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Time-Temperature Superposition and Linear Viscoelastic Behaviour of EPDM Networks with Various Degrees of Crosslinking

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SUMMARY

Conventional time-temperature (t-T) superposition appears to be inappropriate to the viscoelastic behaviour of amorphous, peroxide cured EPDM networks. A phenomenological approach is presented that reduces these permanent elastomers to thermorheologically simple materials. Although the origin of the anomalous behaviour observed is not yet completely understood, it is attributed to an unusual variation of the equilibrium modulus with temperature.

INTRODUCTION

As a result of very long relaxation times and the possible onset of chemical degradation, the determination of the equilibrium modulus of rubber vulcanizates is both time consuming and disputable. Therefore, the evaluation of the modulus or compliance at equilibrium is usually accomplished by fitting stress relaxation or creep data in the terminal zone, covering several decades of time, by an empirical equation (e.g. FERRY, 1970, ch. 14). Besides, t-T superposition is a well known method of extending viscoelastic measurements on amorphous polymers over several decades (e.g. FERRY, 1970, ch. 11), thus offering another method of approaching the equilibrium properties of permanent networks more closely or quickly. However, to our knowledge the applicability of the superposition principle to vulcanized networks has never been subjected to a critical examination.

This short communication describes some preliminary results that were obtained by employing t-T superposition to several permanent, non-crystalline EPDM networks.

EXPERIMENTAL

Use was made of various ethylene-propylene terpolymers differing in type (dicyclopentadiene, DCPD, 5-

ethylidene-2-norborne, EN, and 1-4-hexadiene, HD) and content (0.8-2.7 mole %) of termonomer. As was verified by DSC measurements (Perkin Elmer DSC-2), all samples were essentially non-crystalline in the relevant T-range (300-435 K) due to their relatively high propylene content (33-41 mole %).

The raw rubbers were mixed with small amounts (0.2-1.6 phr) of dicumyl peroxide (> 98 %) on a two-roll mill (10 min at 350 K) and subsequently cured in a press at 20 MPa (12 min at 450 K) in a parallel plate mold of 3 mm thickness.

At temperatures of 300, 345, 390 and 435 K, dynamic mechanical measurements were performed in torsion with a mechanical spectrometer (Rheometrics) employing parallel plate geometry. At strain amplitudes below 0.05, the absolute value of the complex shear modulus G^* and the phase shift δ were determined as functions of the angular frequency ω in the range of 6×10^{-2} to 10^2 rad.s^{-1} (five points per decade). The absence of slip between sample and plates was checked by varying the strain amplitude and the pressure on the sample while recording the stress signal.

RESULTS AND DISCUSSION

The viscoelastic characteristics of permanent rubbers in the terminal zone are usually (very) smooth functions of frequency, the more as the crosslink density increases. Therefore, the appropriate frequency shift factors were firstly determined for the corresponding uncrosslinked samples. Really uncrosslinked elastomers, which exhibited a steady growth of δ to 90° with decreasing frequency, were found to be thermorheologically simple materials: δ vs log ω curves could be superimposed merely by a shift of log a_T along the log ω-axis, whereas G^* vs log ω curves and those of the storage and loss moduli, G' and G'' respectively, required an additional vertical shift factor b_T, that was equal for all moduli but in general much closer to unity than the theoretical value of $\rho_o T_o/\rho T$. In Figures 1 and 2, we present the master curves of $G'(\omega a_T)$, $G''(\omega a_T)$ and $\delta(\omega a_T)$ for one sample characteristic of these entanglement networks (solid lines).

The presence of even the slightest amount of crosslinks, either caused by the peroxide or by ageing (primarily for EPDMs containing DCPD or relatively large amounts of EN), impeded the construction of a proper master curve for $\delta(\omega)$ (broken lines in Figures 2) or $G^*(\omega)$ in the way indicated. However, we found that at low degrees of crosslinking, $G''(\omega)$ could still be superposed with the same frequency shift factor a_T after application of an additional vertical shift

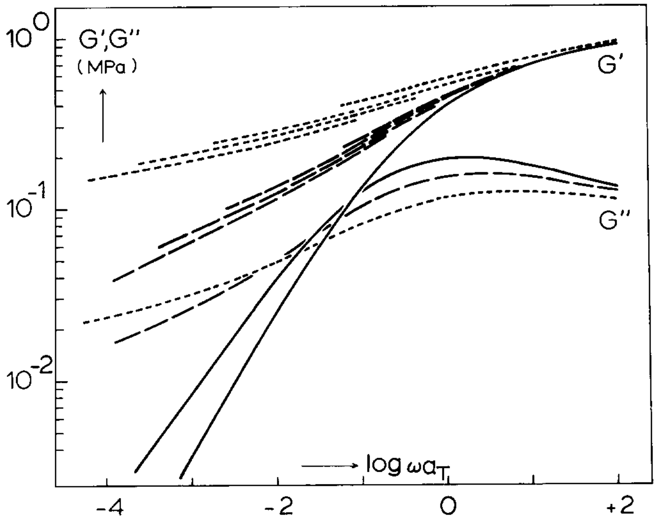

Figure 1. Storage and loss moduli of an uncrosslinked and two lightly cured (0.2 phr peroxide) EPDMs plotted against radian frequency (rad . s^{-1}) at 300 K; solid and broken lines refer to sample A, containing 41 mole % P and 0.8 EN, the dotted lines to sample B with 33 mole % P, 2.2 EN and 0.8 DCPD

