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THE EFFECTS OF POLYETHYLENE AND POLYPROPYLENE ON THE THERMAL PROPERTIES OF ETHYLENE-PROPYLENE TERPOLYMER

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The effects of low-density polyethylene or isotactic polypropylene on the thermal properties of ethylene-propylene-diene rubber were examined by using a rheometer and a derivatograph. Pronounced changes in the thermal properties of the rubber were observed as a result of the polyolefin addition.

Blends of elastomers and plastomers are mostly microheterogeneous. As a rule, the continuous phase consists of an elastomer, while a plastomer forms the discrete phase; the shape of the particles is usually spherical [1-3]. The dimensions of the particles in the dispersed phase depend on the viscosity of both the polymeric components and are the smaller, the lower the viscosity of the dispersed phase [3, 4]. Depending on the solubility parameters of the two polymers, a diffusion layer with varying thickness is formed in these systems [5]. There are promising prospects of useful modification of the ethylene-propylene elastomer by using homopolymers of polyethylene or polypropylene. Therefore, a knowledge of the thermal properties of such blends is needed for a choice of reasonable parameters for the processing of the blend under consideration.

Experimental

Materials

The following polymers were studied: Polish low-density polyethylene (0.916 g/cm^3) (PE), Polish isotactic polypropylene with a density of

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0.920 g/cm^3 (PP) and a Dutch terpolymer of ethylene, propylene and ethylidenenorbornene (EPDM), Keltan 712.

Methods

Blends consisting of 100 parts by wt. of Keltan 712 and 5, 10, 15, 20 or 25 parts by wt. of PE or PP were prepared by mixing in a rolling mill (David Bridge Co. Ltd., England). The rolling temperature was 165° when mixing PE, and 190° when mixing PP.

The melt flow indices $MFI_{(190,\ 211.8)}$ of the blends were determined according to Polish Standard PN 80/C 89069 under the following conditions: measuring temperature 190°, reference time 600 s, nominal load 211.8 N.

Measurements of the plasticity of the blends of the elastomer with the plastomers were carried out with a Vuremo rheometer. The shear modulus G_T was measured *vs.* temperature. Samples were put in the rheometer chamber and heated at 90° for 1 h. Then, after a constant G_T level was reached, the temperature was raised by 10 deg and the shear modulus was measured; this procedure was repeated until a temperature of 190° was reached.

The thermal stabilities of PE, PP, EPDM and their blends were measured with a derivatograph (Paulik, Paulik, Erdey system) under the following conditions: environment air, standard substance Al_2O_3, temperature range 25 800° sample size 60 or 80 mg, heating rate 7.9 deg/min.

The samples were disintegrated or made in form of a film before being examined. The PE and PP films were prepared by pressing in a steel mould for 5 min at 160° and 180°, respectively.

Results and discussion

Changes in the shear modulus of the elastomer-plastomer blends are illustrated in Fig. 1 a, b. It follows from this Figure that the shear modulus of both plastomers is increased at moderately elevated temperature, with G_T of PP being increased to a somewhat higher extent than that of PE. As the temperature increases, this effect gradually disappears. The conclusion arises that the crystalline phases of PE and PP remain stable at 130° and 180°, respectively. The sharp decrease in the shear modulus of the blends is then a sign of the melting of the crystalline phase in the plastomers. We also observed that the melt flow indices of the plastomers are considerably increased at 190° (Fig. 2). The melted plastomers, with lower molecular weights than that of the elastomer, in this case play the role of plasticizers.

