

The Effect of Fillers on Relaxation Phenomena of Vulcanized Styrene–Butadiene Elastomers

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SYNOPSIS

Standard recipe mixtures, based on styrene/butadiene rubber SBR 1500 and oil-extended SBR 1712, with varying amounts of carbon black, silica, or kaoline fillers were prepared and the stress relaxation curves of vulcanized samples were determined. The measurements were restricted to slow relaxation phenomena, observed after 50% initial elongation. Three λ -processes and a fourth ϕ -process, existing only in filled rubbers, were observed. The relaxation times and activation energies, determined graphically, reflect the amount and activity of the fillers. All relaxation times are lower for filled vulcanizates and decrease with increasing temperature; however, the type of filler does not affect the activation energy. The higher parameters observed for the ϕ -processes are discussed in terms of filler particle mobilities and rearrangements and of filler/rubber contact layer phenomena. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Elastomers demonstrate a multiplicity of relaxation phenomena that can be linked to the kinetics in the polymer structure. All relaxation phenomena in elastomers can be divided into groups according to the mobility of single groups, chain segments, or the molecule as a whole. All phenomena are characterized by relaxation times ranging from 10^{-10} to 10^{10} s. The relaxations can be analyzed and the relaxation times determined by relaxation spectrometry involving dynamic or static measurements. Discrete relaxation phenomena of elastomers can be described by generalized Maxwell models. Figure 1 represents a typical relaxation spectrum of a cross-linked elastomer containing a reinforcing filler.¹

The designation of relaxation peaks in a relaxation spectrum is more or less a matter of convention. The most pronounced relaxation maximum in the region of the glass transition temperature is designated as the α -transition, where the kinetic unit involved is the segment. Two groups of relaxation peaks are recognized in the region of very short re-

laxation times. β -Transitions result from conformational changes of small substituent groups, such as methyl, ethyl, or phenyl, taking place even at very low temperatures. γ -Transitions with slightly longer relaxation times represent restricted kinetic movements of small-chain or substituent segments. The third group of α -transitions involves the segment as the kinetic unit, with linear dimensions of the order of 3–4 nm at 293 K. This type of transition is present in every rubber, irrespective of the presence of fillers. In composites, an α' -transition can be observed, with a slightly higher relaxation time than for the α -process, resulting from the mobility of the segments adsorbed on the surface of the filler particles. The α' -transition is characterized by the same preexponential factor B as is the α -transition, but with a higher energy of activation U_i . This transition is observed at a temperature slightly above the α -transition^{1–3} and results from the mobility of the segment in the boundary interphase layer.^{1,4} According to published investigations, the mobility of the segments in the interphase layer does not depend on the filler activity.^{5–7} The fourth group of phenomena are λ -transitions, which are observed above the T_g in the viscoelastic region. Very often, as many as three relaxations, λ_1 , λ_2 , and λ_3 , are observed. In copolymers, this number can be even higher. The

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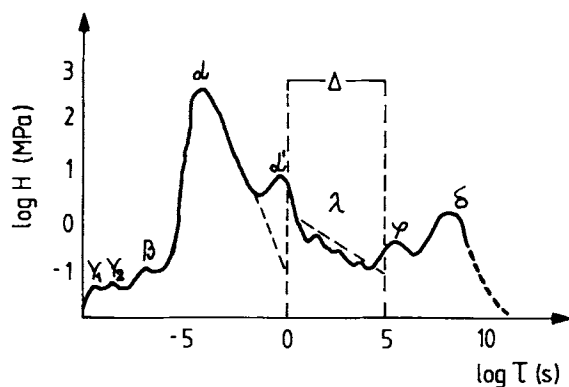


Figure 1 The continuous spectrum of relaxation phenomena in cross-linked elastomers containing reinforcing fillers^{1,2}: (Δ) the region investigated in this research.

transitions of this group result from ordered domains in the matrix, i.e., the supramolecular structures. Relaxations of this type are slow and are usually manifested as creep or viscous flow. In the case of cross-linked polymers, these relaxations involve mainly physical cross-link knots of the polymer net. The fifth group represents ϕ -relaxations, linked to the mobility of colloid filler particles and their rearrangements within the matrix. From the previous considerations, it is evident that α' and ϕ -transitions are present in the continuous relaxation spectrum only when polymers containing fillers are considered. The peaks of these two transitions will be proportional to the content of the filler in the system.

