

Effect of Curing Time and Sulfur Content on the Dielectric Relaxation of Styrene Butadiene Rubber

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Received 4 December 2001; accepted 23 April 2002

ABSTRACT: Dielectric investigations were carried out on styrene–butadiene rubber cured by an increase in either the sulfur content or curing time in a wide range of frequencies from 100 Hz up to 10 MHz and at room temperature ($\approx 25^\circ\text{C}$). After subtraction, the losses due to the Maxwell–Wagner effect, the dielectric data showed deviation from the Debye formula but were found to be fitted in the frequency domain by the Havriliak–Nagami function, which is a combination of Cole–Cole and Cole–Davidson functions. This function describes the relaxation mechanisms of the aggregates caused by the movement of the main chain that were expected to be formed by the addition of the different ingredients to the investigated rubber. These mechanisms are also discussed in terms of the distribution function of Fröhlich between two limiting values of relaxation times τ_1

and τ_2 . The relaxation times obtained from both functions increased with an increase in either sulfur content or curing time. The data obtained are discussed in terms of the crosslinking density determined from the Flory–Rehner relation. The effect of thermal aging on such systems was also studied, and the data obtained were compared with those before aging. This investigation led us to conclude that to get an end product that is highly resistant to thermal aging, the system should be cured for a time greater than 30 min with the addition of more than 5 phr sulfur. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1613–1621, 2003

Key words: crosslinking; curing of polymers; dielectric properties; relaxation; rubber

INTRODUCTION

One of the most important and widely used synthetic rubbers is styrene–butadiene rubber (SBR), a copolymer of styrene and butadiene. For such importance, this research work was directed to carry out some improvements on SBR to be used in industrial applications such as tires and related products, wires, and cables.^{1–3}

The study of the physical parameters in relation to the curing process of polymers is of both practical and fundamental interest.⁴ A number of methods, especially calorimetry^{5–9} and dielectric relaxation spectroscopy have been utilized to study the kinetics of the cure process.^{5,8–17}

The dipolar relaxation time (τ) has a direct relationship with bulk viscosity and is considered to be a good detection characteristic for the changes that occur during the curing of polymeric materials.^{18,19} The increase in the average τ through an increase in the curing time was interpreted according to the network formation.⁵

The viscoelastic properties of polymers are markedly dependent on the type of crosslink and on the degree of crosslinking.²⁰ It is well known that poly-

sulfidic bonds are predominant with the conventional sulfur vulcanizate at relatively high sulfur levels. The sulfur also introduces main-chain modifications either in the form of pendant groups or cyclic sulfide linkages that have a large influence on the viscoelastic properties.²⁰

The aim of this study was to investigate the effect of curing time and sulfur content on the vulcanization process of SBR rubber through the study of dielectric relaxation in relation to the degree of crosslinking. The effect of thermal aging on such systems was also considered.

EXPERIMENTAL

Materials and sample preparation

The material used in this study was SBR 1502, with a styrene content of 23.5% and a specific gravity of 0.945 ± 0.005 . Keeping all conditions of mixing the same, we mixed the rubber mixes according to the standard recipe in a two-roll laboratory mill with a gear ratio of 1 : 1.9. All specimens contained 100 phr SBR 1502, 2 phr zinc oxide, 2 phr stearic acid, 2 phr dibenzothiazyl disulfide and sulfur in increasing quantities (0, 2, 5, 10, and 15 phr). After they were mixed completely, the rubber mixes were subjected to sheeting on the mill. The vulcanization was carried out in a heated flat press under a pressure of about 4 MPa (40 Kg/cm²) and at a temperature $142 \pm 1^\circ\text{C}$. The curing times of different samples were 10, 20, 30, 40, 50, and 60 min.

