 DOI: 10.1002/masy.200650110

Mechanical and Rheological Behavior of Unvulcanized and Dynamically Vulcanized i-PP/EPDM Blends

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Summary: The mechanical and rheological behavior of dynamically vulcanized PP/EPDM blends is examined and compared with those of unvulcanized blends. The effect of blend ratio and dynamic vulcanization of EPDM rubber on tensile properties and flow are investigated. The mechanical properties of the blends are strongly influenced by the blend ratio. With the increasing of EPDM content the value of yield stress in a solid state decreases with the elastomer volume fractions less than 0.45 for the unvulcanized blends. For the dynamically vulcanized blends the interval of EPDM content, at which the yield peak is seen, is rather limited below 0.25 elastomer volume fractions. It is shown that dynamic vulcanization changes the deformational behavior of PP/EPDM blends. The rheological properties of dynamically vulcanized blends depending on the ratio of the components may be similar to the properties of polymer composites containing the highly disperse structuring filler. The distinction between the rheological behavior of unvulcanized and dynamically vulcanized blends is related to differences of their structures and viscoelastic characteristics of unvulcanized and vulcanized EPDM phase.

Keywords: dynamic vulcanization; EPDM-elastomer; mechanical properties; polypropylene; rheological behavior

Introduction

Blends of isotactic PP with rubbers are widely used in industry. Depending on the ratio between components, these blends may be used either as high-impact materials when the rubber content in the blend is low or as thermoplastic elastomers (TPEs) when the rubber content is high [1–3].

Elastomer domains are uniformly distributed in a PP matrix at elastomer content $\phi_{el} \leq 0.25$ volume fractions. At $0.25 < \phi_{el} < 0.50$ volume fractions the matrix is still presented by the thermoplastic polymer but rubber particles agglomerate. When the elastomer content in the blends ranges from 0.50 to 0.60 volume fractions co-continuous phases are observed. With a further increase ϕ_{el} in TPE (above 0.60 volume fractions), phase inversion takes place: the rubber phase becomes continuous [4].

Dynamic vulcanization, at which crosslinking of elastomer proceeds simultaneously with its blending with thermoplastic component, leads to changes in the morphological structure of PP – elastomer blends [4]. Vulcanized elastomer particles with dimensions of about 1–5 μm are dispersed in a continuous thermoplastic matrix at ϕ_{el} less than 0.75 volume fractions. Dynamically vulcanized blends with high elastomer content are identified as thermoplastic vulcanizates (TPVs). The structure of TPV is similar to that of the composite with rigid spherical filler.

The characteristics of the elastomeric phase can significantly affect the properties of PP/rubber blends. However the effect of

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the crosslinking degree of the rubber phase on the deformation mechanism and flow of these materials has not been studied in all details.

In this work, we investigated how the ratio of initial components and the amount of vulcanizing agent influence the mechanical and rheological properties of unvulcanized and dynamically vulcanized PP/EPDM blends within a wide concentration range of blend components.

Experimental

Materials

The following commercial materials were used as the basic components of blends:

- isotactic PP (trade mark 210310-16, Russia) with density 0.907 g/cm^3, melting point 165 °C, degree of crystallinity 55%;
- EPDM (trade mark Dutral TER4044, Italy) with density 0,875 g/cm^3, propylene contents 35%, Mooney viscosity 44 (125 °C).

Blend Preparation

The reactive blending of the polymers was carried out at 190 °C for 10 min in an internal mixer of Brabender type. Dynamic vulcanization was realized in one stage using sulfur-containing accelerating system with the sulfur concentration from 0,5 to 1,5 phr [5]. The PP/EPDM ratio was varied from 95/5 to 15/85.

Test Techniques

The stress-strain behavior was investigated at room temperature by means of ''Instron-1122'' at the constant crosshead speed 50 mm/min. The granules of PP/EPDM blends were used to mold plates at 190 °C, pressure of 13 MPa and an exposure of 10 min. The plates were cooled under pressure, then the dog-bone samples with dimensions $35 \times 5 \times 0{,}35$ mm were cut.

The stress σ – strain ε diagrams allow to estimate elastic modulus E, yield stress in a solid state σ_y corresponding to the maximum of yield peak; ultimate tensile strength σ_b, and elongation at break ε_b. The stress was calculated per initial cross section of the sample. The results were averaged over 10–12 samples [6].

