Available online at www.sciencedirect.com

Polymer 47 (2006) 415–423

polymer

www.elsevier.com/locate/polymer

Experimental and theoretical investigations on petroleum-based elastomers with two cross-linking systems of different lengths viewed as bimodal networks

Tarek M. Madkour *, Rasha A. Azzam

College of Arts and Sciences, ABTI-American University of Nigeria, Lamido Zubairu Way, P.M.B. 2250, Yola, Adamawa State, Nigeria

Received 10 October 2005; received in revised form 13 November 2005; accepted 15 November 2005
Available online 28 November 2005

Dedicated to his Excellency, Alhaji Atiku Abubakar, the founder of the ABTI-American University of Nigeria, as the first published research article of AAUN.

Abstract

A review with 36 references discussing the chemistry and the structure–property relationship of elastomers cured with two cross-linking systems of different chain lengths such as sulfur and the polymerization products of *p*-benzoquinone and viewed as bimodal networks. These exceptional networks have shown remarkable improvements in the overall mechanical properties which are anticipated to be due to the non-Gaussian effects known for bimodal networks and evident by the anomalous upturn in the modulus values in Mooney–Rivlin stress–strain data representations. Proton and ^{13}C NMR as well as energy minimization calculations were used to study the chemical structures and single chain contributions of polyquinones. Nuclei bending of these oligomers have shown to be greatly influenced by the restricted torsional behavior due to the presence of the hydrogen bonds between the benzenoid nuclei. Intrinsic atomic-level forces for the networks were evaluated using molecular dynamics techniques and showed that while the forces acting on the junction points of the cross-linking segments and the elastomeric chains had no apparent change as a consequence of the networks' bimodal formation, forces acting on the short chains of the bimodal networks are of much higher values as compared to those of unimodal networks. The presence of the relatively long polyquinone chains in the bimodal networks has caused the short sulfur chains to stretch to its maximum extensibility and no longer can increase its end-to-end distance separation by simple rotations about its skeletal bonds. Limited chain extensibility of the short chains resulting from the deformation of the bond angles and bond lengths has lead to higher potential energies. Studies on the swollen bimodal networks have validated the above conclusions since swelling of the networks will prevent the elastomeric chains from undergoing possible strain-induced crystallization during the stress–strain experiments and any abnormalities in the mechanical behavior of these networks must be therefore the result of the limited extensibility of the short chains of the networks.

Keywords: Bi-modal network simulation; Limited chain extensibility; Stress–strain

1. Introduction

Attention has been recently directed to the use of antioxidants which either have high molecular weights, and therefore of low volatility or extractability, or can chemically bind to the rubber matrix to avoid the blooming tendency, and thus guaranteeing persistence in the final product [1,2]. Surprisingly, enough results were obtained [1,3] showing an anomalous increase in the values of the ultimate tensile strength of samples prepared using both sulfur as the cross-linking agent and a chemically bound antioxidant such as the polymerization products of *p*-benzoquinone acting as a second cross-linking agent. Control samples prepared without the addition of antioxidants did not show [1–3] such anomalous tensile strength behavior. Since an increase in the modulus of elastomers could be explained on the basis of (i) strain-induced crystallization of the elastomeric chains and/or (ii) limited chain extensibility observed for networks with bimodal cross-link length distribution [4,5], it is our intent to focus on the underlying mechanism behind the observed self-reinforcement behavior of these networks. Furthermore, we will also attempt to examine the intrinsic atomic-level forces exerting on the junction atoms, where the cross-linking agents are attached to the elastomeric chains, on the sulfur atoms

---

* Corresponding author. Tel.: +234 805 502 7786.
E-mail address: drmadkour@yahoo.com (T.M. Madkour).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.11.047

connecting the elastomeric chains and on the polyquinone atoms comprising the second cross-linking agent of relatively long chains. The study is also extended to investigate the dynamics of the polyquinone chains through which the various polyquinone forms may decrease their entropies in response to the imposed stress.

2. Elastomers with two cross-linking systems

Three factors affecting the antioxidants performance [6] are the intrinsic activity of the antioxidants itself to interfere with and retard radical-chain oxidation processes, its incompatibility with the rubber matrix, which may result in the aggregation of the stabilizer and its spewing or blooming, and thirdly the volatility or fugitive nature of the antioxidant. Losses due to extraction or volatility immediately affect the ultimate performance of the final product. Of the three factors mentioned, the third is probably the most important, as it affects the antioxidant's persistence directly [2]. Basically, there are two approaches to increasing the persistence of an antioxidant. The first is to produce antioxidants of high molecular weights, and therefore of low volatility or extractability [7]. The other is to chemically bind the antioxidant of the polymer thereby guaranteeing its persistence in the final product [8,9] product In this case, the vulcanized rubber will possess two crosslinikng systems, the short sulfur crosslinks and the relatively longer chemically bound antioxidant.

2.1. Polymerization products of p-benzoquinone as bound antioxidants for SBR

Polymerization products of *p*-benzoquinone were therefore prepared [10] and its antioxidizing efficiency as bound antioxidants for styrene–butadiene rubber (SBR) was investigated [2]. Three forms of polyquinones, polyquinone (AQ), which consists of both benzenoid and quinonoid nuclei, Fig. 1(a), the fully reduced form, polyhydroquinone (HQ), Fig. 1(b), and the fully oxidized form, polybenzoquinone (BQ), Fig. 1(c) were all used and tested against two control elastomeric samples containing no commercial antioxidants and containing the commercial antioxidant, phenylene diamine (6PPD), respectively.