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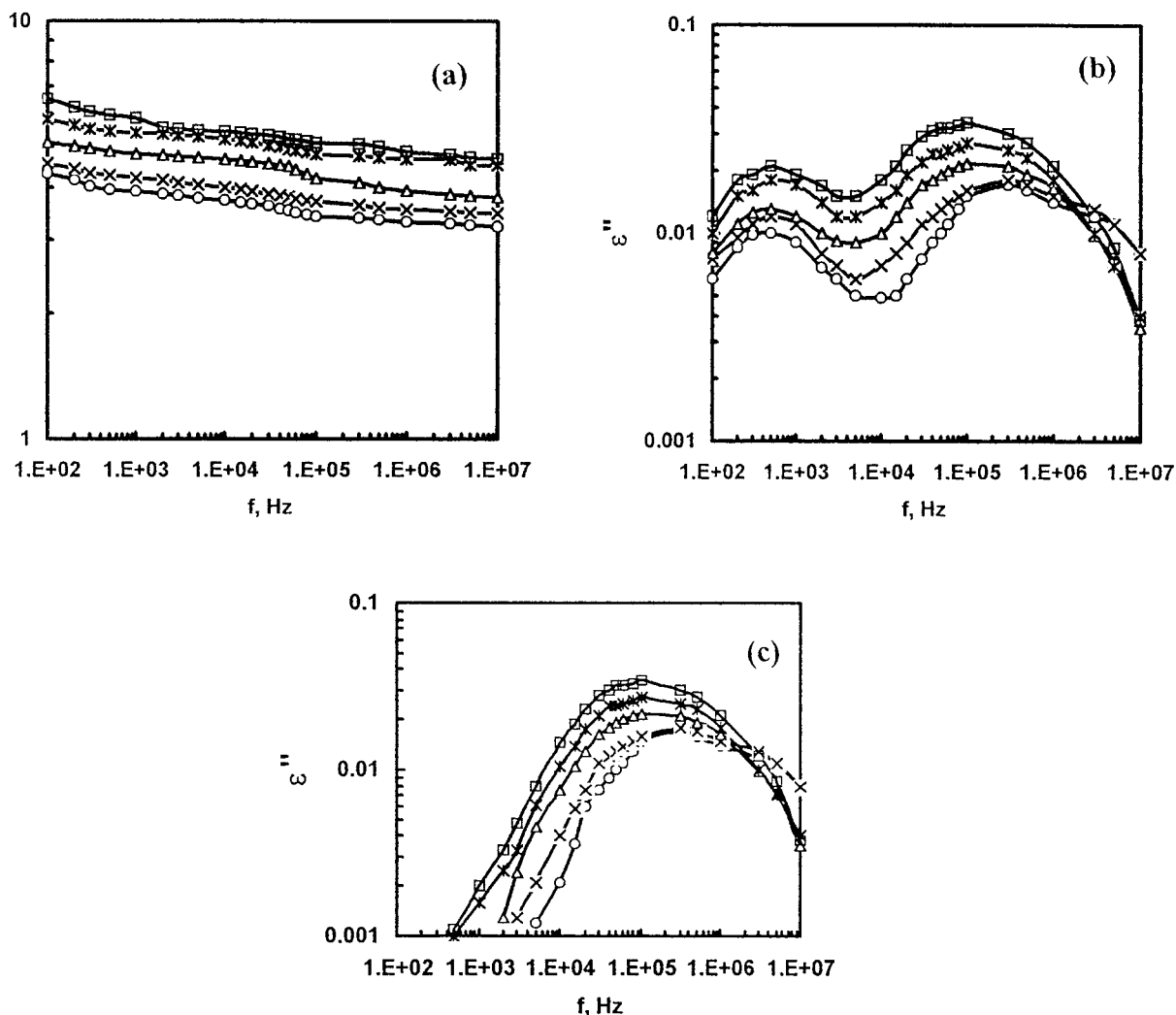


Figure 1 (a) ϵ' (b) ϵ'' and (c) ϵ'' after subtraction of the losses due to the Maxwell-Wagner effect versus f for SBR with different sulfur contents: (○) 0, (×) 2, (△) 5, (●●●) 10, and (□) 15 phr.

Square sheets 15 cm on a side and 2 mm thick were finally obtained and were then cut into pieces that suited the measurements.

Technique

The permittivity (ϵ') and dielectric loss (ϵ'') were measured in a frequency range from 100 Hz to 10 MHz. From 100 Hz to 100 kHz, an LCR meter type AG-411 B (Ando Electric Ltd., Japan) was used. From 100 kHz to 10 MHz, a circuit magnification meter (Q meter) instrument type TF 1245 A with an oscillator type TF 1246 from Marconi Instrument Ltd. (England) was used. The cell used in both instruments was a guard ring capacitor type NFM/5T (Wiss Tech. Werkstätten GMBH, Germany). The cell was calibrated with standard materials (trolitul, glass, and air) with different thicknesses ranging from 1 to 5 mm. For each sample, a relation between the thickness and capacitance (C_M) was plotted as a standard curve. C_M for the standard

materials obtained from the standard curves was plotted versus the known ϵ' of each material ($\epsilon' = 2.5, 7,$ and 1) for trolitul, glass, and air, respectively. The relation between C_M and ϵ' was linear, and thus, the permittivity corresponding to any measured C_M could be deduced. To check the standard curve, we used two Teflon samples ($\epsilon' = 2.0$)²³ with different thicknesses. The experimental error in ϵ' for both instruments was found to be $\pm 3\%$, whereas the expected error in ϵ'' for the whole measurements did not exceed 5%.

RESULTS AND DISCUSSION

Effect of sulfur

ϵ' for SBR cured for 30 min by the addition of sulfur in increasing quantities (2, 5, 10, and 15 phr) was measured in the frequency range from 100 Hz to 10 MHz at room temperature ($\approx 25^\circ\text{C}$). The measured values of ϵ' are illustrated graphically versus the applied fre-

TABLE I
Relaxation Parameters with the Havriliak–Nagami Function and the Crosslinking Density of SBR

Sulfur content (phr)	$\tau_1 \times 10^6$ (s)	$\tau_1\beta \times 10^6$ (s)	S	$\alpha\tau$	β	Crosslinking density $\times 10^4$ (mol/cm ³)
Before aging						
0	1.90	0.52	0.072	0	0.27	0
2	2.22	0.67	0.079	0.08	0.3	0.38
5	1.65	1.07	0.078	0.20	0.65	1.09
10	1.40	1.19	0.093	0.25	0.85	2.71
15	1.40	1.25	0.118	0.27	0.89	5.74
After 7 days of thermal aging at 90°C						
0	1.32	0.40	0.128	0	0.3	
2	1.61	0.48	0.111	0.08	0.3	
5	1.20	0.80	0.087	0.22	0.65	
10	1.40	1.19	0.093	0.25	0.85	
15	1.40	1.25	0.118	0.27	0.89	

