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# The Effect of the Density and Nature of Spatial Network in Elastomers on Their Viscoelastic Characteristics

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We have studied the effect of the density of the networks formed by fluctuating entanglements and chemical crosslinking on the relationships between the circular frequency  $\omega$  and the storage and loss moduli,  $G'$  and  $G''$ , for polybutadienes of narrow and wide molecular weight distributions (the ratio  $M_w/M_n$  varied from 1.1 to 3.35) and different microstructure. Polybutadienes were crosslinked by thermal, radiation, and sulphur vulcanization. With increasing density  $\nu$  of a network of chemical crosslinks, which is characterized by the average molecular weight of a chain length ( $M_e$ ), pseudo-equilibrium plateau extends to the side of low frequencies with a certain small increase of its level. This increase becomes noticeable when  $M_e$  is approximately equal to the average molecular weight  $M_e$  of the chain length between the fluctuating entanglements of an uncrosslinked elastomer. At the same time the maxima on the curves of  $G''(\omega)$  are smoothed out and the losses reduce to negligibly small values with decreasing frequency.

## INTRODUCTION

The effect of structural factors (molecular weight, polydispersity, microstructure, the degree of crosslinking) on the visco-elastic characteristics of uncrosslinked and crosslinked elastomers has been studied in a number of works.<sup>1-5</sup> Measurements were made predominantly by the rebound resilience

method, the time of loading being uncontrollable. In these works, however, the following important inferences have been made: the dynamic modulus of elasticity and rebound resilience increase with increasing molecular weight, these parameters are independent of the fractional composition and microstructure of polymer (in the absence of crystallization), and the dynamic modulus of an elastomer is governed by a network of fluctuating entanglements while the equilibrium elastic deformation at constant stress is determined by a network of chemical nodes.

The effect of the density of a spatial network on the frequency dependences of the elastic compliance  $J'$  and the loss compliance  $J''$  in shear has been studied by Ferry and his coworkers<sup>6-8</sup> for vulcanizates of noncrystallizable polybutadienes of different molecular weight ( $1.8 \times 10^5$  and  $5.1 \times 10^5$ ) and narrow molecular weight distribution (MWD), and also for natural rubber (NR). Rubbers were crosslinked with sulphur and dicumyl peroxide. It has been shown for one of the polybutadiene samples that the change of  $\nu$  from  $0.57 \times 10^{-4}$  to  $1.85 \times 10^{-4}$  mole/cm<sup>3</sup> (as determined from the equilibrium swelling in n-heptane) does not practically affect  $J'(\omega)$  when the circular frequency changes from 10 to  $10^5$  sec<sup>-1</sup>, which corresponds to the high-elasticity plateau. At the same time, in the region of low frequencies the function  $J''(\omega)$  strongly depends on the density of chemical nodes. This difference decreases with increasing frequency and becomes insignificant in the region of high frequencies. The effect of the vulcanizing agent (sulphur or dicumyl peroxide), which is but slightly noticeable at equal values of  $\nu$ , tells but relatively little on the dependences of  $J'$  and  $J''$  on  $\omega$ . Dickie and Ferry<sup>8</sup> extended the frequency range into the region of infralow values of frequencies (up to  $\omega = 10^{-4}$  sec<sup>-1</sup>) by recalculating the data on creep for vulcanized NR to the corresponding values of  $J'(\omega)$  and  $J''(\omega)$ . As the frequency decreases the difference between the functions corresponding to different networks increases. The analysis of the question however is complicated by the fact that the comparison was made between NR samples that differed not only in values of  $\nu$  but also in molecular weight. Nevertheless it is clear that with decreasing frequency  $J'$  approaches the value of equilibrium compliance, which is different for samples with different values of  $\nu$ . The losses decrease the faster the higher the value of  $\nu$ . When the frequency increases, the value of  $J'(\omega)$  corresponding to different  $\nu$  values approach each other, which is associated, as pointed out in the literature,<sup>1,2</sup> with the increase of the role of fluctuating entanglement. The values of  $J''(\omega)$  for samples with different densities of a network of chemical crosslinks also come closer together with increasing frequency, but this approach is not so marked as for  $J'(\omega)$ . At low frequency values the difference in  $J''(\omega)$  becomes more pronounced than that in  $J'(\omega)$ . Thus, measurements of  $J''(\omega)$  are more sensitive to the structural features of polymers.

