Acta Chim. Slov. **1999**, *46*(1), pp. 69-86

STUDY OF SECONDARY MORPHOLOGICAL STRUCTURES IN POLAR RUBBERS BY RHEOLOGICAL MEANS[†]

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(Received 21.12.1998)

Abstract

Work presents an attempt to show how secondary networks in polar rubbers, formed by orientational and dispersional molecular interactions, affect the rubbers' rheological behavior. Secondary networks are weak and hence strongly susceptible to strain and temperature. Their strain and thermally induced breakdown can suitably be followed by rubbers' mechanical dynamic functions. For this purpose a model is chosen, whose result is dependence of these functions on strain and temperature during such process, also enabling determination of two energies characteristic of the network: the one for its mechanical and the other for its thermal breakdown. The model, originally devised to describe rheological properties of carbon black filled rubbers, is based on statistical mechanics of chain molecules and a few additional assumptions, yielding good agreement with experiment.

Introduction

In polar rubbers, such as butadiene- acrylonitrile (NBR) and polychloroprene (CR), *orientational* and *dispersional* interactions between molecules [1] create associations acting as secondary intermolecular linkages and thus constituting a secondary network that represents morphological structure of rubbers when in amorphous state. To rubbers' morphology also contribute molecular entanglement formed mainly by larger molecules and acting as a kind of slipping pseudo linkages [2].

Orientational and dispersional interactions, termed *secondary*, are of short range type with energies decreasing with the mutual molecular distance to the sixth power. They are also considered weak since characteristic values of their energies, ranging fro

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[†] Dedicated to the memory of Professor Anton Šebenik

about 5 kJmol^{-1} to 15 kJmol^{-1}, are low in comparison with energies of primary (covalent) network linkages (e.g. C-S_x-C obtained by sulfur crosslinking or C-C by peroxide crosslinking). Nevertheless, the intermolecular linkages produced by the foregoing secondary interactions crucially affect rheological properties of rubbers, regardless if crosslinked by primary linkages or not. In both cases secondary linkages form a network which considerably augments the rubbers' moduli of elasticity. However, unlike primary linkages that decay under extreme deformational and/or thermal conditions, the secondary linkage breakdown already begins at low strains and at relatively sma increase in temperature. Hence, rheological properties of rubbers with such secondar morphology, either uncrosslinked or crosslinked by primar linkages, strongly depend on strain and temperature. It is important to notice that once broken, the primary linkage network never restores when left at rest, whereas the secondary network gradually reforms, regaining the properties it possessed before the breakdown.

The a of this work is to show relationship between secondary networks in polar rubbers and their rheological properties, concurrently enabling determination of characteristic energies for secondary network breakdown by mechanical means, as we as determination of characteristic (activation) energies for its thermal breakdown.

Theoretical

An eligible way (among several equivalent ones) to study rheological properties of rubbers is pursuing behavior of their *dynamic mechanical functions*, i.e. the *storage* and *loss moduli*, under various strain, frequency and temperature conditions. Regardless of the strain type, the theory of rubber elasticity predicts the storage modulus, a measure of material's resistance to strain, to be proportional to the intermolecular linkage (primary and/or secondary) density and temperature [3]. In the presence of secondar network, the storage modulus monotonically decreases with increasing strain due to gradual network breakdown, i.e. diminution of secondary linkage density. The storage modulus decreases toward a low but finite terminal value, when the network is completely destroyed.

The loss modulus, on the other hand, representing the measure for energ dissipation in form of generated heat, displays different behavior. The usual cause for energy dissipation in rubbers is internal friction [4] whose intensity strongly depends on strain rate. In the case of secondary network structure, strong energy dissipation occurs also due its breakdown, the loss modulus being proportional to the secondary linkage density change. Thus the loss modulus first increases up to a maximum value, when the network breakdown rate is the highest, and then, similarly as the storage modulus, decreases toward a low finite value. Dependence of storage shear modulus, G', and loss shear modulus, G'', on shear strain amplitude, γ, in the plateau frequency zone, i.e. from a few parts of s^{-1} to about 10^3 s^{-1}, during a typical strain-induced secondary network breakdown is schematically given in Fig. 1 [5,7].

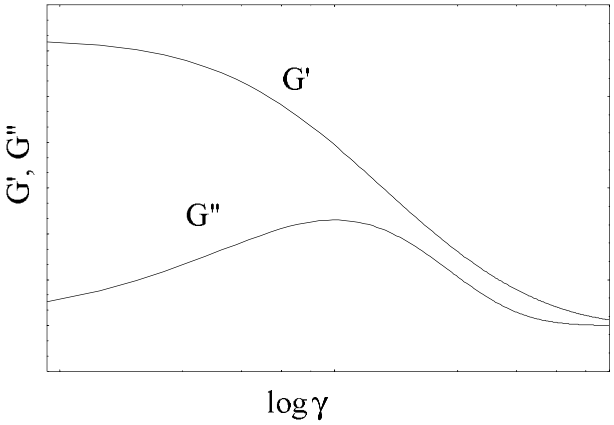

Fig. 1. Dependence of storage and loss shear moduli, G' and G'', on shear strain amplitude.

The secondary linkage density decreases also with increasing temperature. Since the effect of linkage density diminution on G' exceeds the one of its entropic increase with temperature, as asserted by the theory of rubber elasticity [3], in total, G' decreases with increasing temperature, but not as strongly as the linkage density. The same is true with G'', but to its decrease also contributes reduction of internal friction. It should be mentioned, however, that the effect of temperature on G' and G'' diminishes with increasing strain, to be annulled entirely at high strains, which is plausible since the network is completely destroyed.

