

Dynamic mechanical properties of natural rubber vulcanizates with different curing systems and static strain

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The glass transition temperatures of natural rubber compounds cured with dicumyl peroxide and sulphur were measured on a Metravib Viscoelasticimeter. $\tan \delta$ versus temperature curves of compounds vulcanized with peroxide show two well defined relaxations associated with the glass transition. Compounds cured with sulphur show only one relaxation. Dynamic deformations of small amplitude were superimposed on large static deformations. It was found that the intensity of the loss tangent associated with the glass-rubber transitions tends to decrease with increasing static deformation.

(Keywords: natural rubber; dynamic mechanical properties; static strain; glass transition; loss tangent; network)

INTRODUCTION

The characterization of the network structure of a crosslinked polymer is important because of its complex chemical nature and its strong relationship with many physico-chemical properties of the material. The dynamic-mechanical method is a powerful technique for the study of the effect of not only the molecular structure, but also of phase morphology, regarding the physical properties required in component design. This technique allows quantitative measurements of modulus changes during thermodynamic transitions and other molecular relaxations¹⁻⁵ to be obtained.

The effect of stretching on the glass transition temperature (T_g ; the α -relaxation) of rubber has been studied. It is known to be an interesting subject with important basic implications and conflicting results. The T_g has been shown to increase, decrease or remain invariant with increasing deformation⁶⁻¹².

The crosslinking of rubber decreases the mobility and conformational entropy of the network chains. On the other hand, the static strain of the networks decreases the conformational entropy and increases the free volume. The location of the glass-rubber transition for elongated networks shifts to lower temperatures in some systems, in others an increase is observed. Both parameters, free volume and conformational entropy, can be considered as two properties with opposite effects¹³.

This study attempts to provide some additional insight into the dependence of T_g on the degree of crosslinking, the cure systems (sulphur and peroxide) and large static strain¹⁴. The chosen polymer was a natural rubber (NR), which undergoes strain induced crystallization¹⁵⁻¹⁷. The presence of small crystallites also can affect the T_g . This

paper verifies how the locations of the T_g s of networks prepared with sulphur are easily distinguished from peroxide cured networks, in the $\tan \delta$ versus temperature plot for elongated networks. Moreover, in the latter type of network a new α -relaxation appears, which is more clearly manifested by increasing dicumyl peroxide level or by increasing static strain of the network.

This paper suggests some explanations for the variations which take place in the relaxation spectra of strained networks.

EXPERIMENTAL

Materials

All the compounds are based on standardized NR (NR SMR). The sample was provided by Malaysian Natural Rubber, Kuala Lumpur. The crosslinking was effected using dicumyl peroxide and sulphur. *Table 1* gives details of the compounds prepared.

Sheet production

NRs were compounded using a two-roll mill (friction ratio 1:1.14) using conventional mixing procedures.

Physical properties were determined, according to national standards, on test specimens cured at 160°C, in a thermo-fluid heated press, at their respective optimum (t_{c90} from a rheogram). Optimum cure times were determined using a Monsanto rheometer.

Dynamic mechanical measurements

Viscoelastic dynamic measurements were conducted on strips, cut from the network sheets, with a Metravib Viscoelasticimeter at frequencies of 5, 7, 10 and 15 Hz. The dynamic deformation was 15 μm . The heating of the samples was not carried out continuously but in stages,

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Table 1 Rubber vulcanizate formulations (phr)

Sample	NR3	NR6	NR9	NRS
Natural rubber (SMR 5)	100	100	100	100
DiCup 40C ^a	3	6	9	—
Zinc oxide	—	—	—	5
Stearic acid	—	—	—	1
MBTS ^b	—	—	—	1
Sulphur	—	—	—	2

^aDicumyl peroxide on calcium carbonate, 40% pure

^bBenzothiazildisulphide

in the range of -90 to 25°C . Before any measurement was taken the sample was held at the chosen temperature for 10 min. The strip (30 mm long \times 5 mm wide \times 2 mm thick) was stretched in the measuring frame until it reached the desired elongation. The strip was permitted to relax for 24 h at room temperature in nitrogen atmosphere. When the force became constant, the sample was rapidly cooled, and the viscoelastic dynamic measurements were carried out.

