Local dynamics and viscoelastic properties of vulcanisates based on butadiene–acrylonitrile rubbers

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The viscoelastic properties of elastomers are known to depend on the level of intermolecular interaction (IMI). Butadiene–acrylonitrile elastomers (BNK) are characterised by the appearance of specific interactions of nitrile groups in the relaxation spectra [1] in the form of the corresponding relaxation transitions. It is obvious that the dynamics of the given interactions should change under the influence of chemical crosslinking during vulcanisation of the rubber. Earlier [2, 3], using the molecular dynamics method, we showed that the factor determining the level of intermolecular interactions and the dynamics of local motions in butadiene–acrylonitrile copolymers is the configuration of the double bonds of the butadiene units. Here, copolymers containing butadiene units in 1,4-trans-configuration are characterised by a high level of IMI and lower mobility.

The aim of the present work was to assess the influence of crosslinking by sulphur bonds on the local dynamics of intermolecular interactions in the copolymers examined, and also to analyse the strain properties of BNK vulcanisates within the framework of a physical network model [4, 5]. For modelling, use was made of the molecular dynamics method [6] with force-field potential functions complying with the IMI parameterisation of the molecular mechanics method [7, 8].

The copolymers under investigation were modelled by two chains consisting of two triads of the BNBBNB type (where B represents a butadiene unit, and N an acrylonitrile unit), crosslinked via one or two butadiene end units by a monosulphide bond. In the case of crosslinking by one bond, the local dynamics of the end chain of the network was modelled. In the case of crosslinking by two bonds, the local dynamics of the inner chain was modelled. The butadiene units of the copolymers of each chain had a 1,4-trans-configuration only. In the process of integration of the equations of motion of the obtained complex, the average distances and their fluctuations (rms deviations) were calculated for the selected groups of atoms. A diagram of the calculated distances is shown in Figure 1 for the case of a complex that is crosslinked via one end unit by a monosulphide bond. The calculations were carried out from a starting configuration corresponding to the minimum potential energy of the complex, which hypothetically was considered to be a temperature of 0 K, by assigning initial random pulses to the atoms and by a gradual velocity renormalisation corresponding to a gradual increase in temperature to 400 K.

The dynamics of complexes crosslinked by a single bond is characterised by the presence of three qualitatively different types of motion. At low temperatures the molecules of the complex perform regular vibratory motions close to the minimum potential energy. With increase in temperature, the nature of motion changes from regular to stochastic, but the molecules of the complex remain connected to each other by chemical crosslinking by intermolecular bonds. Although in this case the fluctuations in the interatomic distances during motion are fairly great, a molecular “associate” is retained through non-valent interactions. With further increase in temperature, the intermolecular associate breaks down, and the molecules are held in the complex only as a result of chemical crosslinking.

According to the data obtained, the probability of associate formation when the molecules are connected by a single monosulphide bond depends substantially...
on the configuration of the diene units forming the chain. In particular, in the modelling of an associate of two copolymer chains with 1,4-trans-butadiene units connected by a single monosulphide bridge, it proved impossible to obtain numerical results since, at a temperature of 30 K, the system lost stability of motion on account of the disruption of valent interactions, i.e. a structure of this kind is in a high-stress state and breaks down with increase in temperature. On this basis it can be assumed that, in real systems, the formation of monosulphide crosslinks between butadiene units in 1,4-cis configuration is unlikely.

In the case of the crosslinking of molecules with 1,4-trans-butadiene units by a single monosulphide bridge, the nature of the temperature dependences of the distances assessed and their fluctuations corresponds to the sequence of three stages of dynamic behaviour that has been described above (Figure 2). The change from regular to stochastic motion occurs at a temperature of about 200 K. It begins with the transition to stochastic dynamics of the intermolecular bond between nitrile groups that is furthest away from a crosslink, which can be seen from the increase in standard deviation for distance $L_3$ (see Figure 1). At a temperature of 250 K, the complex is in the state of an intermolecular associate sustained by intermolecular interactions. Here, a maximum is observed on the curves of fluctuations in distances. With further increase in temperature, the average distance $L_3$ begins to grow, and the average distances $L_1$ and $L_2$ decrease. This indicates that, instead of an intermolecular associate, the end units of the chains form two independent intramolecular associates.

