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Mobility of Rubber Chains Near Above the Glass Transition Temperature

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Summary

Detailed viscoelastic measurements of natural and ethylene-propylene rubbers cross-linked by sulphur and dicumyl peroxide to various degrees were performed. Main attention is devoted to lightly cross-linked systems where two relaxation processes occur near above the glass transition temperature. The two peaks of the relaxation spectra corresponding to these two relaxation processes begin to overlap as the cross-linking density increases. The simple structural interpretation of the observed features using the entanglement concept is given.

Introduction

It is well known that the main polymer chains begin to move as the temperature of the sample exceeds the glass transition temperature T_g. This process is common for all polymer samples. The movement of the chains is stopped by different mechanisms depending on polymer morphology. In crystalline polymers the restraints to motion are often so high that the activation of polymer chain mobility above T_g is hardly recognizable. In rubbers, however, the activation of the chain mobility above T_g is a dominant effect. The restraints to such a chain mobility in rubbers cross-linked to various degrees will be studied in this article. The restraints were detected by viscoelastic means and the main attention was devoted to lightly cross-linked rubbers. Such viscoelastic measurements were already performed and discussed, e.g. by MAEKAWA et al.(1965), MANCKE and FERRY(1968), VALENTINE et al.(1968). We hope that on the basis of our detailed measurements the simple explanation of the viscoelastic

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behaviour of rubbers in the early stages of cross-linking may be given.

Experimental

Natural rubber (NR) and ethylene-propylene terpolymers (EPR) cross-linked by sulphur (S) and dicumyl peroxide (DCP) were the main systems under investigation. The natural rubber used is the partially purified crepe produced by the MRPRA; the ethylene-propylene terpolymer is Keltan produced by the Shell Company, which is the random ethylene-propylene copolymer with approximately 4% of dicyclopentadiene added.

Viscoelastic measurements were performed by creep method (HAVRÁNEK 1965) in the time interval 3×10^{-2} - 10^{3} s and in the temperature range 200 - 360K; the strain does not exceed 3%. Some complementary measurements were performed on torsion pendulum (ZIMOLA and HAVRÁNEK 1981) in the same temperature range and in the frequency range approximately 10^{-1} - 10^{1}Hz. Retardation spectra L were calculated by approximation method of SCHWARZL and STAVERMAN (1952). The time interval of the creep experiments is sufficiently broad so that the directly measured creep curves may be used in the calculations instead of the superimposed ones. This procedure is necessary as the superposition principle does not hold in the whole measured time-temperature range where two relaxation mechanisms occur.

The cross-linking densities ν of the samples were determined from the equilibrium compliance D_e by the simple (front-factor = 1) formula

$$\nu = 1/3D_e RT \qquad (1)$$

of the rubber elasticity theory (TRELOAR 1975) and/or from swelling eqilibrium by the formula (FLORY 1950)

$$\nu = -\left[\ln(1 - v_r) + \chi v_r^2\right] / V_s(v_r^{1/3} - v_r/2) \qquad (2)$$

The symbols R and T in eq. (1) have the usual meaning, universal gas constant and Kelvin temperature, respectively. In eq. (2) V_s is the molar volume of the swelling agent, v_r is the volume of the swelling liquid in the swollen sample, χ is the interaction parametr between the sample and the swelling agent. The results obtained by the two methods coincide reasonably well (HAVRÁNEK 1971)

Results

The changes of viscoelastic behaviour in the early stages of cross-linking are demonstrated in Fig.1, where the retardation spectra of four typical NR samples are given. The first peak at lower retardation times is present in all the samples including the uncross-linked one. The amount of sulphur is less than 2% in all the samples of Fig.1 (cross-link density is varied by DCP content), and therefore the position of the first peak on the τ axis is nearly the same for all the curves (HAVRÁNEK and BAKULE 1975). The retardation spectrum L of the sample with cross-link density ν_1 has two peaks, the L spectrum of the ν_2 sample one broad peak and the sample with the highest cross-link density has one narrower peak. The second peaks, such as that of the ν_1 curve of Fig.1, were detected in all lightly cross-linked NR and EPR samples. The τ axis positions of these second peaks shift towards the positions of the first peaks with increasing cross-linking density. We denote ${}^{I}\tau_m$ the time at which the first peak reaches its maximum and the same value for the second peak we denote ${}^{II}\tau_m$. The first peak is closely connected with the glass transition temperature T_g and its ${}^{I}\tau_m$ appears approximately 30K above T_g for NR samples and approximately 15K above