The aim of the present work is to elucidate the relative effect of a fluctuating

network of entanglements and a network of chemical nodes on the viscoelastic properties of elastomers.

## EXPERIMENTAL

### Materials

Three noncrystallizable polybutadienes obtained by anionic polymerization with secondary butyl-lithium were used for our investigations. They had a narrow MWD ( $M_w/M_n = 1.1$ ), an approximately equal content of cis- and trans-groups, and molecular weights ( $M_w$ ) of  $2.2 \times 10^5$ ;  $0.85 \times 10^5$ , and  $4.47 \times 10^5$ . The first one was used as such ( $M_w = 2.2 \times 10^5$ ). The two others were mixed in the proportion 1.68:1 to give a polydisperse polybutadiene having a comparatively wide MWD ( $M_w/M_n = 2.36$ ). It had a molecular weight of  $M_w = 2.2 \times 10^5$  (the calculated value) and  $M_v = 1.98 \times 10^5$  (the experimental value). Polybutadiene with a narrow MWD is abbreviated here to PBM ("monodisperse") and the one with a wide MWD, to PBP ("polydisperse").

Besides, sulphur-vulcanized commercial, polydisperse ( $M_w/M_n = 3.35$ ;  $M_v = 10^5$ ) crystallizable cis-PB (the content of cis-groups being 93.5 per cent) produced with a catalyst of the Ziegler type has also been studied.

Thermovulcanized PBM and PBP were prepared at  $240^\circ\text{C}$ <sup>9</sup> for 10, 20, 30, and 40 min (PBM) and 10, 30, 55, and 80 min (PBP). Radiation-crosslinked PBM was prepared by irradiation with doses of 7 to 60 Mrads. Crosslinked cis-PBM was prepared from a standard mixture<sup>5</sup> containing no carbon black and with various contents of sulphur (1, 2, 6, 10, 24, and 44 parts by weight per 100 parts of rubber). Samples of cis-PB were vulcanized for 40 min at  $143^\circ\text{C}$ . Besides, two of these samples were additionally maintained at  $180^\circ\text{C}$  for 45 and 30 min, respectively.

### Methods of determining the components of the complex modulus

These components were determined by means of a vibrometer NV-N1, a modified version of the test apparatus "Dynatron" (O. Wolpert-Werke G.M.B.H., GFR)<sup>10</sup> at the frequencies of the harmonic shear deformation ranging from 5 to 100 cps, an amplitude of 0.01 and temperatures of from  $-70$  to  $+100^\circ\text{C}$ . The samples had the form of sandwiches made of two rectangular prisms ( $2.5 \times 1 \times 1$  cm) placed between three steel plates.

The experimental data obtained were used to plot master curves for the functions  $G'(\omega)$  and  $G''(\omega)$  by the temperature-frequency reduction method through the use of the Williams-Landel-Ferry equation<sup>11</sup> with universal values of the constants. The reduction temperatures  $T_s = T_g + 50^\circ\text{C}$ ,

where  $T_g$  is the glass-transition temperature determined dilatometrically.<sup>12</sup> For the polymers under study  $T_g = -101 \pm 3^\circ\text{C}$ .

In the infra low-frequency region ( $10^{-5} < \omega < 10^{-2}\text{sec}^{-1}$ ) the functions  $G'(\omega)$  and  $G''(\omega)$  were calculated from the creep curves which were plotted with the aid of an instrument for measurement of creep at small displacements.<sup>13</sup> In this apparatus the same sample that was used on NV-N1 was subjected to shear deformation under the action of constant stress. The loads were selected so that the maximum (equilibrium) deformation did not exceed 0.005. The displacement was measured with the aid of an electro-contact system which relieved the sample of the load imposed by the measuring instrument—a multi-revolution indicator of the clock type with a scale division of 1 micron. The samples were tested at  $70^\circ\text{C}$ .