![Figure 1. Diagram of calculated distances between atoms: $L_1$ – distance between end carbon atoms; $L_2$ – distance between nitrogen atoms of nitrile groups of same chain; $L_3$ – distance between nitrogen atoms of nitrile groups of different chains that are far away from crosslink; $L_4$ – distance between nitrogen atoms of nitrile groups of different chains that are closest to crosslink.](image1)

![Figure 2. Temperature dependence (a) of average distances between atoms and (b) of standard deviations in complex consisting of two chains of 1,4-trans-copolymer BNBBNB connected by single monosulphide bridge: 1 – $L_4$; 2 – $L_3$; 3 – $L_2$; 4 – $L_1$.](image2)
In this case the intermolecular bond between the nitrile groups is transformed into an intramolecular bond. This is accompanied with a reduction in fluctuations, which can be seen from the maximum on the standard deviation curves. It must be pointed out that the intermolecular interaction between nitrile groups lying at a shorter distance from a chemical crosslink, $L_4$, hardly changes with increase in temperature, i.e. the given intermolecular bond is not broken, although certain fluctuations are observed for this bond also, the maximum of which coincides with the position of the maximum for fluctuations of the remaining distances. It can be said that free end units introduce a disturbance into the motion of the units adjacent to the chemical crosslink but do not entirely disrupt intermolecular interactions.

For complexes crosslinked by two monosulphide bridges via both end units, the temperature dependence of dynamic behaviour proves to be more complicated. In spite of the apparent symmetry of the nitrile groups located at an identical distance from the ends of the chains, their spatial arrangement at the minimum potential energy of the complex is non-equivalent. In this case, on account of the short length of the monosulphide bridge, the complex of two chains crosslinked via the end groups proves to be stressed by comparison with a non-crosslinked complex. This has a considerable influence on its dynamic behaviour. As can be seen from Figure 3, in the given case, with increase in temperature, fluctuations begin with the bond that corresponds to distance $L_4$ (see Figure 1) which, in the given complex, proves to be unstable, in spite of the fact that the initial distance between the nitrogen atoms is identical for the two pairs of nitrile groups. Then the entire complex acquires a stochastic nature of motion, which is manifested by an increase in fluctuations in distances $L_2$ and $L_1$. Here, the average values of these distances decrease, and conversely the average values of distances $L_3$ and $L_4$ increase. At a temperature of 300 K, the fluctuations reach a maximum, beyond which they begin to decrease. An analysis of the geometric structure of the complex indicates that at this instant it undergoes a conformation transition in which, from its original state corresponding to a linear arrangement of molecules with converging nitrile groups of the various molecules and with the end atoms, with sulphur bridges, far away from each other, the complex acquires the form of a twisted figure of eight (a twist-conformation) with converging sulphur bridges and with the nitrile groups of the various molecules far away from each other. Here, both intermolecular bonds of the nitrile groups are broken, whereas the sulphide bridges together bear a certain resemblance to an intermolecular bond.

Thus, it has been shown that the crosslinking of a butadiene–acrylonitrile copolymer with butadiene units in a 1,4-trans-configuration has different effects on the intermolecular interactions of the nitrile groups, depending on the density of the chemical network. For a sparse chemical network and end chains, the monosulphide bridge may fix the IMI of the nitrile groups of different chains that are closest to it. At the same time, if two monosulphide crosslinks are closely positioned along the chain, which should be characteristic of dense networks, the sulphur bridges introduce stress into the IMI of the nitrile groups, as a result of which, under the action of thermal motion, new stable conformations may arise, with which the intermolecular bonds of the nitrile groups of the various molecules will be broken, and in their place associates of sulphur bridges may be formed.

