Effect of New Additives on the Ultrasonic Attenuation and Mechanical Properties of Styrene–Butadiene Rubber

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SYNOPSIS

The change in attenuation of longitudinal ultrasonic waves has been measured as a function of frequency and temperature for styrene–butadiene–rubber (SBR) mixed with Ismacorr 141 as plasticizer and antioxidant. Analysis of the results showed relaxation processes and the activation energies for these processes were calculated and found to be related to the plasticization of samples. Also the velocity of the ultrasonic longitudinal waves through different samples was measured. The effect of Ismacorr 141 on the physical and mechanical properties of SBR was also studied.

INTRODUCTION

Many studies have been done on styrene–butadiene rubber as ultrasonic attenuation and physicomechanical properties.[1] Also the effects of oils and amines, which were used as antioxidant[2,3] and plasticizers,[4,5] were studied.

In this study the adduct used consists of a vegetable oil (linseed oil) and aniline. This adduct incorporated in the styrene–butadiene rubber is formulated to act as antioxidant and as antioxidant/plasticizer. The relaxation mechanism, which occurs in polymers under the action of temperature, was studied by several authors.[6-10]

The present investigation is devoted mainly to studying the effect of the compound under investigation on the physical properties of Styrene-Butadiene Rubber (SBR) using ultrasonic technique.

EXPERIMENTAL

Materials

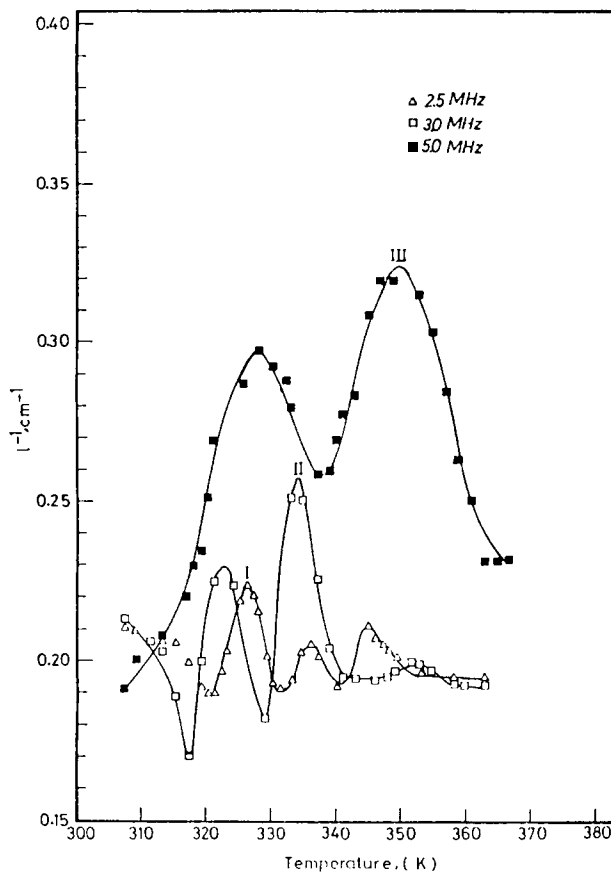SBR (1502) was used, Ismacorr 141 is a product of the Ismadye Company, Kafr-El-Dawar, Egypt, and

Figure 1 Relationship between attenuation l^{-1} (cm^{-1}) and temperature (K) at frequencies 2.5, 3, and 5 MHz for sample no. 1.

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Table I Formulations Containing the Prepared Compound (Ismacorr 141)

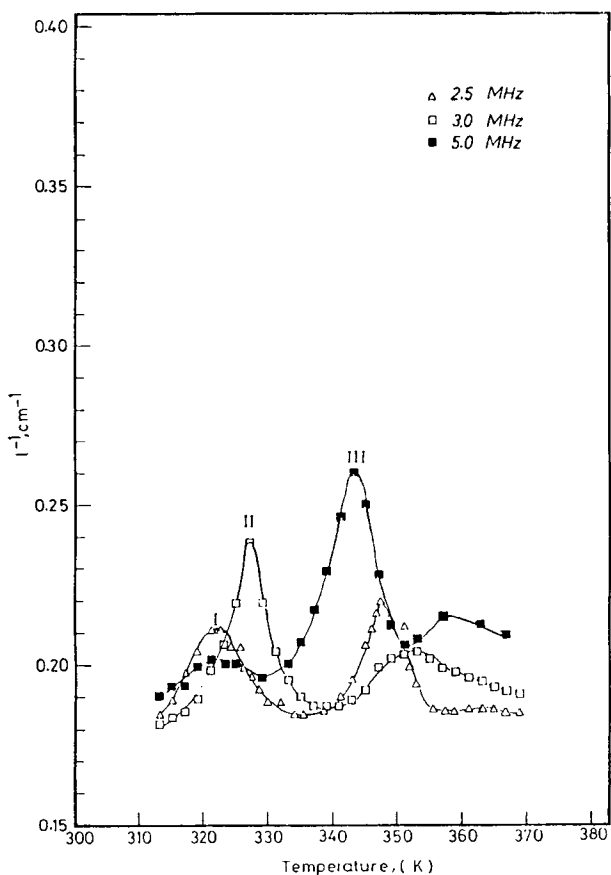| Ingredient \ Sample No.	1	2	3	4	5	6	7
SBR	100	100	100	100	100	100	100
Stearic acid	2	2	2	2	2	2	2
Zno	5	5	5	5	5	5	5
HAF carbon black	50	50	50	50	50	50	50
Processing oil	7	7	7	7	7	7	7
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5	2.5
MBTS	2	2	2	2	2	2	2
PBN	—	1	—	—	—	—	—
Prepared compound Ismacorr (141)	—	—	2	3	4	5	6