The time dependence of the high-elasticity modulus was calculated from the data of creep measurements by using the Leaderman equation<sup>11</sup>:

$$G(t) = \frac{\sin m\pi}{m\pi} \cdot \frac{1}{J(t)} \quad (1)$$

where  $J(t) = \gamma(t)/\tau$  is the compliance at shear,  $t$  is the time,  $\tau$  is the preset shear stress,  $\gamma(t)$  is the time-dependent shear strain and  $m = d \log J(t)/d \log t$  is the slope of the compliance (or deformation) curve in logarithmic coordinates. Since for all the crosslinked rubbers under study  $m \leq 0.1$ , and  $\sin m\pi/m\pi$  is approximately equal to 1, then it follows that

$$G(t) = 1/J(t) = \tau/\gamma(t) \quad (2)$$

The functions  $G'(\omega)$  and  $G''(\omega)$  were calculated with the aid of the Nino-miya-Ferry equation:<sup>11</sup>

$$G(t) = G'(\omega) - 0.4G''(0.4\omega) + 0.014G''(10\omega) \Big|_{\omega = 1/t} \quad (3)$$

and the equation derived by R. Buchdahl and L. Nielsen<sup>14</sup> for  $\tan \delta = G''/G'$ :

$$\tan \delta = \frac{\pi}{2} \frac{d \log \gamma(t)}{d \log t} = 1.57m(t) \quad (4)$$

whence

$$G''(\omega) = 1.57G'(\omega) \cdot m(t) \Big|_{\omega = 1/t} \quad (5)$$

For all the crosslinked rubbers studied  $G''(\omega) \leq 0.06G'(\omega)$ . Since the values of  $m$  are small, it may be assumed, by taking into account the values of the coefficients for  $G''$ <sup>15</sup> in Equation (3), that

$$G'(\omega) = G(t) \Big|_{\omega = 1/t} \quad (6)$$

The density of the spatial structure was characterized by the values of  $M_c$  and  $M_e$ , which are the average values of molecular weight of elastically active

lengths of molecular chains between chemical crosslinks and fluctuating entanglements of the corresponding networks. It is supposed that  $M_c$  and  $M_e$  can be determined by the equation of the kinetic theory of rubber elasticity:<sup>16</sup>

$$M_c = \rho RT/G_e \text{ or } M_e = \rho RT/G_p' \quad (7)$$

with an accuracy of up to a constant factor equal for static and dynamic measurements. Here  $\rho$  is the density of polymer at temperature  $T$ , °K;  $R$  is the gas constant;  $G_e$  is the equilibrium elastic modulus;  $G_p'$  is the storage modulus at a frequency  $\omega$ , corresponding approximately to the middle of the high-elasticity plateau.

Thus the density of the spatial network is estimated by the values of  $G_e$  and  $G_p'$ . Since the width of the high-elasticity plateau varies with change of the degree of crosslinking, different samples were compared by using the values of  $G_p'$  measured at  $\omega = 10^3 \text{ sec}^{-1}$ , which corresponds approximately to the middle of the plateau for uncrosslinked PBM. The value of  $M_e$  determined in this way for PBM and PBP is about 2400. The value of  $G_e$  for uncrosslinked PBM, according to the data reported in the literature,<sup>17</sup> is equal to about  $10^5$  dynes per  $\text{cm}^2$ . The value of  $G_e$  for vulcanizates was calculated from the equilibrium region of the creep curve.

The time during which the equilibrium deformation was attained for different vulcanizates varied from  $3 \times 10^3 \text{ sec}$  (for radiation-crosslinked PBM with  $M_c = 4000$ ) to 10–20 sec (for cis-PB crosslinked with sulphur,  $M_c \leq 2000$ ). At  $M_c = 15500$  (thermovulcanized PBM) the equilibrium was not reached during the loading of a sample for  $10^4 \text{ sec}$ . The magnitude of elastic deformation was determined from the elastic recovery of the sample after removal of the load. The value of the difference  $\gamma_{\max} - \gamma_{\text{res}}$  was used to calculate  $G_e$  ( $\gamma_{\max}$  is the deformation at the moment of unloading and  $\gamma_{\text{res}}$  is the residual deformation).