Rheological measurements were conducted on a capillary microviscometer at 190 °C under the constant load regime [7]. The values of the effective shear viscosity η were calculated as a function of the blend composition under flow through a capillary with the length to the diameter ratio equal to 15. The entrance correction may be ignored in this case.

Results and Discussion

Mechanical Properties

Figure 1a shows the σ–ε diagrams of some uncured samples. The profiles of these diagrams are controlled by ϕ_{el}. For example, for the blend with $\phi_{el} = 0.15$ volume fractions, the stress – strain diagram is similar to that of the initial PP. In this case, the value of yield stress in a solid state σ_y is less than σ_y of the initial PP and the width of the yield tooth increases. With increasing the EPDM content, σ_y decreases, and as a result of elastomer particles agglomeration, the deformation mechanism is changed. For the uncured blend with $\phi_{el} = 0.45$ volume fractions, a well-pronounced yield peak is still observed but its value is ~2.5 times lower than that of the initial PP. After the yield point, tensile stress decreases; then, a uniform polymer strengthening takes place as in the case of the initial PP. With increasing the EPDM content further ($\phi_{el} = 0.50$ volume fractions), the yield peak is less pronounced and its width markedly increases. It is absent at $\phi_{el} \geq 0.60$ volume fractions. In the $\sigma - \varepsilon$ diagrams, one may initially observe a fast growth in tensile stress; upon further deformation, the slope of the curve decreases, and σ almost linearly increases with ε until fracture occurs.

Figure 1b presents the $\sigma - \varepsilon$ diagrams for several samples prepared by the dynamic vulcanization. It is seen that the dynamic vulcanization changes deformational processes in studied blends. The presence of

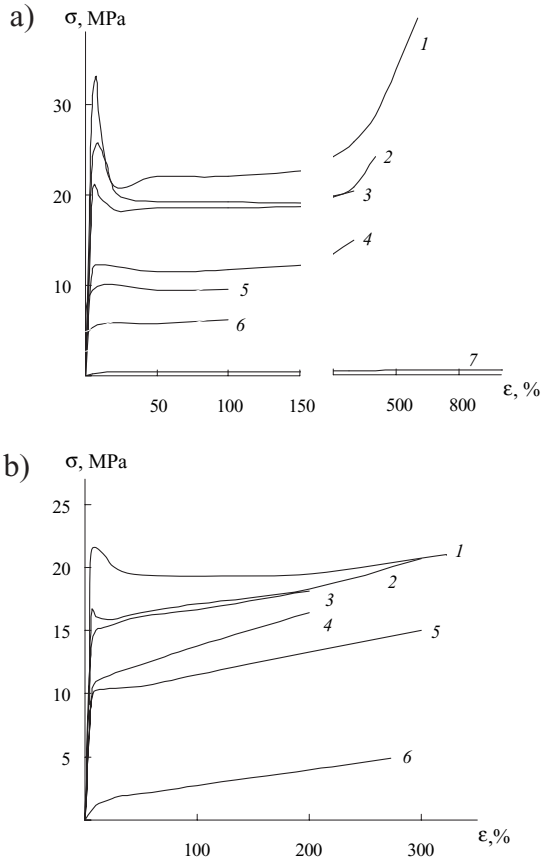

Figure 1.
(**a**) $\sigma - \varepsilon$ diagrams of initial PP (*1*) and uncured blends. $\phi_{el} = 0.15$ (*2*), 0.25 (*3*), 0.45 (*4*), 0.50 (*5*), 0.60 (*6*) and 0.75 (*7*) volume fractions. (**b**) $\sigma - \varepsilon$ diagrams of cured blends. $\phi_{el} = 0.15$ (*1*), 0.25 (*2*, *3*), 0.45 (*4*, *5*) and 0.25 volume fractions (*6*); [S] = 0.5 (*2*, *4*, *6*) and 1.0 phr (*1*, *3*, *5*).

the yield peak depends on both the ratio between the initial components of the blend and the content of the crosslinking agent (sulfur) [S]. For example, the yield stress in a solid state disappears at [S] = 1.0 phr for PP/EPDM blend with $\phi_{el} = 0.25$ and [S] = 0.5 phr for the blend with $\phi_{el} =$ 0.45 volume fractions. The test samples are deformed without neck formation, and prior to fracture one may observe the deformational strengthening of the test samples.