Figure 2 Relationship between attenuation l^{-1} (cm^{-1}) and temperature (K) at frequencies 2.5, 3, and 5 MHz for sample no. 2.
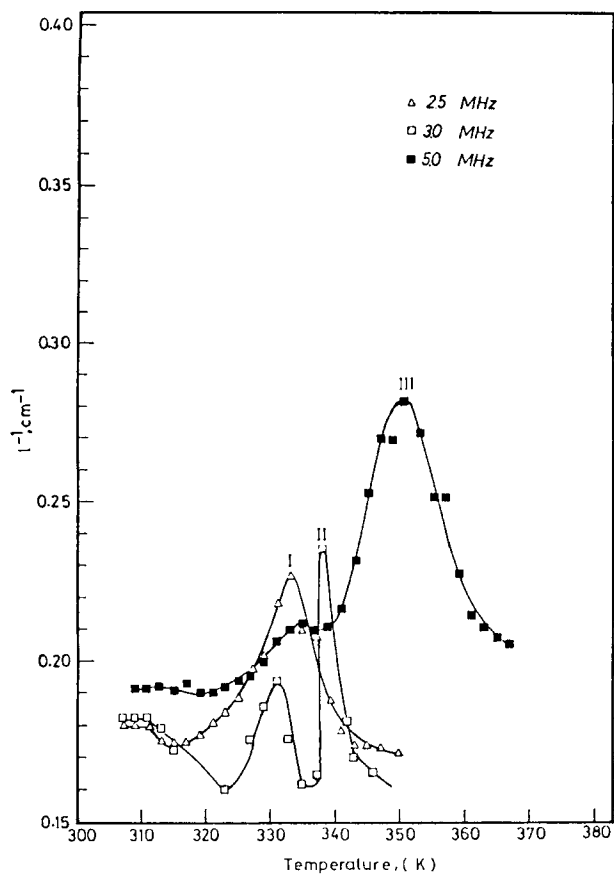

Figure 3 Relationship between attenuation l^{-1} (cm^{-1}) and temperature (K) at frequencies 2.5, 3, and 5 MHz for sample no. 3.

Table II   Formulations Containing the Prepared Compound (Ismacorr 141)

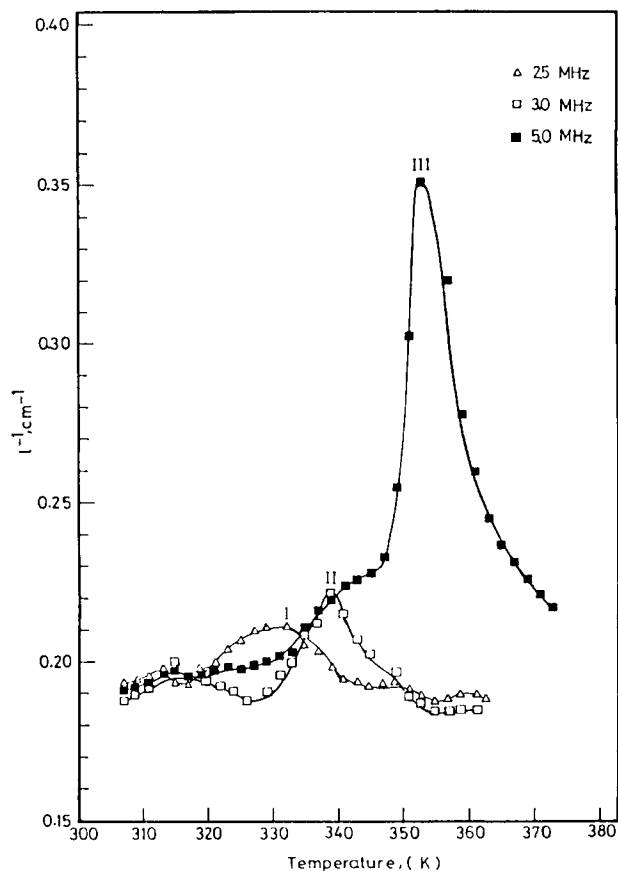| Ingredient \ Sample No.	1	2	8	9	10	11	12
SBR	100	100	100	100	100	100	100
Stearic acid	2	2	2	2	2	2	2
Zno	5	5	5	5	5	5	5
HAF carbon black	50	50	50	50	50	50	50
Processing oil	7	7	—	—	—	—	—
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5	2.5
MBTS	2	2	2	2	2	2	2
PBN	—	1	—	—	—	—	—
Prepared compound Ismacorr (141)	—	—	2	3	4	5	6

Figure 4   Relationship between attenuation l^{-1} (cm^{-1}) and temperature (K) at frequencies 2.5, 3, and 5 MHz for sample no. 4.
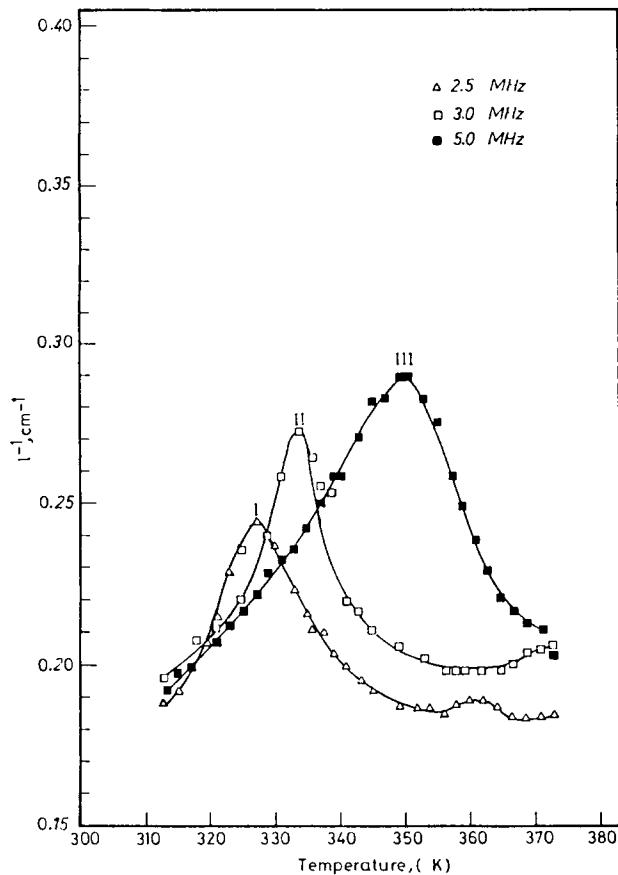