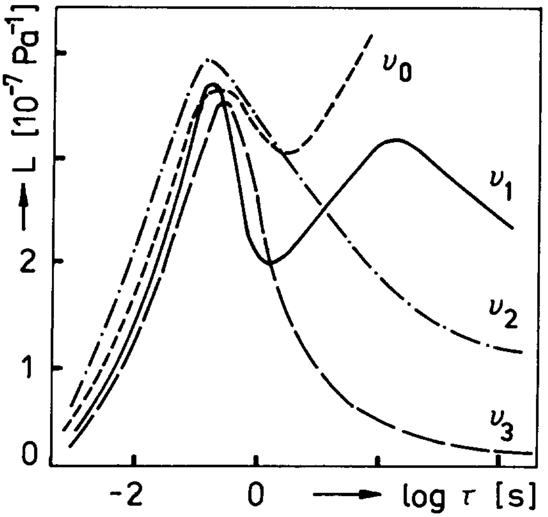

Fig.1 Retardation spectra L as functions of retardation time τ of the NR-S- DCP system cross-linked to the degrees: $\nu_0 = 0$, $\nu_1 = 0.6 \times 10^{-4}$ mol/cm^3, $\nu_2 = 0.9 \times 10^{-4}$ mol/cm^3 and $\nu_3 = 1.8 \times 10^{-4}$ mol/cm^3

T_g for EPR samples, if the time of observation is 1s. To eliminate the increase of T_g, which take place in samples with more than 2% of sulphur, the τ_m values will not be referred to the fixed temperature but to the temperature Tg + 30K. Such values of τ_m will be denoted by a dash: ${}^{I}\tau'_m$ and ${}^{II}\tau'_m$. The τ'_m vs. ν plots of NR and EPR samples are given in Fig.2. The ${}^{I}\tau'_m$ values are nearly constant, the constant for NR is higher than that for EPR in agreement with the different temperature shifts between T_g and the first spectrum peak in the two systems. The positions ${}^{II}\tau'_m$ of the maxima of the second spectrum peaks decrease with increasing cross-linking density ν and approach the constant values of ${}^{I}\tau'_m$. The ${}^{II}\tau'_m$ and ${}^{I}\tau'_m$ curves join when the cross-linking density reaches the value 1.8×10^{-4}mol/cm^3 in the NR samples and 3.2×10^{-4}mol/cm^3 in the EPR ones. The overlapping of the two spectrum peaks (see curve ν_2 in Fig.1) is finished at these values of ν. The separation of the two relaxation processes, the first which is finished just above T_g, and the second which take place at higher temperature (or longer time) and is sensitive to the number of chemical cross-links, was detected also in other lightly cross-linked rubbers investigated in our laboratory; namely in butadiene rubbers, butadiene oligomers prolonged and cross-linked by epoxy resins or diisocyanates (liquid rubbers) and in polyoxypropylene triols cross-linked by diisocyanates.

Discussion

The observed dependence of the form of retardation spectrum L on cross-linking density is schematically given in Fig.3. In the same Figure the creep curves - tensile compliances D - from which the retardation spectra L were derived are given. It ought to be remembered that in the first approximation (e. g. SCHWARZL and STAVERMAN 1952) the L curve is proportional to the logarithmic derivative of the D curve, L=dD/d logt. The plateau modulus D_{eN} is detectable for samples where this plateau is beneath the true rubber plateau with D equal to the equilibrium compliance of chemical cross-links D_e. It means that D_{eN} is detectable in lightly cross-linked samples (Figs. 3a-3c). In all these samples D_{eN} has the same value

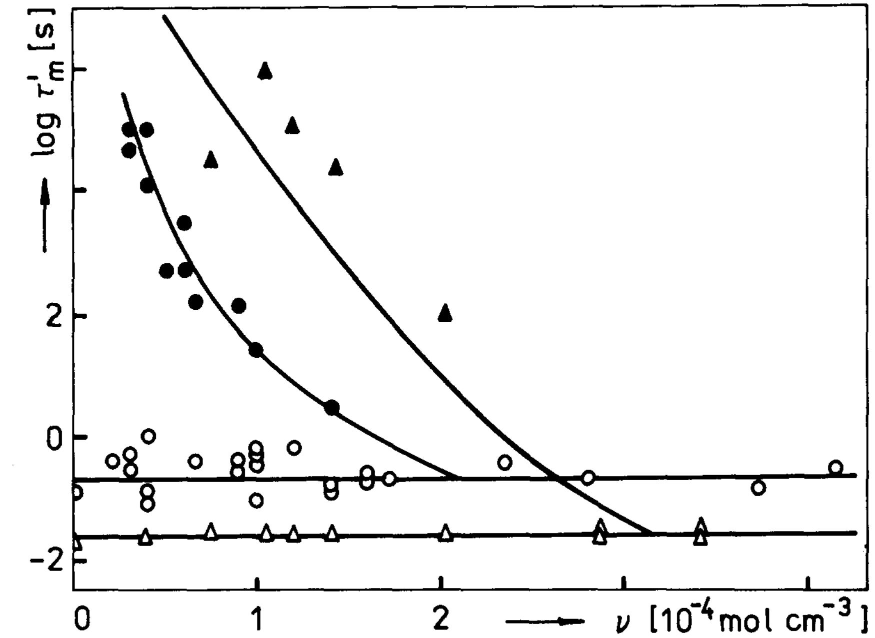

Fig. 2. The retardation times ${}^{I}\tau'_m$ ○ and ${}^{II}\tau'_m$ ● of the NR-S-DCP system and ${}^{I}\tau'_m$ △ and ${}^{II}\tau'_m$ ▲ of the EPR-S-DCP system as functions of cross-linking density ν