Curing time (min)	$\tau_1 \times 10^6$ (s)	$\tau_1\beta \times 10^6$ (s)	S	α	β	Crosslinking density $\times 10^4$ (mol/cm ³)
Before aging						
10	2.1	0.74	0.110	0	0.35	0.16
20	1.8	0.90	0.094	0.16	0.50	0.50
30	1.42	1.04	0.077	0.23	0.73	1.09
40	1.36	1.11	0.066	0.25	0.82	3.40
50	1.29	1.20	0.058	0.29	0.93	3.65
60	1.32	1.32	0.052	0.31	1.00	3.77
After 7 days of thermal aging at 90°C						
10	1.77	0.62	0.120	0	0.35	
20	1.55	0.78	0.100	0.16	0.50	
30	1.22	0.90	0.085	0.23	0.73	
40	1.36	1.11	0.066	0.25	0.82	
50	1.29	1.20	0.058	0.29	0.93	
60	1.32	1.32	0.052	0.31	1.00	

quency in Figure 1(a). ϵ' increased with increasing the sulfur content, whereas it decreased with increasing applied frequency, which showed anomalous dispersion. With regard to the relaxation mechanisms associated with such dispersion, the dielectric loss values ϵ'' are plotted graphically versus the applied frequency, (f), as shown in Figure 1(b). At the lower frequency range, an absorption region with maximum loss at frequency 500 Hz was detected and was independent of the sulfur content in the sample. This region could be attributed to the Maxwell–Wagner effect, the origin of which is an alternating current that is in phase with the applied potential. This current results from the difference in ϵ' and resistivity of the ingredients added to rubber.²⁴ This region was comparable with those found in different types of rubber.^{23,25–27}

Figure 1(c) represents the variation of ϵ'' and f after subtraction of the losses due to the Maxwell–Wagner effect from the total absorption curves. It is clear that the rest of these curves are broad, and their maxima seem to be shifted to the lower frequency range with increases in the sulfur content. This result is considered to be good evidence for the presence of superim-

posed processes due to the orientation of the main chain and its related motions.^{23,26,27}

It is interesting that these data were fitted by Havriliak–Nagami function,²⁸ which is a combination of the Cole–Cole²⁹ and Cole–Davidson³⁰ functions:

$$\epsilon''(\omega) = \frac{(\epsilon_s - \epsilon_\infty)\cos(\beta\theta)}{[(1 + 2(\omega\tau)^{1-\alpha}\sin(\pi\alpha/2) + (\omega\tau)^{2(1-\alpha)})]^{1/\beta}}$$

where $\theta = \arctan[(\omega\tau)^{1-\alpha}\cos(\pi\alpha/2)/1 + (\omega\tau)^{1-\alpha}\sin(\pi\alpha/2)]$; α and β are constants called the Cole–Cole and Cole–Davidson distribution parameters, respectively, ϵ_s and ϵ_∞ are the static permittivity and the permittivity at infinite frequency; ω is the applied frequency = $2\pi f$; and τ is the relaxation time. τ and the related parameters obtained with this function are given in Table I. An example of the analyses for SBR containing 0 and 10 phr sulfur are illustrated graphically in Figure 2. The effective relaxation time ($\tau\beta$), which is more sensitive and usually taken instead of τ could be attributed to the orientation of the aggregates caused by the movement of the main chain, which were expected to be formed by the addition of the

different ingredients to the investigated rubber. From Table I, it is clear that $\tau\beta$ and the other parameters describing the investigated systems increased with increasing sulfur content. This increase could be attributed to the formation of polysulfidic crosslinks and cyclic sulfide structures.²⁰ These crosslinks increased the molar volume of the relaxed units and, consequently, $\tau\beta$.

The formation of crosslinking was achieved through the determination of the density from equilibrium swelling measurements through the molar mass between crosslinks, which is M_c according to the Flory-Rehner relation:³¹

$$M_c = \frac{-\rho_p V_s V_r^{1/3}}{[\ln(1 - V_r) + V_r + \chi V_r^2]}$$

where ρ_p is the density of the polymer (SBR) = 0.945 g/cm³, V_s is the molar volume of the solvent (toluene) = 106.35 cm³/mol, χ is the interaction parameter be-