Figure 5   Relationship between attenuation l^{-1} (cm^{-1}) and temperature (K) at frequencies 2.5, 3, and 5 MHz for sample no. 5.
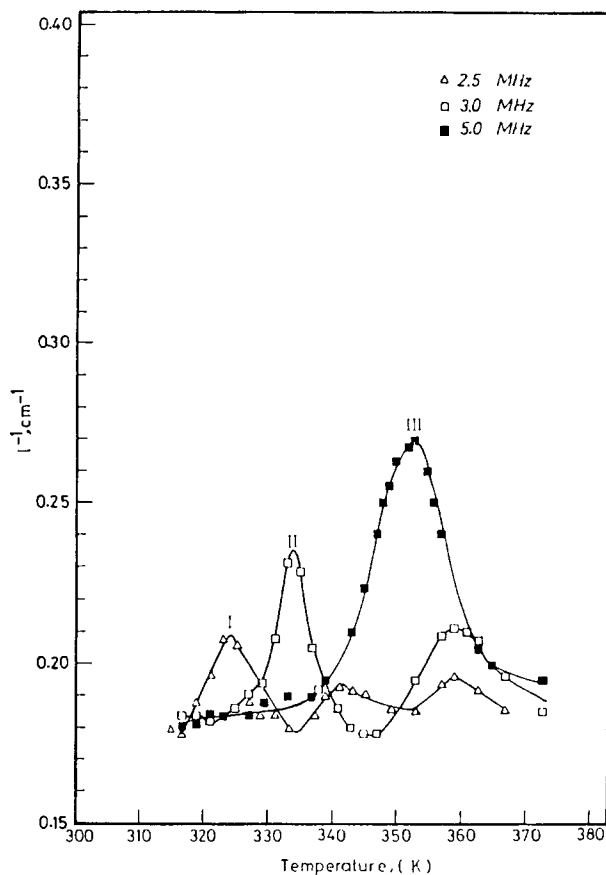
Figure 6 Relationship between attenuation l^{-1} (cm^{-1}) and temperature (K) at frequencies 2.5, 3, and 5 MHz for sample no. 6.

the rubber additives (stearic acid, ZnO, S, PBN, MBTS, and processing oil) are used in industry.

The basic formulae used for preparing the rubber samples, the control formulation, in addition to the formulation containing commercial antioxidant (PBN) which are used for the purpose of comparison, are given in Tables I and II.

Techniques

All rubber mixes were prepared on a two-roll mill 460 mm in diameter, working distance 250 mm, speed of slow roll 16 rpm, and gear ratio 2. The curing characteristics of the rubber compounds were measured using a Monsanto oscillating disc reometer Model 100. The vulcanization process was operated at 152 ± 1°C under a pressure of 140 kg/cm².

Ultrasonic measurements were carried out by a flaw detector USM2 produced by Kraut Kramer.[11]

The apparatus is capable of producing high frequency pulses in the frequency range 5-12 MHg.

The velocity of the ultrasonic longitudinal waves through the samples was measured using an experimental setup for measuring the flight time of the ultrasonic pulse in the rubber samples at room temperature, which consists of:

(a) Radio-frequency pulse source Model 755 RF, plugged in with the Model "660" pulse modulator and receiver in one main frame (Matec Inc., USA).

(b) Hewlett Packard oscilloscope Model 1743A with a capacity of 100 MHz.

Since the ultrasonic absorption α in polymers is much higher than that in metals, usually only one or two echos are observed in the oscilloscope screen.
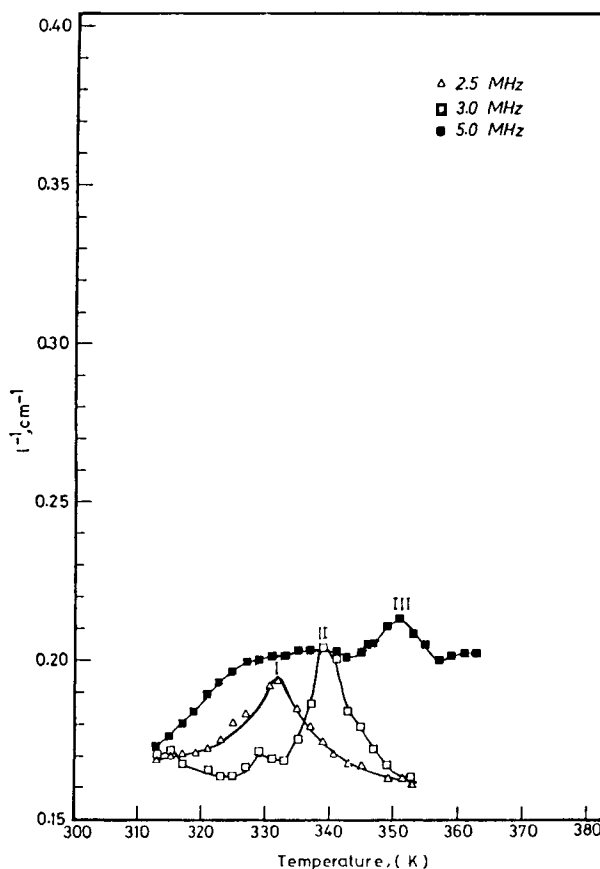

Figure 7 Relationship between attenuation l^{-1} (cm^{-1}) and temperature (K) at frequencies 2.5, 3, and 5 MHz for sample no. 7.

