Effect of Oil and Cured Agent Content on the Structure and Properties of Thermoplastic Vulcanizates

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Summary: The effect of oil and curing agent content on the mechanical behavior of thermoplastic vulcanizates, based on a polypropylene (PP) and ethylene-propylene-diene copolymer (EPDM), was investigated. Mechanical properties such as Young's modulus, stress at 100% elongation and ultimate stress were investigated as a function of blends' composition and phase morphology. Experimental studies show that the Young's modulus of the vulcanizates depends on both PP/EPDM ratio and oil content in the blends; both ultimate strength and stress at 100% elongation increase with curing agent content.

Introduction

The dynamic vulcanization is an efficient process for the production of polymer materials in which chemical reactions occur alongside the mechanical mixing of components. Materials prepared by dynamic vulcanization of blends of thermoplastics and rubbers are known as thermoplastic vulcanizates (TPV). In general, TPV are materials in which cured micron-size rubber particles are dispersed in continuous thermoplastic matrix[1]. Due to such morphology TPV show elastomeric properties at ambient temperature but are processable as thermoplastics at high temperatures. Incorporation of additives such as fillers and plasticizers affects significantly changes in structure, rheological, elastic and ultimate mechanical properties of TPV.

To realize the dynamic vulcanization process in one stage it is important that the mixing conditions used would ensure vulcanization of the rubber phase within short period of polymer blending. Previously[2], we have described the criteria that have enabled us to choose the agents for the curing system, temperature and type of mixing elements to attain both mixing and vulcanization successfully. These criteria are as follows: $\tau_{mix} \leq \tau_i \leq \tau_{res}$, where τ_{mix} is the time of components' mixing, τ_i is the induction period of vulcanization reaction and τ_{res} is the residence time of components in the mixer.

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In this work, the effects of the content of both oil and the curing agent on the morphology and the mechanical properties of TPV, based on isotactic polypropylene (PP) and ethylene-propylene-diene copolymer (EPDM), were studied.

Experimental

Materials

Commercial isotactic PP (density 0.907 g/cm^3, melting point 165°C, degree of crystallinity 55%), oil-extended and oil-free Dutral TER EPDM were used. The characteristics of EPDM used are as follows:

EPDM-1: density 0.875 g/cm^3, propylene contents 35%, Mooney viscosity 44 (125°C), oil content 0%;

EPDM-2: density 0.880 g/cm^3, propylene contents 32%; Mooney viscosity 32 (125°C), oil contents 50%.

Blend preparation

Reactive blending of the polymers was carried out at 190°C in Brabender type internal mixer. Dynamic vulcanization was achieved in one stage using a sulfur-accelerating system[3], with sulfur content ranging from 0.5 phr to 1.5 phr; PP/EPDM ratio was varied between 40/60 and 25/75.

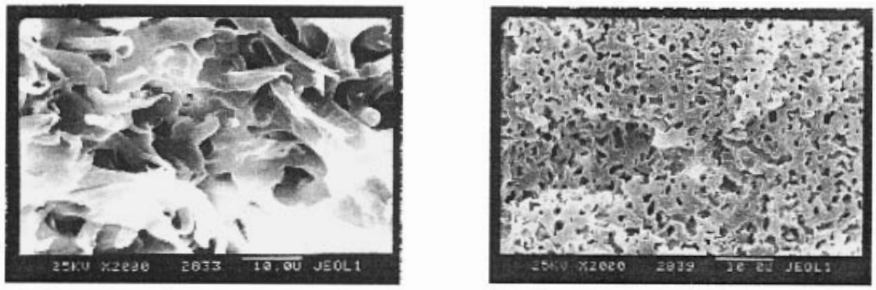
Test techniques

The stress-strain behavior of dumb-bell specimens was determined at room temperature using an "Instron-1122" at constant crosshead speed. The TPV granules were compression molded into sheets at 190°C, under pressure of 13 MPa for 10 min. The sheets were cooled under the same pressure and samples cut (12.0 x 1.4 x 0.35 mm). The morphology of cryogenically (liquid nitrogen) fractured surfaces of the uncured blends were examined by scanning electron microscopy (JEOL JSM-35C).

Results and discussion

The presence of oil in the EPDM phase leads to completely different morphology of TPV prepared at the same PP/rubber ratio (without oil) and mixing parameters (Figure 1). It is shown that the structure of PP/EPDM-1 blends resembles that of an interpenetrating network (Figure 1a). It means that in this case too high viscosity of oil-free EPDM phase does not permit adequate mixing to achieve the degree of dispersion required during the short residence time of the material in the mixer, e.g. $\tau_{res} \leq \tau_{mix}$. The presence of oil in the PP/EPDM-2 blend appears to drastically change the situation sharply (Figure 1b) because of

lowering viscosity, hence achieving the high extent of dispersion of the rubber phase in the PP matrix.



(a) **(b)**

Figure 1. Scanning electron microscope images of uncured TPV at the PP/EPDM ratio 1.33: PP/EPDM-1 **(a)** and PP/EPDM-2 **(b)**.

These morphological peculiarities should obviously lead to absolutely different deformation behaviour and mechanical characteristics of cured TPV based on EPDM-1 and EPDM-2. To verify this, the mechanical properties such as Young's modulus (E_0), stress at 100% elongation (σ_{100}) and tensile strength (σ_b) of PP/EPDM-1 and PP/EPDM-2 blends were investigated as a function of sulfur (S) content.