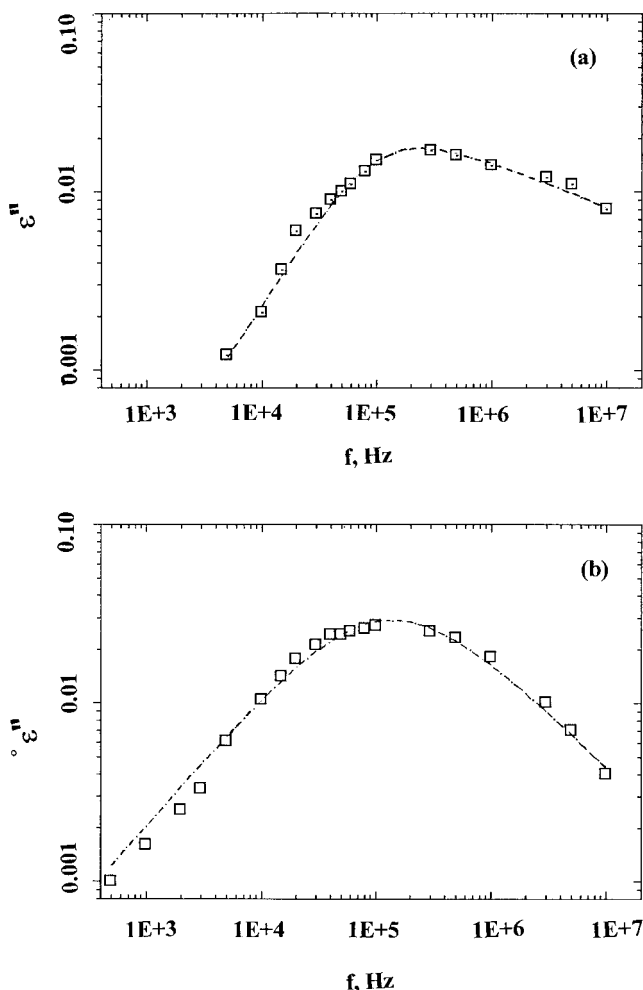


Figure 2 Example of the analyses of the data after subtraction of the losses due to the Maxwell-Wagner for samples containing (a) 0 and (b) 10 phr sulfur fitting the (□) experimental data with the Havriliak-Nagami function.

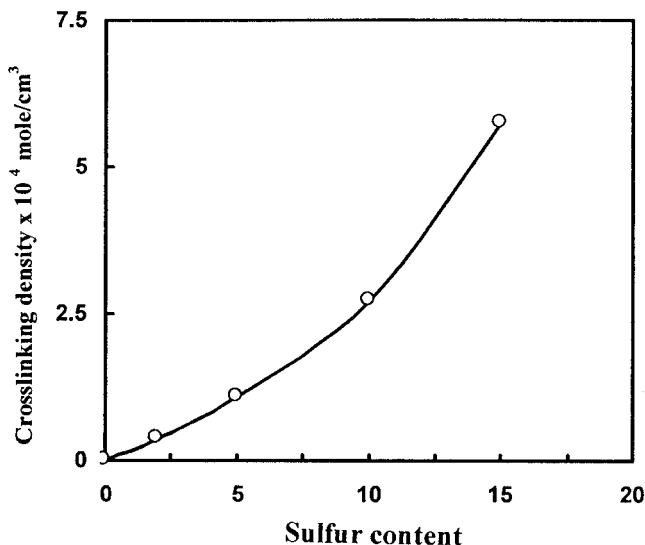


Figure 3 Relation between sulfur content and crosslinking density.

tween SBR and toluene = 0.378,³² and V_r is the volume fraction of swollen rubber and can be obtained from the masses and densities of the rubber sample and the solvent.³³ The degree of crosslinking (ν) is given by³⁴

$$\nu = 1/(2M_c).$$

Table I gives the values of ν for the different samples. The value zero was assigned to ν for the sample free from sulfur because this sample was totally dissolved in toluene.

From this table and from the graphical illustration of the data shown in Figure 3, it is clear that the degree of a crosslinking increased with increasing sulfur content as a result of the continuous formation of bridges between the polymer chains.

Effect of curing time

To study the effect of curing time on the dielectric properties of SBR, ϵ' and ϵ'' were measured for SBR samples containing 5 phr sulfur and cured at increasing curing times (10, 20, 30, 40, 50, and 60 min). The obtained data are illustrated graphically in Figure 4. From this figure, it is clear that the values of ϵ' slightly increased with increasing curing time, whereas those of ϵ'' decreased with increasing f . The variation of ϵ'' with f given in Figure 4(b) indicates a clear absorption region in the lower frequency range with a maximum frequency at about 500 Hz. For such process, the maximum values of ϵ'' decreased with increasing curing time, but the value of τ associated with such a process was the same and equal to 3.2×10^{-4} s. This process could be attributed to the Maxwell-Wagner effect, as mentioned earlier.

