

Mixtures of ethylene-propylene copolymer with atactic polypropylene

Efficiency of crosslinking by dicumyl peroxide

V. POLLÁK, A. ROMANOV, and K. MARCINČIN

*Polymer Institute, Slovak Academy of Sciences,
809 34 Bratislava*

Received 24 May 1971

The crosslinking efficiency of partially compatible mixtures of ethylene-propylene copolymer (EPc) with atactic polypropylene (aPP) by means of dicumyl peroxide (DCP) has been studied. The results have been compared with crosslinking efficiency of EPc of appropriate composition.

The crosslinking of statistical EPc by peroxides has been investigated by several authors [1–6]. They found that crosslinking efficiency decreases with increasing content of the propylene component in copolymer. It may well be explained by the fact that polypropylene branches and decays due to peroxide action. The present paper has been aimed at the investigation of crosslinking of the mixtures of EPc with aPP which are partially compatible.

Experimental

EPc, commercial mark Dutral, $M_n = 7 \times 10^4$, propylene content 50 mole %; aPP $M_n = 5 \times 10^4$, solubility in *n*-heptane at room temperature 100%; DCP twice recrystallized from ethanol, were used.

The mixtures of EPc with aPP of various composition were prepared on laboratory masticator at room temperature. The dynamic-mechanical tests were performed on torsion pendulum at the frequency of about 1 Hz. The crosslinking was carried out on a laboratory press at 160°C for 45 minutes with a content of 2.5 weight parts of DCP per 100 weight parts of mixture. The network density was determined from the equation of the dependence of the equilibrium force f on the sample elongation [7]

$$f = 2A_0(\alpha - \alpha^{-2}) (C_1 + C_2 \alpha^{-1}),$$

where $2C_1 = \nu_{\text{eff}} RT$, and

$$\nu_{\text{eff}} = \nu(1 - KM_c M_n^{-1}),$$

$$M_c = \frac{\rho}{\nu},$$

$$\nu = \nu_{\text{eff}} + 2\rho M_n^{-1}.$$

A_0 — cross-section of the sample, α — relative elongation, C_1, C_2 — constants, ν_{eff} — number of elastically active network chains per unit volume, ν — number of total network chains per unit volume, $K = 2$ [8], M_c — the average molecular weight of the polymer between crosslinks, ρ — density.

The values of the equilibrium force f in dependence on the elongation were obtained on a Cambridge Textile Extensometer. The measurements were made after 5–6 hours of sample relaxation at 70°C. The relative elongation α ranging from 1.2 to 1.65.

Results and discussion

The properties of mixtures used for crosslinking studied by dynamic-mechanical tests are shown in Figs. 1 and 2, respectively. When compared with the components the mixtures exhibit an enlarged transition region which may be regarded as the reflex of microheterogeneity and existence of almost continual series of phase composition, respectively. Each composition has a specific contribution to the dynamic-mechanical properties [9]. This may probably cause the dependence of T_G of the mixtures on the content of propylene component to be S shaped (Fig. 2). (In statistical EPc this dependence exhibits a negative deviation from linearity [10].) This may suggest the limited compatibility of the components.

In Fig. 3 there is plotted the dependence of the crosslinking efficiency E ($E = 100$ times the ratio of the actual crosslinking density to the theoretical maximum density based on one theoretical crosslink per molecule of peroxide) on the mole concentration of the propylene component in the mixture. Owing to experimental difficulties associated with the preparation of appropriate samples, this dependence has been determined

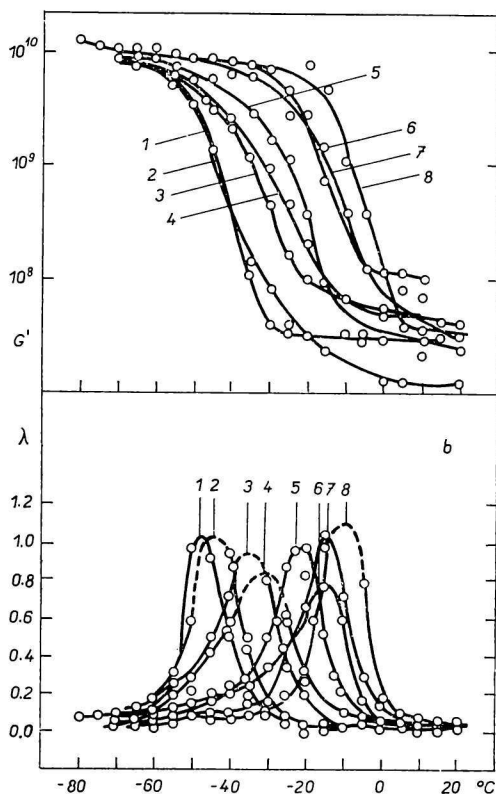


Fig. 1. Dependence of G' (a) and the logarithmic decrement λ (b) on the temperature for the mixtures of EPc with aPP.

