

Elastomers with Two Crosslinking Systems of Different Lengths Viewed as Bimodal Networks

TAREK M. MADKOUR* and MOHAMED S. HAMDI

The Department of Chemistry, Helwan University, Cairo, Egypt

SYNOPSIS

Elastomers cured with two crosslinking systems such as sulfur and the polymerization products of *p*-benzoquinone are shown to have much improved overall mechanical properties. It was thought that this was because of the antioxidizing potency of the quinone polymers that act as radical traps during the oxidative degradation process. However, if the polyquinone crosslinks of the greater length themselves act as elastomeric network chains, then a bimodal network with its exceptional mechanical properties is produced. Adding commercial antioxidants to the samples will even harvest much tougher samples. The antioxidant added, along with the quinone polymers, will reserve the integrity of the bimodal network produced and lead to better mechanical properties. Tests were also done to examine the effect of the quinone polymers on the hardness and on the onset of the vulcanization process. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Recently, we showed that the incorporation of the polymerization products of *p*-benzoquinone into a sulfur-cured rubber matrix such as styrene-butadiene rubber (SBR) has a profound effect on the mechanical properties of the elastomeric networks.¹ That was attributed at the time 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, and/or the adsorption onto the surface of the filler present within the matrix. Surprisingly enough results were obtained showing a gradual increase in the values of the ultimate tensile strength of the samples during the early stages of the accelerated aging process which is followed by a breakdown in the ultimate tensile strength of the samples but to a lesser extent to that of materials treated with commercially available antioxidants. The values of the ultimate tensile strength of the latter have normally degraded with the continuing aging process, which indicates that the observed ab-

normal 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 (1) strain-induced crystallinity and (2) limited chain extensibility observed for networks with bimodal chain lengths distributions^{2,3} and since the rubber material used in the study, SBR, has little or no tendency to undergo strain-induced crystallization,⁴ the focus of attention on the nature of the quinone polymer crosslinks was assumed.

Sharaf and Mark⁵ theoretically investigated the elastomeric networks with two crosslinking systems, namely, the very short sulfur cures and the sufficiently long polysulfidic crosslinks 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 will lead to the superior mechanical properties bimodal networks are known to have.⁶⁻⁹ 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.

* To whom correspondence should be addressed.

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.¹ 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 the sulfur cures. Alternatively, it will take place during the degradation process and a true bimodal chain length distribution is thus anticipated to transpire in time.

The present investigation explored the above-mentioned "non-Gaussian" behavior of the quinone polymer crosslinked elastomers viewed as bimodal networks. The study focuses on the effect of aging time on the reduced stress values of the networks in relation to the elongation of the samples. The study is also extended to cover the possible effect of these bound antioxidants on the onset of the vulcanization process and the hardness values of the elastomeric networks.

EXPERIMENTAL

Preparation of Crosslinked Samples

Different sheets of the elastomeric networks were prepared according to the recipe described by Stern¹¹:

Oil-extended SBR	100 g
ISAF carbon black	45 g
Zinc oxide	3 g
Stearic acid	1.50 g
Dutrex or other softner	2 g
Antioxidant	1 g
Diphenyl guanidine	0.14 g
Santocure	0.17 g
Sulfur	1.27 g

Sheets of the polymer were pressed at 144°C for 50 min to a thickness of 0.2 cm. With the exception of the antioxidant used, all the recipes had essentially the same chemical configuration. According to the type of the antioxidant used in the preparation, the networks were given their code names. Three major different recipes were prepared and used throughout the study: the PQ-0.8% H₂SO₄ recipe processed according to the above method with the appropriation of the polymerization products of *p*-benzoquinone that was prepared using sulfuric acid as a catalyst; the PQ-0.8% H₂SO₄, oxidized,

recipe with essentially the same configuration as the latter with the exception that the quinone polymers were oxidized with iodine to increase the percentage of the quinone nuclei within the samples; and the PQ-0.8% H₂SO₄/6PPD recipe with the added *N*-(1,3-dimethylbutyl)-*N*-phenyl-*p*-phenylenediamine antioxidant (6PPD), as a recipe of this kind has shown the highest ultimate tensile strength when studied earlier.¹ Equal proportions of the two antioxidants were thus used in preparing this latest recipe. A full description of the cationic and anionic polymerization of *p*-benzoquinone together with the structures, properties, chemical, and spectral analyses of the nonoxidized and oxidized products was presented elsewhere.¹⁰ Another SBR network with the commercially known 6PPD antioxidant was also prepared for hardness measurements and used as a reference sample such as in the case with studies done on the ultimate tensile strength.