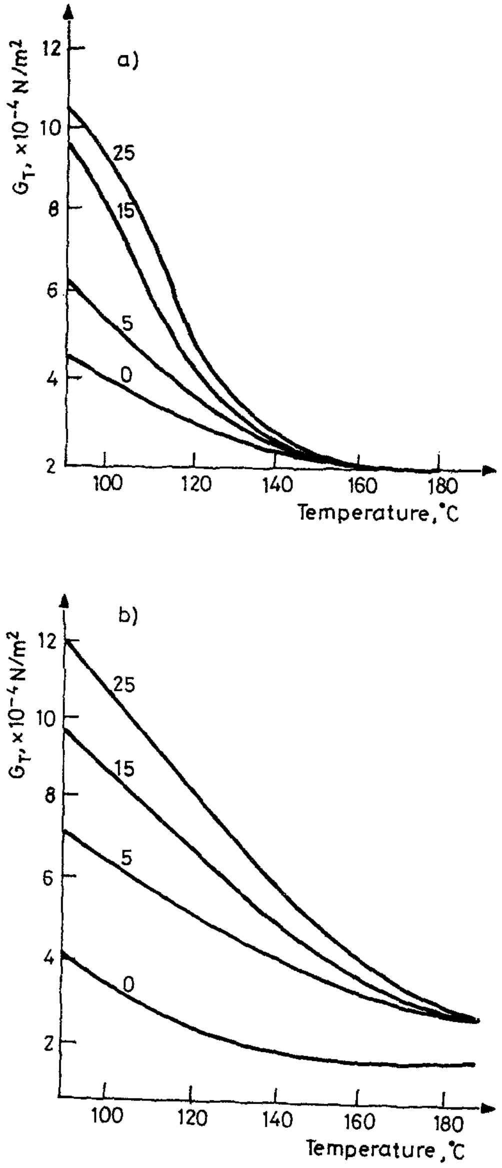

Fig. 1 Shear modulus of EPDM blends with a) PE, b) PP *vs.* temperature

Figures 3, 4 and 5 show thermoanalytical curves of the EP rubber, PE and PP, respectively. In the case of the elastomer the exothermic change at 230° is associated with cross-linking and thermooxidative processes. Its thermooxidative destruction begins at 330° (Fig. 3).

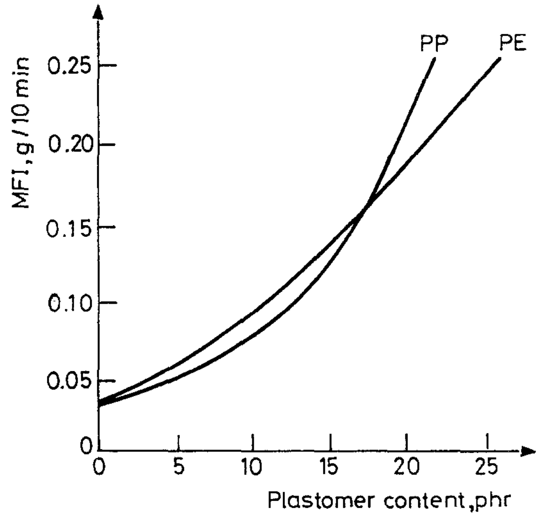

Fig. 2 Melt flow index of EPDM blends with PE or PP (%)