RESULTS AND DISCUSSION

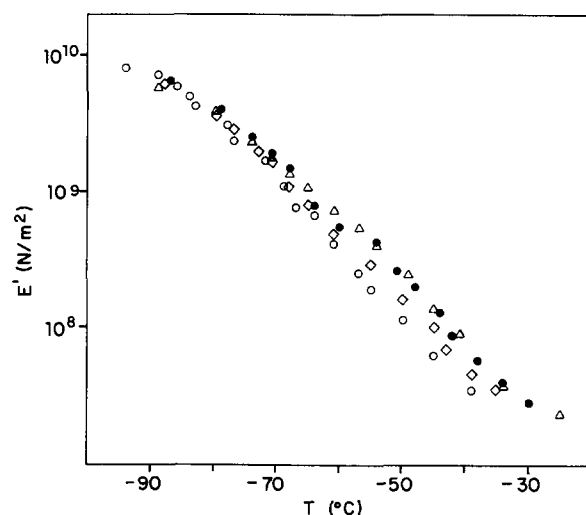
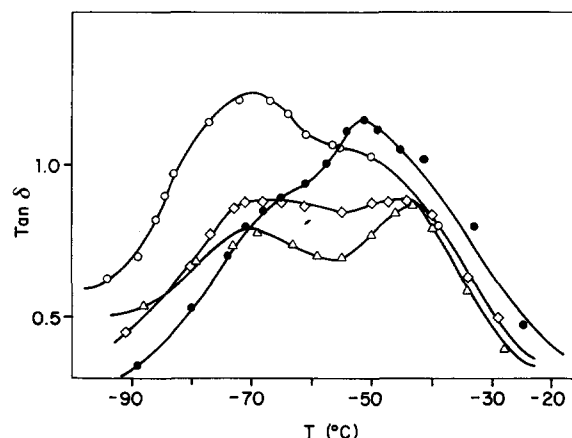
Influence of the type of curing agent

Variation of the dynamic storage modulus E' as a function of temperature is shown in *Figure 1* for the four NR samples, the first three of which were cured with peroxide and the fourth with a sulphur accelerated system. In the glassy region E' is little affected by the crosslinking density, as density increases cause but slight increments in the modulus.

Figure 2 shows $\tan \delta$ variation with temperature for the different samples. In the glassy region there appear two peaks for the peroxide cured samples, and a single peak, at $\sim -52^{\circ}\text{C}$, for the sulphur cured compound.

For the peroxide cured samples the lower peak is attributed to the T_g (the α -relaxation) and is associated with co-operative movements within the polymeric chain. With increasing crosslinking density $\tan \delta_{\max}$ diminishes. The second peak of these vulcanizates is likewise attributable to restrictions in polymeric chain mobility, as it is displaced towards higher temperatures with increasing crosslinking density.

In NR curing with peroxide, the crosslinking is produced by a free radical initiated chain reaction, formed through thermal peroxide decomposition, and during which all the individual steps occur that are typical of this kind of reaction, such as propagation, chain transfer and termination, in order to achieve crosslinking of the polyhydrocarbon chain. The propagation of the crosslinking process, which is strongly exothermal, gives rise to a relatively small volume of densely crosslinked polymer, no more than a spherical body of a few hundred nanometres in diameter, until this chain reaction is interrupted by the termination process. As a result, the crosslinked nodes will not be uniform, but have a grainy texture with highly reticulated spaces embedded in the less firmly crosslinked polymer¹⁸. This texture obviously presents lower moduli (*Table 2*). This grainy structure will show a similar behaviour to that of a reinforcing filler, which strongly adsorbs the polymer, thus giving rise to a T_g relaxation at slightly higher temperatures due to reduced molecular mobility and different from the classical T_g of the amorphous polymer without restrictions. In *Figure 2* this relaxation is better defined


Figure 1 Storage modulus (E') as a function of temperature (T) at a frequency of 5 Hz: (○) sample NR3; (◇) sample NR6; (△) sample NR9; (●) sample NRS. Static deformation $\varepsilon = 1$

Figure 2 Loss tangent ($\tan \delta$) as a function of temperature (T) at a frequency of 5 Hz. Symbols as in *Figure 1*
Table 2 Physical properties of the compounds

Sample	NR3	NR6	NR9	NRS
Cure time at 160°C (min)	55	40	35	10
Shore A hardness	42.6	52.4	60.3	38.6
Stress at 100% (MPa)	0.52	0.85	—	1.84
Stress at 300% (MPa)	1.30	2.75	—	4.67
Tensile strength (MPa)	2.33	3.09	1.04	9.90
Elongation at break (%)	440	320	60	530
Tear strength (N) (die Delft)	8.78	7.80	5.25	39

the higher the proportion of peroxide and it shifts to a slightly higher temperature.