RESULTS AND DISCUSSIONS

Ultrasonic Results

The variation of absorption of longitudinal ultrasonic waves with temperature as a function of frequency is studied for the carbon-black-filled SBR vulcanizate samples. This variation was measured at frequencies ranging from 1 to 5 MHz and temperatures between 30 and 100°C. Also, the ultrasonic velocity of the same vulcanization was measured at room temperature only, because it was difficult to determine the thickness of the samples precisely as soon as the temperature changes.

Figure 1 represents the variation of attenuation of the ultrasonic waves, as a function of the reciprocal of the echo height l^{-1} (cm^{-1}) and T (K) at three different frequencies of the control sample no. 1. It is clear that the absorption of the ultrasonic waves increases with temperature to reach maximum
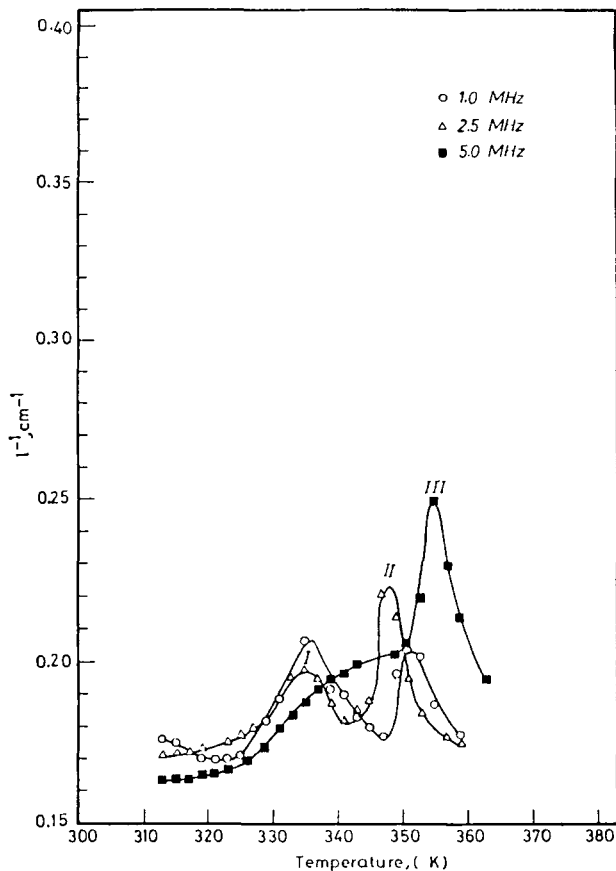
Figure 8 Relationship between attenuation l^{-1} (cm^{-1}) and temperature (K) at frequencies 1, 2.5, and 5 MHz for sample no. 8.

Accordingly, measurements were taken on a comparative basis where the variation of l^{-1} (l is the height of a particular echo on the oscilloscope) with temperature is considered to represent the variation of α with temperature, since they are related to each other by the equation $l = l_0 e^{-\alpha d}$, and have the same dimension of reciprocal height,[11,12] d the distance traversed and l_0 the amplitude of the pulse at $d = 0$. The measurements of the height of a particular echo l, on the face of the oscilloscope, was made by means of calibrated scale capable of measuring with an accuracy of ±0.2 mm. The temperature was achieved by an electric furnace.

A Zwick tensile testing machine 1497 was used for measuring the tension tests. The samples were measured at room temperature according to ASTM D-638. Thermal oxidative aging of vulcanized rubber was carried out in an oven at 90°C for different periods up to 7 days.
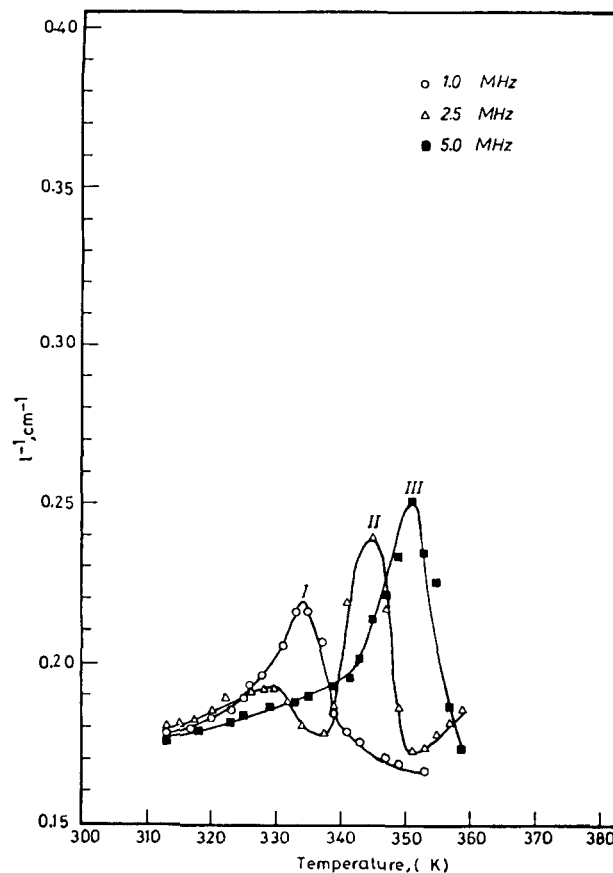
Figure 9 Relationship between attenuation l^{-1} (cm^{-1}) and temperature (K) at frequencies 1, 2.5, and 5 MHz for sample no. 9.
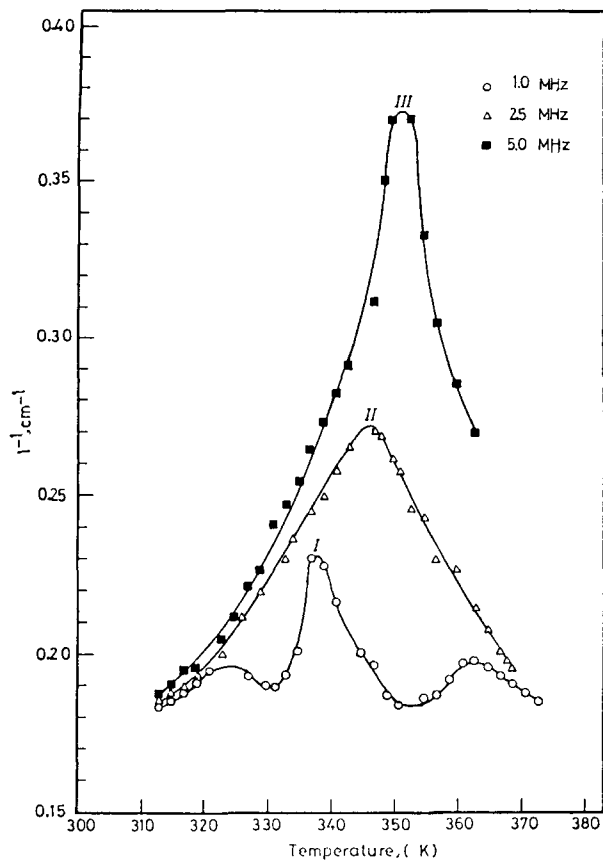
Figure 10 Relationship between attenuation l^{-1} (cm^{-1}) and temperature (K) at frequencies 1, 2.5, and 5 MHz for sample no. 10.