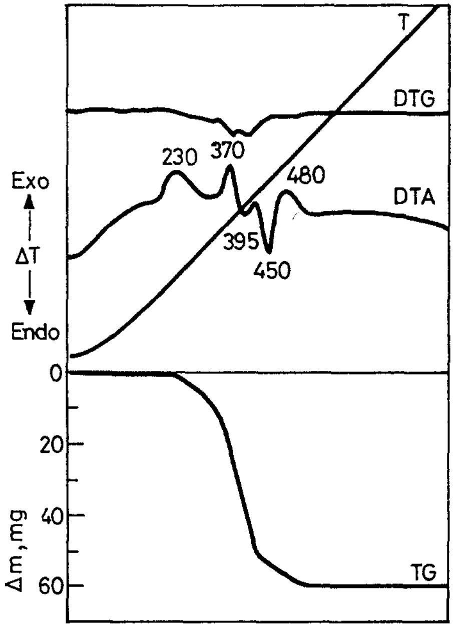

Fig. 3 Thermoanalyitical curves of EPDM

The endothermic processes at 395° and 450° result from the thermal destruction of the elastomer. The combustion of a small residue from the polymer decomposition takes place at 480°. Clear differences in relation to the elastomer can be observed in the curves of the homopolymers. The first endothermic process, associated with the melting of the crystalline phase, reaches the maximum rate at 115° for PE (Fig. 4) and at 140° for PP (Fig. 5). These endothermic processes disappear at 135° (PP) and at 180° (PP), respectively, which corresponds well with the results of examination of the changes in the shear modulus of blends of EP copolymer with the homopolymers. The exothermic changes in the DTA curve of PE at 230° and 350° are associated with thermooxidative processes, while the endothermic one at 415° is due to the thermal decomposition of the sample. The exothermic peak at 453° points to the combustion of the solid polymer residue resulting from polymer decomposition (Fig. 4).

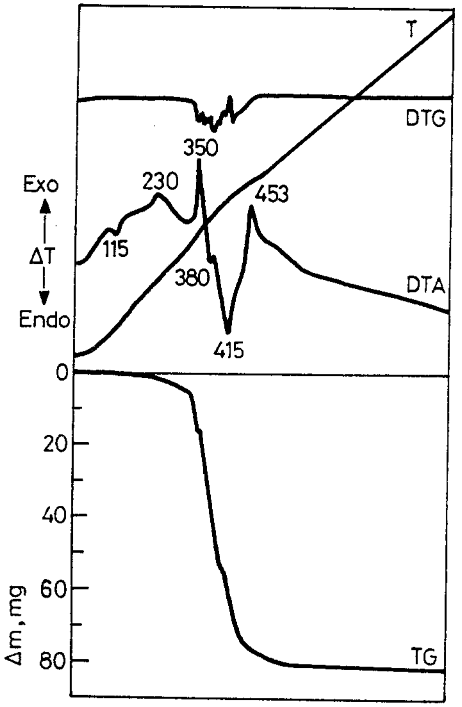

Fig. 4 Termoanalytical curves of PE

The thermal destruction of PP begins at 300° (Fig. 5) and brings about an abrupt weight loss, down to practically zero.

The addition of PE or PP to the elastomer in amounts of 5 to 25 parts by wt./100 parts by wt. of EPDM does not cause any significant changes in the thermal curves, but affects the temperatures of particular processes. Figure 6 a and b shows thermoanalytical curves of blends containing 25 parts by wt. of PE or PP with EP elastomer. There are no changes associated with the melting of the crystalline phases of the plastomers.The apparatus used was probably not sensitive enough.

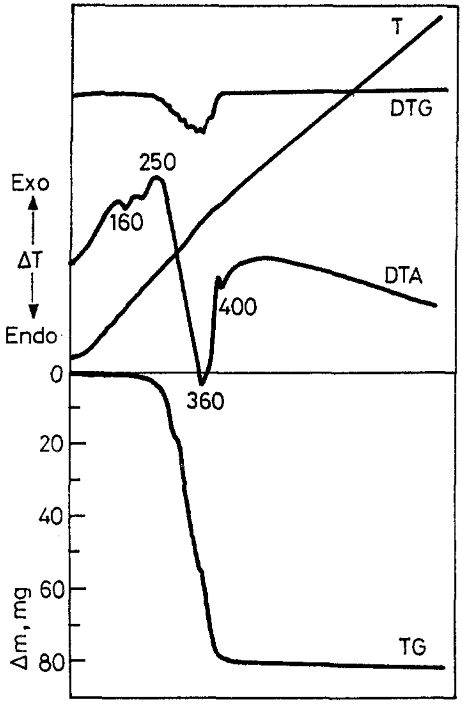

Fig. 5 Termoanalytical curves of PP

In order to confirm the conclusion about the appearance of a crystalline phase in the elastómer/plastomer blends, measurements of density were performed. Blends of EPDM with PP were selected for the examination (Fig. 7). It turned out that the densities of the blends reach higher values than those calculated additively. This would suggest that molecules of PP contained in the blend play the part of crystallization nuclei in relation to the sequences of the PP units in the copolymer. In light of the results obtained, one may assume the presence of crystalline phase to be proved.