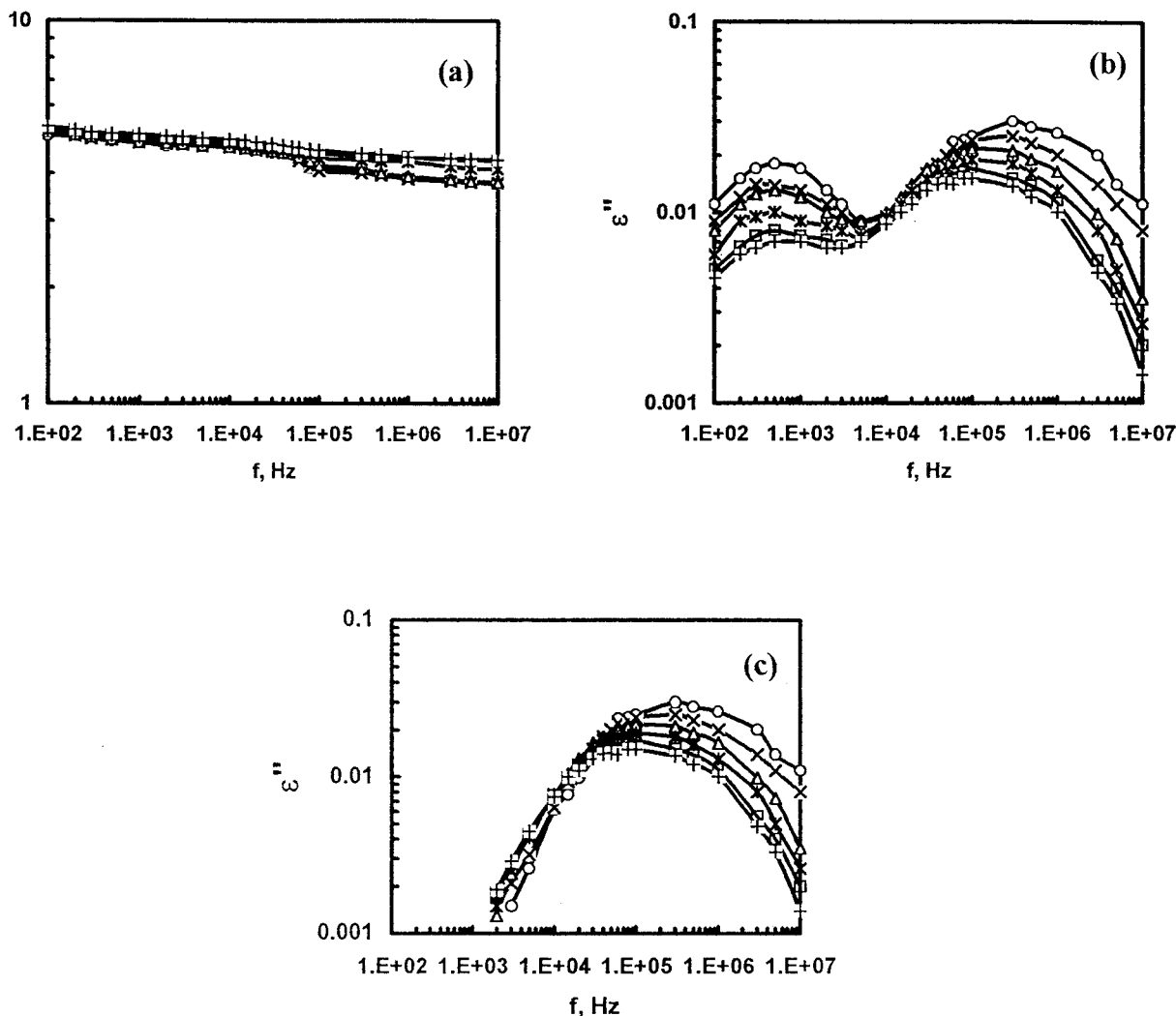


Figure 4 (a) ϵ' (b) ϵ'' and (c) ϵ'' after subtraction of the losses due to the Maxwell-Wagner effect versus f for SBR with different curing times: (○) 10, (×) 20, (△) 30, (●●●) 40, (□) 50, and (+) 60 min.

With regard to the changes in the other relaxation mechanisms, the losses due to the Maxwell-Wagner effect were subtracted from the total absorption as done before, and the obtained data are given in Figure 4. From this figure, it is clear that these curves are also broad, indicating that more than one relaxation process was present. The data were also found to be fitted by Havriliak-Nagami.²⁸ $\tau\beta$ and the parameters describing these systems are given in Table I. From this table, it is clear that the values of τ , which were expected to ascribe the orientation of the aggregates, increased with increasing curing time. The increase in τ , which was followed by a pronounced decrease in the relaxation strength (S), could be attributed to the increase in crosslinking.

To study the effect of the increase in the curing time on the formation of such crosslinking, we determined the crosslinking density using the Flory-Rehner equation, given previously, and the data obtained are depicted in Table I and illustrated graphically in Figure

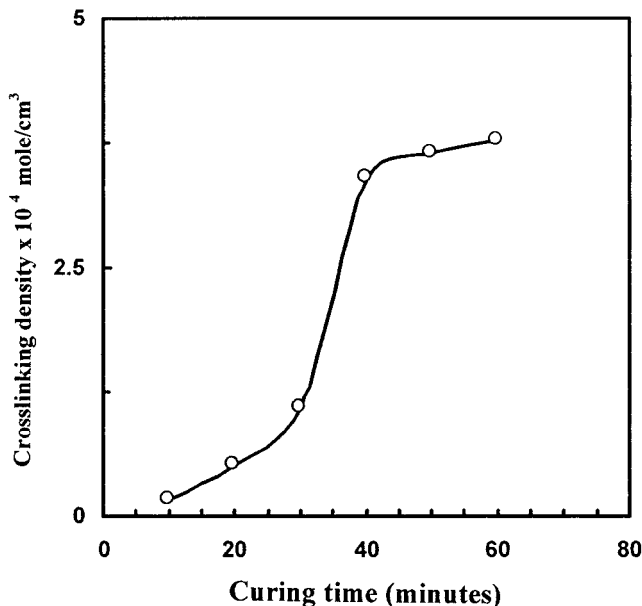


Figure 5 Relation between curing time and crosslinking density.