and then decreases, i.e., a peak is observed. This may be attributed, at the maximum absorption, to the order of magnitude of the molecular motion when it is comparable to the wavelength of the frequency used. The observed relaxation peaks shifted to higher temperatures and become higher with increasing frequency. The peaks are observed at 325, 334, and 350 K for frequencies 2.5, 3, and 5 MHz, respectively.

Figure 2 shows the results obtained for sample no. 2 containing the commercial antioxidant PBN and processing oil. The peaks are found to shift to a higher temperature and become higher with increasing frequency as shown in case of sample no. 1. These peaks are observed at 315, 327, and 343 K at frequencies 2.5, 3.0, and 5 MHz, respectively.

Figures 3–7 represent the behavior of the carbon-black-filled SBR samples containing different amounts of the compound under investigation, which is used as antioxidant, in the presence of pro-

cessing oil as a plasticizer. All the peaks are observed nearly in the same region of temperature 332 K (2.5 MHz), 338 K (3 MHz), and 353 K (5 MHz). From these figures, it can be noticed that the observed relaxation peaks for all samples (nos. 1–7) appear nearly at the same range of temperature, i.e., the increase of the concentration of Ismacorr 141 has no effect on the position of the relaxation peaks. Also, it can be said that the relaxation peaks of sample no. 2, which contained the commercial antioxidant PBN, slightly shifted towards a lower temperature. This may be attributed to the fact that PBN reduces the crosslinking density.

Figures 8–12 represent the carbon-black-filled SBR samples containing different concentrations of the compound under investigation (Ismacorr 141) as a bifunctional ingredient (antioxidant and plasticizer), i.e., without any addition of PBN or the processing oil. All the relaxation peaks are observed
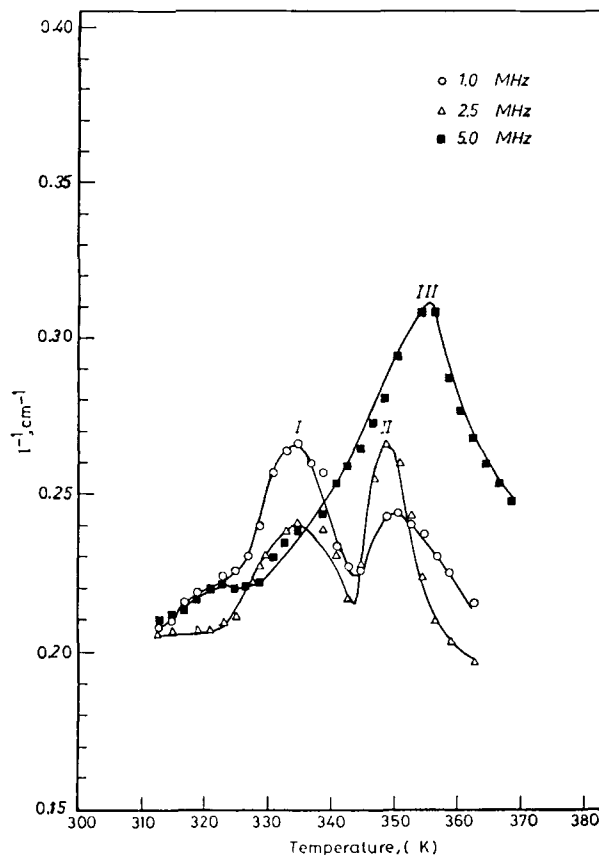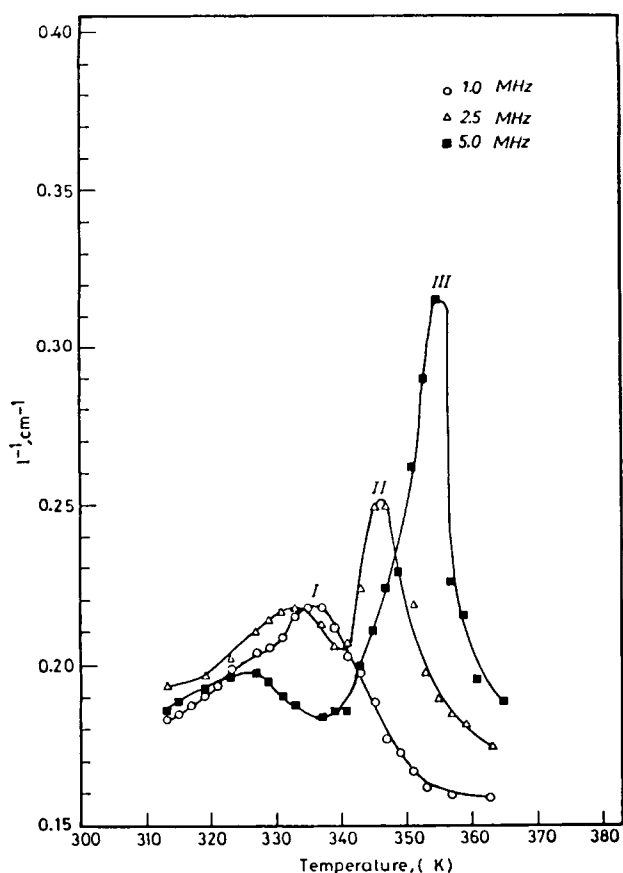