The behaviour of TPV under deformation and their dependence of their mechanical properties on sulfur content, especially E_0, appears to depend on the type of EPDM. In the case of the oil-free system, the E_0 values show a drop down with increasing of sulfur content (Figure 2a).

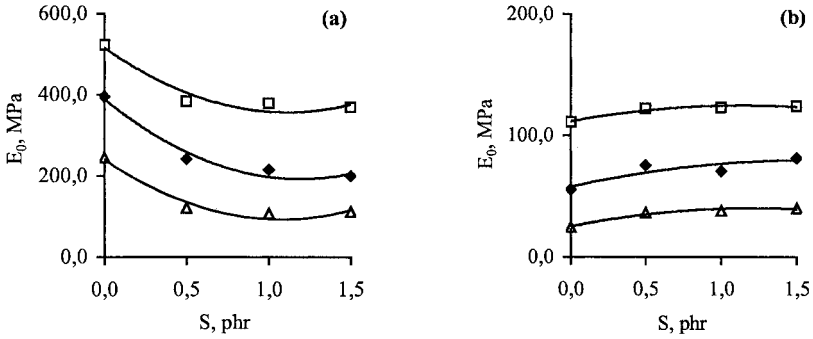


Figure 2. Dependences of the Young's modulus on sulfur contents in TPV samples: PP/EPDM-1 **(a)** and PP/EPDM-2 **(b)**; PP/EPDM ratio: □=1.33, ♦=1, Δ=0.67.

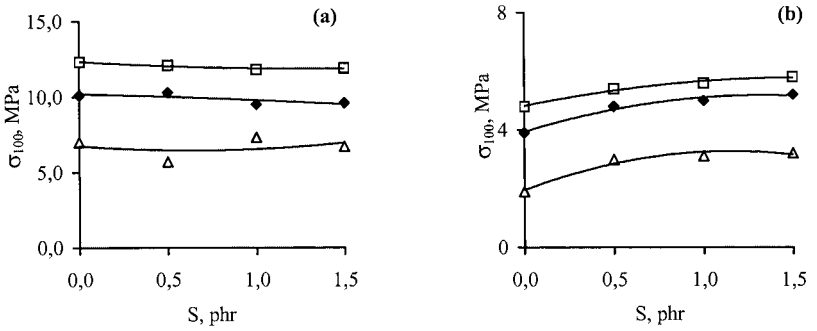


Figure 3. Dependences of σ_{100} on the sulfur contents in TPV samples: PP/EPDM-1 **(a)** and PP/EPDM-2 **(b)**; PP/EPDM ratio: □=1,33; ♦=1; =0,67.

It is clear from figures 2 and 3 that higher degree of curing of the EPDM phase is accompanied by increased viscosity of EPDM resulting in a coarse dispersion of EPDM. As a result, the PP matrix develops many defects and regions of discontinuities. It is clear from figure 3 that the elongation values σ_{100} do not depend on sulfur content (Figure 3a) whereas the ultimate stress increases with sulfur content (Figure 4a) for PP/EPDM-1 blends. These results confirm the mechanism of TPV stretching strain[4]: at the initial stage, the PP matrix is predominantly deformed, but with the development of TPV elongation, both PP and the dispersed rubber phase are jointly deformed.

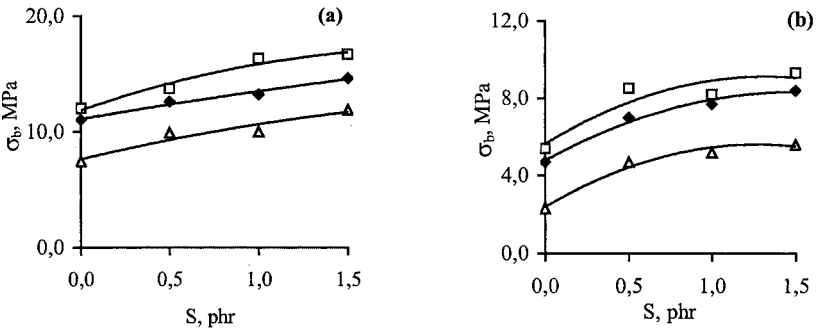


Figure 4. Dependences of σ_b on the sulfur contents for TPV samples: PP/EPDM-1 **(a)** and PP/EPDM-2 **(b)**; PP/EPDM ratio: □=1.33, ♦=1, Δ=0.67.

Compared to PP/EPDM-1, the dependences E_0 on sulfur content of the oil-extended material show slight increases with increasing sulfur content. In this case, the PP matrix is deformed

only and the effect of the presence of the curing agent is not displayed initially (see Figure 2b). Subsequently, PP and EPDM are deformed jointly (as mentioned above) and dependences σ_{100} on sulfur content, and particularly σ_b vs S, develop more sharply (see Figure3b and 4b). It should be noted, however, that the absolute values of all the measured properties of PP/EPDM-2 are lower when compared to those of PP/EPDM-1. These results suggest that lowereing of these properties is attributed to diffusion of some of the oil from EPDM into the PP matrix.

Conclusions

Structure and composition of the polymer blends influence the stress-strain properties of TPV. The experimental studies show that the Young's modulus (E_0) depends on both PP/EPDM ratio and contents of oil in the polymer blends. The value E_0 decreases with growth of sulfur concentration in cured system for oil-free TPV, but it increases insignificantly in case of oil-extended blends. Ultimate strength and stress at 100% elongation grow with the sulfur concentration independently on oil contents. The oil-extended TPV have a structure with a high degree of dispersion of rubber particles in thermoplastic matrix.

Acknowlegments

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