## RESULTS AND DISCUSSION

The dependences  $G'(\omega)$  and  $G''(\omega)$  reduced to 24°C for the samples investigated are presented in Figures 1–4.

From Figures 1 and 2 it is seen that up to considerable degrees of crosslinking ( $M_c \approx 4000$ ) the level of the high-elasticity plateau remains practically the same as for unvulcanized PB. At the same time  $G_e$  varies from about  $1 \times 10^5$  dynes/ $\text{cm}^2$  (for uncrosslinked PB<sup>16</sup>) to  $5.2 \times 10^6$  dynes/ $\text{cm}^2$ , i.e., increases by 50 times and even more. This lends support to the assumption made earlier<sup>1,2</sup> as to the decisive effect of a fluctuating network of entanglements on the value of the storage modulus in the presence of a network of chemical crosslinks of low density. It thus becomes possible to determine  $M_e$  for uncrosslinked rubber on weakly crosslinked samples.

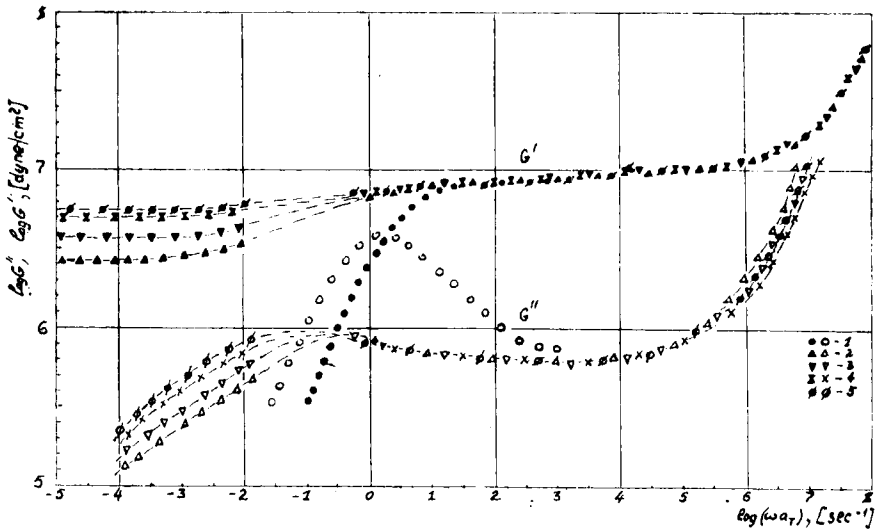


FIGURE 1 Frequency dependences of  $G'$  and  $G''$  for uncrosslinked polybutadienes of narrow molecular weight distribution and its thermovolcanizates with different values of  $M_c$ : 1—uncrosslinked polymer; 2—8500; 3—6000; 4—4400; 5—4000.

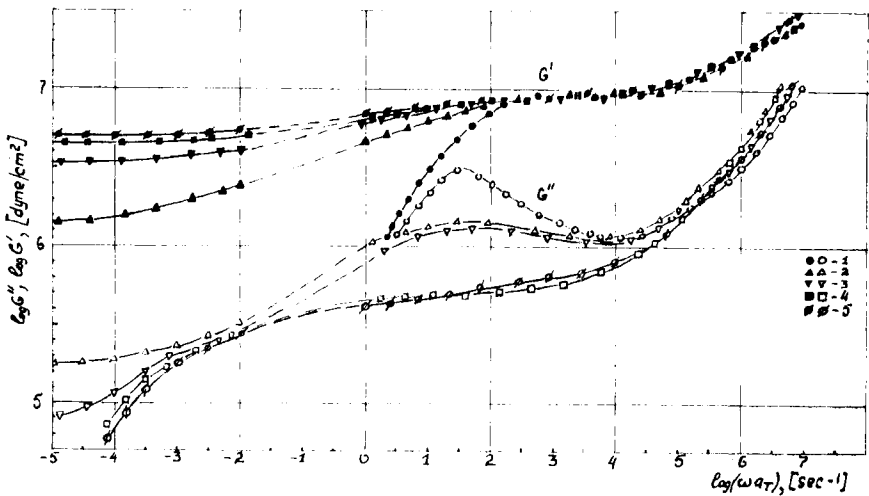


FIGURE 2 Frequency dependences of  $G'$  and  $G''$  for uncrosslinked polydisperse polybutadiene and its thermovolcanizates with different values of  $M_c$ : 1—uncrosslinked polymer; 2—15,500; 3—6500; 4—4900; 5—4400.