Regarding experimental techniques, dynamic relaxation measurements are applied for relaxations involving relaxation times up to 1 s, designated as fast relaxations. Static methods are applied for processes represented by relaxation times between 1 and $1 \cdot 10^{10}$ s, designated as medium or slow relaxations.

It is believed that the adsorption and interaction of rubber molecules on the filler particle surface is equivalent to the formation of additional cross-links in the vulcanized matrix⁸ and that, as a consequence, due to the reduced mobility of polymer segments, the relaxation times should increase.⁹ Other authors expressed the opposite opinion, expecting faster relaxation times in filled elastomers.¹⁰ Payne¹¹ studied the dynamic properties of carbon black-loaded natural rubber vulcanizates and demonstrated the effect of the filler, viz., the carbon black type on the dynamic shear modulus G_0 . The results are attributed to the chainlike structure of the carbon black particles in the rubber matrix. Lobe and White¹² performed stress-relaxation measurements similar to our investigation on a carbon black-loaded polysty-

rene melt: The relaxation modulus increased with carbon black loading and generally decreased with time, tending to zero for the unloaded melt and to small but finite values for the loaded melt. The aim of the present work should shed more light on the problem of the relaxation of styrene-butadiene vulcanizates with various types of fillers.

EXPERIMENTAL

Two basic vulcanization mixtures were prepared, based on the styrene-butadiene rubbers SBR 1500 and SBR 1712, both products of the Synthetic Rubber Factory, Elemir, Yugoslavia. The following fillers were used: The first was carbon black N-330, a product of INA-Petrokemija, Kutina, designated as ROF 58, with an iodine absorption number of 83.8 mg/g and a dibutylphthalate absorption of 105 ccm/100 g. The second filler was Vulkasil C, a product of Bayer, Germany, and the third, Kaolin BG of Tamnava, Donje Crniljevo, Yugoslavia. Sulfur was a product of Zorka, Sabac, and the accelerator was Vulkacit CZ, representing *N*-cyclohexyl-2-benzothiazole sulfenamide, from Bayer. The vulcanization activators were zinc oxide and stearic acid of commercial origin. The ISO test mixture 2322/75E was prepared for all investigations, with variations of the filler content, as outlined in Table I.

The mixing was performed on a laboratory two-roller mixer according to the (Yugoslav) JUS G.Cl.071 standard. The optimal time of vulcanization was determined on a Monsanto 100 rheometer according to the JUS G.S2.118 standard. The cross-linking was performed at 433 K and 18 MPa in a standard vulcanization press.

The activity of the fillers was determined from the mechanical properties of the vulcanized rubber, prepared either with styrene/butadiene standard-

Table I Recipes for the Preparation of Rubber Mixtures (Mass Parts)

Component	Mixture Based on SBR 1500	Mixture Based on SBR 1712
SBR	100	100
Mineral oil	—	37.5 ^a
Filler	0, 20, 40, 60	0, 60
Sulfur	1.75	1.75
Stearic acid	1.00	1.00
Zinc oxide	3.00	3.00
Vulkacit CZ	1.00	1.00

^a Incorporated in the 100 parts of SBR 1712.

type rubber SBR 1500 or with oil-extended SBR 1712 and 40 parts of filler, as presented in Tables II and III. According to the data presented, the most active filler was carbon black N-330, followed by Vulcasil C and, finally, Kaoline BG.