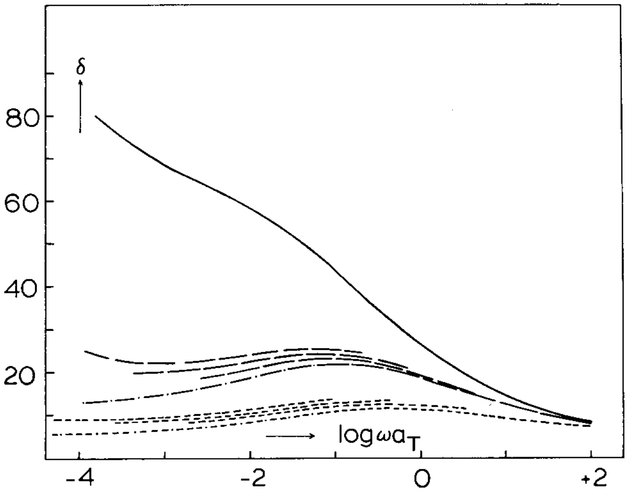

Figure 2. Loss angle versus frequency reduced to 300 K. The curves pertain to the same samples as in Figure 1. The dot and dash master curves were obtained after modification according to Equations 1 and 3

factor b_T. For moderately and strongly cured preparations we assumed, with PLAZEK (1966), that the same shift function a_T could still be applied. For these vulcanizates, b_T was rougly equal to $\rho_o T_o/\rho T$, whereas for the lightly crosslinked EPDMs, with $G'(0)$ at 300 K $\lesssim$ 0.15 MPa, this factor was usually substantially nearer to unity, similar to that for the uncured preparations. In addition, we found that superposition of the $G'(\omega)$ curves with the pertinent shift factors did not result in one composite curve, but, when plotted semi-logarithmically, in a set of virtually parallel curves. This anomalous behaviour is exemplified by the interrupted curves in Figure 1, which represent shifted $G'(\omega)$ and $G''(\omega)$ curves for two different preparations.

Accordingly, master curves could be obtained for all viscoelastic characteristics by the following modification of the original curves:

$$G'_{mod}(\omega a_T) = b_T\cdot G'(\omega a_T) + G'_T \qquad (1)$$

$$G^*_{mod}(\omega a_T) = \left(\left[G'_{mod}(\omega a_T)\right]^2 + \left[b_T\cdot G''(\omega a_T)\right]^2\right)^{0.5} \qquad (2)$$

$$\delta_{mod}(\omega a_T) = \tan^{-1}\left[b_T\cdot G''(\omega a_T)/G'_{mod}(\omega a_T)\right] \qquad (3)$$

where G'_T represents the empirically found difference between the $G'(\omega)$ curve at the reference temperature T_o and the $G'(\omega)$ curve at T as obtained after the usual horizontal and vertical shifting. The results of this modification are shown graphically by the two dot and dash curves in Figure 2, representing the master curves of $\delta(\omega a_T)$ obtained from the corresponding sets of broken curves, and by the $G'_{mod}(\omega a_T)$ master curves in Figure 3, derived from the two sets of disconnected curves of Figure 1. The proposed reduction scheme was verified by comparing these master curves with $G'(\omega)$ values calculated from stress relaxation measurements at T_o (the star shaped symbols in Figure 3) using SCHWARZL's (1971) interconversion formula with a relative error always smaller than 4 %. It is evident that the agreement is excellent.

Vulcanizates of other types of EPDM and peroxide showed very similar behaviour, G'_T depending on temperature, degree of crosslinking and type of elastomer. In Figure 4, this dependence is plotted for two types with various degrees of crosslinking (giving rise to different values of $G'(0)$ at 300 K). Equation (1) seems to indicate that the value of G'_T greatly depends on the choice of a_T and b_T. However it was found by plotting $b_T\cdot G'(\omega)$ versus $b_T\cdot G''(\omega)$ (independent of a_T) and by the trial and error evaluation of the value of G'_T/b_T which provided the

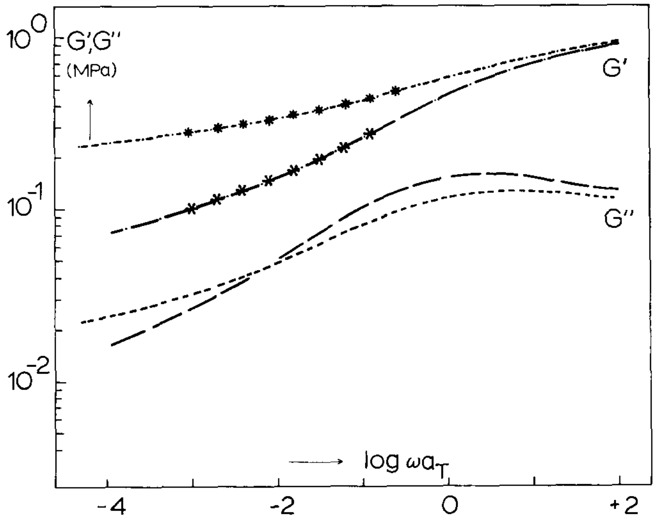

Figure 3. Storage and loss modulus master curves for the two permanent networks of Figure 1 after modification, reduced to 300 K. The points represent $G'(\omega)$ values calculated from $G(t)$ at 300 K

best master curve for tan δ (independent of b_T), that only slight variations in G_T' could be obtained.