It seems that different mechanical behavior of unvulcanized and dynamically vulcanized PP/EPDM blends results from their different morphology. The domains of uncured elastomer could be exposed to unlimited deformations in a thermoplastic matrix. Whereas cured rubber particles are boundedly deformed and they are more elastic than uncured ones. The presence of crosslinks increases a rigidity of rubber particles. Therefore, the dynamically vulcanized blends with high cure agent concentration characterized by high values of tensile strength.

Figure 2 presents elastic modulus and ultimate characteristics of the blends plotted against elastomer content. As ϕ_{el} is increased, E and σ_b are seen to decrease. Uncured PP/EPDM blends with $\phi_{el} \leq 0.60$ volume fractions are characterized by low values of elongation at break $\varepsilon_b \approx 150$–350%. These values are lower than those of

the initial components. The $\varepsilon_b - \phi_{el}$ curves show a minimum at $\phi_{el} = 0.60$ volume fractions. With increasing the elastomer content above 0.60 volume fractions, ε_b almost linearly increases in the concentration range under study.

For dynamically vulcanized blends with $\phi_{el} \leq 0.75$ volume fractions, the corresponding ε_b values slightly exceed ε_b of uncured materials of the same composition and depend on the EPDM content in the blend. At the same time, for the samples with $\phi_{el} \geq 0.75$ volume fractions, when the rubber phase becomes a matrix, the ε_b of cured blends is lower than that of the uncured ones (Figure 2c). Therefore, as a result of dynamic vulcanization, phase inversion boundary is shifted: for uncured blends phase inversion is observed at $\phi_{el} \sim 0.40$–0.50 volume fractions; but for dynamically vulcanized materials phase inversion takes place at a volume fractional content of elastomer higher than 0.75 volume fractions.

As was mentioned above, the structure of uncured blends at low concentrations of the elastomer phase and dynamically vulcanized materials with $\phi_{el} \leq 0.75$ volume fractions (i.e, at the content below phase inversion point) is similar to the structure of dispersion filled polymer composites. This fact allows one to analyze yield stress in a solid state in terms of the models proposed for this class of composites. The equation describing the dependence of the yield stress of the composite σ_{yc} on the filler content ϕ_f was considered within the minimally effective cross section model [8]:

$$\sigma_{yc} = \sigma_y^0(1 - 1.21\,\alpha\,\phi_f^{2/3})$$

where σ_y^0 is the yield stress of a matrix, α is the fractional content of particles which were separated from the matrix prior to the initiation of plastic flow. With a good adhesion between filler and matrix, filler particles do not separate from matrix before the onset of plastic flow and $\alpha = 0$. In this case, $\sigma_{yc} = \sigma_y^0$. When the adhesion between filler and matrix is low and the particles separate from the matrix before the onset of plastic flow, $\alpha = 1$.

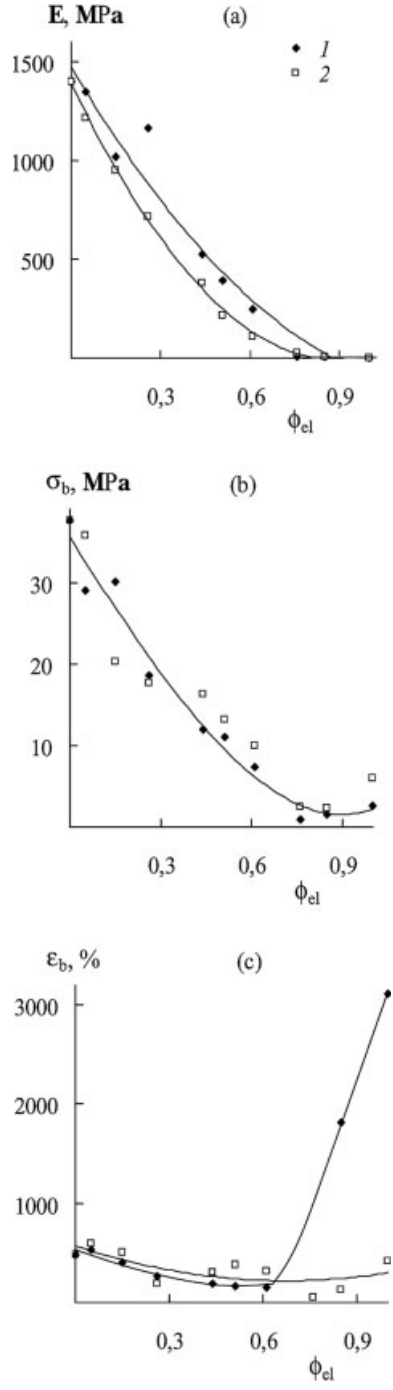

Figure 2.
Elastic modulus E (a), ultimate tensile strength σ_b (b), and elongation at break ε_b (c) vs. ϕ_{el} for uncured (*1*) and cured (*2*) blends. [S] = 1.0 phr.

