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The High Temperature Dispersion in Rubbers

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Summary

Results obtained by measuring dielectric absorption spectra in a 10^{-3} up to 10^{7} Hz frequency region as well as depolarisation currents, showing the existence of a high-temperature maximum in both natural and synthetic cis-1, 4-polyisoprene, are given. The influence exerted by the network density and the degree of quenching of the sample upon this maximum is explained by the orientation of the microblock arrangements in the polymer.

Introduction

Measurement results embracing the relaxation regions, relatively high above the glass transition temperature, have been published in some papers. It is mainly in natural rubber samples and butadiene-acrylonitrile copolymers where these relaxation regions, which we are going to mark as λ, have been observed. We believe that satisfactory interpretation of the mechanism of this relaxation region has been furnished by MAEKAWA et al. /1965/, who followed his measuring of the mechanical properties of crosslinked natural rubber and by PLAZEK /1966/, who followed the torsional creep measurements on four natural rubber vulcanisates. According to them the existence of this relaxation region results from the changing number and distribution of physical crosslink points. In a similar way BARTENEV and LYALINA /1977/ explained this phenomenon by means of large clusters of macromolecular chains shifting in and out of the larger blocks in the polymer. BARTENEV and ZELENEV /1976/ were prone to explain this by the motions of microblocks with different hypermolecular structures. High-temperature relaxation regions have been also observed by means of dielectric methods /BAKULE et al. 1971, 1977/.

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Experimental

Samples of MRPRA, partially purified crepe, and synthetic cis-1, 4-Polyisoprene Cariflex IR 305 were prepared for the purposes of measuring. Using natural rubber we also prepared a crosslinked sample with 60 mg of sulphur per 1 g of rubber.

For the same period of time /10 minutes/ all the samples were calendered at 333 K and the sheets obtained pressed for 3 hours at 420 K.

Using a constant brenting rate the frequency dependence of complex permitivity and the temperature dependence of the depolarisation current were measured. In order to measure complex permitivity a lowfrequency bridge /STOLL 1975/ for the 10^{-3} up to 40 Hz regions, a transformer bridge /General Radio/ for the 40 Hz up to 20 kHz, and Q-meter for the 80 kHz up to 1.6 MHz ones were used.

While measuring the depolarisation currents the following procedure was applied: the sample to be tested was heated up to a preselected temperature /375 K/ in a testing capacitor and the electric field of an intensity of about 1.9 MV/M was applied hitherto. With the voltage remaining at the same level all the way through, the sample was cooled at approximately constant rate of 4 K/min down to the temperature of 175 K. The discharging short-circuit current was measured at $q = 4.5$ K/min.

Results

While examing the frequency region in question /10^{-3} up to 1.6×10^6 Hz, in samples of both natural and synthetic rubber dielectric absorption maxima being in relationship with the relaxation of the main chain motion /the α-region/, occuring at temperatures of about 210 to 275 K, were observed. With the sulphur crosslinked sample the relaxation appears to be shifted by about 10 K towards higher temperatures. This phenomenon is identical to the glass transition temperature increase, which takes place due to polarity rise of the chain while sulphur is being added.

On the dielectric spectrum of samples made of natural rubber the high-temperature relaxation region /λ-region/, which is of greatest interest to us in this study, can be seen within the 10^{-2} up to 10^3 Hz frequency region at temperatures of approximately the 275 to 400 K region. The frequency dependence of the imaginary part of permitivity, the λ-region of the specimen of non-crosslinked natural rubber, are shown in Fig. 1. The frequency logarithm values /log f_m/ as well as those of the maximum /ε''_m/, taken from the chart and refering to the individual temperatures T, can be found in the first three columns of TABLE 1. In figure 1 the relaxation α-region has not been plotted since for the curve, measured even at the very lowest marked temperature of 296 K, the maximum would be attained at the frequency of the order of 100 MHz, in other words beyond the scope of the measured frequency only.

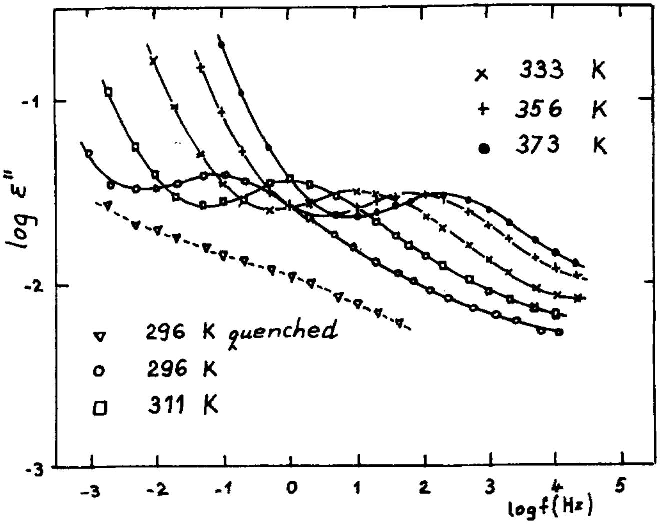

Figure 1. The frequency dependence of the logarithm of the imaginary part of permitivity of non-crosslinked natural rubber.