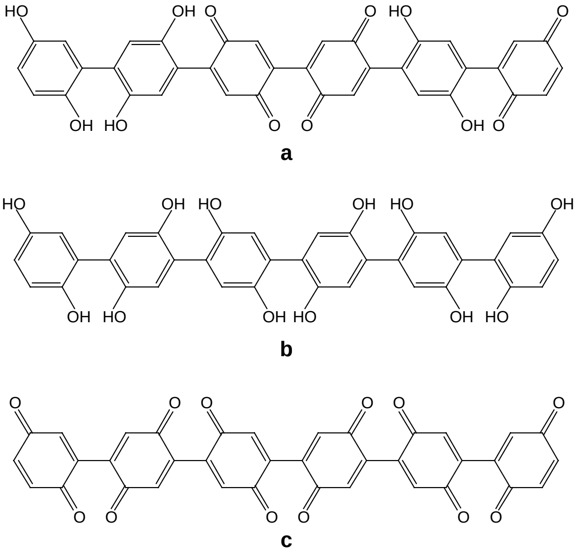


Fig. 1. Sketches of the three products resulting from the polymerization of *p*-benzoquinone.

It was envisaged that these compounds will be excellent candidates for stable antioxidants due to the well-known antioxidizing capabilities of hydroquinone and the higher molecular weight expected for these polymeric materials thus lowering their volatility. This has been investigated by measuring the percentage deterioration of tensile strength and ultimate elongation for the thermally aged rubber samples after up to 14 days in an air oven at 100 °C as described by ASTM 0573-99. The results indicate the remarkable antioxidizing efficiency of these products for SBR as compared to common industrial antioxidants as shown in Fig. 2.

The antioxidizing efficiency of the polyquinone products seems to be due to the ability of both the hydroquinone and benzoquinone nuclei to react with the radical intermediates of the degradation process as well as their ability to block the odd electron sites created on the rubber chains, thus disrupting the chain degradation process as represented by Scheme 1. According to this mechanism, the OH radical formed, being of higher mobility, probably abstracts the hydrogen atom from the hydroquinone nuclei of the stabilizer, thus leading to the formation of highly stabilized semiquinone radical. The latter, due to its high stability, can probably recombine with the alkoxy radical derived from the rubber molecule leading not only to the blocking of the odd electron site formed on the rubber chain, but also to the bonding of the antioxidant molecule with its effective hydroquinone and benzoquinone nuclei.

This has been experimentally proven [2] by the non-extractability of the investigated products from the rubber vulcanizates when subjected to boiling tetrahydrofuran (in which the products are freely soluble) in a Soxhlet apparatus for 24 h. The profound effect on the tensile strength values due

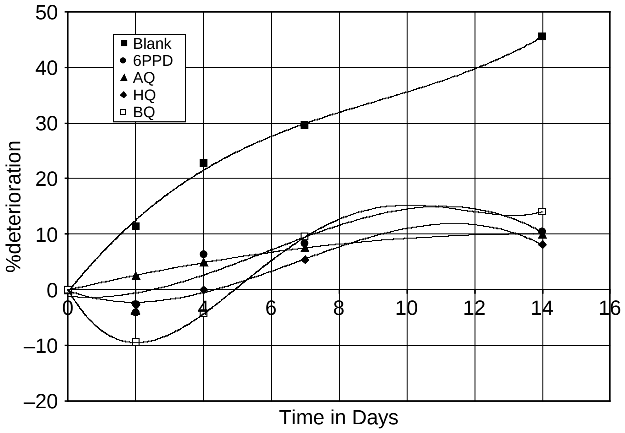
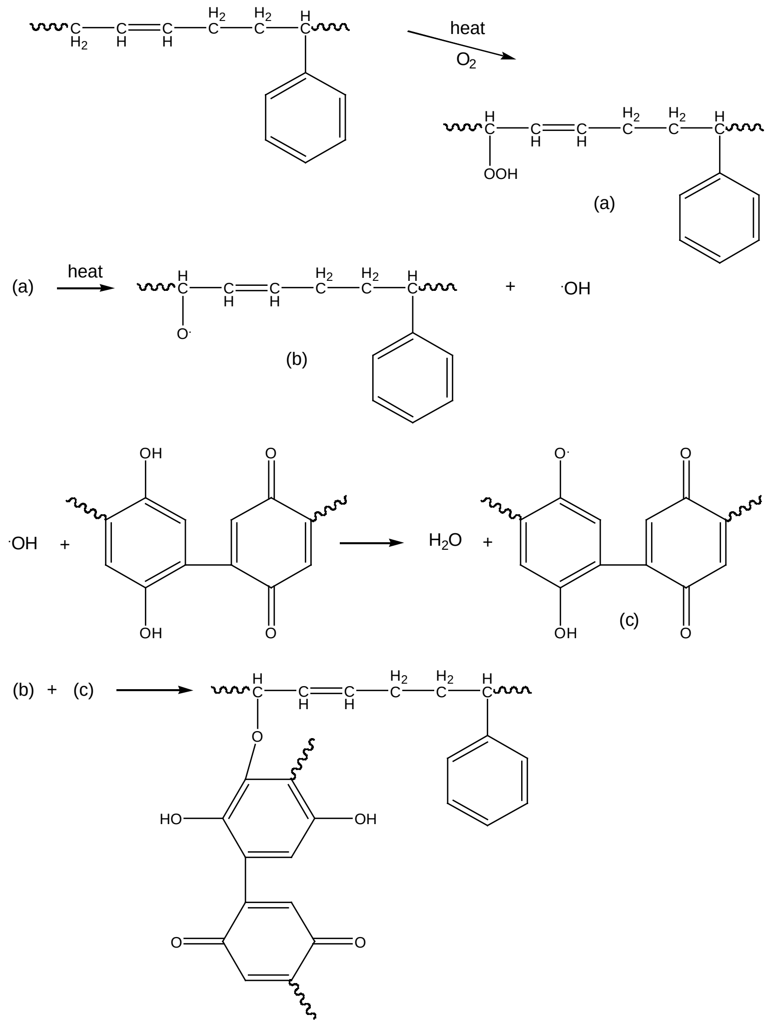


Fig. 2. Percentage deterioration of the tensile strength for various SBR samples subjected to an accelerated thermal degradation using the oven method at 100 °C.