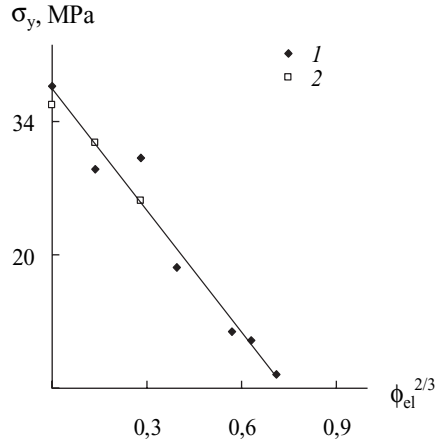

Figure 3.
The dependences of yield stress in a solid state σ_y vs. $\phi_{el}^{2/3}$ for uncured (1) and cured (2) blends. [S] = 1.0 phr.

As was found, the yield stress σ_y of the uncured and cured PP/EPDM blends linearly decreases with increasing ϕ_{el} to 0.50 volume fractions as (Figure 3):

$$\sigma_y = \sigma_{y\,PP}(1 - 1.18\,\phi_{el}^{2/3}) \quad (1)$$

Therefore, the adhesion between rubber particles and the matrix is low, as a result, the matrix is separated from the disperse phase upon tensile drawing and micropores are formed. Upon further deformation, one may observe the growth and the coalescence of pores which lead to the fracture of the sample.

Figure 4 shows the mechanical characteristics of dynamically vulcanized samples plotted against the concentration of the crosslinking agent (sulfur). As is seen, changes in elastic modulus E upon varying the concentration of sulfur are controlled by the blend composition (Figure 4a).

For example, E is independent on the sulfur content for the blends with ϕ_{el} ranging from 0.40 to 0.60 volume fractions, E decreases with increasing the concentration of the crosslinking agent for samples with $\phi_{el} = 0.25$ volume fractions, and E increases slightly for the blends with $\phi_{el} \geq 0.75$ volume fractions. In the latter case, the matrix is represented by the

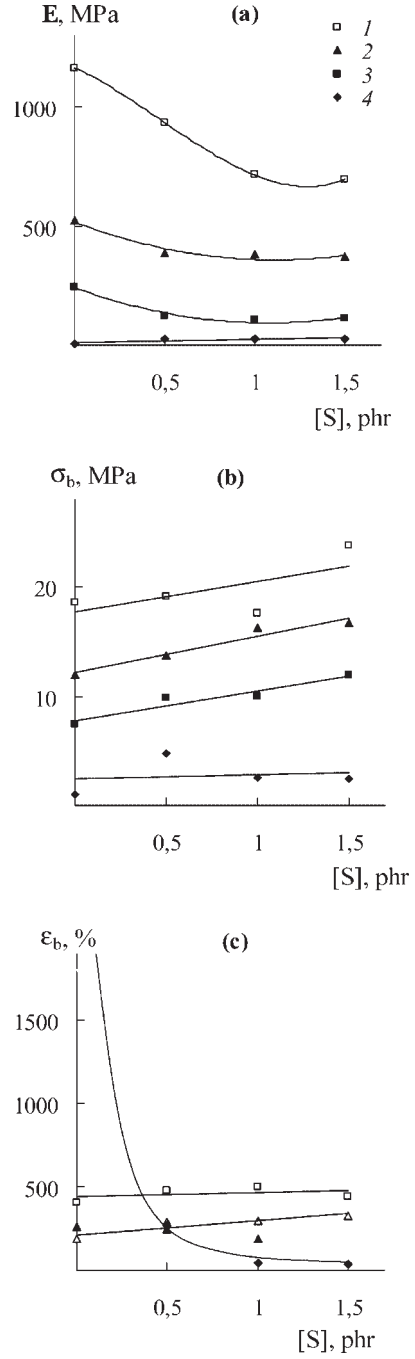

Figure 4.
Elastic modulus E (a), ultimate tensile strength σ_b (b), and elongation at break ε_b (c) vs. the sulfur concentration [S] for cured blends with $\phi_{el} = 0.25$ (1), 0.45 (2), 0.60 (3), and 0.75 (4) volume fractions.

rubber phase. Therefore, with growth of the sulfur concentration, the elastic modulus of the rubber increases and, correspondingly, the elastic modulus of cured blends increases too. Polypropylene as a more rigid filler also increases E. As a result of dynamic vulcanization of the rubber phase, the elastic modulus of dynamically vulcanized blends is changed as compared to the samples containing the nonvulcanized elastomer. This change depends on the ratio between the components and the amount of crosslinking agent.

