Rheological Behavior of Thermoplastic Vulcanizates

E. Prut,* T. Medintseva, D. Solomatin, O. Kuznetsova

Summary: Dynamic and steady shear rheological properties of dynamically vulcanized iPP/EPDM blends were investigated. Two different curing systems based on sulfur or phenolic resin were applied on iPP/EPDM blends. The use of phenolic resin system allows producing materials with lower viscosity at higher rubber content in comparison with sulfur-cured compositions. Melt rheological properties of iPP/EPDM blends with different loading levels of paraffinic oil were studied. Significant improvement in the flowability is observed for TPVs extended with 50 wt% oil. A partial replacement of EPDM on rubber powder decreases the viscosity of materials.

Keywords: blends; poly(propylene); rheology; vulcanization

Introduction

Thermoplastic vulcanizates (TPVs) are a particular group of thermoplastic elastomers. These materials combine the melt processability of the thermoplastics and the elastic and mechanical properties of the thermoset cured rubbers. TPVs are produced via dynamic vulcanization of immiscible blends of a thermoplastic and an elastomer.[1]

The most commercial TPVs are based on the blends of ethylene-propylene-diene rubber (EPDM) as a dispersed cured rubber and isotactic polypropylene (iPP) as thermoplastic matrix. Dynamically vulcanized iPP/EPDM blends showed much better performance than uncured blends. It would be desirable to prepare new TPV with a good processability.

The processing of TPVs is a function of their rheology. The rheological properties of the uncured and cured iPP/EPDM blends were examined by several authors.[2–7] It was shown that rheology of these materials is determined by a number of parameters including molecular characteristics of the basic components. In this paper, some factors affected on the rheological behavior of dynamically cured TPVs based on iPP/EPDM are discussed.

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Experimental Part

Commercial available polymers with following characteristics were used in this study: iPPs (Petrochemical Company, Tomsk (Russia)) – PP-1 ($M_w = 150000$ g/mol, MFI = 10.0 dg/min), PP-2 ($M_w = 210000$ g/mol, MFI = 2.6 dg/min), PP-3 ($M_w = 280000$ g/mol, MFI = 0.3 dg/min), EPDMs – EPDM-4044 and EPDM-4535 contained 50 wt% of paraffinic oil (Dutral® TER 4044 and Dutral® TER 4535, Polimeri Europa, Milan (Italy)), EPDM-6470 (Buna® EPG 6470, Bayer AG, Leverkusen (Germany)).

Blends with various iPP/EPDM ratios were prepared in Brabender® mixer at 190 °C and 100 rpm for 10 min. Dynamic vulcanization was performed in one stage using sulfur-accelerated system or phenolic resin system (PhR).[8,9] Ground rubber tire powder (GRT) and powder of EPDM-4044 vulcanizates (RP) were produced by mechanical grinding.[10,11]

The rheological properties were analyzed using capillary and parallel-plate rheometers at 190 °C.[5–7] Dynamic frequency scan tests were conducted in the linear viscoelastic region. MFI values were measured at 190 °C.

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Results and Discussion

Effect of Curing Systems and PP Molecular Weight on Rheological Behavior of TPVs

The melt shear viscosity η vs. shear stress τ and complex viscosity η^* vs. frequency ω of dynamically cured iPP/EPDM-4044 blends as the function of iPP molecular weight, blend ratio, and curing systems exhibit a classical viscoelastic behavior of the non-Newtonian fluids and shear thinning behavior.

The logarithmic plots of melt viscosity vs. shear stress for TPVs based on three types of iPPs and EPDM-4044 are presented in Figure 1. The addition of 25 wt% EPDM-4044 and dynamic vulcanization increases the melt shear viscosity of initial PP-1, PP-2, but reduces it for PhR-cured blend based on PP-3. Sulfur-cured iPP/EPDM blends have a much more viscosity in comparison with PhR-cured blends.

It should be noted that in studied shear stress range (log $\tau = 3.5–5.0$ [Pa]) it is impossible to observe a melt flow of sulfur-cured TPVs based on 50 and 60 wt% of EPDM-4044. The increase of EPDM-4044 content in PhR-cured TPVs leads to a permanent growth of their viscosity. It is important that such materials flow even at high EPDM content. The melt shear viscosity of TPVs increases with iPP molecular weight.

