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Rheological behaviors of blends based on polypropylene and EPDM rubber powder

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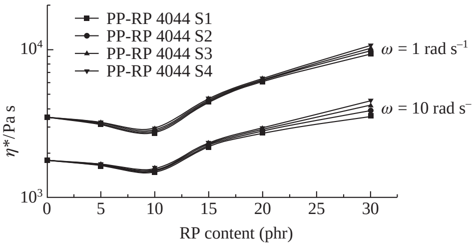
A significant improvement in the melt flowability of polypropylene/rubber powder (RP) blends was found to depend on the RP content. The viscosity of polypropylene decreased significantly with the addition of up to 10 phr RP.



The recycling of waste rubber products is a serious environmental problem of considerable current importance.[1–3] A high-temperature shear deformation (HTSD) technique[4] developed at N. N. Semenov Institute of Chemical Physics of the Russian Academy of Sciences is a promising method of rubber recycling. It is based on the fracturing of solids with the formation of individual particles under the joint action of compression and shear deformation at elevated temperatures. The grinding of crosslinked rubbers occurs under the joint mechanical and thermal impact. During HTSD, the action of mechanical factors initiates chemical processes such as oxidation, degradation and secondary structurization. In this context, the composition and properties of rubbers used for the production of rubber powders (RPs) play an important part.

A tire is a composite involving complex elastomer formulations, fibers, textiles and steel cord. Therefore, to produce RPs by the HTSD method, the characterized vulcanizates of ethylene–propylene–diene monomer (EPDM) rubbers with different crosslink densities and paraffin oil contents were used. This made it possible to study the physicochemical processes taking place during the vulcanization of ethylene–propylene–diene elastomers at 190 °C and to suggest the mechanism of their grinding. Moreover, the effect of the properties of EPDM vulcanizates on the characteristics of the resulting RPs was estimated.[†]

Under the HTSD grinding conditions, the inevitable thermal and mechanical degradation is an important factor. The basic characteristic of powder materials is their dispersity, that is, the characteristic size of the material structures. Hence, the experimental methods of measuring the dispersity and estimating the particle size are relevant to the above materials.

Figure 1 shows the particle-size distribution curves of RPs prepared from EPDM vulcanizates with different crosslink densities and plasticizer contents.[8] The curves have an asymmetrical shape with the asymmetry increasing with the crosslink density of EPDM vulcanizates regardless of the plasticizer content. This indicates that the grinding of a more densely crosslinked EPDM vulcanizate results in a larger fraction of finer RP particles.

Using the mathematical methods of statistics,[9] the following parameters were calculated from the particle size distribution curves of RPs:

– arithmetical weighted mean

$$\bar{X} = \frac{\sum x_i f_i}{\sum f_i},$$

where x_i is the RP particle size and f_i is the fraction of RP particles with size x_i;

– median

$$Me = X_{Me} + h_{Me}\frac{\frac{1}{2}(\sum f) - S_{Me-1}}{f_{Me}},$$

where X_{Me} is the lower boundary of the median interval, h_{Me} is the width of the median interval, S_{Me-1} is the sum of cumulative frequencies of an interval preceding the median interval, and f_{Me} is the local frequency of the median interval;

[†] The RPs were prepared by HTSD method using a rotor disperser constructed on the basis of a single-screw extruder.[5]

The following EPDM elastomers (Polimeri Europa, Italy) were used: Dutral TER 4044 (EPDM 4044) with 35% propylene units and a Mooney viscosity of 44 (at 100 °C); Dutral TER 4334 (EPDM 4334) with 27% propylene units, 30% paraffin oil and a Mooney viscosity of 28 (at 125 °C); and Dutral TER 4535 (EPDM 4535) with 32% propylene units, 50% paraffin oil and a Mooney viscosity of 32 (at 125 °C). The EPDM vulcanization was carried out using a multicomponent vulcanization system of sulfur (1.0–4.0 phr), tetramethylthiuram disulfide (0.73 phr), di(2-benzothiazolyl) disulfide (0.25 phr), zinc oxide (2.53 phr) and stearic acid (1.0 phr).

The particle size distribution of RPs in an aqueous medium was determined by laser diffraction on a Fritsch Analysette 22 Microtec Plus particle size analyzer (Germany) with a resolution from 0.08 to 2000 μm.[6]

Blends with different compositions were prepared by mixing the components in Plastograph EC (Brabender, Germany) at 190 °C and 100 rpm for 10 min.

For mechanical testing, the blends were molded into plates with a thickness of 1 mm for 10 min at 190 °C and 10 MPa with the subsequent cooling at a rate of ~15 K min^{-1} under pressure.