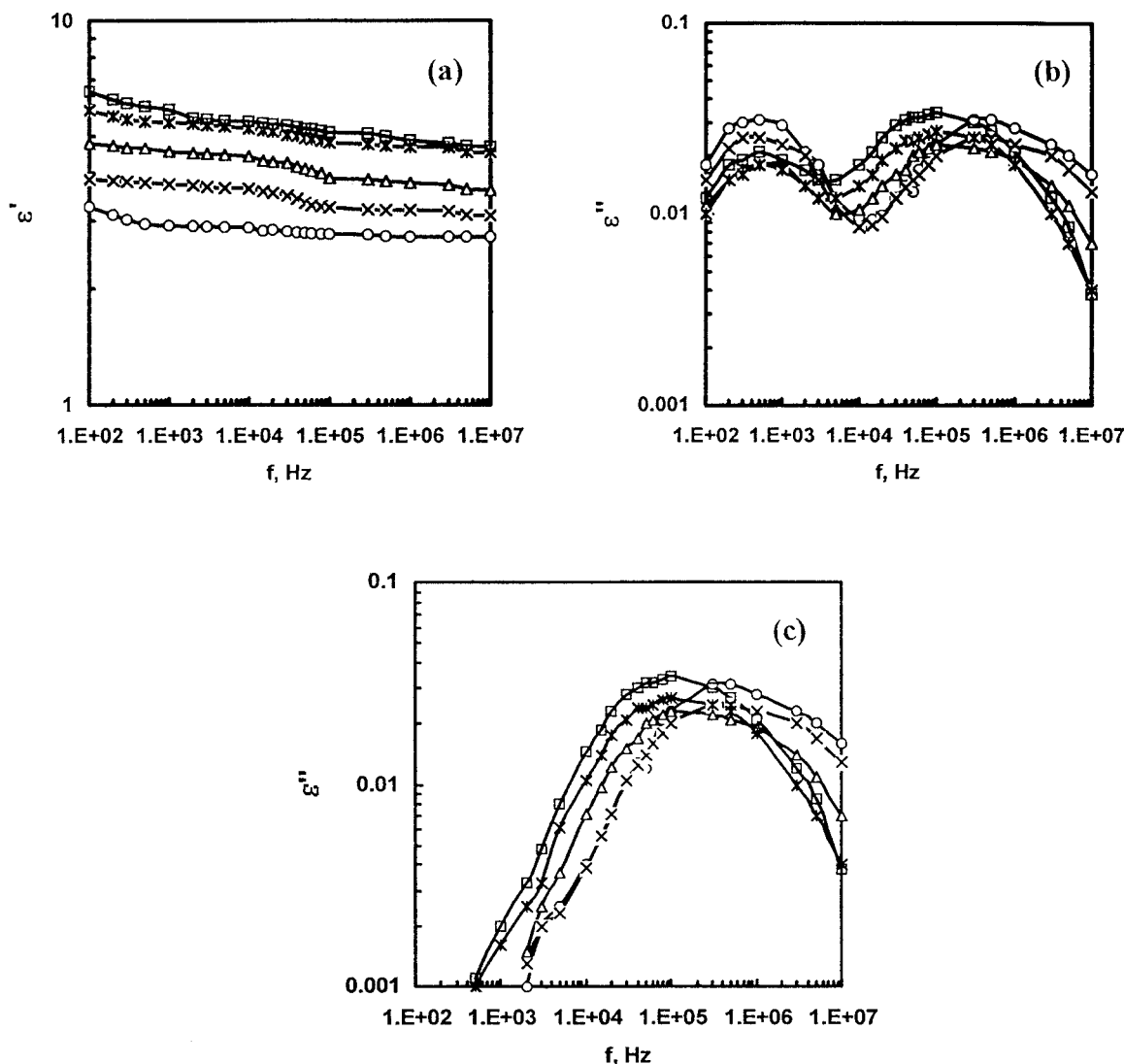


Figure 6 (a) ϵ' (b) ϵ'' and (c) ϵ'' after subtraction of the losses due to the Maxwell-Wagner effect versus f for SBR after 7 days of thermal aging at 90°C with different sulfur contents: (○) zero, (×) 2, (△) 5, (●●●) 10, and (□) 15 phr.

5. From this figure, it is clear that the crosslinking density increased with increasing curing time. This increase was much more pronounced up to 40 min, after which a slight increase was noticed and a plateau was reached; that is, a stable matrix was formed. This means that when the time was less than 40 min, the rubber matrix contained too many loose ends that were not connected in the network structure. This result was supported by the $\tau\beta$ data given in Table I.

Effect of thermal aging

Effect of sulfur

ϵ' and ϵ'' were remeasured for the previous samples after exposure to thermal aging for 7 days at 90°C , and the data obtained are illustrated graphically in Figure 6. From this figure, it is clear that the values of ϵ' increased with increasing sulfur content in the sample.

When the values of ϵ' obtained before aging (Fig. 1) are compared with those obtained after aging (Fig. 6), it is clear that a pronounced decrease in ϵ' occurred for samples containing 0, 2, and 5 phr sulfur, whereas no significant change was noticed for those containing 10 and 15 phr sulfur. However, ϵ'' increased markedly for the samples with low sulfur contents (< 10 phr), whereas it became less for samples with higher than 5 phr sulfur. This was contrary to that found before aging, as a continuous increase in ϵ'' was noticed when the sulfur content was increased. This increase, which was followed by a decrease in ϵ' , indicates that the samples cured for 30 min containing less sulfur than 10 phr lost to some extent their insulating properties. However, the samples that were cured for 30 min and having a sulfur content more than 10 phr were unchanged, indicating that these samples were good insulators and could resist thermal aging.