Although the present phenomenological description of the viscoelastic behaviour of peroxide cured EPDM networks seems to be consistent, the molecular origin of the phenomena observed is still obscure. There seems to be a close correspondence with the McCRUM-MORRIS (1964) reduction scheme. Since G_T' is independent of ω and is only a necessary parameter for crosslinked EPDM samples, the reduction could also be represented by an empirical reduction factor of the equilibrium modulus $G'(0)$, obtained by extrapolation of log ω to $-\infty$. Incorporation of G_T'/b_T into $G'(0)$ enables the dependence of $G'(0)$ on T to be derived, as shown in Figure 5 for two types of terpolymers with various degrees of crosslinking. In deviation from theoretical predictions, $\partial G'(0)/\partial T$ is negative at low degrees of crosslinking, whereas it increases with an increase in modulus. Eventually, at the highest levels of crosslinking, $G'(0)$ grows with T even more than proportional to ρT. A behaviour similar to the latter has also been observed by POLLAK and ROMANOV (1979) for all crosslink densities in a study on the thermoelastic properties of cured ethylene-propylene and ethylene-vinylacetate copolymers. They attributed this effect to a temperature dependence of the front factor (energy

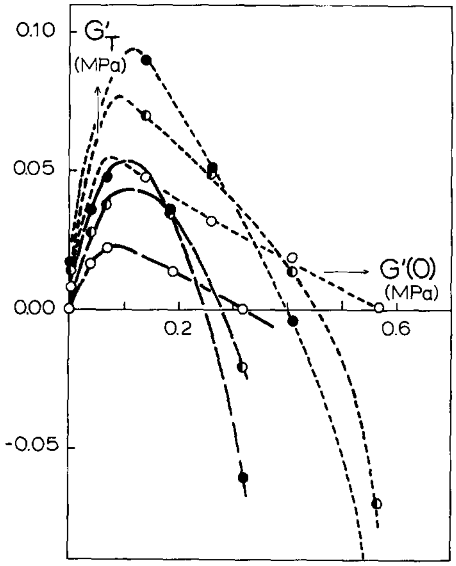

Figure 4. Dependence of the empirical correction quantity G'_T at 345 (o), 390 (◐) and 435 K (●), on the equilibium modulus at 300 K. Broken lines correspond to sample A, dotted lines to B, both at various degrees of crosslinking

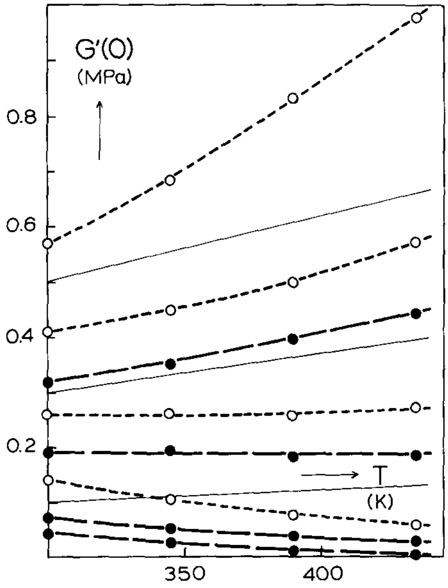

Figure 5. Dependence of the equilibrium modulus, obtained by extrapolation of G'(ω), on the absolute temperature; ● refers to sample A, o to B; the solid lines represent the theoretical behaviour (G'(0)~ρT)

elasticity).

In view of the facts that the value of G'_T was not dependent on whether T was reached starting from a higher or a lower temperature, and that a given rubber behaved as usual in both completely uncured and the moderately cured states, but not at intermediate and high crosslink densities, traces of crystallization undetectable by DSC can be excluded as the cause of the peculiarities found. Similarly, conventional energy elasticity due to intramolecular processes can also be ruled out, as this has always been found to be independent of crosslink density (MARK 1973 and 1976, SHEN and CROUCHER 1975). Nevertheless, we think that for all permanent networks with some kind of energy elasticity, time-temperature superposition would pose the same difficulties that are to be attacked in a similar way. However, we suspect the origin for our findings to be related to embedded orientations or perturbed chains, introduced during the crosslinking process, or to intermolecular energetic effects. These factors may depend strongly on the amount of peroxide present during the pressing and curing stage.

In order to get more insight into this new and still unexplained behaviour, oscillation measurements in the swollen state or equilibium swelling measurements at different temperatures may prove to be useful. Research in these fields is in progress.

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