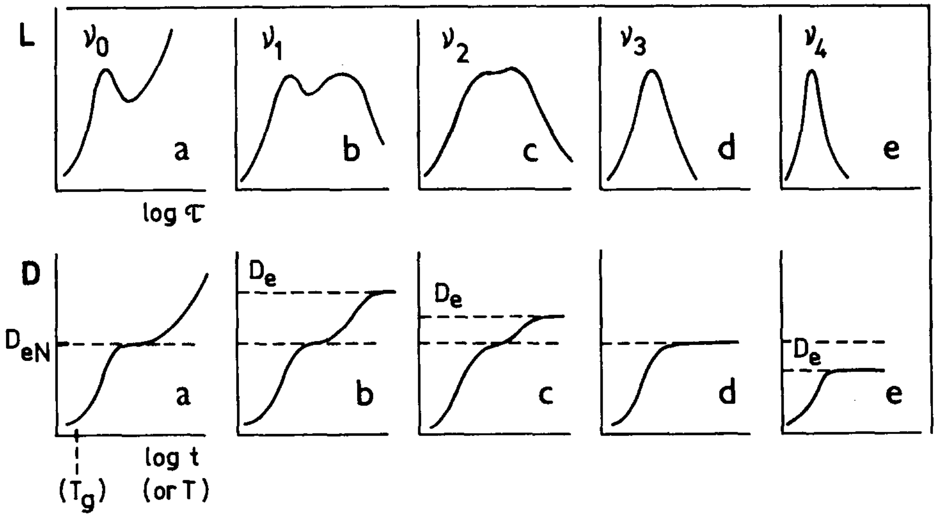

Fig. 3. The evolution of the form of retardation spectrum L and tensile compliance D with increasing cross-linking density: $\nu_0=0$, $\nu_1<\nu_2<\nu_3<\nu_4$. Time is denoted t, temperature T

and the creep curves up to it have the same form which is reflected in the same form of the initial part of the retardation spectra L. The average molecular mass $\overline{M}_e$ of chains between two neighbouring coupling points were calculated using eq. (1) where D_e was replaced by D_{eN} and ν was taken equal to the moles of these chains per cubic centimter (density of the samples is known). The values in the range $2000<\overline{M}_e<6000$ were obtained for various rubbers. This values and also the differences between various rubber types are in good agreement with the values of entanglement chain length given by other authors and collected by FERRY (1980). Therefore, it seems natural to assign the first plateau and subseqently also the first peak of the L spectra to the effect of entanglements; the restraints which stop the chain motion in lightly cross-linked rubbers just above T_g are entanglements (compare MANCKE and FERRY 1968).

The entanglement restraints have temporary character and therefore at longer times (or higher temperatures) the samples begin to creep again, either without limit (Fig. 3a) or to an equilibrium value D_e, if some chemical cross-links are present (Fig.3b). The two-step creep curves of the lightly cross-linked samples correspond to the two-peak L spectra of these samples. The increase of the number of chemical cross-links (increase of ν) causes the lowering of D_e, the entanglement and cross-link restraints of chain motion approach and the L spectrum peaks begin to overlap (Fig.3c). The number of chemical cross-links is lower than the number of entanglement coupling points in Figs. 3b and 3c. If the number of entanglements and chemical cross-links is approximately the same the simple one-step creep curve and one-peak L spectrum occur (Fig. 3d). This situation corresponds to the point where the ${}^{I}\tau'_m$ and ${}^{II}\tau'_m$ curves join (Fig. 2). If we calculate the $\overline{M}_e$ values from the cross-link densities (1.8×10^{-4} mol/cm^3 for NR and 3.2×10^{-4} mol/cm^3 for EPR) at the joining points we obtain $\overline{M}_e = 5500$ for NR and $\overline{M}_e = 3000$ for EPR, again in satisfactory agreement with values collected by FERRY (1980). Further increase of cross-linking density in the range where $D_e < D_{eN}$ causes the reduction of the retardation step $D_e - D_g$ (D_g is the compliance in the glassy state) and the decrease of the spectrum width (Fig. 3e). This reduction in the spectrum width was also verified experimentally (HAVRÁNEK 1971, HAVRÁNEK et al. 1980).

This description of the evolution of the spectra form with increasing cross-linking density is a qulitative one. Therefore it is not possible at the present stage of investigation to distinguish between the various front-factors in eq.(1) (e.g. FLORY 1976) and to state whether, in the situation given in Fig. 3d, the entanglement and cross-link densities should be added or not.

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