1), so, probably, a contribution of the thermoplastic matrix to complex viscosity of TPE is reduced. Thus, PP molecular weight noticeable effects on viscosity of unvulcanized TPEs contained 25 wt% EPDM, but it practically does not influence the rheological behavior of TPEs based on 50–60 wt% EPDM (Figure 2).

3.3. Rheological properties of dynamically vulcanized TPVs

Figure 4 displays the plots of $\log \eta^*$ vs. $\log \omega$ for dynamically vulcanized PP/EPDM blends. As one can see, the complex viscosity depends on a blend composition, PP molecular weight, and the type of curing system. The values of η^* increases with the elastomer content for all dynamically vulcanized blends.

The $\log \eta^*$ values decrease monotonously with the increase of ω magnitude. TPVs exhibit shear-thinning behavior in all frequency range. The magnitudes of flow index n for TPVs determined at three zones are summarized in Table 4. One can observe that the values of n decrease with the PP/EPDM ratio. But the magnitude of this index weakly depends on the PP molecular weight at a given PP-EPDM ratio.

The complex viscosity of all blends cured by PRS and PP/EPDM = 75/25 blends cured by SAS increases with PP molecular weight. However, as ω value increases, the curves for PP/EPDM = 75/25 vulcanized by SAS become close to each other and coincide at very high frequencies (Figure 4a). The viscosities of PP-1/EPDM and PP-2/EPDM dynamically vulcanized by SAS, which contained 50 and 60 wt% of elastomer, are coinciding in the whole range of frequencies, but the viscosity of TPVs based on PP-3 is much greater (Figures 4b, 4c). The $\log \eta^*$ vs. $\log \omega$ curves for SAS-blends with high elastomer content are parallel. At low frequencies, the complex viscosity of SAS-blends is significantly higher than those of the PRS-blends. The difference in viscosity decreases with an increase of ω values, and $\log \eta^*$ vs. $\log \omega$ curves become closer to each other.

The process of dynamic vulcanization increases the complex viscosity of PP/EPDM blends (cf. Figure 2 and Figure 4). However, the values of η^* depend on

Table 4. The flow index for dynamically vulcanized PP/EPDM blends.

Sample	n			n		
	$\log \omega = 0$	$\log \omega = 1$	$\log \omega = 2$	$\log \omega = 0$	$\log \omega = 1$	$\log \omega = 2$
	SAS-blends			PRS-blends		
PP-1/EPDM = 75/25	0.52	0.51	0.37	0.63	0.53	0.38
PP-2/EPDM = 75/25	0.55	0.47	0.31	0.71	0.57	0.39
PP-3/EPDM = 75/25	0.52	0.40	0.25	0.70	0.51	0.33
PP-1/EPDM = 50/50	0.18	0.26	0.22	0.50	0.46	0.36
PP-2/EPDM = 50/50	0.17	0.26	0.21	0.54	0.47	0.35
PP-3/EPDM = 50/50	0.16	0.26	0.22	0.55	0.46	0.33
PP-1/EPDM = 40/60	0.09	0.15	0.17	0.46	0.43	0.34
PP-2/EPDM = 40/60	0.12	0.13	0.12	0.54	0.48	0.36
PP-3/EPDM = 40/60	0.10	0.18	0.17	0.53	0.44	0.32

Figure 4. Plots of $\log \eta^*$ vs. $\log \omega$ for dynamically vulcanized PP/EPDM blends. PP/EPDM ratio is (a) 75/25, (b) 50/50, and (c) 40/60.

the nature of the crosslinking agents. The viscosity of SAS-blends significantly exceeds the viscosity of unvulcanized TPEs, especially at low frequencies, whereas the curves become very close while the ω values increases. The application of PRS practically does not change the viscosity of an unvulcanized blend containing 25 wt% EPDM at low frequencies but exceeds it at high ω magnitudes. The viscosity of TPVs contained 50–60 wt% elastomer and cured by PRS is less than one of analogous TPEs at low frequencies and more at high frequencies. Obviously, the peculiarities of rheological behavior of studied TPVs are determined by the difference of their morphology and viscoelastic properties of EPDM vulcanized by SAS and PRS, as well as a different curing degree of elastomer phase.

Our investigations show that the morphological structure of dynamically vulcanized blends depends on the PP/EPDM ratio and the nature of the crosslinking agent, but it is practically independent of PP molecular weight. So, we discuss below the comparison of morphological features of TPVs vulcanized by SAS and PRS on the example of PP-2/EPDM blends. The AFM phase images of TPVs are shown in Figure 5 and Figure 6. Dynamic vulcanization by means of SAS substantially changes the structure of PP/EPDM blends, and it was accompanied by a size reduction of the rubber domains. All TPVs have a structure characterized by a relatively homogeneous distribution of small EPDM domains in the continuous thermoplastic matrix (Figure 5). The structures of TPVs and filled composites are similar, so the

rheological properties of TPVs resemble the properties of composites containing a highly dispersed filler [10, 12, 13].