For the vulcanisates of butadiene–acrylonitrile rubbers that are used in practice, the degree of crosslinking is normally low, and, on the basis of the results presented, it can be concluded that, at temperatures above 300 K, a large proportion of the intermolecular interactions of the nitrile groups should be disrupted. Interactions of groups adjacent to a chemical crosslink should be an exception. Furthermore, in the present work, the dynamics of nitrile groups positioned in blocks along

![Figure 3. Temperature dependence (a) of average distances between atoms and (b) of standard deviations in complex consisting of two chains of 1,4-trans-copolymer BNBBNB connected by two monosulphide bridges: 1 – $L_4$; 2 – $L_3$; 3 – $L_2$; 4 – $L_1$.](image-url)
the chain was not examined. As shown by estimates by the molecular mechanics method, their IMI energy is considerably higher, and consequently the temperature transitions corresponding to their breakdown should lie at temperatures higher than 300 K. Evidently, even for such block-arranged nitrile groups, \( r \)-relaxation transitions were recorded [1]. Since the proportion of block-arranged groups during radical polymerisation should be small, it is natural for the observed contribution of processes of \( r \)-relaxation, even in copolymers with a relatively high content of nitrile groups, to be small.

It was of interest to assess the contribution of intermolecular interactions of nitrile groups to the elastic properties of the network during the strain of BNK vulcanisates at the rate normally used in uniaxial tensile tests. During the elongation of standard vulcanisate specimens at rates of 10–1000 mm/min, the strain curves, especially on the initial section, do not differ too greatly, the only difference being the strain at which failure of the specimen occurs, i.e. the elongation rate in the given range determines the durability of the vulcanisate more than its elastic properties. Under these conditions, with some allowance it can be assumed that the loading of the specimen is quasi-equilibrium, so that the stress in the specimen occurs, i.e. the elongation rate in the given range determines the durability of the vulcanisate more than its elastic properties. Under these conditions, with some allowance it can be assumed that the loading of the specimen is quasi-equilibrium, so that the stress in the specimen, \( f \), will be proportional to the concentration of high-elastic (rubbery) chains, \( v \), determined by the total number of crosslinked points, \( n \), both chemical (sulphur crosslinks) and physical (nitrile groups):

\[
f = v k T \left( \frac{1}{n} - \frac{1}{N} \right) \left( \frac{\lambda - 1}{\lambda^2} \right) + \frac{9}{10 N} \left( \frac{\lambda^3 - 2}{\lambda^2 + 3} + 1 \right)
\]

where \( k \) is Boltzmann’s constant, \( \lambda \) is the elongation factor, and \( N \) is the number of chain segments between the crosslinked points.

In expression (1), use was made of an approximation for the non-Gaussian distribution function of the distances between the chain ends in order to allow for the finiteness of the number of chain segments between crosslinked points, \( N \). This is necessary, since, with loading of the specimen and with increase in temperature, the physical network should break down, and therefore \( n \), together with \( v \) and \( N \), should be functions of \( T \) and \( \lambda \). In order to allow for this, in the present work, use was made of an equilibrium model of the physical network [4, 5], in accordance with which

\[
n = \frac{n_0}{\lambda^2 + 1} + n_0
\]

\[
x = \frac{\lambda^2 - 2}{\lambda} - 3 - \frac{E - TS}{k T}
\]

where \( n_0 \) is the concentration of chemical crosslinks, \( n_0 \) is the maximum possible temperature- and strain-independent concentration of physical crosslinks, and \( E \) and \( S \) are respectively the energy and entropy of a physical crosslink.

If we confine ourselves to an examination only of tetrafunctional crosslinks and ignore rings and the ends of chains, then it is possible to assume that

\[\nu = 2n, \quad N = \frac{1}{v M_0}\]