TABLE 1
The dependence of the frequency logarithm values /log f_m/ and the maxima of the imaginary part of permitivity /ε''_m/ on the temperature

1st NR measurement			2nd NR measurement			Crosslinked		
T/K/	ε''_m	$\log f_m$	T/K/	ε''_m	$\log f_m$	T/K/	ε''_m	$\log f_m$
296	0.039	-1.07	371	0.043	0.66	275	0.019	-1.83
311	0.036	0.1	389	0.04	1.47	289	0.018	-0.5
333	0.031	1.1	404	0.038	2.1	305	0.018	0.67
355	0.03	1.93	419	0.037	2.67	331	0.019	2.03
						371	0.018	2.7
						391	0.02	3.23

Compared to the non-crosslinked sample, the relaxation α-region of the sample crosslinked by 60 mg S/1g NR appears to be shifted by about two orders towards the lower frequencies. Contrary to that the high-temperature λ-region will slide towards higher frequencies. With the rise of network density both the relaxation regions will get nearer to each other. In Fig. 2 the two relaxation regions are shown. For better illustration the high-frequency side of the λ-region, lying out the limits of the limits of the measured frequency region, has been included too; to this purpose the principle of the time- temperature superposition was used.

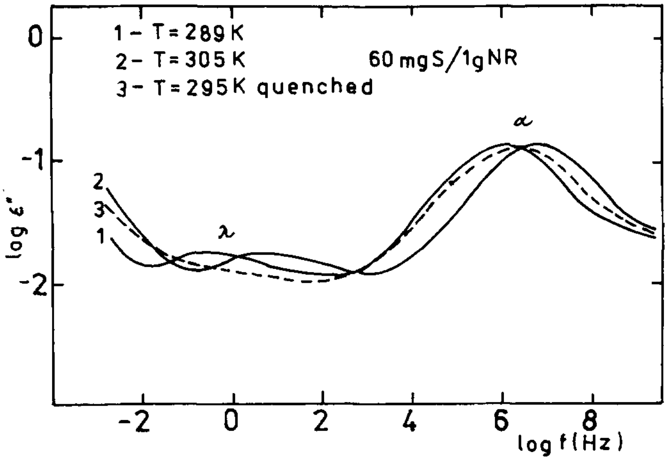

Figure 2. The frequency dependence of the logarithm of the imaginary part of permitivity of crosslinked natural rubber.

In case of the non-crosslinked sample the high-temperature λ-maximum is three times as high as the α-maximum. Through crosslinking the value of the λ-maximum will decrease /BAKULE at al. 1970/, while the value of α-maximum will increase. The α-maximum of a crosslinked sample is by about ten times higher than the λ-maximum. As the sulphur content reaches 80 mg of sulphur per 1 g of rubber, no λ-region is detected. During the measurements we found that the λ-region was not stable enough. There has been found that after quenching the specimen, heated to 420 K, in water with ice no λ-maximum was observed in the measured frequency range. This frequency dependence of the permitivity was changed in the way shown by the dashed curve in Fig. 1 and 2.

It was possible to assume that a shift towards the lower frequencies could take place as in the case of a non-crosslinked quenched sample the λ-maximum could again be noticed whenever the sample was subjected to malleableization at a temperature of 420 K and afterwards slowly cooled down at the rate of q=1 K/min. The frequencies f_m and values ε''_m of the maximum achieved when the sample, after being quenched, was subjected to malleableization for three hours at the above temperature, are shown in TABLE 1 under 2nd NR measurement. By measuring the depolarisation currents we were trying to prove the shift of the maximum towards the lower frequencies /or to the higher temperatures when the measurement had been realised at a constant frequency/. For non-crosslinked samples the dependences of densities of the depolarisation currents on the temperature are shown in Fig. 3. From said figure we can clearly see to what an extent the charakteristic of the depolarisation current within the high-temperature region is being influenced by the degree of quenching of the samples.

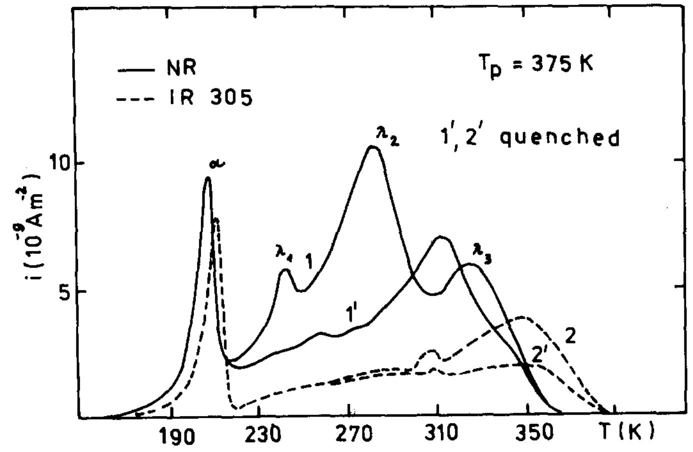

Figure 3. The temperature dependence of the depolarization current of non-crosslinked rubbers.