Although such interpretation of dynamic functions' behavior is in qualitative agreement with observation, there have been no attempts to quantitatively describe thei dependence on strain and temperature, based on more primary principles. For this purpose, therefore, a model has been chosen, originally devised for description of dynamic functions' strain and temperature dependence for rubber with carbon black [6,7], but judging by analogy, suitable to treat dynamic functions of polar rubbers. The model is based on statistical mechanics of chain molecules and some additiona assumptions.

First assumption accounts for secondary network breakdown in rubbers while being strained. The network decays, when the network linkages break and disappear. According to the theory of elasticity of free chain molecules, the elastic force, $\boldsymbol{f}$, deforming a molecule has the following form [8]:

$$\boldsymbol{f} = 3kT\boldsymbol{r} / < r^2 > \qquad (1)$$

where $\boldsymbol{r}$ is the molecular end-to-end distance, called the *chain vector*, $< r^2 >$ the mea square of the chain vector, T the temperature and k the Boltzmann constant. Elastic force has completely the same form for *network chains*, i.e. parts of molecules between topologically adjacent linkages, the chain vector representing here the distance between the latter. The linkages break, when acted upon by a pendant chain with a certain *critical* force, $\boldsymbol{f}_c$, proportional to a *critical* chain vector, $\boldsymbol{r}_c$ (depending on network chain length), and given as

$$\boldsymbol{f}_c = 3kT\boldsymbol{r}_c / < r^2 > . \qquad (2)$$

Second assumption considers *distribution* of *network chain lengths*. If such distribution exists, then in strained network only chain vectors of a certain fixed length will undergo affine transformation, whereas all chain vectors differing in length will be transformed nonaffinely

As for the effect of temperature, it is additionally assumed that the secondar network breakdown in polar rubbers is a thermally activated process.

Effect of strain amplitude

It is well known from statistical mechanics of chain molecules that the chain vector distribution in undeformed state is Gaussian of the following form [9]:

$$w_0(\boldsymbol{r}) = (3/2\pi < r^2 >)^{3/2} \exp(-3r^2 / 2 < r^2 >), \qquad (3)$$

where $r^2 = x^2 + y^2 + z^2$ in Cartesian coordinate system with one end of a network chain in its origin. For affinely transformed chain vectors in strain, i.e $\boldsymbol{r} = \{\lambda\}\boldsymbol{r}_0$, where $\{\lambda\}$ is the gradient deformation tensor and $\boldsymbol{r}_0$ the chain vector in unstrained state, the distribution function (3) is transformed accordingly into [9]

$$w(\boldsymbol{r}, \lambda) = (\det\{\lambda\})^{-1} w_0(\{\lambda\}^{-1} \boldsymbol{r}) \qquad (4)$$

The determinant factor responsible for volume changes can be neglected at low strains.

For shear strain, used in this work, the principal values of the tensor $\{\lambda\}$ are $\lambda_1 = \lambda,\ \lambda_2 = 1$ and $\lambda_3 = 1/\lambda$ where λ represents the deformatin ratio [10], i.e. the ratio of specimen's lengths in strained and unstrained state, respectively. Substituting this into (4) and negleting the determinant term, distribution of affinely transformed chain vectors turns into

$$w(\boldsymbol{r}, \lambda) = (3/2\pi < r^2 >_{aff})^{3/2} \exp\left[-r^2(\lambda^2 + \lambda^{-2} + 1)/2 < r^2 >_{aff})\right] \qquad (5)$$

Since shear strain is expressable in terms of deformation ratio as $\gamma = \lambda - \lambda^{-1}$ [10], the distribution (5) can be written as a function of γ in the following way:

$$w(\boldsymbol{r}, \gamma) = (3/2\pi < r^2 >_{aff})^{3/2} \exp\left[-(3 + \gamma^2)r^2 / 2 < r^2 >_{aff})\right] =$$

$$= w_0(\boldsymbol{r}) \exp(-\gamma^2 r^2 / 2 < r^2 >_{aff}) \qquad (6)$$

As assumed, network linkages break when subjected to a certain critical force proportional to a critical chain vector. Thus, the fraction of unbroken linkages a deformation γ is simply given by the fraction of network chains whose affinely transformed vectors do not exceed the critical chain vector r_c. This fraction is given as

$$n_{aff}(\gamma) = \int_0^{r_c} w(\boldsymbol{r}, \gamma) 4\pi r^2 dr = 4\pi \int_0^{r_c} w_0(\boldsymbol{r}) \exp(-\gamma^2 r^2 / 2 < r^2 >_{aff}) r^2 dr \qquad (7)$$

where $4\pi r^2 dr$ is the volume element dV in Cartesian coordinate system. It is worth noting here that the integral (7) for $\gamma = 0$,

$$n_{aff}(0) = 4\pi \int_0^{r_c} w_0(\boldsymbol{r}) r^2 dr\,, \tag{8}$$

representing the fraction of unbroken linkages in unstrained state, is not equal to unity, which can be attributed to thermal breakdown of linkages in the moment of formation. For small deformations, the value of integral (7) is approximately

$$n_{aff}(\gamma) \approx n_{aff}(0) \exp(-r_c^{\,2}\gamma^2 / 2 < r^2 >_{aff})\,, \tag{9}$$

or, in terms of the critical force, f_c,

$$n_{aff}(\gamma) \approx n_{aff}(0) \exp\left[-(f_c / 3kT)^2 < r^2 >_{aff} \gamma^2 / 2\right]. \tag{10}$$

Such would be low strain functional dependence of G' (proportional to linkage density and in this case, therefore, to the fraction of unbroken linkages), if all network chains were of equal

length, with $< r^2 > = < r^2 >_{aff}$, since the length of a chain is proportional to its $< r^2 >$ [8].