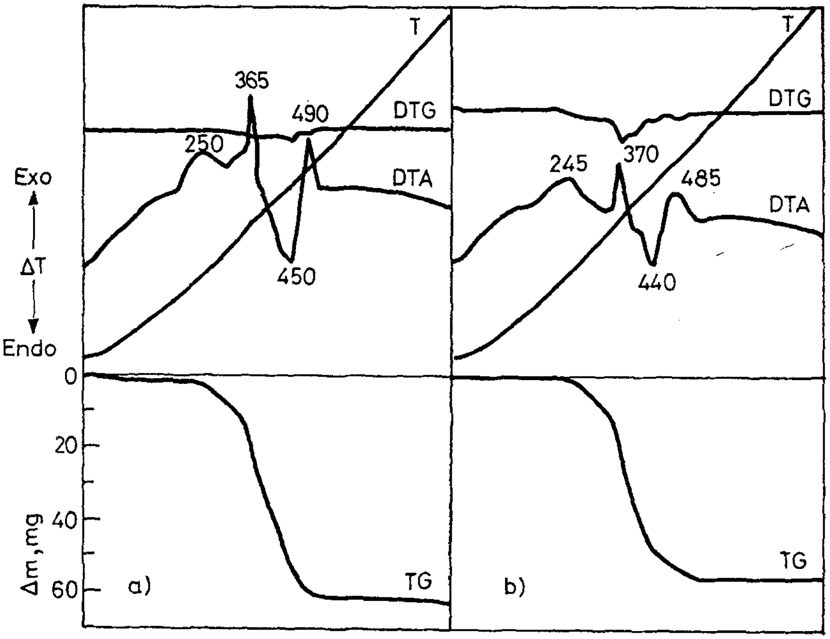

Fig. 6 Termoanalytical curves of EPDM blends with a) PE, b) PP/25 parts by wt. of PE or PP/100 parts by wt. of EPDM

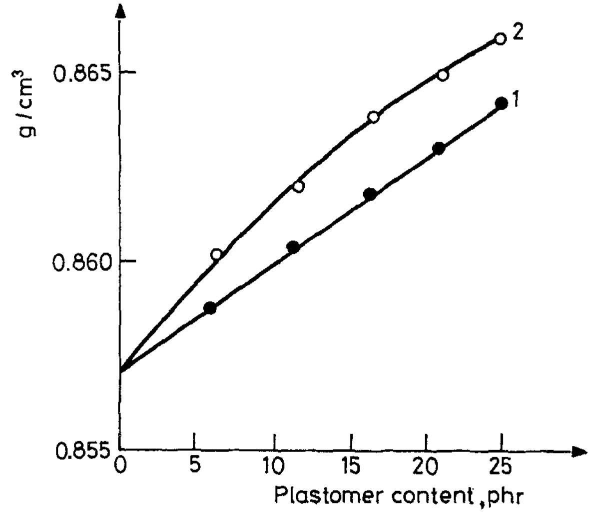

Fig. 7 Density of EPDM with PP vulcanizates 1. calculated additively; 2. experimental

Conclusions

1. The addition of a low-density PE or an isotactic PP affects the properties of the ethylene-propylene rubber considerably.

2. There is an increase in the shear modulus at a temperature below the melting point of the crystalline phase of the plastomers. When the melting point is exceeded, a sharp decrease in the viscosity of the system takes place.

3. Particles of PP are probably nuclei of crystallization of PP units in the ethylene-propylene terpolymer.

References

1 L. Šlusarski, J. Kuczynski and M. Zaborski, Preprints of the VI International Rubber Conference, Kijev 1978, A33.

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Zusammenfassung – Der Einfluss hochdruck Polyäthylen und isotatisches Polypropylen auf die thermischen Eigenschaften von Äthylen-Propylen-Terpolimer, Keltan 712, wurde mittels Rheometer, Plastometer und Derivatograph untersucht. Es wurde festgestellt das, der Zusatz von Polyolefine hat grossen Einfluss auf die thermische Eigenschaften des Kautschuks.