Figure 11 Relationship between attenuation l^{-1} (cm^{-1}) and temperature (K) at frequencies 1, 2.5, and 5 MHz for sample no. 11.

Table III   The Apparent Activation Energies (W) of the Relaxational Processes for Samples Nos. 1–12

Sample No.	The Fitting (r)	ln f_0	(W/K)	W (kcal/mol)
1	0.995	11.17	3350.78	6.655
2	0.9998	11.828	3503.7	6.958
3	0.9996	14.516	4531.4	8.999
4	0.996	12.737	3932.58	7.81
5	0.998	11.584	3493.75	6.939
6	0.994	9.475	2782.6	5.526
7	0.991	13.923	4329.4	8.598
8	0.995	28.776	9664.7	19.194
9	0.995	32.595	10897.1	21.642
10	0.993	36.821	12420.66	24.667
11	0.992	26.552	8907.22	17.690
12	0.999	30.132	10119.65	20.100

Figure 12   Relationship between attenuation l^{-1} (cm^{-1}) and temperature (K) at frequencies 1, 2.5, and 5 MHz for sample no. 12.

in the same temperature range (334 K (1.0 MHz), 345 K (2.5 MHz), and 355 K (5 MHz).

The apparent activation energies of the relaxational processes of the whole vulcanizates under investigation were calculated using the Arrhenius equation $f = f_0 e^{-E/KT_m}$, where f is the operating frequency of the ultrasonic wave, f_0 is the natural frequency of the relaxation process, T_m is the absolute temperature corresponding to the peak, and K is the Boltzman constant. The relation between ln f and $1/T_m$ can be represented as a straight line of the form

$$\ln f = \ln f_0 - (W/K)(1/T_m)$$

from the slope of this straight line, the activation energies of the samples (nos. 1–12) were calculated and listed in Table III.

The values of the apparent activation energies lead to the conclusion that the relaxation is of secondary or β type, which could be attributed to the playable side groups in the amorphous region.[13-15] It was also suggested that the motion associated with the β-relaxation is possible even in crystalline defects because this type of relaxation is local. Accordingly, the β-relaxation due to amorphous phase can be distinguished from the β-relaxation due to crystalline defects where the former is a high-temperature process and the latter a low-temperature one. These relaxations are comparable with those found before at frequencies 10^5–10^7 Hz in the range

Table IV   Rheometric Characteristics of SBR Mixes at 152 ± 1°C and Physicomechanical Properties of Vulcanizates

Sample No. Character	1	2	3	4	5	6	7
Minimum torque M_L (dN m)	26.5	26.5	25.0	24.0	23.0	20.5	21.5
Maximim torque M_L (dN m)	94.0	94.0	100.5	97.5	97.0	99.0	94.5
Torque at 90% of maximum torque M_{c90} (dN m)	87.25	87.25	92.95	90.15	89.60	91.15	87.20
Scorch time t_{S2} (min)	4.25	3.75	3.625	3.50	3.30	3.15	2.15
Cure time t_{c90} (min)	40.0	39.0	33.25	31.0	26.0	19.25	17.5
Cure rate index (CRI) (min^{-1})	2.80	2.84	3.376	3.640	4.405	6.21	6.78
Tensile strength (MPa)	144.7	158.2	166.3	150.0	156.1	146.5	150.0
Modulus at 200% (MPa)	71.0	71.9	72.0	70.0	69.7	62.0	63.7
Elongation at break (%)	330	370	375	370	365	395	390
Equilibrium swelling (%)	198.0	190.8	190.82	191.22	193.02	195.0	196.5

Table V   Rheometric Characteristics of SBR Mixes at 152 ± 1°C and Physicomechanical Properties of Vulcanizates