However, all network chains are not equally long and chai n vector transformations of those wit $< r^2 > \neq < r^2 >_{aff}$ are nonaffine in strain. Deformati ratio, say λ', of such chain vectors is not equal to deformation ratio of affinely transformed vectors λ, but is related to it through the relationship between their corresponding relative deformations ε' $(\varepsilon' = \lambda' - 1)$ and ε $(\varepsilon = \lambda - 1)$, respectively:

$$\varepsilon' = \varepsilon < r^2 >_{aff}^{1/2} / < r^2 >^{1/2}. \tag{11}$$

By taking account of this relation and of the fact tha $\gamma = \lambda - \lambda^{-1} = 1 + \varepsilon - (1+\varepsilon)^{-1} \approx 2\varepsilon$ for small ε, replacement o γ in Eq. (10) by the expression $\gamma < r^2 >_{af}^{1/2} / < r^2 >^{1/2}$ would make Eq. (10) valid also for network chains of an arbitrary $< r^2 >$. So the fraction of unbroken linkages in this generalized case, n_g, is

$$n_g(\gamma) \approx n_g(0) \exp\left[-(f_c < r^2 >_{aff} / 3kT)^2 \gamma^2 / 2 < r^2 >\right]. \tag{12}$$

To obtain the total fraction of unbroken chains as a function of strain, it i necessary to consider distribution of network chain lengths, or, more precisely, distribution of average absolute values of chain vectors $<r^2>^{1/2}$. It is natural to assume this distribution to be Gaussian, too, possessing the form:

$$w(<r^2>^{1/2}) = (3/2\pi<\overline{r^2}>)^{3/2}\exp(-3<r^2>/2<\overline{r^2}>), \qquad (13)$$

where $<\overline{r^2}>$ is the overall average of the chain vector mean squares in the system. The total fraction of unbroken linkages at given deformation γ, $n(\gamma)$, is obtained by combination of Eq. (12) and distribution (13) in the following manner:

$$n(\gamma) = 4\pi\int_0^\infty <r^2> n_g(\gamma)w(<r^2>^{1/2})d<r^2>^{1/2} \qquad (14)$$

where integration is carried out over the entire space, since $<r^2>^{1/2}$ can theoretically assume any value. By designating the quantity $3/2<\overline{r^2}>$ from distribution (13) wit the letter a and the quantit $(f_c<r^2>_{aff}/3kT)^2/2$ from Eq. (15) with the letter b, substitution of (12) and (13) into (14) yields

$$n(\gamma) = B\int_0^\infty <r^2>\exp(-a<r^2>-b\gamma^2/<r^2>)d<r^2>^{1/2} =$$

$$= (B/2)\int_0^\infty <r^2>^{1/2}\exp(-a<r^2>-b\gamma^2/<r^2>)d<r^2>, \qquad (15)$$

where $B \equiv 4\pi n(0)\ (3/2\pi<\overline{r^2}>)^{3/2}$. Evaluation of this integral gives the final results:

$$n(\gamma) = n(0)\left(1+2a^{1/2}b^{1/2}\gamma\right)\exp\left(-2a^{1/2}b^{1/2}\gamma\right) \qquad (16)$$

and

$$-dn(\gamma)/d\gamma = 4n(0)ab\gamma\exp\left(-2a^{1/2}b^{1/2}\gamma\right). \qquad (17)$$

The expression $2a^{1/2}b^{1/2}$ in these equations is strain independent for low strain amplitudes and is of the following form:

$$2a^{1/2}b^{1/2} \equiv f_c<r^2>_{aff}/3^{1/2}<\overline{r^2}>^{1/2}kT = W_b/3^{1/2}RT \qquad (18)$$

where

$$W_b = N_A f_c<r^2>_{aff}/<\overline{r^2}>^{1/2} \qquad (19)$$

(N_A being the Avogadro number) is a quantity with the unit of energy per mol, characteristic of material. It may be called *characteristic energy for secondary linkage* and subsequently *secondary network breakdown*. As shown later, the values of W_b are typically within the range of energies characteristic for secondary interactions.

The storage shear modulus G', being proportional to the linkage density in rubber and thus to the total fraction of unbroken linkages, is then given as dictated by Eq. (16):

$$G'(\gamma) = G'(0)\left(1 + W_b\gamma / 3^{1/2} RT\right) \exp\left(-W_b\gamma / 3^{1/2} RT\right) \tag{20}$$

where $G'(0)$ is the initial storage shear modulus, i.e. at $\gamma = 0$.