The complex viscosity of sulfur-cured TPVs is higher than ones of PhR-cured blends. But this parameter is not practically depends on EPDM content and iPP M_w (Figure 2).

Effect of Paraffinic Oil on Rheological Behavior of TPVs

Rheological properties of iPP blended with oil-extended EPDM are strongly determined by amount of oil and its distribution between EPDM and iPP phases. The viscosity of oil-extended TPVs based, for example, on iPP-2 and EPDM-4535 decreases in comparison with that of oil-free TPVs contained iPP-2 and EPDM-4044.[5–7]

It should be noted that a method of incorporation of a paraffinic oil into EPDM rubber strongly determined rheological behavior of TPVs. Figure 3 shows logarithmic plots of melt viscosity vs. shear stress for uncured and dynamically cured by sulfur system blends based on PP-2 and EPDM-4044 which was extended by 30 and 50 wt% of paraffinic oil in Brabender® mixer. One can see that a mechanical addition of oil into elastomer leads to a significant decrease of melt viscosity of uncured blends, but in fact does not improve that of TPVs based on EPDM-4044 + 30 wt% oil. It is observed a weak decrease of melt viscosity for TPV contained EPDM-4044 + 50 wt% oil.

Figure 4 depicts plots of melt shear viscosity and complex viscosity vs. rubber content for sulfur-cured TPVs based on oil-

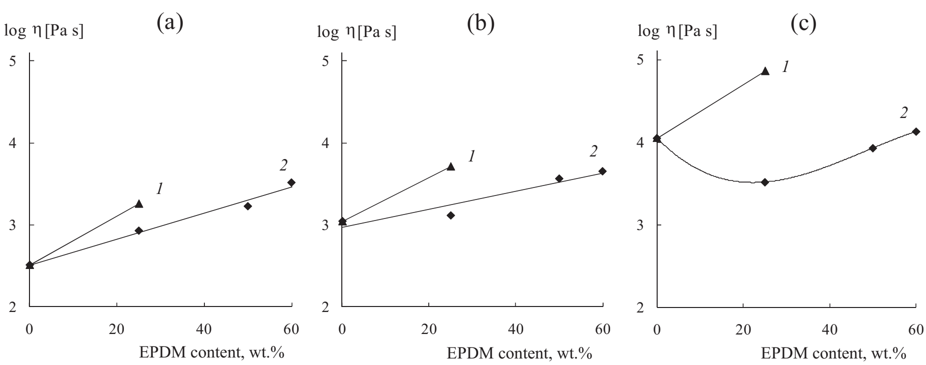

Figure 1.
Plots of melt shear viscosity log η vs. rubber content for iPP/EPDM-4044 blends based on (a) PP-1, (b) PP-2, (c) PP-3 and dynamically cured by (1) sulfur and (2) PhR systems. log $\tau = 4.22$ [Pa].

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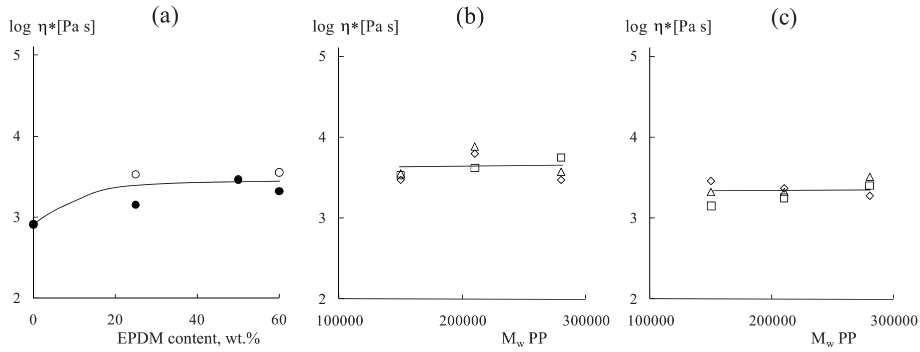

Figure 2.
Plots of complex viscosity log η^* vs. (a) rubber content and (b, c) iPP M_w at $\omega = 10$ rad/s for iPP/EPDM blends. (a) PP-1/EPDM-4044 cured by (○) sulfur and (•) PhR systems. (b) sulfur- and (c) PhR-blends with iPP/EPDM-4044 ratio: (□) 75/25, (◇) 50/50, (Δ) 40/60.

extended EPDM-4535. The melt viscosity of studied TPVs exceeds iPP melt viscosity only when a content of EPDM-4535 is high than 40 wt%, and this parameter is sensitive to a change of iPP molecular weight (Figure 4, curves 1).