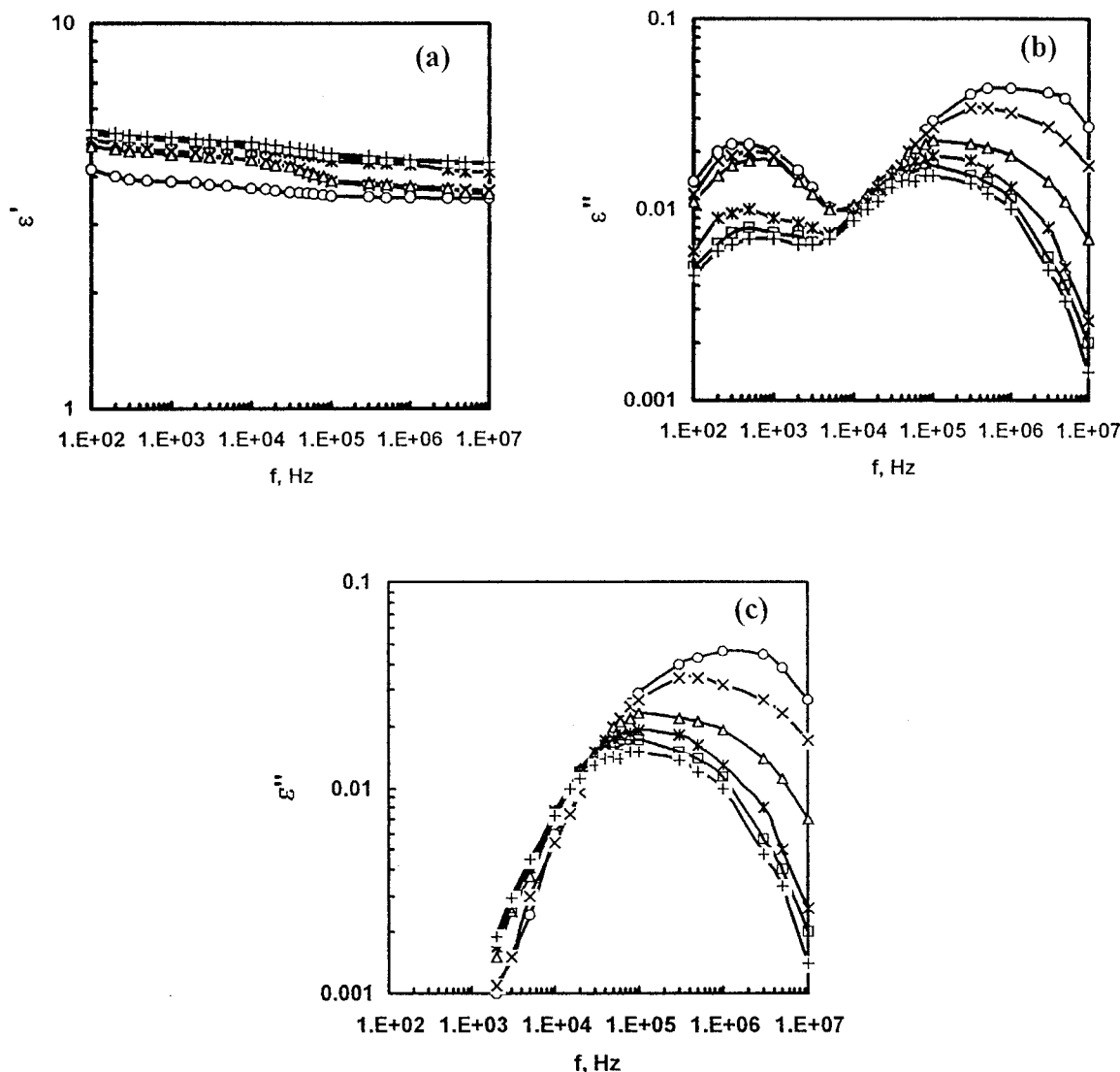


Figure 7 (a), ϵ' (b) ϵ'' , (c) ϵ'' after subtraction of the losses due to the Maxwell–Wagner effect versus f for SBR after 7 days of thermal aging at 90°C with different curing times: (○) 10, (×) 20, (△) 30, (●●●) 40, (□) 50, and (+) 60 min.

The relation between ϵ'' and the applied frequency, illustrated graphically in Figure 6, indicates a clearly detected absorption region in the lower frequency range with a maximum at a frequency of 500 Hz, which was ascribed to the Maxwell–Wagner effect, as mentioned previously. This means that this region was not affected by thermal aging. After subtraction of the losses due to the Maxwell–Wagner effect from the total absorption curves, the values of ϵ'' were still broad; this was analyzed with Havriliak–Nagami, and the obtained data are listed in Table I. From this table, it is interesting to find that at lower contents of sulfur (0, 2, and 5 phr), some sort of degradation of the formed crosslinking took place as the values of $\tau\beta$ decreased. After this concentration, no significant change was noticed, indicating some sort of stability for the formed polysulfidic crosslinks.

Effect of curing time

ϵ' and ϵ'' were also remeasured for SBR samples containing 5 phr sulfur and cured for increasing curing times (10, 20, 30, 40, 50, and 60 min) after exposure to thermal aging for 7 days at 90°C . The obtained data are illustrated graphically in Figure 7. From this figure, it is clear that the values of ϵ' increased with increasing curing time, whereas ϵ'' decreased, which was similar to that noticed before aging. When the data given before aging (Fig. 4) are compared with those after aging (Fig. 7), it is clear that ϵ' decreased markedly compared to samples cured at times up to 40 min. This decrease was followed by a pronounced increase in ϵ'' compared with those detected before aging. However, for the samples cured for times higher than 30 min, no pronounced change in either ϵ'

or ϵ'' was noticed, indicating good resistance to thermal aging.