Scheme 1. Action of the polyquinone antioxidants on blocking active sites created on the rubbery chains during the degradation process.

to the incorporation of the polymerization products of *p*-benzoquinone into a sulfur-curd rubber matrix such as SBR is attributed to the excellent antioxidizing efficiency of the quinone polymers along with their ability to bind chemically to the rubbery chains, thus avoiding the blooming tendency, escaping the rubber matrix, and eventually being vaporized off the surface. However, enough results [1] were obtained showing a gradual increase in the value of the ultimate tensile strength of the samples during the early stages of the accelerated aging process which is followed by breakdown in the ultimate tensile strength of the samples but to a lesser extent than the materials treated with commercially available antioxidants. The value of the ultimate tensile strength of the latter have normally degraded with the continuing aging process, which indicates that the observed abnormal behavior is related directly to the quinone polymers added to the rubber matrix. Since an increase in the modulus of elastomers could only be explained on the basis of strain-induced crystallinity of the polymeric chains or a limited chain extensibility observed for networks with bimodal chain lengths distributions [5,11], the focus on the nature of the quinone polymer crosslinks was assumed.

2.2. Elastomeric networks with bi-modal cross-link length distribution

Sharaf and Mark [12] theoretically investigated the elastomeric networks with two cross-linking systems, namely, the very short sulfur cures and the sufficiently long polysulfidic cross-links which then were assumed to be elastically effective and would thus contribute to the modulus of the samples by increasing their end-to-end distances and decreasing their entropies in response to the imposed stress. Eventually, this would lead to the superior mechanical properties bimodal networks are known to have [13–16]. If, however, the longer crosslinks are replaced by an antioxidizing polymeric material, the effect will even be more profound, such as the case with SBR materials treated with the polymerization products of *p*-benzoquinone. In this system, the quinone polymers themselves will act as elastomeric chains and a bimodal network is produced.

As a consequence of the polymerization of *p*-benzoquinone, the products would contain both quinone and hydroquinone nuclei [10], which are characterized by their high efficiency as radical traps and as blocking agents for radical sites created on the rubbery chains during the degradation process [2]. Consequently, crosslinking of the quinone polymers to the elastomeric chains is not expected to occur during the molding process as would be the case with sulfur cures. Alternatively, it will take place during the degradation process, i.e. post-cure, and a true bimodal chain length distribution is thus anticipated to transpire by time.

2.3. Stress–strain measurements of the dry rubber vulcanizates

Representations of the stress–strain data of styrene–butadiene rubber vulcanizates in the dry state, cross-linked with two different cross-linking systems, the short sulfur cures and the relatively long polyquinone chains are based on the Mooney–Rivlin equation:

$$[f^*] = 2C_1 + 2C_2\alpha^{-1} \tag{1}$$

where $2C_1$ and $2C_2$ are constants. Typical isotherms of this type are shown in Figs. 3 and 4. Each one of these figures corresponds to a different recipe and every isotherm in the figures represents the stress–strain behavior of the sample after being subjected to a definite aging interval. Results shown in the figures show clearly the 'non-Gaussian' behavior of the samples. According to the above equation, the reduced stress of the sample should decrease with an increase in the elongation.

This did not occur until high elongations were reached. Instead of continuing to decrease, an upturn in the modulus values was obtained. This would consequently explain the higher values of ultimate tensile strength obtained for these samples when using the oven method, and shown in Fig. 2. In the absence of the strain-induced crystallinity and the influence of fillers, this behavior could only be explained on the basis of the bimodality of the networks and in this case, the limited chain extensibility of the short chains, which is responsible for the increase in the modulus values observed for these samples [5,17].

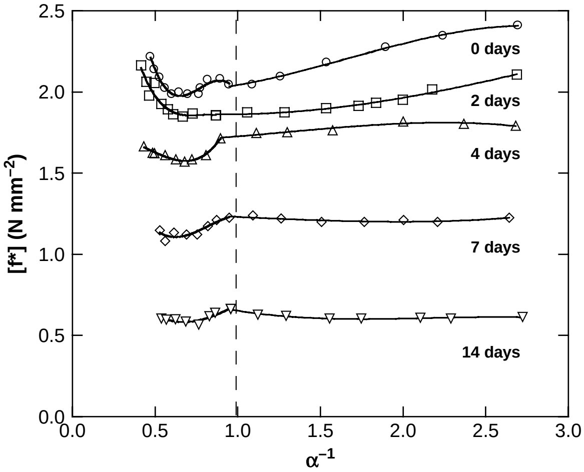


Fig. 3. Stress–strain isotherms for dry rubber vulcanizates prepared using polyquinone.