Rheological Properties

The onset of the vulcanization process was studied using a Rheometer 100 Therm-O-Logger, Monsanto Company, UK. Analysis of the Rheometer curves is based on the following calculations¹²: minimum torque (M_L), the minimum point on the curve (dNm); maximum torque (M_H), the maximum point on the curve (dNm); scorch time (t_{S2}), the time after two torque units from minimum torque (min); torque at 90% cure M_{C90} , $M_L + (M_H - M_L) \times 90/100$ (dNm); optimum cure time t_{C90} , the time which corresponds to 90% cure (min); and cure rate index (CRI), $100/t_{C90} - t_{S2}$ (min⁻¹).

Accelerated Aging of Vulcanized Rubber

This was performed by the oven method as described by the American Association ASA No. J 5.1.^{1,13} The specimens for aging were placed vertically in the oven after it had been preheated at 100°C. The aging interval began at the time the specimens were placed in the oven and continued for time intervals of 1, 2, 3, 4, and 5 days. These intervals were chosen to study the "non-Gaussian" behavior of the samples observed during the early stages of the aging process. At the end of the aging interval, the specimens were removed from the oven, cooled to room temperature on a flat surface, and allowed to stand for not less than 16 h and not more than 48 h before the determination of the physical properties.

Hardness Measurements

Hardness measurements were performed using a standard type D durometer Model 307L, PTC In-

Table I Data from the Rheometer Curves for Various Networks at 186°C, Chart Motor 9 min, Range Sel. 100, Preheat Nil, Arc 3°

Recipe	M_L	M_H	t_{S2}	M_{C90}	t_{C90}	CRI
PQ-0.8% H ₂ SO ₄	15	55	2.7	51.0	9.4	14.9
PQ-0.8% H ₂ SO ₄ , oxidized	15	55	2.6	51.0	9.1	15.4
PQ-0.8% H ₂ SO ₄ /6PPD	15	53	2.5	49.2	9.3	14.7
6PPD	14	53	2.7	49.1	9.2	15.3

struments, USA, in accordance with the standard test method for rubber property (ASTM designation: D2240-86). Five measurements of hardness at different positions on the specimens were made which were at least 6 mm apart and the arithmetic means of the hardness values were determined. All measurements were carried out in the vicinity of room temperature.

Stress-Strain Measurements

Stress-strain isotherms at 25°C were obtained on strips cut from various network sheets, using standard techniques.¹⁴ The strips had cross-sectional areas A^* of approximately 4 mm² and the lengths of the central portions of the strips were approximately 12 mm. The apparatus used for the stress-strain measurements is described elsewhere.³ The sample, held vertically between two clamps, was placed into a glass cell which was enclosed in a thermostatted water bath. The lower clamp was fixed and the upper clamp was suspended from a strain gauge (Statham Model G1-16-350). A constant voltage dc power supply (Hewlett-Packard 6217) was used to supply approximately 14 V potential to the transducer. The transducer was frequently calibrated using a set of standard weights. Its output was found to remain constant over the usual time span of an experiment.

Prior to attaching the clamps to a sample, two thin lines were drawn on it by means of a white powder. The sample clamps were lined with thin sheets of rubber to minimize premature rupture or slippage of the samples at the contact points. The exact length of the thus-demarcated section of the sample was measured precisely at the desired temperature using a cathetometer (Gaertner Scientific Corp., Model M940-303P, precision 1 micron), and the thickness and width were determined with a micrometer. Three measurements, each along the thickness and width of the strip, were taken, and the average cross-sectional area A^* was determined.

The upper clamp was raised to a position giving the desired elongation of the strip. The distance between the two lines was measured with a catheto-

meter and recorded as the length L . The ratio of L to L_0 (initial length) presents the elongation. The potential from the stress gauge was calibrated in terms of Newtons (N). Stress-strain measurements were made using a sequence of increasing values of the elongation up to rupture point of the sample. The values of the elastic force f were recorded only after they had become sensibly constant for at least 15 min. The elastic quantity of primary interest was the reduced stress or modulus defined by³

$$[f^*] = f/[A^*(\alpha - \alpha^{-2})] \quad (1)$$

RESULTS AND DISCUSSION

Rheological Properties

The influence of the polyquinone antioxidants on the rheological properties of SBR networks and the reference sample is summarized in Table I. The results of the nonoxidized and the oxidized polyquinone samples given in Table I reveal that both types of the product have only a slight effect on the major rheological properties. The effect is probably due to their hydrogen-donating properties, which might interfere with the action of the accelerator in its abstraction of the hydrogen atoms from the rubbery chains.¹ In general, one could conclude that the usage of the polymerization products of *p*-benzoquinone as antioxidants does not have much influence on the onset of the vulcanization process.