Overall molar content of propylene component:

1. 54.3%; 2. 58.6%; 3. 63.2%; 4. 67.8%;
5. 72.8%; 6. 77.8%; 7. 85.8%; 8. 94.2%.

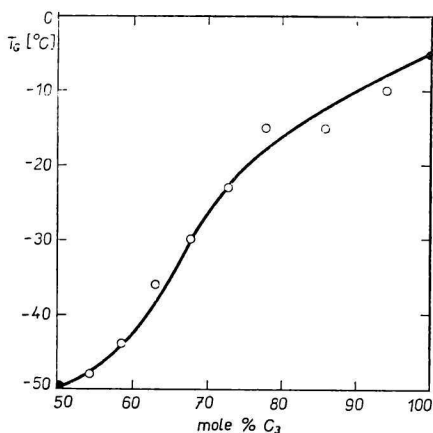


Fig. 2. Dependence of T_g of the mixtures of EPc with aPP on the molar content of the propylene component.

only to 73 mole % of the propylene component. Comparison of the crosslinking efficiency of the studied mixtures with the statistical EPc is complicated due to different crosslinking methods or the way of E determination and may only be approximative. In Table 1 there are, for the purpose of comparison, shown the E values from three authors.

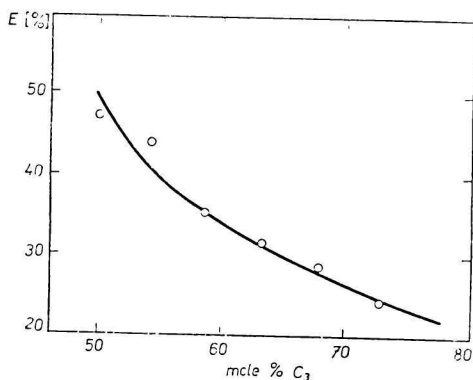


Fig. 3. Dependence of the crosslinking efficiency E of the mixtures of EPc with aPP on the molar content of the propylene component.

Though in the literature a larger extent of EPc composition is referred to, in Table 1 only the comparable data are given. As may be seen, the difference in E between the data taken from the reference [2] and [6], respectively, is a considerable one. Unlike [2, 3] and our results, the authors [6] obtained by straight line extrapolation of the E values determined at a relatively low content of the propylene component the value $E = 0$ at a content of the propylene component of about 68 mole %. In the present case, similarly as in [2, 3], the value E decreases with increasing content of the polypropylene component, and the curve extrapolation towards pure aPP leading to negligible E values. In DCP crosslinking, the mixtures of EPc with aPP may be presumed to behave in a way approximately equal to that of the statistical EPc having a corresponding composition.

Table 1

Efficiency values of EPC crosslinking by peroxides

Peroxide	Propylene content [mole %]	Efficiency E [%]	Ref.
Dicumyl peroxide	33	65	[2]
Dicumyl peroxide	50	55–60	[2]
Dicumyl peroxide	35	40	[3]
Dicumyl peroxide	42	34	[3]
α, α' -Di(<i>tert</i> -butylperoxy)diisopropylbenzene	32	145	[6]
α, α' -Di(<i>tert</i> -butylperoxy)diisopropylbenzene	38	107	[6]
α, α' -Di(<i>tert</i> -butylperoxy)diisopropylbenzene	50	75	[6]
Dicumyl peroxide	50	47	This work

References

1. Natta, G. and Crespi, G., *Rubber Age* (N. Y.) **87**, 459 (1960).
2. Robinson, A. E., Marra, J. V., and Amberg, L. O., *Ind. Eng. Chem., Prod. Res. Develop.* **1**, 78 (1962).
3. Loan, L. D., *J. Polym. Sci. A*, **2**, 3053 (1964).
4. Loan, L. D., *J. Polym. Sci. B*, **2**, 59 (1964).
5. Dunn, J. R., *J. Macromol. Sci.* **1**, 739 (1966).
6. Flisi, U. and Crespi, G., *J. Appl. Polym. Sci.* **12**, 1947 (1968).
7. Mullins, L., *J. Appl. Polym. Sci.* **2**, 1 (1959).
8. Meissner, B., *J. Polym. Sci. C*, **16**, 781 (1967).
9. Sperling, L. H., Taylor, D. W., Kirkpatrick, M. L., George, H. F., and Bardman, D. R., *J. Appl. Polym. Sci.* **14**, 73 (1970).
10. Illers, K. H., *Kolloid-Z. Z. Polym.* **190**, 16 (1963).

Translated by J. Mynafik