The relaxation times and the energies of activation, U_i , of the relaxation transitions were calculated from the stress-relaxation measurements. These were performed on an Instron tensile table tester model 1122 at 293, 303, 313, 323, 333, 343, and 353 K and at 50% elongation. The test samples were rectangular, and the working length was 30 mm; width, 15 mm wide; and thickness, about 1 mm. The deformation rate was 1000 mm/min, and the ultimate deformation, 50%. The stress relaxation of the samples was followed for 5 h and occasionally even longer, but not to complete relaxation.

Determination of the Relaxation Curves and Relaxation Time¹³

The stress-relaxation curves of the cross-linked polymers, presented in Figure 2, consist of two parts: a nonlinear part AB, which corresponds to the physical relaxation, and a linear part BC, which corresponds to the process of relaxation of the network knots in its primary stadium, as the period of investigation was considerably shorter than the relevant relaxation time.

The net stress at any time can thus be described by the following equation:

$$\sigma'(t) = \sigma'_1(t) + \sigma'_2(t) + \sigma'_3(t) \quad (1)$$

The measurement of time in our experiment started from 1 s, i.e., the fast stadium of relaxation was not investigated. Therefore, $\sigma'_1(t)$ in the previous equation equals zero and the relaxation curve in Figure 1 is therefore represented by

$$\sigma'(t) = \sigma'_2(t) + \sigma'_3(t) \quad (2)$$

Table II Rheometric Values of the Mixture Based on SBR 1500 with 40 Mass Parts of Filler, 353 K

Filler	t_2 (min)	t_{90} (min)	M_{90}
Carbon black	6	16	40.48
Vulkasil C	9	20	31.55
Kaolin BG	10	35	28.45

To obtain the curve of the slow physical relaxation $\sigma'_2(t)$, it is necessary to separate the relaxation curve ABC from the linear part DBC. The nonlinear part represents the physical relaxation and BC corresponds to the chemical relaxation $\sigma'_3(t)$:

$$\sigma'_2(t) = \sigma'(t) - \sigma'_3(t) \quad (3)$$

In the case of linear viscoelasticity, the expression for the relaxation stress can be written in the following form:

$$\sigma'_2(t) = \epsilon_0/E(t) = \epsilon_0 \sum_{i=1}^m E_i \cdot e^{-t/\tau_i} \quad (4)$$

where ϵ_0 is the zero time of deformation; $E(t)$, the modulus that characterizes the slow stadium of the viscoelastic deformation; τ_i , the relaxation time of the i -th element of the elementary relaxation mechanism; and E_i , the contribution of the i -th relaxation process to the overall relaxation.

If it is assumed that the distribution of the relaxation times for elastomers can be described by a discrete distribution, then from eq. (4),

$$E(t) = E_1 e^{-t/\tau_1} + E_2 e^{-t/\tau_2} + \dots + E_n e^{-t/\tau_n} \quad (5)$$

The experimental data of the stress relaxation were treated graphically according to a method proposed by Tobolsky and Murakami.¹⁴ This approach is based on the assumption that the real relaxation process is composed of separate elemental relaxation processes, with individual relaxation times that differ considerably among themselves. The $E(t)$ dependence is represented in the coordinate system $\log(E)t$ vs. t . For sufficiently high values of t , all the exponential members of eq. (5) are practically equal to zero, except for the last one. The longest relaxation time τ_i is determined from the slope of the linear part of the curve. The intercept obtained by the extrapolation of the lower linear part of the ordinate equals $\log E_n$. $\log[E(t) - E_n \exp - t/\tau]$ vs. t is then found in an analogous way, followed by other relaxation times τ_i and the coefficient E_i .