| Sample No. Character	1	2	8	9	10	11	12
Minimum torque M_L (dN m)	26.5	26.5	15.25	17.75	18.5	17.0	16.25
Maximum torque M_L (dN m)	94.0	94.0	102.0	110.0	111.0	108.0	106.0
Torque at 90% of maximum torque M_{C90} (dN m)	87.25	87.25	93.33	100.78	101.75	98.9	97.08
Scorch time t_{S2} (min)	4.25	3.75	3.5	3.69	3.25	3.00	3.00
Cure time t_{c90} (min)	40.0	39.0	37.50	28.75	22.50	18.00	16.25
Cure rate index (CRI) (min^{-1})	2.80	2.84	2.94	3.99	5.19	6.67	7.55
Tensile strength (MPa)	144.7	158.2	193.9	194.8	186.00	197.50	206.50
Modulus at 200% (MPa)	71.5	71.9	101.0	114.75	114.88	110.25	103.0
Elongation at break (%)	330	370	310	315	300	295	290
Equilibrium swelling (%)	198.0	190.8	171.4	165.6	162.18	165.1	168.0
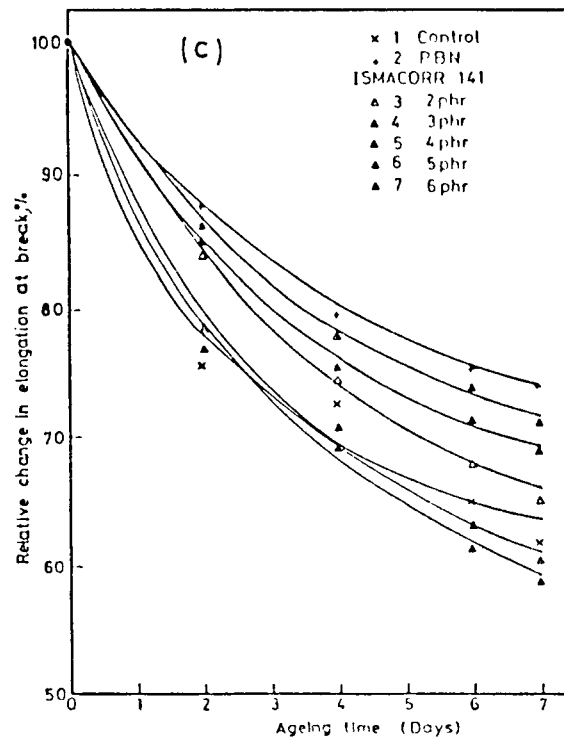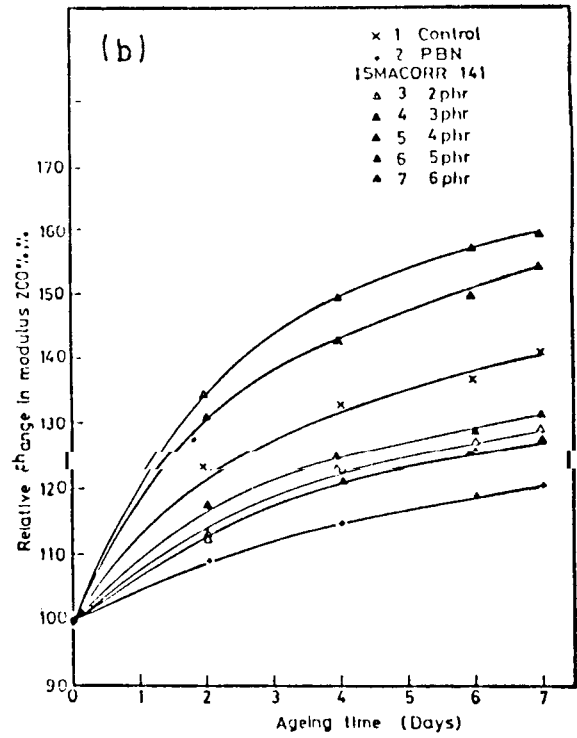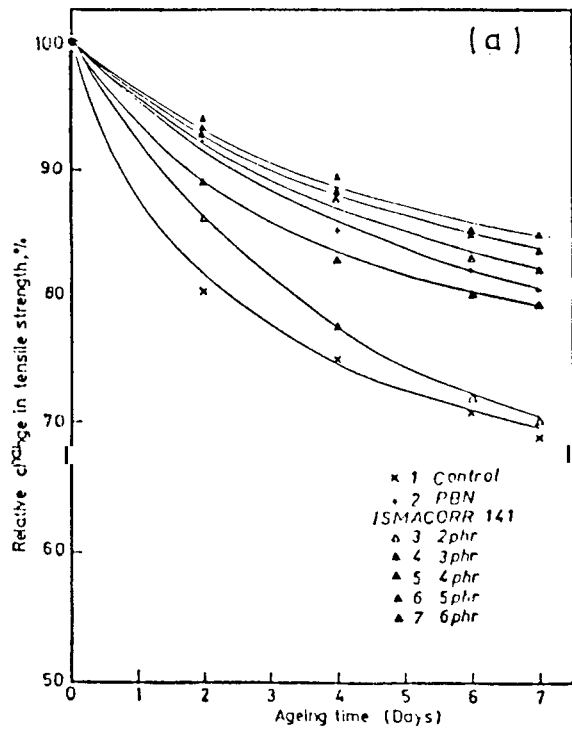
Figure 13 (a) Relationship between relative change in tensile strength (%) and aging time (days). (b) Relationship between relative change in modulus 200% elongation and aging time (days). (c) Relationship between relative change in elongation at break (%) and aging time (days). For samples 1, 2, and from 3 to 7.
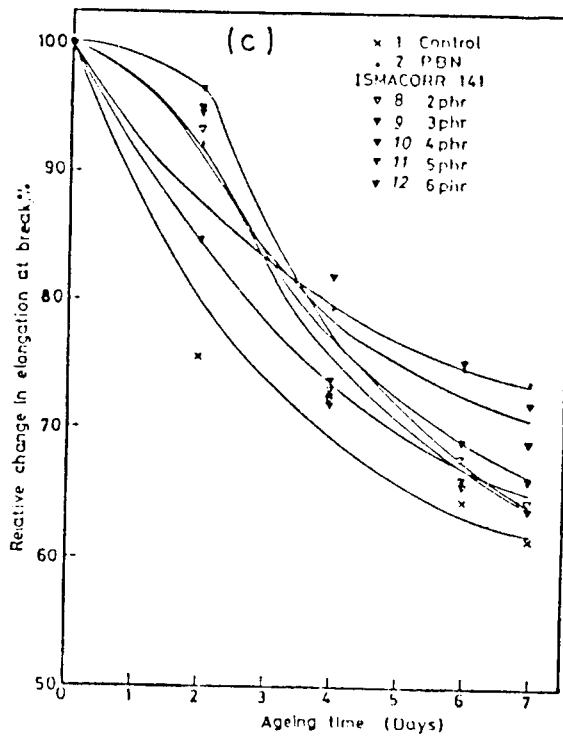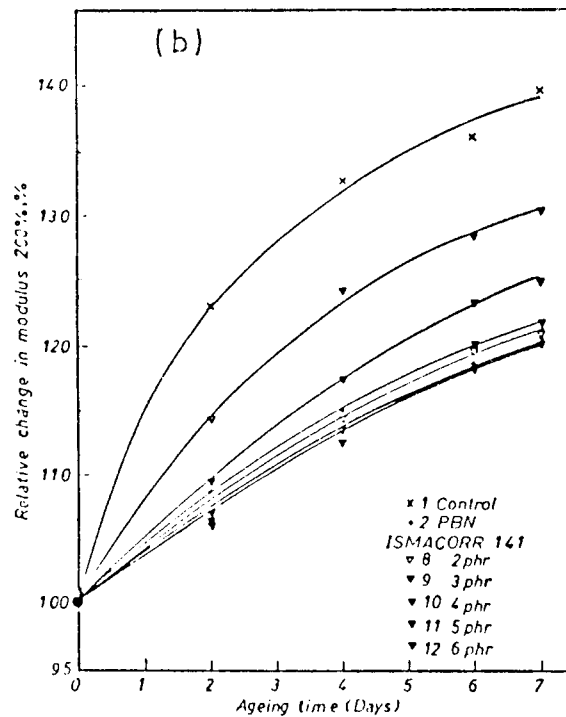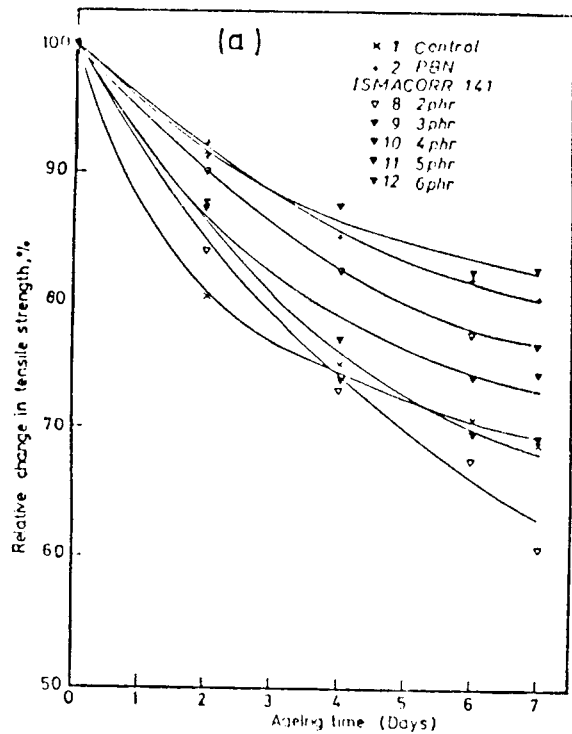
Figure 14 (a) Relationship between relative change in tensile strength (%) and aging time (days). (b) Relationship between relative change in modulus 200% elongation and aging time (days). (c) Relationship between relative change in elongation at break (%) and aging time (days). For samples 1, 2, and from 8 to 12.