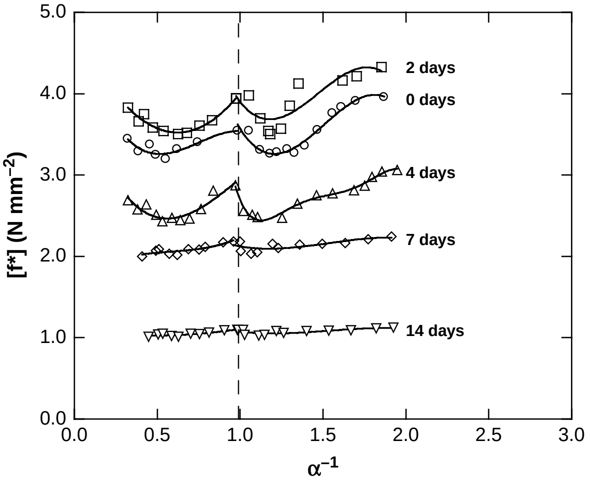


Fig. 4. Stress–strain isotherms for dry rubber vulcanizates prepared using oxidized polyquinone.

2.4. Stress–strain measurements of the swollen rubber vulcanizates

It is envisaged that stress–strain measurements of swollen rubber networks having bimodal cross-link length distribution may provide a clear revelation on the effect of the limited chain extensibility of the short cross-links on the moduli of these networks. This is because swelling of the networks will prevent the elastomeric chains from undergoing possible strain-induced crystallization during the stress–strain measurements.

Mckenna and co-workers [18] have studied the mechanical and swelling behavior of cross-linked natural rubber in the dry and swollen states. They indicated that the mechanical and swelling responses in their studies have been treated within the context of the Frenkel [19]–Flory–Rehner [20] (FFR) hypothesis. The hypothesis states clearly that the elastic free energy of a swollen network is normally balanced by the free energy of mixing at the vicinity of the swelling equilibrium and is generally expressed as:

$$-RT\left[\ln(1-v_2) + v_2 + \chi v_2^2\right] = \frac{V_1}{\lambda^2}\frac{\partial \Delta A}{\partial \lambda} \tag{2}$$

where R is the gas constant, T the absolute temperature, v_2 the volume fraction of rubber in the swollen state, χ the Flory–Huggins interaction parameter, V_1 the molar volume of the solvent, λ the stretch ratio given by $v_2^{-1/3}$ and ΔA the elastic free energy per unit volume of dry rubber. They reported that, for the experimental results to be consistent with the FFR hypothesis, the Flory–Huggins χ parameter need to be dependent upon the cross-link density, v. Nevertheless, they showed that an apparent universal relationship between the value of χ_{eff} and the cross-link density, which is independent of the solvent used during the swelling experiments, persists.

Mark [21] has reported the results of simple tension experiments on dry and swollen *cis*-1,4-polyisoprene networks of various cross-link densities having unimodal cross-link length distribution. The modulus or the reduced force of these networks showed as expected a significant decrease with extension and swelling. The dependence of the observed moduli on extension and swelling, was shown to be well-represented by the results of calculations based on the Flory–Erman theory of networks with constrained junctions [22]. Other studies were also performed on expanded natural rubber vulcanizates. Sombatsompop [23] illustrated the effect of the cross-link characteristics on the mechanical and swelling behavior of these foams. He showed that the properties of the expanded networks are dependent not only on the degree of cross-linking, but also on the type of chemical structure of the cross-link.

The reduced stress or modulus for the swollen samples is given by [5]:

$$[f^*] = \frac{(f/A^*)v_2^{1/3}}{(\alpha - \alpha^{-2})} \tag{3}$$

where f is the equilibrium elastic force, v_2 the volume fraction of polymer in the stretched swollen network, and $\alpha = L/L_{\mathrm{i,v}}$ the extension ratio relative to the length $L_{\mathrm{i,v}} = L_0(V/V_0)^{1/3}$ of the unstretched (isotropic) specimen at the volume V prevailing in the elongated state. The application of swelling on the stress–strain measurements of styrene–butadiene rubber vulcanizates in the swollen state cross-linked with two different cross-linking systems, the short sulfur cures and the relatively long polyquinone chains had a much more pronounced effect. The resulting isotherms [24] are shown in Figs. 5 and 6.

The effect of swelling on the isotherms of the bimodal networks is quite different from that of the unimodal ones. In the usual case of unimodal networks, the application of swelling causes a decrease in the modulus. However, the opposite effect is observed with bimodal networks. The higher the cross-link density of bimodal networks the higher the influence of the swelling on the modulus so that the upturn in the modulus values appears at lower deformations. These enhanced upturns are apparently due to the diluent stretching the short chains closer to the limits of their extensibility [5]. The results presented here for the elongation region are similar to those also obtained for bimodal PDMS networks in elongation [25] and in compression [26].

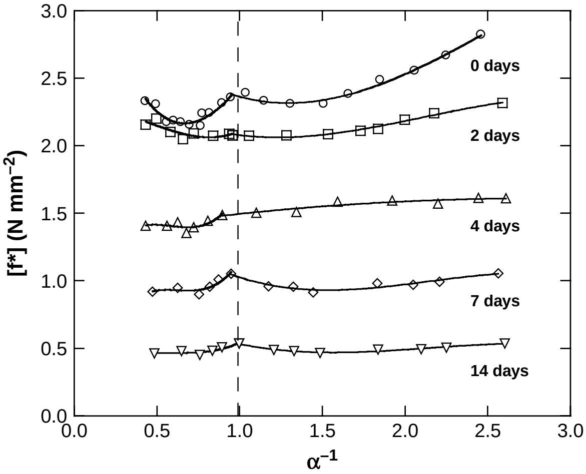


Fig. 5. Stress–strain isotherms for swollen rubber vulcanizates prepared using polyquinone antioxidants.