The values of complex viscosity steadily increase with rubber content for TPVs based on PP-1 and PP-2, but is not practically depended on iPP M_w (Figure 4, curves 2). A complex viscosity of oil-extended TPV based on PP-3 does not varied with growth of EPDM-4535 content.

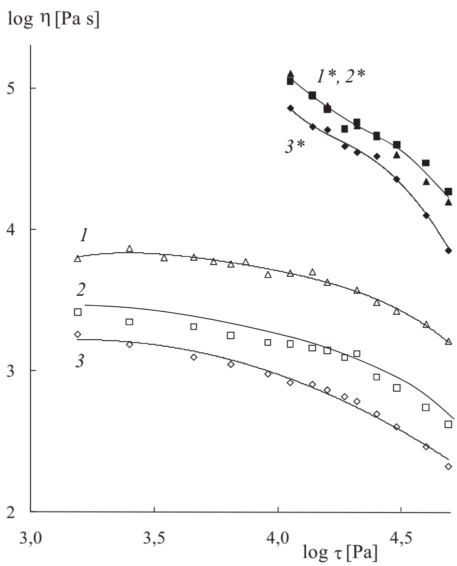

Figure 3.
Plots of melt shear viscosity log η vs. shear stress log τ for (1, 2, 3) uncured and (1*, 2*, 3*) dynamically sulfur-cured blends based on PP-2 and (1, 1*) EPDM-4044, (2, 2*) EPDM-4044 plus 30 wt% of oil, (3, 3*) EPDM-4044 plus 50 wt% of oil. PP-2/EPDM ratio is (1, 1*) 57/43, (2, 2*) 48/52, (3, 3*) 40/60.

TPVs contained a great content of EPDM oil-extended during synthesis possess a better melt flowability than the corresponding TPVs based on oil-free EPDM as it follows from comparison of Figures 1 and 4.

Effect of Rubber Powder on Rheological Behavior of TPVs

In recent years, a potential way to use GRT in thermoplastic elastomers has been developed [14–16]. Rubber powder was used for partial replacement of virgin elastomer. So, a rubber phase of such materials consists of a mixture of virgin rubber and GRT. In this paper we discuss how an addition of GRT influences on rheological behavior of TPVs based on iPP/EPDM.

The compositions of PP-2/EPDM-6470 = 50/50 and 30/70 were chosen. The ratio of the GRT to virgin EPDM was 1/3, keeping the total rubber content constant.

Our experiments show that the addition of GRT powder promotes the flowability of uncured iPP/EPDM = 50/50 and these TPVs (Table 1). The MFI values of TPVs contained GRT are higher than those of TPVs without GRT. One can see that

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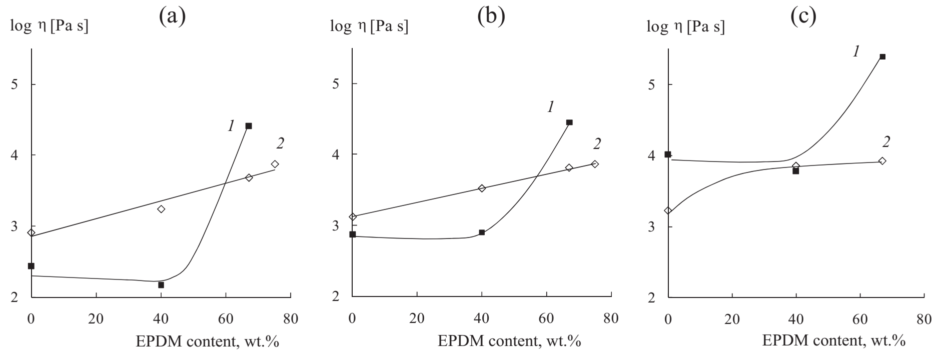

Figure 4.
Plots of log η and log η^* vs. oil-extended rubber content for dynamically sulfur-cured iPP/EPDM-4535 blends based on (a) PP-1, (b) PP-2, (c) PP-3. (1) log $\tau = 4.33$ [Pa], (2) $\omega = 10$ rad/s.

blends with iPP/EPDM ratio 30/70 do not flow at low and medium loads, but an increase of a load to 10 kg leads to a weak flow.