For the sulphur cured sample the T_g presents at $\sim -52^{\circ}\text{C}$, intermediate between the relaxations found for the peroxide vulcanizates. In the sulphur cured sample the matrix lattice is uniform, the whole volume has a similar response, there appear no topological differences and hence the physical properties are better than those obtained in peroxide vulcanizates (*Table 2*).

Effect of deformation on T_g

Subsequently the influence of static deformation on the dynamic properties was studied in NR vulcanizates

cured with 3 phr of DiCup 40C. The results obtained indicate that E' and the position of the peak associated with the main glass transition, to lower temperature, are affected by increments in static deformation.

The temperature dependence of E' and $\tan \delta$ for deformed networks with elongation ratio $\epsilon = 1, 2$ and 2.75 are shown in Figures 3 and 4, respectively. In Figure 3 it can be observed how E' increases with deformation in the glassy region. This phenomenon can be explained through the incidence of crystallization, which is generated with NR deformation and produces substantial changes in the mechanical properties. From a mechanical point of view, crystalline nucleus formation is equivalent to the incorporation of additional crosslinks, which in turn will increment the rubber moduli.

With regard to $\tan \delta$ variation with temperature, both relaxations were observed as described above for this type of vulcanizate and proved to be influenced by the degree of static deformation. The peak appearing at lower temperatures and indicative of the amorphous phase (T_g of the polymer) decreases with the degree of crystallinity, which increases in proportion to the previous deformation undergone by the crosslinked rubber network. The

relaxation recorded at higher temperatures, which had been attributed to the influence of the grainy texture, does not seem to change with deformation. The elongation stresses undergone by the sample are relatively too low to deform the grain sites embedded in the polymeric matrix. This new relaxation, which we call α' , shows no significant dependence on the degree of crystallinity.

As a subsequent step, the degree of crystallization was varied, but now not only by means of static deformation of the vulcanized NR network, in order to study its impact on the mechanical dynamic properties. The following procedure was adopted: the sample subjected to $\epsilon = 2$ was kept at -25°C for 12 h to enhance the crystallization rate in the deformed polymer. Another sample, which had been deformed likewise at $\epsilon = 2$, was kept at 50°C for 24 h (in nitrogen atmosphere to avoid oxygen induced ageing) and then rapidly quenched in liquid air in order to maintain the amorphous rubber. Figures 5 and 6 show the variation of E' and $\tan \delta$ with

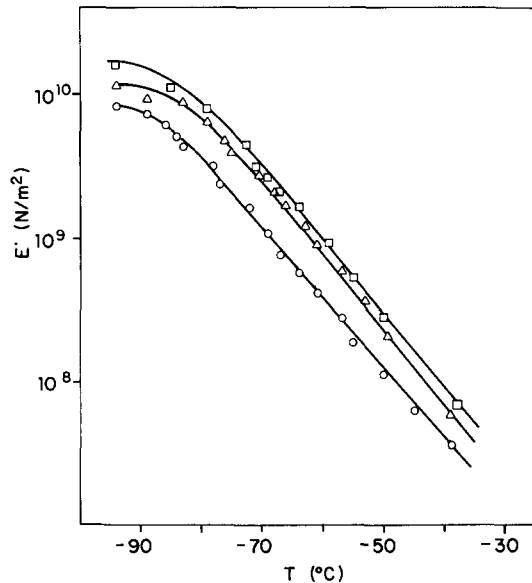


Figure 3 Storage modulus (E') as a function of temperature (T) for sample NR3 at a frequency of 5 Hz at different static elongation ratios: (O) $\epsilon = 1$; (Δ) $\epsilon = 2$; (\square) $\epsilon = 2.75$

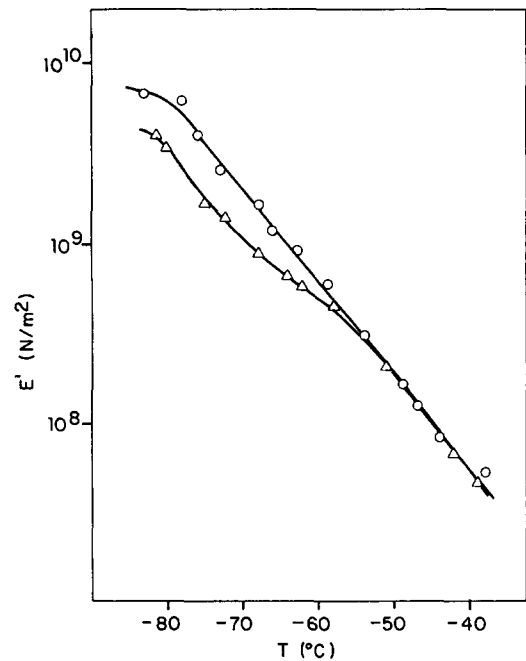


Figure 5 Storage modulus (E') as a function of temperature (T) for sample NR3 under static deformation $\epsilon = 2$: (O) 12 h at -25°C ; (Δ) 24 h at 50°C and later quenched