Discusion

As per the results of VOLKENSTEIN´s and PTICYN´s work /1956/ there should be a correlation between the course of the depolarisation current, obtained through measuring /Fig. 3/ and the characteristic of the temperature dependence ε''/T/ measured at a constant frequency of 10^{-3} Hz. The high-temperature maximum, evaluated for natural rubber by means of measuring the frequency dependence of permitivity, then corresponds to the λ_2-maximum of the depolarization current characteristic. In all probability the maximum shows up in such a poor way that it remains just unobserved in the ε''/f/ characteristic. The λ_3-maximum is likely to be caused by polarization of the volume charge. There is no linear dependence of the value of this maximum on the intensity of the electric field and the value of said maximum considerably increases with the rising contennts of crosslinking agents in the specimens. Augmenting the contents of crosslinking ingredients and agents results in raising the portion of low-molecular dissociating matters and increasing conductance. The λ_3-maximum overlaped the λ_1 and λ_2 maxima of the crosslinked samples. Juding from the characteristic of curve 1 in Fig. 3, a shift of the λ_2-maximum towards the higher temperatures is to be taken for granted. In a quenched specimen the value of this maximum changed linearly with the intensity of the field.

The depolarization current characteristic of synthetic polyisoprene /curve 2 in Fig. 3/ makes it possible for us to follow up the high-temperature maximum. The shift of this maximum towards the higher temperatures of about 70 K in comparison with natural rubber, seems to explain the reason for which this maximum cannot be observed in the frequency dependence of the permitivity and why any change of the characteristic ε' with quenching was not observed in this sample. In contrary to ε''/f/ the depolarization current is influenced by the quenching /curve 2/. As it seems, no temperature shift of the maximum was ever observed since temperature T_p, at which the sample had been polarized, is comparable with the temperature of the maximum. It is quite impossible to raise the temperature T_p as the quenching influence would be paralyzed thereby.

Several interpretations of the mechanism of high-temperature maxima have been mentioned in the introductory part. As long as the loosening of the relevant motion mode results in an increase of dielectric losses, chances are that either a translational motion of the charge or a rotating motion of a group with a non-zero dipole moment are involved. In the first case, though, the frequency and /or temperature dependence of the dielectric losses mostly does not show any maximum and polarization is not a linear function of intensity. Our observations are not of this kind. That´s why we are ready to support the idea of a certain microblock /domain/ of the polymer being in rotating motion, while the chains in the microblock are at least partially arranged in a way to add up the dipole moments of monomer units. The whole group, containing arranged polar groups, then orients itself as a total in the direction of the electric field. An approximate estimate of the size of the rotating domain can be made if we suppose a spherical particle of <u>a</u> diameter to be rotating in a viscous medium of η viscosity at T temperature. The time of relaxation, τ, is then proportional to $\eta a^3 T^{-1}$. Basilically the temperature dependence of the relaxation time is then determined by the temperature dependence η mostly given in the well known form of $\eta \sim \exp A/(T-T_\infty)$. The values of the A parameter, given by the temperature dependence of the relaxation time τ characteristic of the α-region, are 3200 K for non-crosslinked rubber and 2600 K for the crosslinked one of 60 mg S/1 g NR as long as the temperature $T = 153$ K for the non-crosslinked sample and $T = 163$ K for the crosslinked one. The values of the parameter A_λ, stated by the temperature dependence of the relaxation time characteristic of the λ-region are 2140 K for the non-crosslinked sample and 1870 K for the crosslinked one. With regards to the temperature instability of the λ-region, we consider the conformity of A_α and A_λ to be acceptable. Obviosly the diameter a changes with temperature too.

If we know the relaxations between the relaxation times of the α -region $/\tau_\alpha/$ and the λ -region $/\tau_\lambda/$, then at a certain temperature the relations between the effective diameters a_α and a_λ of the structual units, the motion of which results in creating these regions, will equal p $a_\lambda/a_\alpha = /\tau_\lambda(T)/T_\alpha(T)/^{-1/3}$. For non-crosslinked natural rubber the value of quantity $p = 5\text{x}10^2$, for crosslinked 60 mg S/1 g rubber with a crosslinked density $\gamma \doteq 5\text{x}10^{-5}\text{mol/cm}^3$ we have got $p \doteq 100$. Should we anticipate that the diameter of the particle, relaxing in the α-region, is comparable to the magnitude of the monomer unit $a \triangleq 5\text{x}10^{-10}\text{m}^3$, then $a_\lambda = 3\text{x}10^{-7}\text{m}$ for non-crosslinked sample and it drop down to a_λ $1\text{x}10^{-7}\text{m}$ for the crosslinked one. These values are well comparable to those found by BARTENEV and ZELENEV /1976/, who, of course, used a little different method of mechanical measurements.

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