Interesting results are obtained when one considers the curves of  $G'(\omega)$  for PBM crosslinked by radiation. They were vulcanized to higher degrees of crosslinking than rubbers cured by thermovulcanization. Figure 3 shows that, beginning from a certain critical value of  $M_e$  there is observed the effect of a network of chemical crosslinks on the level of the high-elasticity plateau. In this case, with increasing degree of crosslinking  $G_p'$  increases at a slower rate than does  $G_e$ , as a result of which the values of  $G_p'$  and  $G_e$  approach each other. The level of the high-elasticity plateau starts changing noticeably at  $M_e \approx 1.5 M_e$ .

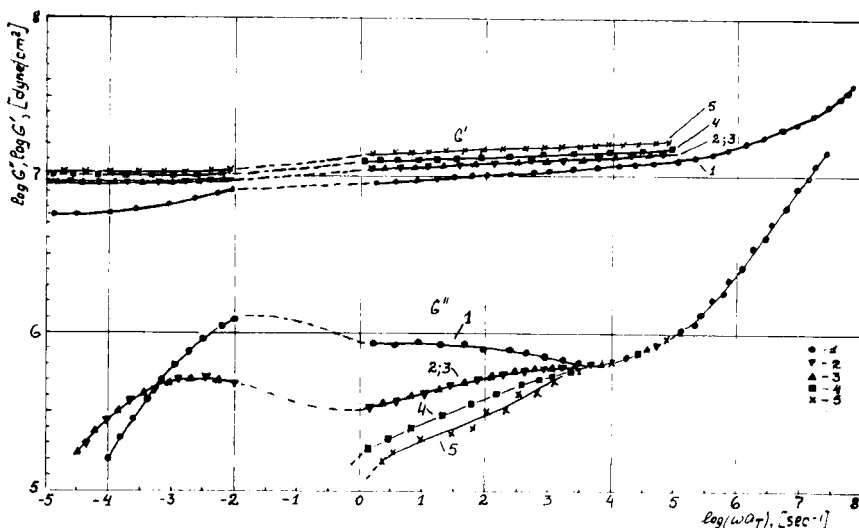


FIGURE 3. Frequency dependences of  $G'$  and  $G''$  for radiation-crosslinked polybutadienes of narrow molecular weight distribution and different values of  $M_e$ : 1—4020; 2—2460; 3—2360; 4—2210; 5—2140.

The process of radiation vulcanization is accompanied by the destruction of the polymer. Starting from a radiation dose of 50 Mrads the value of  $G_e$  does not practically increase, and therefore higher values of the density of the network of chemical nodes were obtained through the vulcanization of cis-PB in the presence of sulphur. The ability of cis-PB to crystallize limited the possibility of using low temperatures, for which reason the master curves of the frequency dependences  $G'(\omega)$  and  $G''(\omega)$  extend in a lesser degree to high frequencies than in the case of noncrystallizable PB. A certain fall of the level of the plateau for a sample most weakly crosslinked with sulphur ( $M_e = 7850$ , Figure 4) is probably associated with the relatively low molecular weight of commercially produced cis-PB.