Hardness Measurements

Results of the hardness measurements for various networks at 25°C in response to the time of the accelerated aging are presented in Table II. As clearly shown, the incorporation of the polymerization products of *p*-benzoquinone as antioxidants in the rubber matrix has a slight increasing effect on the hardness values. This is probably because of the binding nature of the polymeric quinone antioxidants which would result in an increase in the cross-linking density of the elastomeric networks.

Table II Hardness Measurements for Various Networks at 25°C in Response to the Time of Accelerated Aging

Recipe	Hardness Measurements (Points) ^a					
	Days of Accelerated Aging					
	0	1	2	3	4	5
PQ-0.8% H ₂ SO ₄	29	28	28	29	29	30
PQ-0.8% H ₂ SO ₄ , oxidized	28	29	29	30	30	31
PQ-0.8% H ₂ SO ₄ /6PPD	30	30	31	31	32	32
6PPD	26	27	27	27	28	28

^a ASTM designation: D2240-86.

Stress-Strain Measurements

The first representation of the stress-strain data was based on the Mooney-Rivlin equation:

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

where $2C_1$ and $2C_2$ are constants. Typical isotherms of this type are shown in Figures 1-3. Each one of the figures thus 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. As an alternative representation, f^* was plotted against α itself, as is illustrated in Figures 4-6. The ultimate properties obtained from these figures are the elongation at rupture α_r , the nominal stress at rupture $(f/A^*)_r$, and the energy required for rupture E_r . The values obtained are summarized in Table III. The energy required for rupture was calculated by considering the area under the isotherm.

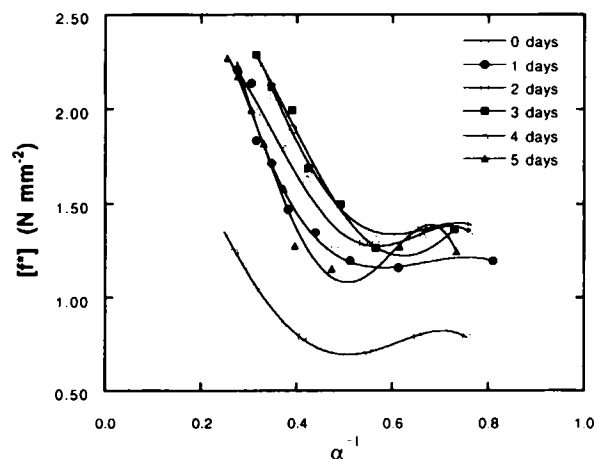


Figure 1 Mooney-Rivlin isotherms for the SBR networks having PQ-0.8% H₂SO₄ antioxidants.

Results of the first three figures show clearly the “non-Gaussian” behavior of the samples. According to eq. (2), the reduced stress of the samples 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 the ultimate tensile strength obtained for these samples when using the oven method.¹ 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 caused by the quinone polymers crosslinks. The limited chain extensibility of the short chains are responsible for the increase in the modulus values observed for these samples.^{3,15}

Figures 4-6 and Table III show the dependence of the ultimate properties of the SBR networks on the type of antioxidant being used and on the time the samples spent in the oven during the accelerated aging process. The figures indicate clearly that max-

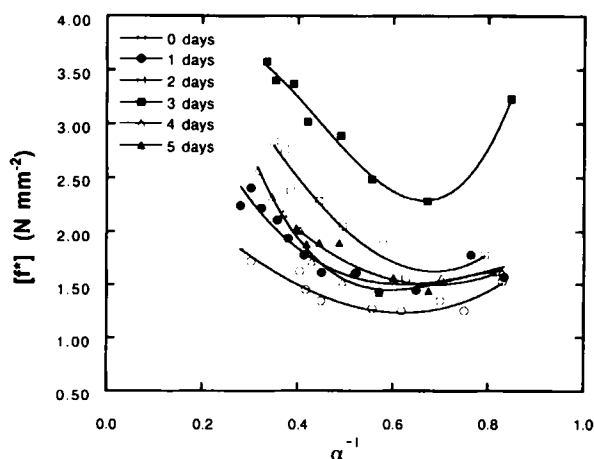


Figure 2 Mooney-Rivlin isotherms for the SBR networks having PQ-0.8% H₂SO₄, oxidized antioxidants.