The loss shear modulus G'' is proportional to deformational change of the total fraction of unbroken linkages. As the function given by Eq. (17) experiences maximum at $\gamma_{\max} = (4ab)^{-1/2}$, i.e. at strain amplitude of the strongest decrease of unbroken linkage density and subsequently G', $G''(\gamma)$ written in terms of its maximum value, $G''_{\max}$ (at $\gamma_{\max}$), thus possesses the form:

$$G''(\gamma) = G''_{\max} (W_b\gamma / 3^{1/2} RT) \exp\left(1 - W_b\gamma / 3^{1/2} RT\right). \tag{21}$$

It should be noted again that this equation accounts only for energy dissipation due to secondary network breakdown and does not consider internal friction. Hence, this fact is expected to worsen its agreement with experiment.

Eqs. (20) and (21) in the foregoing forms are valid only for low strains because approximations made in solving integral (7) and in generalizing Eq. (10) into Eq. (12) are possible only in the low strain range. For higher strains, exact solution of the integral (7) is divergent. Nevertheless, Eqs. (20) and (21) can be generalized to hold at higher strains as well. In doing this, their forms remain unchanged, but the characteristic energy W_b at given temperature becomes strain dependent $W_b(\gamma)$, specifically, it decreases with increasing strain from the initial value, $W_b(0)$, towards a low constant value, $W_b(\infty)$. Mathematically, the reason for strain dependence of W_b is formal, but it also has a physical meaning. For its explanation it is necessary to examine the form of W_b given by Eq. (19). As deformation increases, the linkage density decreases and topologically adjacent unbroken linkages are connected by ever longer network chains.

Hence, the denominater on the right-hand side of Eq. (19) increases, causing $W_b(\gamma)$ to decrease. Namely, from obvious relation

$$n(\gamma) < \overline{r^2} >_\gamma^{3/2} = n(0) < \overline{r^2} >_0^{3/2} \qquad (22)$$

where $< \overline{r^2} >_\gamma^{3/2}$ and $< \overline{r^2} >_0^{3/2}$ are the basic volume elements associated with linkages at shear strains γ and $\gamma = 0$, respectively, it follows

$$d < \overline{r^2} >_\gamma^{3/2} / dn(\gamma) = -n(0) < \overline{r^2} >_0^{3/2} / n^2(\gamma) = - < \overline{r^2} >_\gamma^{3/2} / n(\gamma) \,. \qquad (23)$$

Since, except at very low strains, the function $n(\gamma)$ given by (16) is dominated by the exponential term, which is evident from strong decrease i $G'(\gamma)$, combination of Eqs. (16) and (17) yields approximatel

$$dn(\gamma) / n(\gamma) \approx -W_b(\gamma) d\gamma / 3^{1/2} RT \,. \qquad (24)$$

As ensues from (19),

$$dW_b(\gamma) / d < \overline{r^2} >_\gamma^{1/2} = -N_A f_c < r^2 >_{af} / < \overline{r^2} >_\gamma = -W_b(\gamma) / < \overline{r^2} >_\gamma^{1/2} \,, \qquad (25)$$

and combination of Eqs. (23), (24) and (25) yields by a short calculation the equation

$$dW_b(\gamma) / W_b^2(\gamma) = -d\gamma / 3^{3/2} RT \qquad (26)$$

which, integrated from $W_b(0) - W_b(\infty)$ at $\gamma = 0$ to $W_b(\gamma) - W_b(\infty)$ at γ, gives after rearrangement the following functional form for $W_b(\gamma)$:

$$W_b(\gamma) = W_b(\infty) + \left\{ 1 / \left[W_b(0) - W_b(\infty) \right] + \gamma / 3^{3/2} RT \right\}^{-1} . \qquad (27)$$

Arriving at this result, the critical force f_c has plausibly been assumed to be strain independent. By substitution of Eq. (27) into Eq. (20) excellent agreement is obtained with the measured $G'(\gamma)$, whereas agreement o Eq. (21) with the measured $G''(\gamma)$ may not always be that fine, particularly at low strains. This is because G' depends only network linkage density (and temperature), whil G'', as already mentioned, may, apart from linkage density change, be affected by other energy dissipation processes, such as internal friction.

It is worth noting here that good agreement of this model (which considers the rubbers' secondary structure breakdown only) with experiment in the instance o G' excludes any effects of nonlinear viscoelasticity from being responsible for strai dependence o G'. This simultaneously confirms the fact predicted by the finite strain rheology that, unlike in the case of extension, the stress-strain relation in simple shear remains linear at finite strains, with strain independent shear modulus [11].

Both constants, $W_b(0)$ in $W_b(\infty)$, can simply be determined from measurements and Eq. (20). At low strains, the exponential term on the right-hand side of Eq. (20) can be expanded into series. Keeping only the first two terms, it turns into

$$G'(\gamma) \approx G'(0)\left[1 + W_b(0)\gamma / 3^{1/2} RT\right]\left[1 - W_b(0)\gamma / 3^{1/2} RT\right] =$$

$$= G'(0)\left[1 - W_b^{\,2}(0)\ \gamma^2 / 3(RT)^2\right] \qquad (28)$$

from which $W_b(0)$ can immediately be calculated.

At high strains, $W(\gamma)$ becomes constant, i.e. $W(\gamma) = W(\infty)$, and the function $G'(\gamma)$ can be written as

$$G'(\gamma) \approx G'(0)\left[W_b(\infty)\gamma / 3^{1/2} RT\right] \exp\left[- W_b(\infty)\gamma / 3^{1/2} RT\right]. \qquad (29)$$

Using this equation and measurements, $W(\infty)$ is obtained simply from linear relationship betwee $\ln\left[G'(\gamma)/\gamma\right]$ and γ.