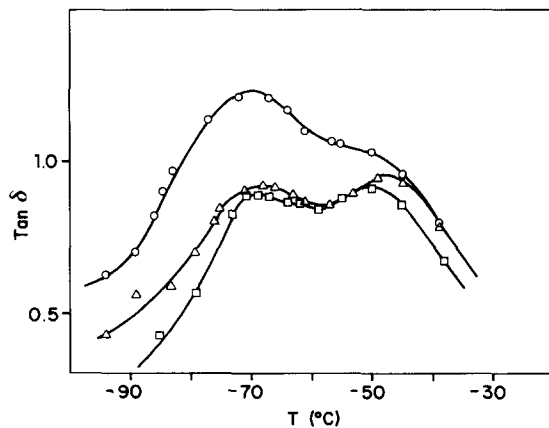


Figure 4 Loss tangent ($\tan \delta$) as a function of temperature (T) for sample NR3 at a frequency of 5 Hz at different static elongation ratios. Symbols as in Figure 3

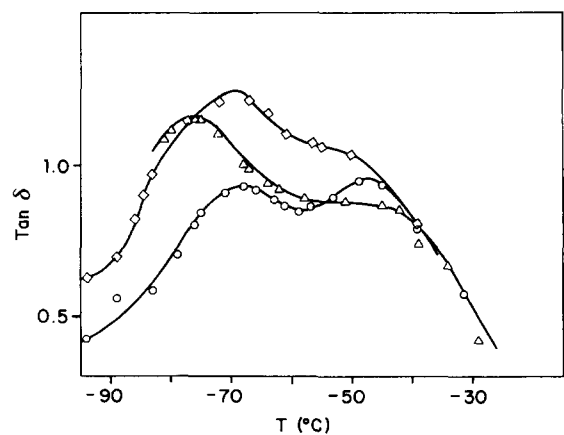


Figure 6 Loss tangent ($\tan \delta$) as a function of temperature (T) for sample NR3 under static deformation $\epsilon = 2$: (O) 12 h at -25°C ; (Δ) 24 h at 50°C and later quenched; (\diamond) 24 h at 20°C

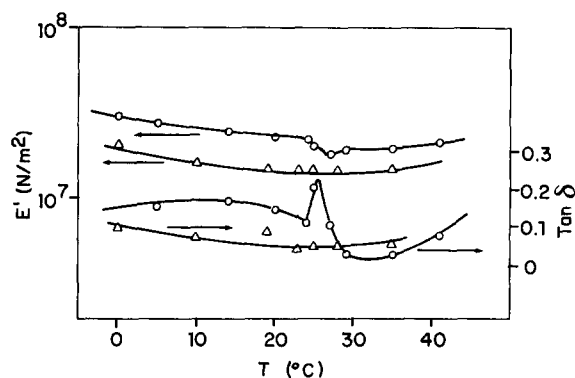


Figure 7 Storage modulus (E') and loss tangent ($\tan \delta$) as a function of temperature (T) for sample NR3 at a frequency of 7 Hz; (○) 12 h at -25°C , $\epsilon = 2$; (△) 24 h at 50°C and later quenched, $\epsilon = 2$

temperature. The disappearance of crystallinity gives rise to a decrease in E' in the glassy region. *Figure 6* shows $\tan \delta_{\max}$ to decrease, as compared to the reference curve, as a consequence of increased crystallinity. For the sample in which crystallinity had been removed, T_g is displaced towards lower temperatures, as the absence of crystallinity increases molecular mobility in the polymer.

Evidence of these variations in crystallinity is gained from the analysis of the changes undergone by E' and $\tan \delta$ in the range in which NR crystals melt. The sample maintained at -25°C for 12 h shows a change of slope in a plot of E' versus temperature (see *Figure 7*) at $\sim 26^\circ\text{C}$, which may be assumed to be associated with crystal melting, as it also shows the respective $\tan \delta$ peak. In contrast, the sample kept at 50°C and rapidly quenched in liquid air does not show any changes in E' and $\tan \delta$ in the melting range.

In conclusion, the above results indicate that the peroxide vulcanized NR exhibits two α -relaxations. These phenomena are significantly more remarkable when the cured sample is submitted to dynamic deformations superimposed on large static deformations. It would be necessary to apply a similar analysis to other elastomers in order to confirm this behaviour.

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