The uniaxial tension of samples was determined on an Instron-1122 tensile test machine at room temperature and an upper crosshead speed of 50 mm min^{-1}.

The rheological properties were analyzed using a parallel-plate rheometer at 190 °C.[7]

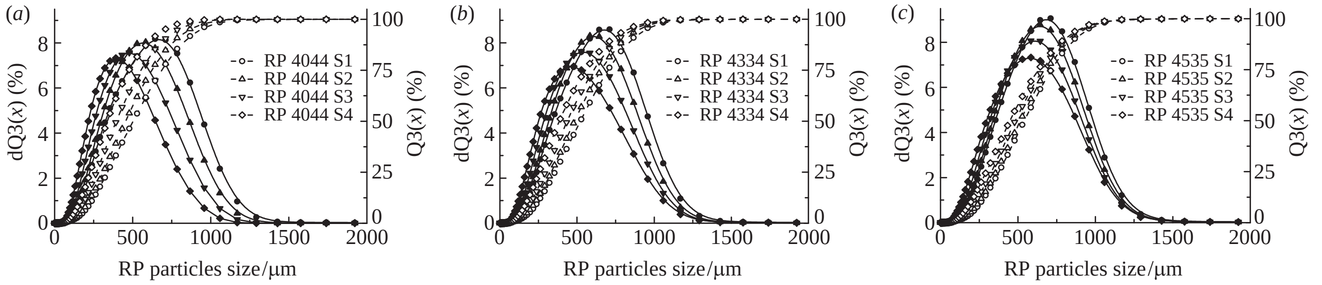


Figure 1 Differential dQ3(*x*) and cumulative Q3(*x*) particle size distributions of (*a*) RP 4044, (*b*) RP 4334 and (*c*) RP 4535.

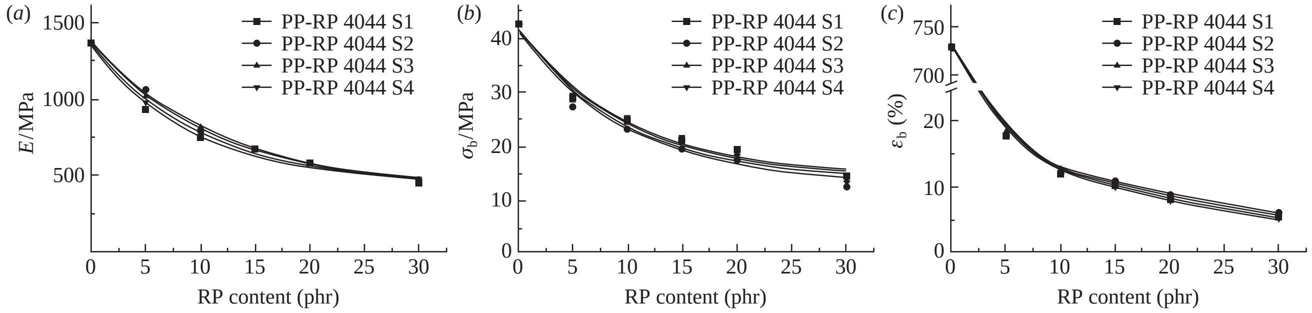


Figure 2 (*a*) Modulus of elasticity *E*, (*b*) ultimate strength σ_b, and (*c*) elongation at break ε_b as functions of the RP content.

– mode

$$Mo = X_{Mo} + h_{Mo}\frac{f_2 - f_1}{(f_2 - f_1) + (f_2 - f_3)},$$

where X_{Mo} is the lower boundary of the modal interval, h_{Mo} is the width of the modal interval, f_1, f_2, and f_3 are the local frequencies of the interval preceding the modal one, the modal interval, and the following interval, respectively;

– asymmetry coefficient $As = \mu^3/\sigma^3$ and excess coefficient $Ex = \mu^4/\sigma^4 - 3$, where μ^3 and μ^4 are the central moments of the third and fourth order, respectively, and σ is the root-mean-square deviation.

The above parameters made it possible to estimate the distribution in more detail. Figure 1 and Table 1 indicate that the distribution curves have an asymmetrical shape with the asymmetry increasing with the crosslink density of EPDM vulcanizates and being virtually independent of the plasticizer content. Thus, the grinding of a more densely crosslinked EPDM vulcanizate results in a greater fraction of finer RPs.

The RP content is a significant factor that influences the structure and properties of blends. The incorporation of RPs into polymer matrices essentially deteriorates the mechanical properties of the blends due to very weak interfacial adhesion between the RP particles and the matrix-forming polymer (Figure 2).

Table 1 Parameters of RP particle size distributions.