Eqs. (20) and (21) predict $G'(\gamma)$ and $G''(\gamma)$ to decrease toward zero when $\gamma \rightarrow \infty$. In reality the functions decrease toward low but finite values $G'(\infty)$ in $G''(\infty)$, respectively. Despite virtually complete destruction of secondary network at high strains, some secondary linkages still form and almost instantly decay, whereas to finite values o dynamic functions may also contribute some molecular entanglements that have not disentangled yet. So, strictly, Eqs. (20) and (21) should be written in terms of function differences rather than functions alone, i.e. $G'(\gamma)$ - $G'(\infty)$ and $G'(0)$ - $G'(\infty)$ in Eq. (20), as well as $G''(\gamma)$ - $G''(\infty)$ and $G''_{\max}$ - $G''(\infty)$ in Eq. (21). But since for all sensible strains $G'(\gamma) >> G'(\infty)$ and $G''(\gamma) >> G''(\infty)$, the forms of Eqs. (20) and (21), as written, are adequate.

It should be noted, finally, that Eqs. (20) and (21) are equally valid for polar rubbers crosslinked by primary linkages (vulcanizates). Albeit higher values o vulcanizates’ dynamic functions, the breakdown course of their secondary networks with increasing strain is the same as in the case o uncrosslinked rubbers. Experiments show that the main contribution t moduli of elasticity at low strains comes from the secondary network.

All findings from this model are in perfect qualitative agreement with those acquired from the study of dynamic mechanical functions of carbon black filled rubbers where carbon black forms its own agglomeration network with van der Waals bonding, strongly susceptible to strain [6,7],. The only exception is that carbon black agglomeration network starts and ends its breakdown at much lower strains, thus making the breakdown characteristic energy independent of strain.

Effect of Temperature

Theory of rubber elasticity predicts the storage shear modulus to be related to the network linkage density and temperature in the following manner: $G' = nkT$ where *k* is the Boltzmann constant [3]. In the case of secondary network, the linkage density itself depends on temperature, owing to the thermal molecular motion. At given temperature secondary linkages form and decay in a dynamic equilibrium and their average density is constant. With increasing temperature more energy is available for linkage breakdown and equilibrium is established at lower linkage density.

It is not difficult to conceive an energy barrier that must be surpassed for a linkage to break. This is supported by experimental evidence suggesting the drop o linkage density with increasing temperature to be of thermal activation nature, i.e. $n \propto \exp(E_a / RT)$ where E_a is the height of the energy barrier called the *activaton energy* for *secondary linkage* and subsequently *secondary network thermal breakdow* . Considering this, $G'(T)$ has the form:

$$G'(T) = CT\exp(E_a / RT) \qquad (30)$$

where C is a constant. For polar rubbers this equation holds with high precision.

Experimental

Using the presented model, secondary networks were studied through dynamic mechanical functions o polychloroprene (CR - Byprene 611, Bayer) rubber and butadiene-acrylonitrile (NBR - Krynac, Polysar) rubber of weight average molecular weights 270000 and 414000, respectively, both uncrosslinked and crosslinked by primar linkages (vulcanized), but without fillers. Measurements o G' and G'' as a function of shear strain amplitude and temperature were performed by the instrument for measuring dynamic mechanical functions (Rubber Process Analyzer - RPA 2000, Monsanto), which also carried out vulcanization, at the frequency of 0.3 Hz, being low enough to allow undisturbed changes of molecular conformations in the entire chosen ranges of strain (from 0.03 to 9) and temperature (from 30^oC to 100^oC) . Characteristic energies for mechanical breakdown of secondary networks and activation energies for their therma breakdown were determined by the measured G' and the model, using Eqs. (28)-(30). Finally, to verify credibility of the model, these energies were then used to make comparison of calculated and measured G' and G'' as a function of strain and temperature.

Results and Discussion

Figs. 2 and 3 demonstrate comparison of measured (points) and by Eq. (20) calculated (curves) storage shear moduli G' of CR and NBR, respectively, as a function of shear strain amplitude at different temperatures. It is immediately noticeable that in all the cases good agreemen is obtained within the whole strain range. Correc prediction of the gradual diminution of the effect of temperature with increasing strain and its total disappearance at high strains when the secondary network is destroyed is another supportive attribute for the model.