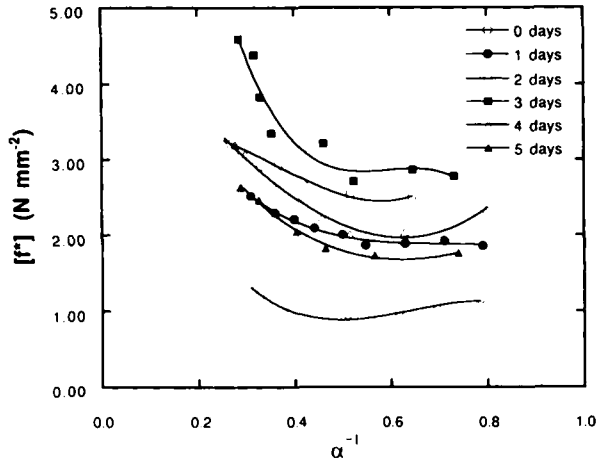


Figure 3 Mooney-Rivlin isotherms for the SBR networks having PQ-0.8% H₂SO₄/6PPD antioxidants.

imum modulus values were obtained after 3 days of continuing aging time. That is probably when the maximum bimodal chain length distribution took place as a consequence of the linking of the quinone polymers to the elastomeric chains during the oxidative aging process. This continues to take place up to a point at which the degradation takes over and a breakdown of the chains and the mechanical properties of the networks prevails.

Of interest here is the PQ-0.8% H₂SO₄/6PPD recipe, which showed the best results obtained in this study. In the earlier investigation, the better mechanical properties obtained in this case was attributed to a synergistic effect between the two antioxidants used. Nevertheless, the current findings indicate that this is probably because of the bimodal chain-length distribution caused by the quinone polymers. The polyquinone antioxidant is not prob-

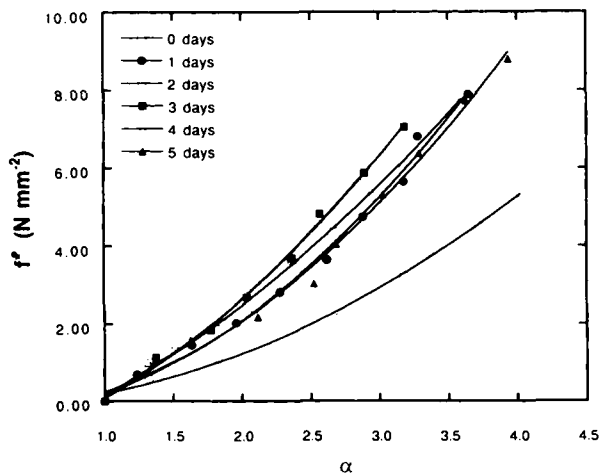


Figure 4 Nominal stress-elongation isotherms for the SBR networks having PQ-0.8% H₂SO₄ antioxidants.

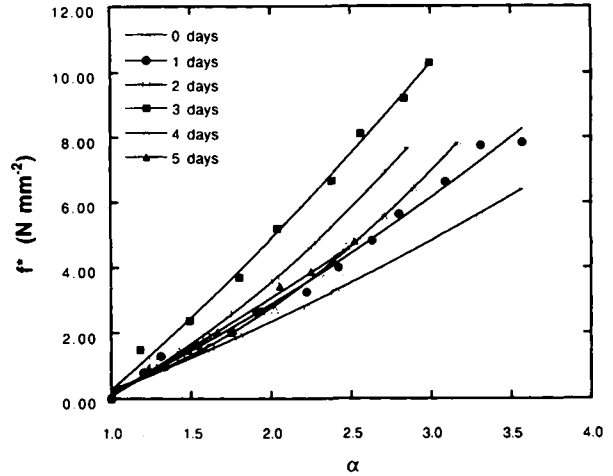


Figure 5 Nominal stress-elongation isotherms for the SBR networks having PQ-0.8% H₂SO₄, oxidized antioxidants.

ably as effective as is 6PPD in inhibiting the oxidative degradation of the elastomers. However, adding the 6PPD antioxidant, along with the quinone polymers, will, consequently, reserve the integrity of the bimodal networks produced and give rise to better mechanical properties. The fifth column of Table III is truly indicative of this, since the values of the energy required for rupture were nearly doubled in the case of networks treated with the two types of antioxidants.