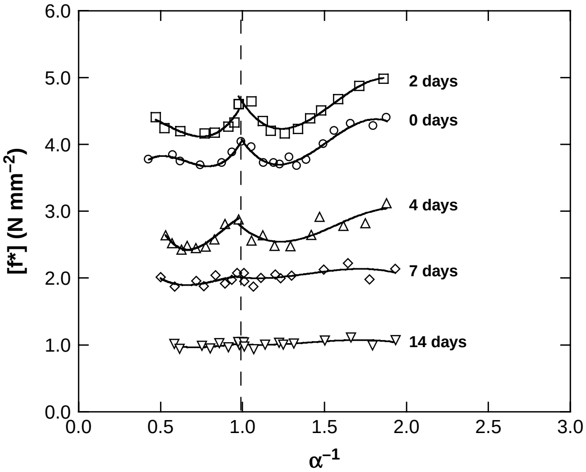


Fig. 6. Stress–strain isotherms for swollen rubber vulcanizates prepared using oxidized polyquinone antioxidants.

2.5. Molecular modeling of the polyquinone structures

In order to gain more insight into the microscopic nature of polyquinone chains and how this may influence its macroscopic characteristics, energy minimization of the three macromolecular structures was performed using steepest descent and dynamic quenching techniques. The polymers under study are polyquinone (AQ), polyhydroquinone (HQ), and polybenzoquinone (BQ). Potential energies of totally minimized structures using the steepest descent and dynamic quenching methods are given in Table 1 [27]. Data obtained from the analysis of the minimized structures indicates that the quenching technique, as expected, was able to overcome the small barriers between the stable points on the potential energy surface to finally approach a new energy minimum. Results shown in the table also indicate that polyquinone and polyhydrquione are greatly stabilized by the presence of the hydrogen bonding which is also expected to limit their number of conformations. Studying the effect of cooling on the system behavior indicated that the nuclear bending dynamics is more restricted than the torsion dynamics causing the range of the former to be much smaller than that of the latter.

The dynamics of bending must therefore require more energy and upon cooling, the system dynamics loses most of the energy available through the more restricted bending fluctuations. Polyhydroquinone being mostly stabilized by hydrogen bonding showed the highest bending movement.

Table 1
Potential energies of polyquinones evaluated using molecular mechanics

Polyquinone type	Potential energy (kcal mol^{-1})	
	Steepest descent	Dynamic quenching
AQ	40.724	37.187
HQ	−0.543	−8.901
BQ	76.749	74.179

The presence of the hydrogen bonds between the hydroxyl groups on neighboring hydroquinone nuclei should restrict to some extent the torsional movement of these nuclei about the bonds connecting them as was evident by the steady behavior of the polymer at low temperatures [27]. The ease of torsional movement of polybenzoquinone is due to the lack of any hydrogen bonding, which led to a moderate fluctuation of its bending behavior. The dynamics in general of polybenzoquinone are much more restricted than that of polyquinone and polyhydroquinone as was determined using molecular dynamics techniques [28]. Not as much as the case with polyhydroquinone, the torsion of polybenzoquinone is somewhat restricted as well. This is because of the partially negatively charged carbonyl oxygen atoms. The maximum repulsion between these charged atoms must take place as the torsional angles approach 180°. Alternatively, torsional angle value of polyhydroquinone is near the 180° to favor the hydrogen bonding formation between neighboring groups. Because of the existing repulsion between the carbonyl oxygen atoms, this value might either go up or down away from the high energy barriers at 180°. These barriers are high enough not to be easily overcome and fluctuations between these barriers are therefore only allowed. Polyquinone in general, shows behavior in-between that of polyhydroquinone and polybenzoquinone. The behavior is, however, more closely related to that of polyhydroquinone, which indicates the stronger presence of the benzenoid nuclei over the quinonoid ones in an equimolar ratio compound. This is due to the more restricted dynamics of the quinonoid nuclei in general. In all three models, the mean square displacement calculations showed a transition temperature at 365 K at which all three systems slow down in terms of their molecular dynamics.

2.6. Evaluation of the intrinsic atomic-level forces in the non-Gaussian polymer networks

In order to evaluate the non-Gaussian effects of the polymer networks cured with two different vulcanizing agents of different lengths, Mark and co-worker [12] theoretically investigated the elastomeric networks with two cross-linking systems, namely, the very short sulfur cures and the sufficiently long polysulfidic cross-links which then were assumed to be elastically effective and would thus contribute to the modulus of the samples by increasing their end-to-end distances and decreasing their entropies in response to the imposed stress. Eventually, this was shown to lead to superior mechanical properties for bimodal networks [13–15,29]. The increase in the modulus and the anomalous improvements in the ultimate properties of the bimodal networks are thought to be due to the intramolecular effects, specifically to the non-Gaussian effects arising from the limited chain extensibility. The hypothesis as outlined by Curro and Mark [30] states that a network chain near its maximum extensibility can no longer increase its end-to-end separation by configurational changes, i.e. by simple rotations about its skeletal bonds. Deformations of bond angles (and possibly even bond lengths) would be required, and the energies for those processes are much greater than those for configurational changes. The forces, acting microscopically, on the individual long and short network chains could be evaluated by considering a bimodal network consisting of N_S short chains and N_L long chains. The free energy change $\Delta A(\alpha)$ due to the deformation of the network long (L) chains and short (S) chains with a uniaxial stretch ratio (α) is given by:

$$\Delta A(\alpha) = \Delta A_\mathrm{L}(\alpha_\mathrm{L}) + \Delta A_\mathrm{S}(\alpha_\mathrm{S}) \tag{4}$$