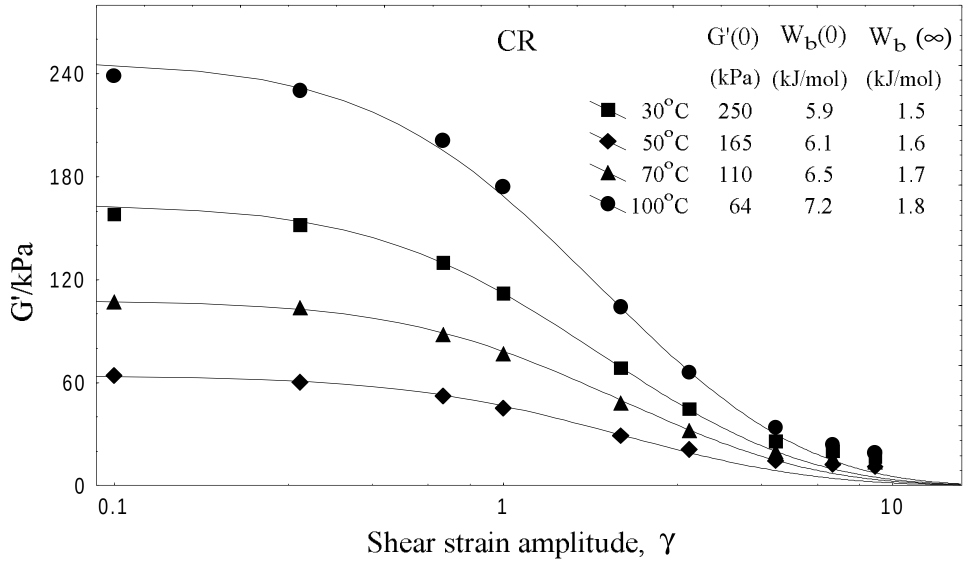

Fig. 2. Shear strain amplitude dependence of storage shear modulus for CR at the frequency of 0.3 Hz and various temperatures (measured: points, calculated: curves).

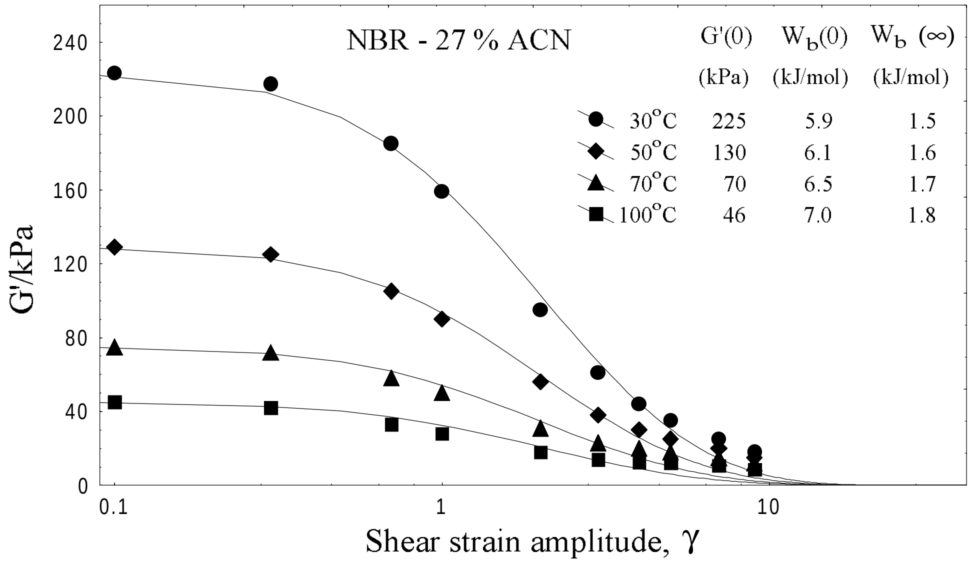

Fig. 3. Shear strain amplitude dependence of storage shear modulus for NBR at the frequency of 0.3 Hz and various temperatures (measured: points, calculated: curves).

The values of characteristic energies for secondary network breakdown $W_b(0)$ and $W_b(\infty)$ obtained by Eqs. (28) and (29), respectively, and given in the figures are a within the range of magnitudes typical for secondary interactions. It can be noticed tha they slightly increase with increasing temperature, which due to the fact that the expressions $W_b(0)/3^{1/2}RT$ and $W_b(\infty)/3^{1/2}RT$ appearing in Eqs. (20) and (21) are virtually independent of temperature. Namely, considering Eqs. (3) and (19), in these expressions temperature cancels out, which is experimentally confirmed.

$W_b(0)$ also slightly increases with electric dipole density in rubbers, presumably due to closer dipole packing. This is demonstrated in Fig. 4 for NBR rubbers o different acriylnitrile (ACN) contents. $W_b(\infty)$, on the other hand, logically remains unchanged.

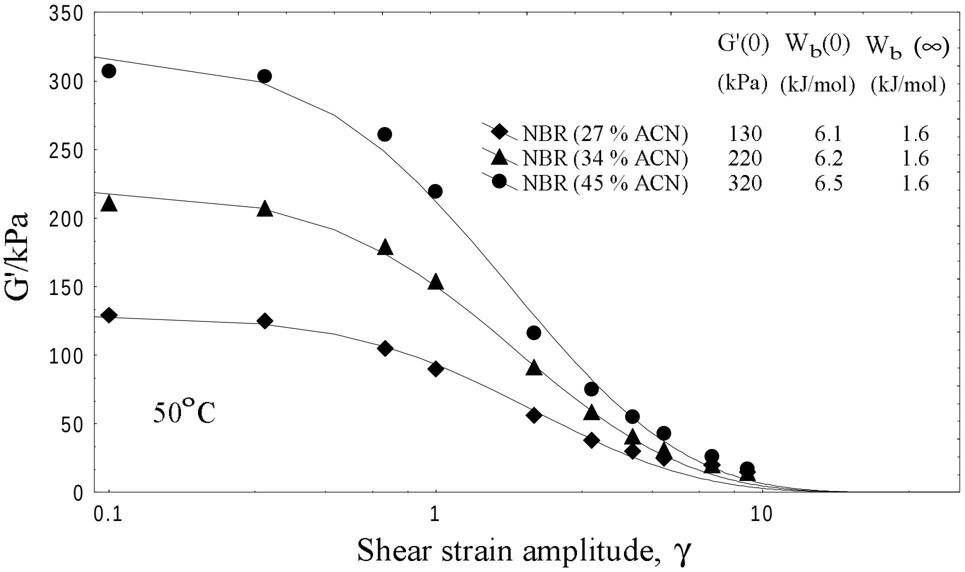

Fig. 4. Shear strain amplitude dependence of storage shear moduli for NBR's with different ACN contents at the frequency of 0.3 Hz and 50 °C (measured: points, calculated: curves).