where \( \rho \) is the density of the polymer, and \( M_0 \) is the molar mass of the chain segment. These equations, together with expressions (1)–(3), give a closed system of algebraic equations for describing the stress–strain relationship of the vulcanisate. On the basis of experimental data on stress–strain relationships at different temperatures for an unfilled sulphur vulcanisate (2 parts sulphur, 0.7 parts N-cyclohexyl-2-benzthiazyl sulphenamide per 100 parts rubber) based on butadiene–acrylonitrile rubber BNKS-40 AN, the least-squares method was used to calculate the parameters of the given model: \( n_0, n_0 \), and \( E \). With an elongation rate of the standard specimen of 600 mm/min, they were as follows: \( n_0 = 21 \text{ mol/m}^3 \), \( n_0 = 21 \text{ mol/m}^3 \), and \( E = 47 \text{ kJ/mol} \). For the entropy of physical crosslinks, on the basis of the increment of the nitrile group to the entropy of evaporation of organic compounds, the estimate \( S = 32.3 \text{ J/(mol K)} \) was adopted [9]. Graphs of experimental and calculated curves are shown in Figure 4. As can be seen, quite satisfactory agreement between experimental and calculated curves is observed. Attention must be drawn to the fact that, on the calculated dependence at \( T = 293 \text{ K} \), with an elongation factor of \( \lambda \), there is a small plateau. This corresponds to the equilibrium process of intense breakdown of physical crosslinks [5]. It is significant that it is at this strain that an inflection is observed on the experimental dependence. Deviations of the experimental and calculated curves occur at the start of deformation

![Figure 4. Strain curves during elongation of BNKS-40 AN vulcanisate at temperature of 293 K (1, 2) and 373 K (3, 4) at rate of 600 mm/min (standard specimen): 1, 4 – experiment; 2, 3 – calculation by means of equilibrium model of physical network](image-url)
and in the region of the plateau. In both cases the experimental curve runs above the calculated curve. This gives grounds for assuming that the divergence is due to the same regular factor – non-equilibrium of the real process of deformation of the specimen. With a large elongation factor, when the initial physical network has broken down, the experimental and calculated strain curves practically merge. At increased temperature, the agreement of experimental and calculated dependences again is quite good.

If in equation (2) it is assumed that \( n_0 = 0 \) (absence of a physical network), then relationship (1) will be the high-elasticity (rubbery) equation of the non-Gaussian chain chemical network. Approximation of the obtained experimental data by such a function turns out to be considerably worse. For the experimental data examined, the variance of inadequacy of the model with no allowance for the physical crosslinks increases by more than a factor of 5. Here, a model taking into account only the chemical network of non-Gaussian chains also gives good agreement with experiment at high elongation factors, but far worse agreement at low elongation factors, and, most importantly, it reproduces the temperature dependence of the initial elastic modulus much more poorly. This just confirms that the intermolecular interactions of nitrile groups contribute to the quasi-equilibrium elastic modulus. Allowance for these interactions makes it possible, by means of the equilibrium model (1)–(3), to describe satisfactorily experimental data relating to the non-equilibrium process of network deformation.

Let us evaluate the import of the parameters of the physical crosslinks that are obtained as a result of approximation. The calculated value of the crosslink energy is roughly twice as high as the increment of the nitrile group to the enthalpy of evaporation of organic compounds [9]. This confirms the remarks made above concerning the fact that only block-arranged nitrile groups should contribute to the elasticity of the network. Their maximum concentration is in fact very low – 4 times lower than the concentration of chemical crosslinks, the stoichiometric concentration of nitrile groups being more than an order of magnitude greater than the maximum possible concentration of sulphur crosslinks. It must be noted that, in reality, the estimate of \( n_0 \) obtained on the basis of the equilibrium model (1)–(3) is still too high. Allowance for processes of viscoelasticity within the framework of phenomenological theory [10] makes it possible to achieve an even better agreement between calculated and experimental curves, and in this case the estimate of the maximum concentration of physical crosslinks is roughly halved by comparison with the equilibrium model. Such an insignificant coefficient of realisation of physical crosslinks is due not only to the small proportion of block-arranged nitrile groups but also to purely topological factors – a low probability of crosslink formation with an irregular arrangement of functional groups along the chain.

Thus, the results of computer modelling make it possible to detail concepts concerning the contribution of intermolecular interactions of nitrile groups to the deformation properties of vulcanised butadiene-acrylonitrile elastomers.

REFERENCES


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