The variation of ϵ'' with f given in Figure 7 indicates a clear absorption region in the lower frequency range due to the Maxwell–Wagner effect in addition to the relaxation, which was tested by the Havriliak–Nagami function to describe the orientation of the aggregates. The data obtained from such analyses are listed in Table I. When these values are compared with those obtained before aging, it is clear that the values of the $\tau\beta$ were lower than those before aging up to 30 min, after which some sort of stability was detected. The decrease in τ at lower curing times indicated some sort of degradation of the formed crosslinking, whereas the stability noticed at higher curing times indicated a high resistance for thermal aging.

In some cases, a distribution of τ s between two limiting values makes better physical sense. So, it was interesting to find that the dielectric data was fitted on the frequency domain by another function, the Fröhlich distribution:³⁵

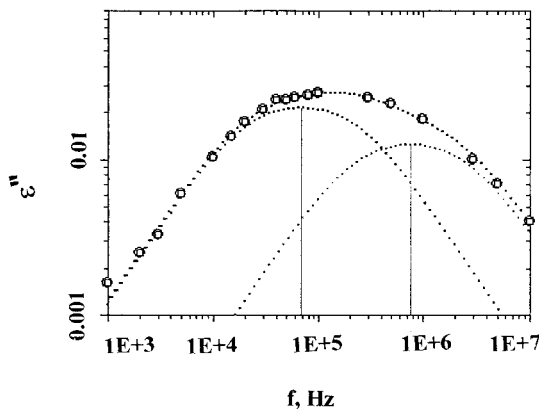


Figure 8 Example of the analyses of the data after subtraction of the losses due to the Maxwell–Wagner effect for a sample containing 10 phr sulfur, fitting the experimental data (○) with two Fröhlich terms.

$$\epsilon''(\omega) = \sum_{i=1}^n \frac{\epsilon_s - \epsilon_\infty}{P_i} \arctan \left[\frac{\sinh P_i/2}{\cosh \ln(\omega\bar{\tau}_i)} \right]$$

where P_i is a parameter that describes the width of distribution of τ s and equals $\ln(\tau_1/\tau_2)$ and $\bar{\tau}_i$ is the mean relaxation time and equals $(\tau_1\tau_2)^{1/2}$.

A computer program based on the Fröhlich equation was used to analyze the data of the whole investigated systems in two absorption regions. The data obtained from the analyses are given in Table II.

An example of the analyses for SBR containing 10 phr sulfur is given in Figure 8. The relaxation time τ_1 and τ_2 , obtained from such detected regions, were expected to ascribe the orientations of the big and small aggregates. Both relaxations increased with increasing sulfur content or curing time. The only difference was that $\tau\beta$, which was expected to ascribe the orientation of aggregates with the Havriliak–Nagami function, was substituted by two mechanisms to specify the orientations of both big and small aggregates between two limiting values, τ_1 and τ_2 .

However, thermal aging affected only the small content of sulfur up to 5 phr and curing times up to 30 min, which was similar to the result obtained in the case of the Havriliak–Nagami function.

TABLE II
Relaxation Parameters with the Fröhlich Equation Function of SBR

Sulfur content (phr)	$(\epsilon''_{\max})_1$	$\tau_1 \times 10^6$ (s)	$(\epsilon''_{\max})_2$	$\tau_2 \times 10^8$ (s)
Before aging				
0	0.015	0.8	0.008	4.0
2	0.016	1.1	0.009	6.4
5	0.018	2.0	0.011	15.9
10	0.022	2.3	0.013	19.0
15	0.028	2.5	0.015	21.2
After 7 days of thermal aging at 90°C				
0	0.028	0.53	0.014	2.7
2	0.022	0.72	0.013	4.0
5	0.02	1.6	0.012	10.6
10	0.022	2.3	0.013	19.0
15	0.028	2.5	0.015	21.2
Curing time (min)	$(\epsilon''_{\max})_1$	$\tau_1 \times 10^6$ (s)	$(\epsilon''_{\max})_2$	$\tau_2 \times 10^8$ (s)
Before aging				
10	0.025	0.9	0.0150	5.7
20	0.022	1.3	0.0130	8.0
30	0.018	2.6	0.0110	15.9
40	0.015	2.5	0.0100	21.2
50	0.013	2.9	0.009	22.7
60	0.012	3.2	0.008	24.5
After 7 days of thermal aging at 90°C				
10	0.033	0.64	0.028	4.0
20	0.028	0.80	0.020	5.3
30	0.020	1.6	0.012	10.6
40	0.015	2.5	0.0100	21.2
50	0.013	2.9	0.009	22.7
60	0.012	3.2	0.008	24.5

The authors are especially grateful to M. H. Youssef, Department of Physics, Faculty of Science, Cairo University, Geza, Egypt, for supplying us with the samples and for helping us with the calculation of the crosslinking density. The authors wish to thank Adel H. Soliman, Department of Physics, La Trobe University, Bundoora, Victoria, Australia, for his kind help with analyzing the data by the Havriliak–Nagami function.

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