As mentioned, dynamic straining of rubber may, apart from secondary linkage breaking, generate other energy dissipation mechanisms, mainly internal friction. The pure effect of secondary linkage breakdown on G'' is thus screened, particularly at low strains, and hence its strain dependence cannot be adequately described b Eq. 21. In rubbers crosslinked by primary linkages (vulcanizates), however, internal friction is somewhat reduced because of shorter network chains. Contribution of secondary linkage breakdown to energy dissipation is therefore manifested more clearly. This is shown in Figs. 5 and 6 for vulcanizates of CR and NBR, respectively, together with the values o characteristic energies and moduli.

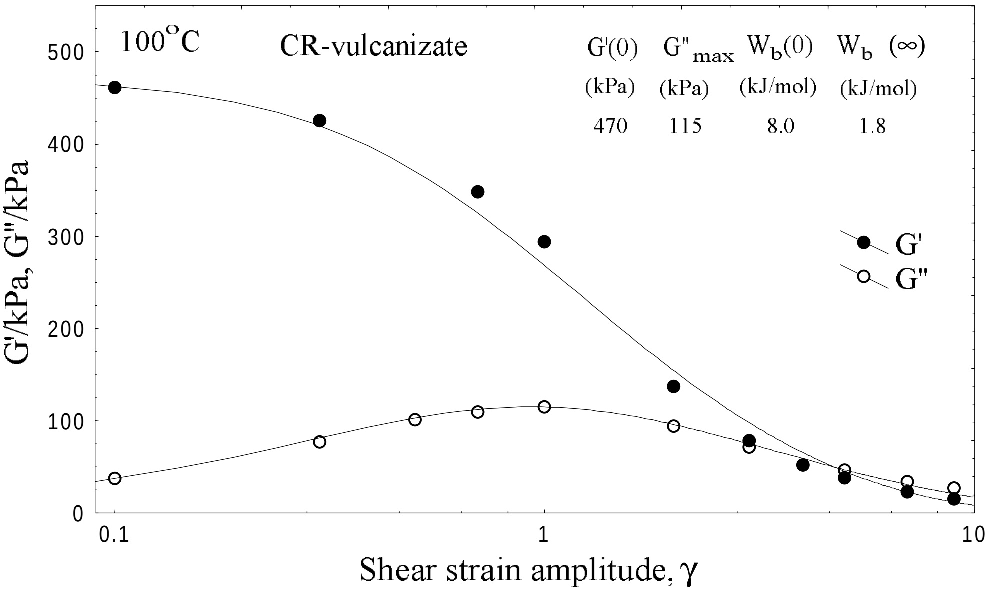

Fig. 5. Shear strain amplitude dependence of storage and loss shear moduli for vulcanized CR at the frequency of 0.3 Hz and 100 °C (measured: points, calculated: curves).

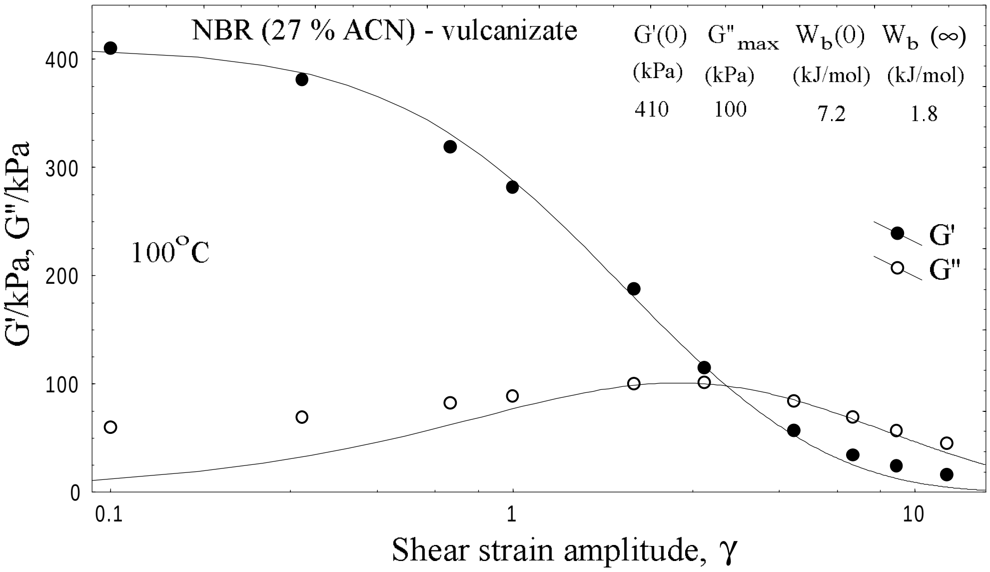

Fig. 5. Shear strain amplitude dependence of storage and loss shear moduli for vulcanized NBR at the frequency of 0.3 Hz and 100°C (measured: points, calculated: curves).