Making use of the conventional rubber-like elasticity theory [31], the free energy change of the long chains is given by:

$$\Delta A_\mathrm{L} = \frac{KTN_\mathrm{L}}{2V}\left(\frac{\alpha_\mathrm{L}^2 + 2}{\alpha_\mathrm{L} - 3}\right) \tag{5}$$

whereas the free energy change of the short chains is given by [32]:

$$\Delta A_\mathrm{S} = \frac{N_\mathrm{S}}{3V}\left[A_0(r_0\alpha_\mathrm{S}) + 2A_0\left(r_0\alpha_\mathrm{S}^{-1/2}\right) - 3A_0(r_0)\right] \tag{6}$$

where r_0 is the root-mean-squared value of the end-to-end distance. The intrinsic microscopic deformation could be thus related to the macroscopic deformation by (i) considering the average microscopic deformation to be affine,

$$\alpha = x_\mathrm{L}\alpha_\mathrm{L} + x_\mathrm{S}\alpha_\mathrm{S} \tag{7}$$

where x_L and x_S represent the fraction of the long and short chains in the network, and by (ii) partitioning the macroscopic deformation between the long and short chains non-affinely according to:

$$\left(\frac{\partial \Delta A}{\partial \alpha_\mathrm{S}}\right)_\alpha = 0 \tag{8}$$

Applying the extreme condition in Eq. (8) into Eqs. (4)–(7) yields the relationship:

$$\frac{r_0}{3}\left[A_0'(r_0\alpha_\mathrm{S})\alpha_\mathrm{S}^{-3/2}A_0'\left(r_0\alpha_\mathrm{S}^{-1/2}\right)\right] = \frac{KT}{x_\mathrm{L}}\left[(\alpha - \alpha_\mathrm{S}x_\mathrm{S}) - x_\mathrm{L}^3(\alpha - \alpha_\mathrm{S}x_\mathrm{S})^{-2}\right] \tag{9}$$

The nominal force, f^*, on the network can be obtained from the following considerations:

$$f^* = KT\left(\frac{\partial A}{\partial \alpha}\right) = KT\left[\left(\frac{\partial A}{\partial \alpha}\right)_{\alpha_\mathrm{S}} + \left(\frac{\partial A}{\partial \alpha_\mathrm{S}}\right)_\alpha\left(\frac{\partial \alpha_\mathrm{S}}{\partial \alpha}\right)\right] \tag{10}$$

The second term on the right-hand side of Eq. (10) vanishes in view of Eq. (8), thus we obtain:

$$f^* = -KT\left(\frac{\partial A}{\partial \alpha}\right)_{\alpha_\mathrm{S}} \tag{11}$$

and finally,

$$f^* = vKT\left[\frac{\alpha}{x_\mathrm{L}} - \frac{x_\mathrm{S}\alpha_\mathrm{S}}{x_\mathrm{L}} - \left(\frac{\alpha}{x_\mathrm{L}} - \frac{x_\mathrm{S}\alpha_\mathrm{S}}{x_\mathrm{L}}\right)^{-2}\right] \tag{12}$$

thus implying the relationship between the microscopic deformation of the individual short chains and the macroscopic deformation, α, which is well described by the virial stress formula [33] where the macroscopic stress tensor in a polymer system may be expressed as a sum of the intrinsic atomic-level stress tensors, with each of the latter associated with a single atom.

The profound effect on the mechanical properties of styrene–butadiene networks resulting from the incorporation of polyquinones into the sulfur-cured rubber matrix was thus elaborated further by considering the intrinsic atomic-level stress tensors associated with each individual atom [34]. This is possible if an assumption was to be made that the relatively long polyquinone chains are elastically effective and would thus contribute to the modulus of the samples by increasing their end-to-end distances and decreasing their entropies in response to the imposed stress. These nuclei, in fact, are planner in nature and changes about the bond angles or the torsional angles within the single nuclei are highly unlikely. The only types of motion these materials might, therefore, perform must involve the bonds connecting the different nuclei. Torsion and/or quinonoid–benzenoid nuclei bending about the connecting bonds are such examples as was elaborated earlier by considering the molecular modeling of the polyquinone chains. The intrinsic forces acting on the various atoms comprising a cross-linked system is normally evaluated during the integration of the classical equations of motion [35]. For a system of atoms, with Cartesian coordinates $\mathbf{r}_i$ and mass of atom m_i, the force exerted on that atom is given by:

$$m_i \cdot \ddot{r}_i = f_i \tag{13}$$

where $\ddot{r}_i$ is the second derivative of $\mathbf{r}_i$ with respect to the time t. The force acting on atom i is related to the potential energy exerted on atom i, V, by:

$$f_i = -\nabla_{r_i} V \tag{14}$$

Integration of the equation of motion during a dynamics run is usually achieved by the evaluation of the total potential energy exerted on atom i and the calculation of the force f_i acting on this atom accordingly. This is done by evaluating all pairwise potentials between atom i and all other atoms in the system within a loop over all pairs of i and j atoms. The pairwise potential energy, $V(r_{ij})$, the pair virial function, $W(r_{ij})$, and the pairwise force directed along the interatomic vector, r_{ij}, are all related according to:

$$f_{ij} = -\frac{1}{r_{ij}}\left(\frac{\mathrm{d}V(r_{ij})}{\mathrm{d}r_{ij}}\right) r_{ij} = -\frac{W(r_{ij})}{r_{ij}^2} r_{ij} \tag{15}$$

Insight II modeling package was employed to perform the dynamics simulation of sulfur-cured butadiene networks either with no incorporated polyquinone cross-links (unimodal networks), Fig. 7, or with the incorporation of the polyquinone chains (bimodal networks), Fig. 8.