The TPVs rheological behavior determines by both a thermoplastic matrix and a cured elastomer phase. As was discussed above, the complex viscosity of TPVs containing 25 wt% EPDM increase with PP molecular weight (Figure 4a) because the rheological characteristics of the thermoplastic matrix, evidently, play a major role. When the EPDM content increase, both the type of thermoplastic and viscoelastic properties of the vulcanized rubber phase determine the rheological behavior of TPV. In the case of

SAS-blends based on 50–60 wt% EPDM, the matrix and rubber phase equally affect the viscosities of TPVs based on PP-1 and PP-2, so their rheological curves coincide (Figure 4b and 4c). In the case of TPVs based on PP-3, which viscosity is much high, probably, the influence of the thermoplastic matrix is stronger than the vulcanized rubber phase.

Rubber domains in SAS-cured blends are smaller (less than 1 μm) than those in unvulcanized blends (cf. Figure 3 and Figure 5). With an increase of EPDM content, the agglomeration of EPDM particles develops [20, 21]. The crosslinked rubber particles form a three-dimensional network, in which

Figure 5. AFM phase images of PP-2/EPDM blends dynamically vulcanized by SAS. PP/EPDM ratio is (a) 75/25, (b) 50/50, and (c) 40/60. The size of images is $15 \times 15 \mu\text{m}$.

density increases with EPDM content; therefore, the rigidity of the whole system also increases. The presence of crosslinks increases the rigidity of dispersed rubber particles and prevents their irreversible deformation in the melt of the polymeric matrix. With increasing test frequency, this network is deformed and even destroyed. It is associated with a pronounced reduction in the complex viscosity values, so at high frequencies, one can observe a convergence of rheological curves of studied TPEs and TPVs.

The structure of PRS-blends is different from SAS-blends (cf. Figure 6 and Figure 5). Generally, the size of EPDM particles cured with SAS is less, and their

distribution is more narrow and uniform. It is noticeable that the domains of EPDM in blends cured by PRS are larger; they have an irregular shape with more coarse external contours. It means, that EPDM cured by PRS, have been dispersed in another way than EPDM cured by SAS.

The distinctions in the rheological behavior of TPVs vulcanized with SAS and PRS are likely to be due to different vulcanization mechanisms and, as a consequence, differences in the morphology and viscoelastic characteristics of resulting products. The rigidity of EPDM particles cured by PRS and their crosslinking density are lower; they form a looser

Figure 6. AFM phase images of PP-2/EPDM blends dynamically vulcanized by PRS. PP/EPDM ratio is (a) 75/25, (b) 50/50, and (c) 40/60. The size of images is $15 \times 15 \mu\text{m}$.

network and are better deformable in the matrix melt [15]. Therefore, in the case of identical component ratio, the viscosity of TPVs cured by SAS is higher than those cured by PRS, especially at low frequencies. The increase of test frequency leads to stronger destruction of the structural framework of SAS-blends and a much greater reduction of their viscosity values.

As was discussed above, the viscosity of PRS-blends increases with PP molecular weight for all PP/EPDM ratios (Figure 4). The lower rigidity of EPDM particles cured by PRS, lower crosslinking density, looser network, and their better deformability in the matrix melt, probably, lead to a stronger influence of PP type on a complex viscosity of PRS-blends.

4. Conclusions

The influence of PP molecular weight on the complex viscosity of unvulcanized TPEs and dynamically vulcanized TPVs based on PP and EPDM was studied. It was shown that the complex viscosity of neat PPs, unvulcanized, and dynamically vulcanized PP/EPDM blends gradually decreases in all studied frequency range. The decrease of complex viscosity with the frequency increase shows a pseudoplastic or shear-thinning behavior of the samples. The shear-thinning of all blends starts early at very low frequencies. The flow index noticeably varies with PP molecular weight for unvulcanized TPEs based on 25 wt% EPDM, but it is practically independent of PP type for other TPEs and dynamically vulcanized TPVs at a given PP/EPDM ratio.

The flow index varied with frequency and elastomer content for all blends.

The value of complex viscosity change depends on PP molecular weight only for unvulcanized blends containing 25 wt% of elastomer and is not practically affected by the variation of PP molecular weight in case of TPEs with higher EPDM content, for which a contribution of elastomer to their complex viscosity begins to grow. The higher its content, the more significant its effect on the viscosity of TPEs.

The complex viscosity of dynamically vulcanized SAS-blends is higher than that of PRS-blends at low frequencies. At high frequencies, the curves of $\log \eta^*$ vs. $\log \omega$ for PP/EPDM = 50/50 and 40/60 are very close to each other, so they are practically independent of the nature of curing agents.

The TPVs rheological behavior determines by both a thermoplastic matrix and a cured elastomer phase.

In some cases, when the influence of the thermoplastic matrix is stronger than the vulcanized rubber phase, the complex viscosity of TPVs changes with PP molecular weight. Thus, the viscosity of all TPVs cured by PRS slightly increases with PP molecular weight, and such a trend is observed for SAS-blends containing 25 wt% of EPDM. The curves of $\log \eta^*$ vs. $\log \omega$ for SAS-blends based on 40–50 wt% PP-1 and PP-2 coincide in all frequency range, but the viscosity of analogous SAS-blends based on PP-3 is much higher.

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