In the case of CR vulcanizate, the model's agreement with experiment is good for both, G' and G''. Agreement is also good for G' of NBR vulcanizate, but less so for its G'' at low strains, owing to the above-mentioned arguments. However, due to growing degree of molecular alignment with increasing strain , internal friction becomes less intensive at higher strains and secondary linkage breakdown turns to be the main energy dissipation mechanism, resulting in good agreement of the model with experiment. It is plausible to suppose, though, that at high strains some primary linkages break, too. But since in the case of vulcanizates G' is proportional to the density of both, primary and secondary linkages, and G'' to the change of this density, the primary linkage breakdown does not affect the result.

Characteristic energies $W_b(0)$ are a little higher for vulcanizates than for unvulcanized rubbers, which can be attributed to somewhat increased firmness of the secondary network when embedded in the strong primary network. $W_b(\infty)$, on the other hand, is expectably unaffected by primary network because the secondary network does not exist any more at very high strains.

Finally, the effect of temperature on G' (taken here at $\gamma = 0.1$) of CR, NBR, and their vulcanizates, is accounted for in Fig. 7, verifying validity of Eq. (30) and determining the activation energy for secondary network thermal breakdown, E_a. The expression $\ln(G'/T)$ is plotted against $1/RT$, the slope representing the value of E_a. In all the cases linear relationship with high correlation is obtained, pointing out that in these rubbers thermal breakdown of secondary networks is indeed a thermally activated process.

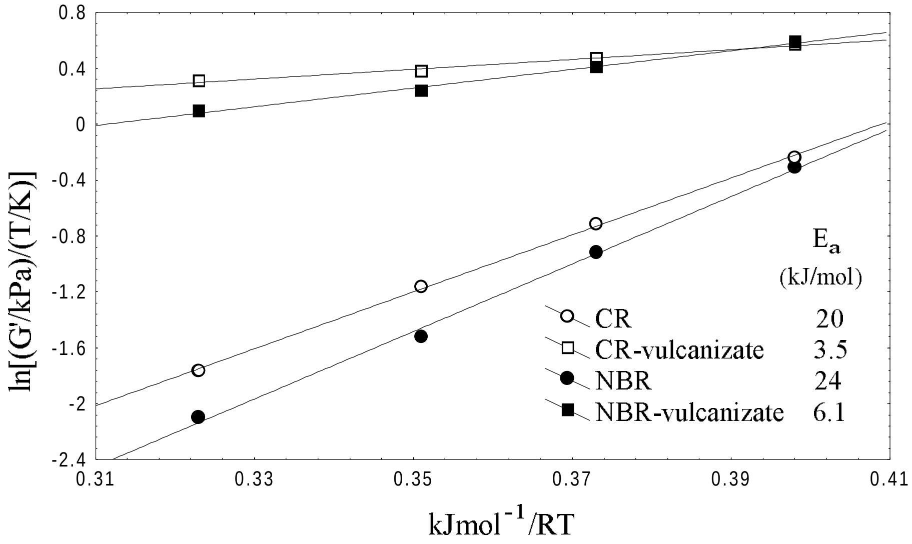

Fig. 7. Plots of $\ln(G'/T)$ against $1/RT$ for storage shear moduli of CR, NBR and their vulcanizates at the frequency of 0.3 Hz and shear strain amplitude of 0.1.

A rather drastic difference can be noticed between thermal breakdown of the secondary network in rubbers and that in their vulcanizates. Activation energies o secondary network breakdown in vulcanizates are lower than those for the breakdown in rubbers by almost an order of magnitude. This, however, is not surprising. It only means that by hindering mobility of network chains, thermally stable primary networks of vulcanizates substantially augment thermal stability of the embedded secondary networks themselves, which is then reflected in low activation energies.

Conclusion

Study of secondary morphological structures in polar rubbers, both uncrosslinked and crosslinked by primary linkages, through dynamic mechanical functions has given some important results. Firstly, good qualitative and quantitative agreement with experiment of the proposed theoretical model for strain and temperature dependence of dynamic functions confirms both the existence of secondary networks formed b secondary interactions in these rubbers and correctness of the assumptions on which the model is based. Secondly, the model's agreement with experiment enables determination of two quantities characteristic of secondary networks: characteristic energy for network's strain induced breakdown and activation energy for its thermal breakdown, their values being in the range typical for energies of secondary interactions. Finally, as the model is rather general, i.e. its assumptions being not associated with any specific polymeric system, it could presumably be used, along with measured dynamic mechanica functions or other equivalent rheologica quantities, for study of secondary morphological structures and subsequent rheologica properties of any related materials - after all, it was originally devised to describe behaviour of carbon black agglomeration network in rubbers.

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Povzetek

V delu je poskušano pokazati kako sekundarne mreže v polarnih kavčukih, ki nastanejo zaradi orientacijskih in disperzijskih molekulskih interakcij, vplivaj na reološko vedenje kavčukov. Sekundarne mreže so šibke in zat močno občutljive na deformacijo in temperaturo. Primere način spremljanja njihovih deformacijskih ali toplotnih porušitev je preučevanje dinamičnih mehaničnih funkcij kavčukov. V ta namen je izbran model, katerega rezultat je odvisnost teh funkcij od deformacije in temperature med takšnim procesom, in ki tudi omogoča določitev dveh energij, značilnih za mrežo: ene za njeno mehanično in druge za njeno toplotno porušitev. Model, ki je bil prvotno zgrajen za opis reoloških lastnosti kavčukov, polnjenih s sajami, temelji na statistični mehaniki verigastih molekul in na nekaj dodatnih predpostavkah, pri čemer je dobljeno dobro ujemanje z eksperimentom.