Type of RP	$\bar{X}$/μm	*Me*/μm	*Mo*/μm	*As*	*Ex*
RP 4044 S1	549	527	667	0.46	0.04
RP 4044 S2	501	477	567	0.50	0.05
RP 4044 S3	444	415	492	0.62	0.12
RP 4044 S4	384	354	396	0.75	0.30
RP 4334 S1	566	548	678	0.44	0.12
RP 4334 S2	530	508	607	0.49	0.18
RP 4334 S3	487	458	539	0.62	0.31
RP 4334 S4	443	406	460	0.80	0.64
RP 4535 S1	583	568	684	0.42	0.21
RP 4535 S2	559	540	642	0.46	0.25
RP 4535 S3	531	507	609	0.54	0.27
RP 4535 S4	501	470	574	0.63	0.32

The incorporation of RPs in a thermoplastic matrix alters its processability *via* a related change in the viscosity. The large surface area of RP particles, which triggers interparticle interactions, also has a major impact on the rheology of PP/RP systems. It is well known that the microstructure markedly influences the rheological behavior of blends. The viscoelastic properties of two-phase polymer materials depend on the size and deformability of the dispersed phase. Note that the deformability of the dispersed domains is also greatly affected by their sizes.

The addition of a relatively small amount of RPs (5–10 phr) reduced the complex viscosity η^* of the corresponding two-phase system compared to the matrix. The values of η^* of PP/RP blends went through a minimum at a loading of about 10 phr RP (Figure 3). Similar curves are observed for all frequencies ω.

The reduction of the particle–particle distance with increasing RP loading restricts the mobility of PP chains and thus increases the complex viscosity of the blend. It is evident that all blends with various RP loadings display increases in elastic response with frequency. The appearance of a minimum in the viscosity curve is most probably associated with the formation of an additional free volume in the polymer layers adjacent to filler particles.[10]

Grinding under the action of the high-temperature shear deformations of EPDM vulcanizates cured by a sulfur-based system up to different degrees of crosslinking was studied. The distribution curves have an asymmetrical shape with the asymmetry increasing with the crosslink density of EPDM vulcanizates.

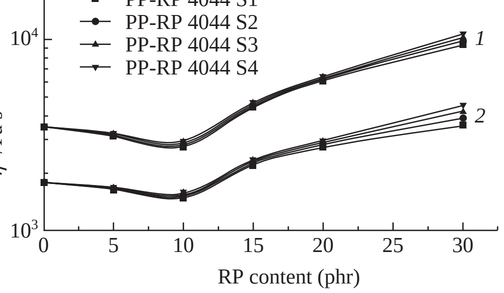


Figure 3 Plots of complex viscosity log η^* *vs.* RP content at ω of (*1*) 1 and (*2*) 10 rad s^{-1}.

The incorporation of rubber powder into polypropylene led to a decrease in the mechanical performance. The addition of a relatively small amount of RP (5–10 phr) reduced the complex viscosity η^* of the corresponding two-phase system compared to the matrix. The complex viscosity of polypropylene decreased significantly with the addition of up to 10 phr of RP. The addition of rubber powder to PP did not change η^* for all frequencies.

The dynamic rheological behavior of composites strongly depended on the degree of agglomeration of the powdery filler. The appearance of a minimum in the viscosity curve was reasoned by supposing the formation of an additional free volume in the interphase adjacent to filler particles.

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References

1 J. Karger-Kocsis, L. Mészáros and T. Bárány, *J. Mater. Sci.*, 2013, **48**, 1.
2 *Rubber Recycling*, eds. S. K. De, A. I. Isayev and K. Khait, CRC Press, Boca Raton, FL, 2005.
3 *The Science and Technology of Rubber*, eds. J. Mark, B. Erman and M. Roland, 4th edn., Academic Press, Boston, 2013.
4 E. V. Prut, *Polym. Sci.*, 1994, **36A**, 493.
5 D. V. Solomatin, O. P. Kuznetsova and E. V. Prut, *Int. Polym. Sci. Technol*., 2012, **39**, 119.
6 H. G. Merkus, *Particle Size Measurements: Fundamentals, Practice, Quality*, Springer, New York, 2009.
7 J. D. Ferry, *Viscoelastic Properties of Polymers*, 3rd edn., John Wiley & Sons, New York, 1980.
8 C. Jacob, P. P. De, A. K. Bhowmick and S. K. De, *J. Appl. Polym. Sci.*, 2001, **82**, 3293.
9 K. Falconer, *Fractal Geometry: Mathematical Foundations and Applications*, 3rd edn., John Wiley & Sons, 2014.
10 E. Prut, O. Kuznetsova, J. Karger-Kocsis and D. Solomatin, *J. Reinf. Plast. Compos.*, 2012, **31**, 1758.

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