Energy minimization of the various unimodal and bimodal cross-linked systems was performed using the dynamic quenching method. The technique involved the coupling of all the systems to a thermal bath as to allow for the temperature variation [36]. This is simulated by constantly monitoring and adjusting the average kinetic energy of the atoms to maintain a newly given temperature during a molecular dynamics run. By setting the target temperature to a very low value (e.g. 1 K) the system overcomes small barriers during the relaxation procedure to finally settle in a lower-energy minimum.

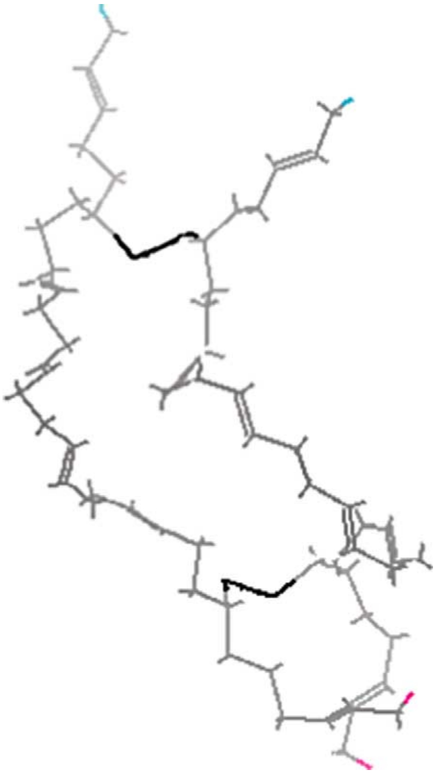


Fig. 7. Graphical representation of a unimodal polybutadiene network cross-linked using only sulfur atoms.

The higher potential energies determined for the bimodal networks as compared to the unimodal ones were explained to be due to the intramolecular effects arising from the presence of the bimodal cross-linking. Since a network chain near its maximum extensibility can no longer increase its end-to-end separation by simple rotations about the skeletal bonds, deformation of the bond angles and lengths leading to a greater potential energy values would be required. Furthermore, potential energy results showed that polyquinone networks (AQ) were greatly stabilized by the presence of the hydrogen bonding between the hydroxyl hydrogen attached to

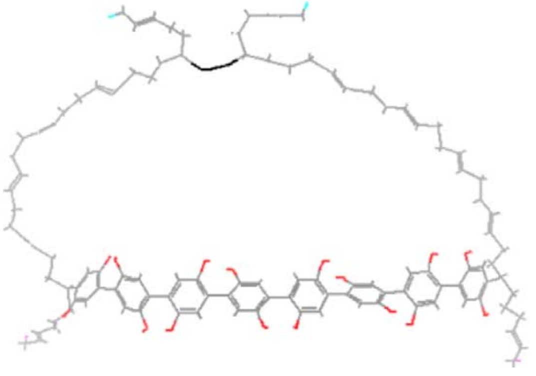


Fig. 8. Graphical representation of a bimodal polybutadiene network cross-linked using sulfur atoms and polyhydroquinone long chains.

Table 2
Intrinsic atomic-level forces acting on the junction atoms of the networks

Segment length	Intrinsic forces (kcal mol^{-1} Å^{-1})					
	Unimodal cross-linking			Bimodal cross-linking		
	AQ	BQ	HQ	AQ	BQ	HQ
3	38.34	40.24	37.56	39.30	39.14	41.17
4	38.69	35.30	39.34	40.06	40.38	39.77
5	37.08	38.27	37.51	38.71	41.28	39.29
6	37.48	39.38	39.66	38.58	40.56	40.66
7	40.23	37.23	39.79	37.94	40.18	39.78
8	37.96	38.17	37.60	39.84	39.92	38.92
9	40.15	37.14	38.61	40.80	40.37	40.30
10	36.26	40.63	37.55	39.48	39.37	40.11

the benzenoid rings and the carbonyl oxygen atoms of the quinonoid ones. Increasing the segment length of the polyquinone chains also resulted in an increase of the total potential energies of these systems.

Values for the intrinsic atomic-level forces acting on the junction atoms of the cross-linking systems and the elastomeric chains as a function of the polyquinone segment length are listed in Table 2. The table shows that these forces have practically similar values irrespective of the type, arrangement or the segment length of the cross-linking agents within the statistical errors. This indicates, however, that the various arrangements of the cross-linking agents do not influence the elastomeric chains but rather affect intrinsically the cross-linking chains themselves. Further results [34] showed that for a network cross-linked using sulfur atoms only, the forces exerting on the sulfur atoms had the lowest values. Replacement of one of the sulfur short chains by a relatively long polyquinone chain has caused the stress on the other sulfur short chain to increase dramatically possibly due to the limited chain extensibility of these short chains. To clarify this further, the forces on the polyquinone atoms in unimodal and bimodal arrangements were also evaluated. In this case, unimodal networks refer to elastomeric networks with only one cross-linking system, either sulfur or polyquinone chains. Bimodal networks refer to elastomeric networks with both cross-linking systems. Comparison of the results from the two arrangements clearly showed that the intrinsic forces acting on the polyquinone atoms have decreased as a result of the formation of the bimodal networks and the limited chain extensibility of the short sulfur chains. The results also showed that for the three chemically different polyquinone chains, BQ-crosslinked networks had the highest stress values, which correspond to elastomeric networks with the lowest percentage deterioration, Fig. 1, and the highest modulus values, Fig. 4. This is due to the absence of any hydrogen bonding formation in BQ chains, which resulted into the easiness of the dynamics of the relatively long chains causing them to be elastically effective and to dramatically contribute to the modulus of the samples by increasing their end-to-end distances and decreasing their entropies in response to the imposed stress. The dynamics of the three polyquinone chain types showed that the motion of AQ and HQ segments were mostly stabilized by hydrogen bonding between the hydroxyl groups on the neighboring hydroquinone nuclei, which restricted to some extent the torsional movement of these chains rendering them less elastically effective.