The elongation at break is virtually independent of the amount of the crosslinking agent; the only exception concerns the blends with $\phi_{el} \geq 0.75$ volume fractions (Figure 4c). For such compositions, ε_b decreases upon vulcanization.

Previous structural investigations shown that the dynamic vulcanization of PP/EPDM blends with the use of sulfur-containing accelerating system leads to the formation of β-phase of PP. However, the studied mechanical characteristics don't depend on the presense of β-PP. They are determined only by PP/EPDM ratio and the amount of crosslinking agent [9].

Rheological Properties

Figure 5 plots the viscosity η versus shear stress τ for the uncured and dynamically vulcanized blends. Two observations are worthy of note.

First, the two systems show substantially different plots at any PP/EPDM ratios. At sufficiently high shear stress values, the viscosity of uncured materials drops as log τ increases, while in the region? less than 3.5. The tendency toward attaining the constant viscosity η_0, corresponding to the Newtonian flow regime, is observed as the shear stress decreases. In other words, the uncured blends behave as melts of common polymers with a wide molecular mass distribution [10]. An appreciable viscosity

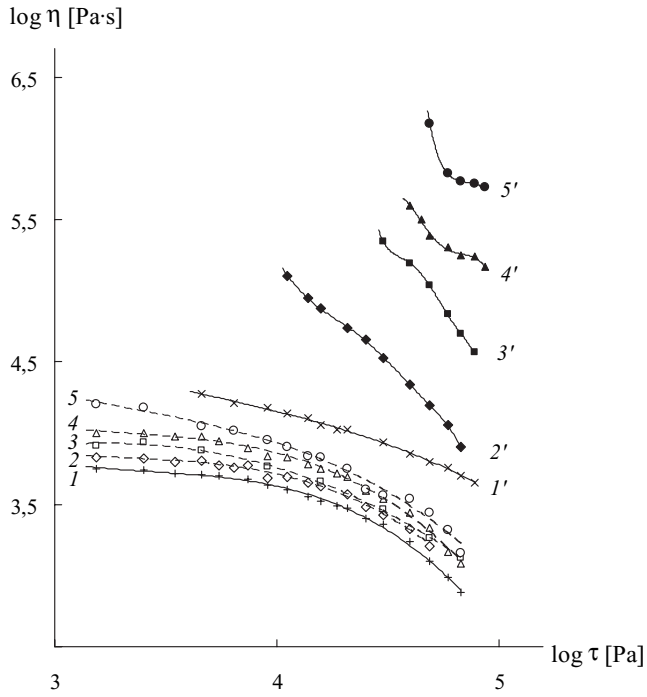

Figure 5.
The viscosity η vs. the shear stress τ for the initial PP (*1*) and EPDM (*1′*), uncured (*2–5*), and cured (*2′ – 5′*) PP/EPDM blends. $\phi_{el} = 0.45$ (*2*, *2′*), 0.50 (*3*, *3′*), 0.60 (*4*, *4′*), and 0.75 (*5*, *5′*) volume fractions. [S] = 1 phr.

anomaly also manifests itself in the case of cured blends. However, a reduction in the shear stress at log τ less than 4.5 leads to a sharp rise in viscosity rather than to the achievement of the region with $\eta_0 = \text{const}$. This effect is typical for heavily structured systems, in particular, polymer composites containing highly disperse fillers for which shear yield stress in a melt state τ_y makes itself evident at sufficiently low values of τ [10].

Second, the viscosity of cured PP/EPDM blends turns out to be much (by tens or hundreds times) higher than that of uncured ones. On the whole, this difference is preserved up to the highest shear stresses tested in this work.