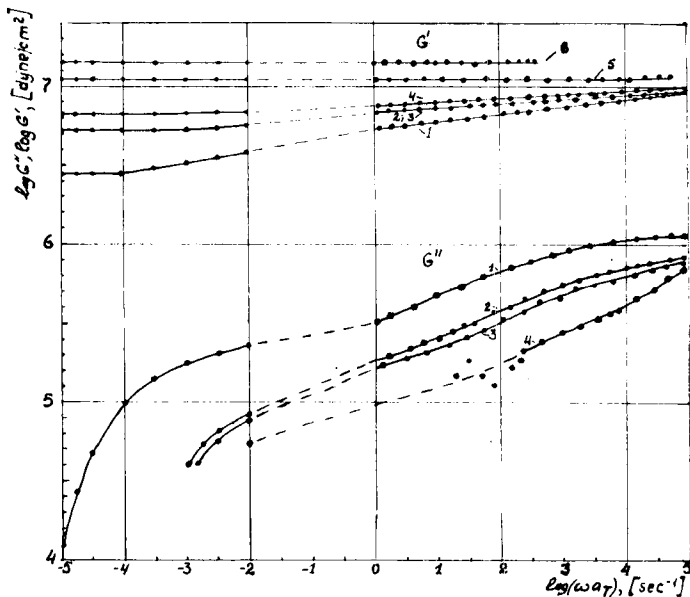


FIGURE 4 Frequency dependences of  $G'$  and  $G''$  for vulcanizates of cis-polybutadienes of different  $M_c$ : 1—7850; 2—4200; 3—4080; 4—3300; 5—2000; 6—1580.

The rise of the plateau level for cis-PB crosslinked with sulphur becomes noticeable at a higher  $M_c$  than in the case of PBM crosslinked by radiation, which is a consequence of the higher value of  $M_e$ , which is approximately 3000 for cis-PB (determined on a vulcanizate with  $M_c = 7850$ ), and therefore the increase of  $G_p'$  must be noticeable already at  $M_c \approx 1.5 M_e = 4500$ .

The increase of the degree of crosslinking up to  $M_c \leq 2000$  leads to the complete coincidence of the values of  $G_e$  and  $G'$  over a wide frequency range. In these cases, only a spatial network formed by chemical crosslinks can be detected.

Figure 5 presents the dependence of  $G_p'/G_e$  on  $M_e/M_c$  ( $M_e$  refer to uncrosslinked rubber) for all the samples investigated. In these dimensionless coordinates the effect of the density of a network of chemical crosslinks on the elastic properties of an elastomer is expressed by a single curve independently of the molecular weight, MWD, microstructure and the method of vulcanization of the starting polymer. The relation between the storage modulus (in the region of the high-elasticity plateau) and the equilibrium modulus of elasticity is determined by the ratio of the number of chemical crosslinks to that of fluctuating entanglements in the network of the elastomer. The increase of  $G_p'/G_e$  for rubbers crosslinked by radiation may be ascribed to their destruction.

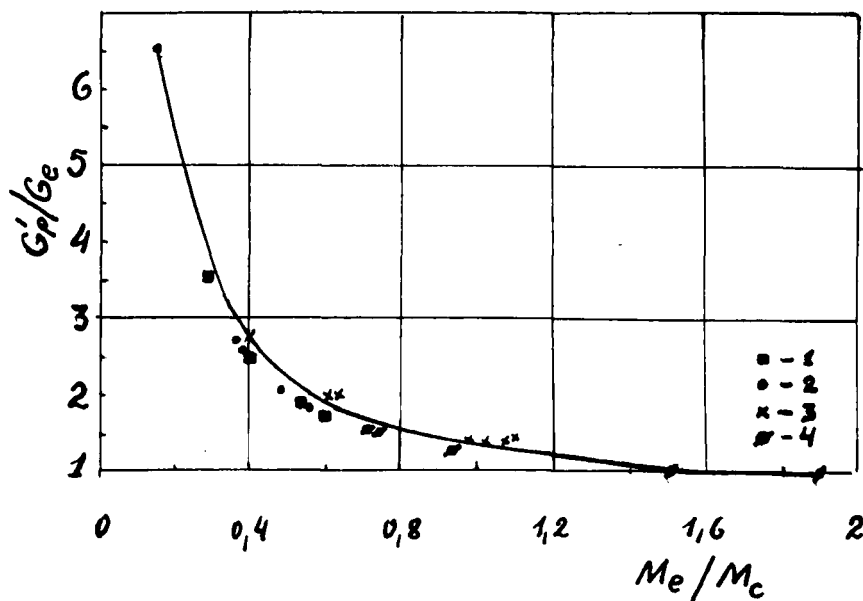


FIGURE 5. The reduced value of the storage modulus on the high-elasticity plateau versus the reduced value of the molecular weight of the chain segments between the crosslinks normalized by the molecular weight of the chain length between the entanglements: 1—polybutadiene of narrow MWD, thermovulcanized; 2—polybutadiene of wide MWD, thermovulcanized; 3—radiation-crosslinked polybutadiene of narrow MWD; 4—cis-polybutadiene of wide MWD, vulcanized with sulphur.