In accordance with other inferences,¹ one may conclude that the incorporation of quinone polymer crosslinks in the rubber matrices will aid tremendously in improving the antioxidizing efficiency of the stabilizers used without affecting the rheological or other mechanical properties such as the hardness

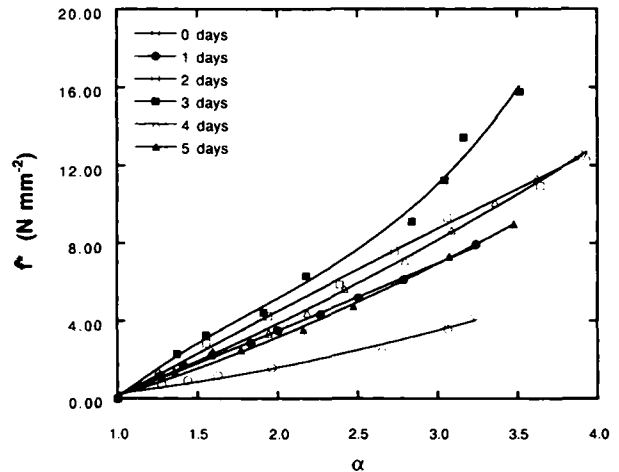


Figure 6 Nominal stress-elongation isotherms for the SBR networks having PQ-0.8% H₂SO₄/6PPD antioxidants.

Table III Ultimate Properties of the Various SBR Networks

Recipe	T_a^a (Days)	α_r^b	$(f/A^*)_r^c$ (N mm ⁻²)	$10^3 E_r^d$ (J mm ⁻³)
PQ-0.8% H ₂ SO ₄	0	4.02	5.344	6.855
	1	3.65	7.893	8.846
	2	3.02	6.485	5.833
	3	3.18	7.056	6.872
	4	3.59	7.785	9.170
	5	3.94	8.799	7.083
PQ-0.8% H ₂ SO ₄ , oxidized	0	3.57	6.494	6.033
	1	3.57	7.838	8.075
	2	2.86	7.772	6.479
	3	2.99	10.295	9.944
	4	3.17	7.871	7.375
	5	2.52	4.807	3.638
PQ-0.8% H ₂ SO ₄ /6PPD	0	3.24	4.283	4.351
	1	3.24	7.932	8.849
	2	3.88	12.616	18.280
	3	3.51	15.781	15.880
	4	3.93	12.448	17.621
	5	3.48	8.956	10.394

^a Time of accelerated aging.^b Elongation at rupture.^c Nominal stress at rupture.^d Energy required for rupture.

or elongation. The ability of the polymeric products to bind to the chains and establish the crosslinks is, however, a prerequisite in creating the mechanically anomalous bimodal networks.

The authors wish to express their deep thanks to the Transport and Engineering Co., Alexandria, Egypt, for providing the necessary materials used throughout this study. Special thanks to Mr. Osama Fadal for carrying out some of the hardness measurements.

REFERENCES

- M. W. Sabaa, T. M. Madkour, and A. A. Yassin, *Polym. Degrad. Stab.*, **22**(3), 205 (1988).
- M. A. Llorente, A. L. Andrady, and J. E. Mark, *J. Polym. Sci. Polym. Phys. Ed.*, **19**, 621 (1981).
- J. E. Mark and B. Erman, *Rubberlike Elasticity. A Molecular Primer*, Wiley-Interscience, New York, 1988.
- L. R. G. Treloar, *The Physics of Rubber Elasticity*, 3rd ed., Oxford University Press, Clarendon, 1975.
- M. A. Sharaf and J. E. Mark, *Macromol. Rep. A*, **28**(Suppl. 1), 67 (1991).
- J. P. Queslel and J. E. Mark, *Encycl. Polym. Sci. Technol.*, **5**, 365 (1986).
- T. M. Madkour and J. E. Mark, *Macromol. Rep. A*, **3**(Suppl. 1-2), 153 (1994).
- V. Galiatsatos and J. E. Mark, *Macromolecules*, **20**, 4521 (1987).
- S. C. Clarson, J. E. Mark, C.-C. Sun, and K. Dodgson, *Eur. Polym. J.* **28**, 823 (1992).
- M. W. Sabaa, T. M. Madkour, and A. A. Yassin, *Polym. Degrad. Stab.*, **22**(3), 195 (1988).
- H. J. Stern, *Rubber, Natural and Synthetic*, 2nd ed., Maclaren, London, 1967.
- R. D. Stiehler, in *Basic Compounding and Processing of Rubber*, H. Long, Ed., Rubber Division, American Chemical Society, Akron, OH, 1985.
- ASTM Designation: D573-45 (1947).
- S. Wang and J. E. Mark, *J. Polym. Sci. Polym. Phys. Ed.*, **30**, 801 (1992).
- A. L. Andrady, M. A. Llorente, and J. E. Mark, *J. Phys. Chem.*, **72**(4), 2282 (1980).

Received August 29, 1995

Accepted November 20, 1995