The viscosity of the unvulcanized and dynamically vulcanized blends increases with the elastomer content. However, this trend is more noticeable in the case of higher viscosity cured blends (Figure 6). The growth in the EPDM content from ~0.25 to 0.75 volume fractions insignificantly increases the viscosity of uncured blends, while this raise in viscosity is as great as 30 times in the case of dynamically vulcanized samples. The different changes in the viscosity are apparently related to different structures of blends, different viscosity variations with the blend composition, and different mechanisms of their flow. Figure 6 shows also the concentrational dependence of the shear yield stress in a melt state τ_y for cured blends. The values τ_y were calculated with the use of the Casson equation at low shear stresses and shear rates [7]. It is seen that τ_y increases with the growth of elastomer content.

Figure 7 plots the viscosity of dynamically cured blends as a function of the amount of the crosslinking agent (sulfur). It is shown that the viscosity increases by two or three times with the sulfur concentration.

The distinction between the rheological behavior of uncured and cured blends is evidently related to differences in their structures and viscoelastic characteristics of the uncured and cured EPDM copolymers. A principal difference between the melts of blends of unvulcanized polymers (polymer emulsions) and filled polymer composites (polymer suspensions) is that the flow of the first is accompanied by the irreversible deformation of particles of both phases, which facilitates the flow. In the second case, solid undeformable particles of the filler hamper the flow of the polymer matrix for purely hydrodynamic reasons.

The presence of crosslinks in the rubber particles prevents their irreversible defor-

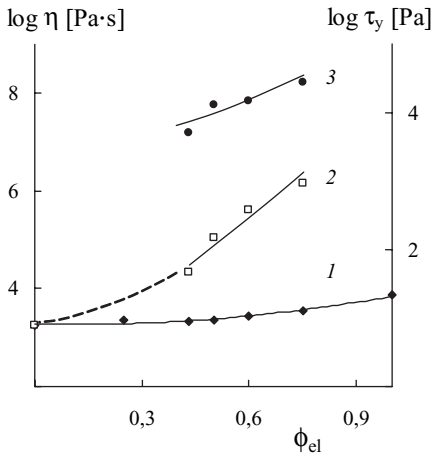

Figure 6.
The viscosity η of uncured (1), cured blends (2) ([S] = 1 phr) and shear yield stress in a melt state τ_y (3) vs. the elastomer content ϕ_{el}. log $\tau = 4.6$.

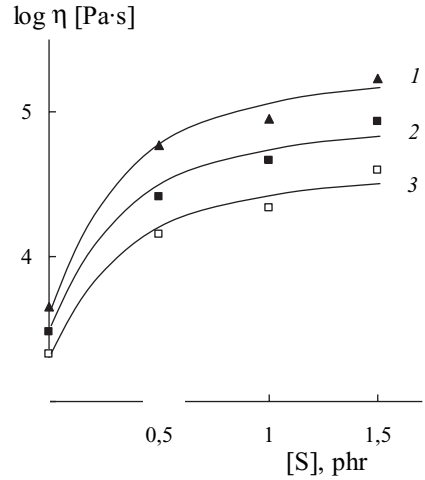

Figure 7.
The viscosity η vs. the sulfur content [S] for cured blend. $\phi_{el} = 0.45$ volume fractions. log $\tau = 4.14$ (1), 4.4 (2) and 4.6 (3).

mation and flow compared to the unvulcanized blend. These difficulties should become more distinct when the rigidity of rubber particles increases and their deformability decreases with the growth of the crosslink density. This results from an increase in the amount of the cure agent and in the concentration of rubber phase particles. Along with the elasticity of crosslinked rubber particles, the viscosity of the blends is also affected by a three-dimensional structural network formed by these particles. This leads to the development of the shear yield stress in a melt state τ_y, as in the case of composites containing highly disperse solid fillers, but at the same time τ_y does not depend practically on the sulfur content [7]. It is this network that increases the viscosity of the material (density of cured samples grows with the concentration of the crosslinked rubber). However, in the flow of cured blends, the breakdown of the network under the high shear stresses should cause a more pronounced viscosity anomaly than that of uncured blends.

Conclusion

Dynamic vulcanization of PP/EPDM blends changes their deformational and rheological behavior as compared with the blends of PP and unvulcanized EPDM. The character of these processes is determined by the components ratio and resulted from the differences in morphology of such materials. The domains of uncured elastomer could be exposed to unlimited deformations in a thermoplastic matrix. Whereas cured rubber particles are boundedly deformed and they are more elastic than uncured ones. The rigidity of cured rubber particles increases and their deformability decreases with the growth of the crosslink density. They are formed a three-dimensional structural network also effected on the deformational and flow behavior of PP/EPDM blends.

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