3. Conclusion

Styrene–butadiene rubber vulcanizates prepared using sulfur as the cross-linking agent and a chemically bound antioxidant such as the polymerization products of *p*-benzoquinone acting as a second cross-linking agent exhibited a significant improvement in the ultimate mechanical properties. The upturn in the modulus values in response to the imposed stress could only be explained on the basis of strain-induced crystallization of the elastomeric chains and/or the limited extensibility of the short network chains. Stress–strain experiments carried out on these networks in the dry and the swollen states emphasized the underlying mechanism of observed 'non-Gaussian' behavior. Since swelling of the networks will prevent the elastomeric chains from undergoing possible strain-induced crystallization during the stress–strain experiments, it must therefore be concluded that the marked improvement in reinforcement has resulted from the very limited extensibility of the short network chains. The higher the cross-linking density of these networks, the higher the influence of the swelling on the modulus so that the upturn in the modulus values appeared at lower deformations. The short chains near its maximum extensibility can no longer increase its end-to-end separation by simple rotations about its skeletal bonds. Therefore, deformation of the bond angles and bond lengths of the short chains will be required in response to the imposed stress. These deformations demand greater energies than those for configurational changes. Intrinsic atomic-level forces evaluated for the various atoms in the polymer networks of unimodal and bimodal chain length distribution indicated that the atoms at the junction points of the cross-linking agents and the elastomeric chains suffer no extra stress due to the change in the network chain length distribution. The intrinsic forces acting on the atoms comprising the short sulfur cross-links has increased dramatically upon the formation of the bimodal networks on the expense of the stress values acting on the relatively long cross-links. The limited chain extensibility, in this case, has acted as to increase the total potential energy of these networks and consequently its nominal force giving rise to the anomalous modulus values, bimodal networks are known to have.

References

[1] Madkour TM, Hamdi MS. J Appl Polym Sci 1996;61:1239.
[2] Sabaa MW, Madkour TM, Yassin AA. Polym Degrad Stab 1988;22:205.
[3] Isayev AI, Kim SH, Levin VY. Rubber Chem Technol 1997;70:194.
[4] Mark JE, Riande E, Scholtens BJR. Rubber Chem Technol 1983;56:1141.
[5] Mark JE, Erman B. Rubber like elasticity. A molecular primer. New York: Wiley-Interscience; 1988.
[6] Scott G. Plast Rubber Process 1977;2:41.
[7] Scott G. In: Scott G, editor. Development in polymer stabilization-4. New York: Applied Science Publishers Ltd; 1981. p. 181.
[8] Otomo S, Sako T, Yamamoto Y, Yamashita S. J Appl Polym Sci 1983;28: 3671.
[9] Otomo S, Kobayashi Y, Sako T, Yamamoto Y. J Appl Polym Sci 1983;29: 89.
[10] Sabaa MW, Madkour TM, Yassin AA. Polym Degrad Stab 1988;22:195.
[11] Llorente MA, Andrady AL, Mark JE. J Polym Sci, Polym Phys Ed 1981; 19:621.
[12] Sharaf MA, Mark JE. Macromol Rep 1991;A28:67.
[13] Queslel JP, Mark JE. Encycl Polym Sci Technol 1986;5:365.
[14] Madkour TM, Mark JE. Macromol Rep 1994;A3:153.
[15] Galiatsatos V, Mark JE. Macromolecules 1987;20:4521.
[16] Clarson SC, Mark JE, Sun C-C, Dodgson K. Eur Polym J 1992;28:823.
[17] Andrady AL, Llorente MA, Mark JE. J Phys Chem 1980;72:2282.
[18] McKenna GB, Flynn KM, Chen YH. Polym Commun 1988;29:272.
[19] Frenkel J. Rubber Chem Technol 1940;13:264.
[20] Flory PJ, Rehner J. J Chem Phys 1943;11:521.
[21] Mark JE. Rubber Chem Technol 1982;55:1123.
[22] Erman B, Flory PJ. Macromolecules 1982;15:806.
[23] Sombatsompop N. Cell Polym 1998;17:63.
[24] Madkour TM, Azzam RA. Rubber Chem Technol 2003;76(2):334.
[25] Clarson SJ, Galiatsatos V, Mark JE. Macromolecules 1990;23:1504.
[26] Xu P, Mark JE. Polymer 1992;33:1843.
[27] Madkour TM. Polym J 1997;29(8):670.
[28] Madkour TM. Chem Phys 2001;274(2–3):187.
[29] von Lockette PR, Arruda EM. Macromolecules 1999;32:1990.
[30] Curro JG, Mark JE. J Chem Phys 1984;80:4521.
[31] Treloar LEG. The physics of rubber elasticity. 3rd ed. Oxford: Clarendon; 1975.
[32] Mark JE, Curro JG. J Chem Phys 1983;79:5705.
[33] Gao J, Weiner JH. J Chem Phys 1989;90:6749.
[34] Madkour TM, Ebaid AH. J Mol Model 2001;7:392.
[35] Allen MP, Tildesley DJ. Computer simulation of liquids. Oxford: Clarendon; 1987.
[36] Berendsen HJC, Postma JPM, van Gunsteren WF, DiNola A, Haak JR. J Chem Phys 1984;81:3684.