The effect of the structural factors on  $G''(\omega)$  is considerably more pronounced than that of  $G'(\omega)$ , especially in the region of the maximum of the loss modulus ( $G_{\max}''$ ) of an uncrosslinked polymer and in the region of low frequencies when  $G''(\omega)$  falls sharply with decreasing frequency.

A comparison of the curves in Figure 1 and 2 shows that the increased polydispersity of uncrosslinked rubbers shifts the maximum of  $G''(\omega)$  to the right along the frequency axis (by about 30 times when the ratio  $M_w/M_n$  changes from 1.1 to 2.36) without a noticeable change of the value of  $G_{\max}''$ , which is consistent with the data reported in the literature.<sup>18</sup>

The formation of even a relatively sparse network of chemical crosslinks ( $M_c \approx 16,000$ ) results in a sharp decrease of  $G_{\max}''$  (by a factor of about 2, Figure 2). On further crosslinking the maximum of  $G''(\omega)$  is shifted to the left, decreases still more, becomes blurred and finally disappears. The function  $G''(\omega)$  is markedly affected by the method of vulcanization. Thus, at equal values of  $M_c$  for cis-PB vulcanized with sulphur the losses are lower than in the case of thermally or radiation crosslinked PBM (the curves 5 in Figure 1;

the curve 1 in Figure 3, and the curve 2 in Figure 4), for which  $G''(\omega)$  does not practically differ up to  $M \approx 4000$ .

The curves of  $G''(\omega)$  have a complicated form and pass through a maximum at different frequencies, and there are many points of intersection in the case of networks of different nature. One should therefore be careful when estimating the effect of the density of networks on the mechanical losses on the basis of data obtained in a narrow frequency range.

The present examination of the viscoelastic properties of unfilled vulcanizates enables one to account for certain specific features of the behaviour of the functions  $G'(\omega)$  and  $G''(\omega)$  for rubbers filled with carbon black. The value of  $G_e$  rises as a result of the increase of the effective density of the spatial network of stable links between macromolecules (chemical crosslinks plus the bonds between the macromolecules and particles of carbon black). The value of  $G'(\omega)$  is also affected by the structural skeleton formed by the particles of carbon black.<sup>19</sup> The addition of carbon black is usually responsible for the increase of losses, which are the greater the higher is the content of carbon black in the polymer and hence the fraction of carbon black not linked to rubber. Therefore the increase of  $G_e$  caused by the introduction of an active filler leads to the rise of not only the storage but the loss modulus as well. The increase of the content of an active filler cannot thus be expected to bring about an effect equivalent to that of the intensive crosslinking of unfilled rubber when the material is produced with negligibly small losses and with the storage modulus being frequency independent.

## CONCLUSION

The formation of a network of chemical crosslinks in the vulcanization of rubbers may lead to the coexistence of two types of network: a network of fluctuating entanglements and a network of chemical crosslinks. As the degree of crosslinking increases the value of the equilibrium modulus of elasticity  $G_e$  also increases. The value of  $G'$  increases also in the region of low frequencies, but the rate of increase falls with rise of frequency. The level of the high-elasticity plateau remains unaltered but the plateau extends to the side of low frequencies.

The high degree of crosslinking ( $M_c < 1.5M_e$ ) enhances the effect of chemical crosslinks on the function  $G'(\omega)$  not only at low frequencies but also in the region of the high-elasticity plateau. The plateau level rises, but the increase of  $G_p'$  observed in this case does not exceed the twofold amount. With decreasing  $M_c$  the mechanical losses decrease, which is evidence of the decisive influence of the fluctuating network on the relaxational properties of the elastomer.

If  $M_c$  is smaller than  $M_e$ , then the difference between  $G'$  and  $G_e$  practically disappears. In this case the high-elasticity plateau extends to any low frequencies and the losses are reduced to such an extent that they are inaccessible to measurement (the mechanical loss angle being lower than  $15^\circ$ ).

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