of temperature between 20 and 50°C.[16] This result is also supported by the activation energies for such relaxations which are found in the order of 6.0–24.6 kcal/mol.

From Table III, no pronounced change in the values of the activation energies is noticed by the addition of Ismacorr 141 with different concentrations in the first group of samples (nos. 3–7). It is interesting to find that the activation energies for the samples which do not contain processing oil (nos. 8–12) are higher than those containing processing oil. In addition, the concentration of the Ismacorr adduct has more or less no effect on the activation energies of this group of samples.

This could be attributed to the increase in the degree of crosslinking which is highly increased due to the absence of the processing oil which causes a restriction in the motion of the playable side groups; this conclusion will be supported by the physicomechanical properties following the latter in Tables IV and V.

The velocity of ultrasonic wave in carbon-black-filled SBR samples was measured at room temperature using a probe at frequency 4 MHz. It is found that the velocity of the ultrasonic waves is nearly the same in all vulcanizates either in those having the processing oil or not. This may be due to the fact that the ultrasonic waves pass through the same matrix, and it is clear that the additives have more or less no effect on the velocity of the ultrasonic waves in this type of matrices.

Physicomechanical Results

The compound under investigation (Ismacorr 141) was incorporated in carbon-black-filled SBR formulations by different concentrations up to 6 phr to study its effect as antioxidant and as antioxidant/plasticizer in the presence of processing oil. The rheometric characteristics of the above-mentioned formulations were studied at 152 ± 1°C and their physicomechanical properties were measured. Both are given in Tables IV and V.

In both cases it is noticed that the cure time (t_{c90}) and the scorch time (t_{s2}) decreased linearly with increasing the concentration (c) of the Ismacorr 141 with fitness ≥ 0.99. The cure rate index (CRI) is found to increase by increasing Ismacorr 141. This indicates that Ismacorr 141 can play the role of secondary accelerator.

Also the apparent activation energy of the vulcanization process was calculated according to Ar-

rhenius equation from the rheometric characteristics at (152 ± 1°C, 172 ± 1°C, and 182 ± 1°C) and it is noticed that the oil/amine did not affect it for all concentrations used.

The rubber vulcanizates were subjected to thermal oxidative aging at 90°C for different periods of time up to 7 days.

The dependance of the relative changes in tensile strength, the modulus at 200% elongation and the elongation at break on the aging time were measured and illustrated graphically in Figures 13 and 14. From these figures it is clear that the behavior of the relative changes of all the properties obeys the power relationship of the general formula

$$R = at^b$$

where R is the relative change of the property, t is the aging time in days ($2 < t < 7$), and a and b are constants.

The first derivative of the above-mentioned equation dR/dt will be the slope of the curve at any point, i.e., (dR/dt) the rate of change in any property. Thus the minimum slope will be the minimum rate of change, i.e.,

$$dR/dt = abt^{(b-1)}$$

From the study of the rate of change of property (dR/dt) with the compound under investigation (Ismacorr 141), it can be concluded that 3 and 4 phr of Ismacorr 141 are considered to be the optimum concentrations which have the higher efficiencies as antioxidant and as antioxidant/plasticizer.

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