As can be seen from Table 1, rubber particle size is an important factor affecting the MFI of TPVs. The reduction of the rubber particle size increases MFI of uncured blends and dynamically cured TPVs. So, the TPVs processability is strongly influenced by a partial substitution of the EPDM rubber by the GRT powders.

GRT contains mineral fillers such as carbon black and other additives, which could vary rheological properties of TPVs. So, it is interested to use RP of cured virgin elastomer without any additives. For these reasons, in this study we used the powder of EPDM-4044 vulcanizates without mineral fillers.

Figure 5 shows plots of PP-2/EPDM-4044 complex viscosity vs. RP content. One can see that a partial replacement of virgin EPDM-4044 by RP increases η^* value of uncured iPP/EPDM-4044/RP blends. But growth of RP content in TPVs steadily decreases their complex viscosity. So, the addition of 25 wt% RP results in one order reduction in η^* value.

Therefore, the partial replacement of traditionally rubbers used in TPV by GRT will make it possible to improve the processability of TPVs and reduce the environmental pollution.

Table 1.
MFI values of uncured blends and dynamically cured TPVs at different conditions.

iPP/EPDM/GRT	Particle size of GRT d, mm	MFI, dg/min					
		2.16 kg		5.00 kg		10.00 kg	
		uncured	cured	uncured	cured	uncured	cured
50/50/0	–	–	–	–	–	–	–
50/37.5/12.5	without fractionation	0.05	0.4	0.4	1.6	2.4	8.4
50/37.5/12.5	$d < 0.1$	0.3	0.4	0.4	1.5	2.4	8.4
50/37.5/12.5	$0.1 < d < 0.4$	0.1	0.2	0.2	1.0	1.8	6.0
50/37.5/12.5	$0.4 < d < 0.63$	–	0.05	0.1	0.6	1.3	5.1
30/70/0	–	–	–	–	–	–	–
30/52.5/17.5	without fractionation	–	–	–	0.1	0.1	0.6
30/52.5/17.5	$d < 0.1$	–	–	–	0.1	0.1	1.2
30/52.5/17.5	$0.1 < d < 0.4$	–	–	–	–	0.1	0.4
30/52.5/17.5	$0.4 < d < 0.63$	–	–	–	–	–	0.05

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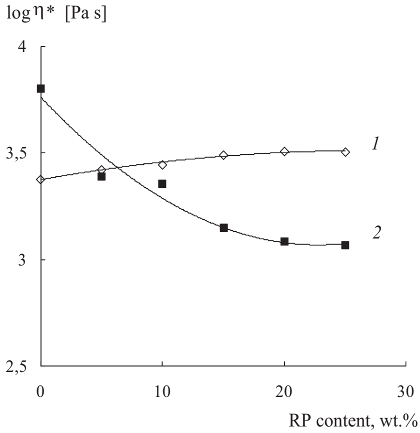

Figure 5.
Plots of complex viscosity log η^* vs. RP content for (1) uncured and (2) dynamically cured by sulfur system PP-2/EPDM-4044 = 50/50.

Conclusion

Some factors influenced on rheological behavior of TPVs based on iPP and EPDM were discussed in the paper. Our experiments showed that iPP molecular weight, blend ratio, type of curing systems, a presence of a plasticizer like paraffinic oil, a method of its incorporation in EPDM, and a partial replacement of a virgin elastomer by rubber powders can essentially change a rheology of TPVs. The use of phenolic resin system, oil-extended during synthesis EPDM, iPP with low molecular weight and rubber powders allows producing materials with lower viscosity at higher rubber content.

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