The energy of activation U_i can be determined from experimental data from the straight lines obtained in the $\log \tau_i$ vs. $1/T$ plot, according to eq. (6). The preexponential constant B_i is calculated from the intercept on the $\log \tau_i$ axis. The slopes and intercepts were evaluated according to the least-squares method:

$$\tau_i = B_i \cdot e^{-U_i/kT} \quad (6)$$

Table III The Activity of the Fillers Expressed in Terms of the Mechanical Properties of the Vulcanizate Based on SBR 1500 with 40 Mass Parts of Filler

Filler	Tensile Strength (N/mm ²)	Elongation at Break (%)	Modulus 300 (N/mm ²)	Hardness (Shore)
Carbon black	27	440	12	70
Vulkacil C	16	700	7	53
Kaolin BG	8	605	3	47

where i represents the relaxation time of the i -th process; U_i , the energy of activation of the i -th process, depending on the character of the interaction of kinetic units; B_i , the preexponential factor, depending on the frequency of collisions and on the size of the kinetic units and interaction forces between them; T , the absolute temperature; and k , the Boltzmann constant.

RESULTS AND DISCUSSION

The results of this investigation are presented in Table IV, referring to vulcanized samples based on SBR 1500 with 0, 20, 40, and 60% carbon black filler. In Table V are the results for samples based on SBR 1500 and Vulkasil and kaolin filler, and in Table VI, for samples based of SBR 1712 and 60% carbon black filler.

From the results presented in Table IV and also in the tables that follow, it can be seen that the slow relaxation is composed of several simple λ -processes. The relaxation times of the three observed λ -processes are numerically different and decrease with increasing temperature both for unfilled and filled mixtures. The relaxation times for unfilled mixtures of all three λ -processes are higher from those with 60 mass parts of filler (Table IV). The relaxation times increase, going from λ_1 to λ_3 , indicating that

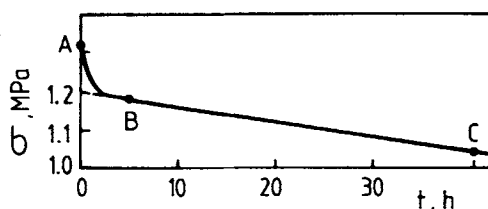


Figure 2 The stress-relaxation curve of a cross-linked elastomer,⁶ represented by ABC; AB, the nonlinear part; BC, the linear part.

microblocks involved in the relaxation phenomena are larger in the case of the λ_3 - than in the λ_1 -process.

The preexponential coefficients B_λ are also different for all three processes. The difference observed can be explained by the size of the microblocks. The probability of disintegration of larger microblocks is lower than that of smaller microblocks and is proportional to the reciprocal of B_i . This observation is linked to the assumption that in unfilled rubbers and in the soft phase of filled rubbers, globular, folded, and micellar microblocks may exist.

The energies of activation U_i of the three λ -processes for samples with and without filler all equal 54 kJ/mol. These values were obtained according to eq. (6); the plots for several cases are presented in Figures 3 and 4. This observation indicates that all three λ -processes of physical relaxations are determined by the same mechanism, linked directly to the mobility of the same kinetic unit, represented by a segment.^{13,15}

The fourth relaxation observed is a ϕ -process, present only in the filled rubbers, resulting from phenomena in the rubber/filler boundary layer. The energy of activation for the mixture with 60 mass parts of filler is 70 kJ/mol (Table IV). In an idealized approach, it is assumed that rubber with a filler represents a tridimensional network in which the filler particles act as binding agents. Active loci on the filler particle surface are bound to polymer chains, so that fillers represent polyfunctional adsorptive binding agents within the polymer matrix. Due to the influence of mechanical stress and the thermal mobility of the filler particles and polymer segments, bonds are disrupted and new bonds formed, leading to a new equilibrium in the system. The relaxation is then attained after disruption and the formation of new bonds in the interphase. The mechanism of this elementary relaxation process is, however, also dependent on the polymer segment mobility as in the case of the previous three processes, but the relaxation times and energies of activation are much higher. The reason for this can

Table IV Parameters of Relaxation Processes of Vulcanized Rubber Based on SBR 1500 with 0, 20, 40, and 60 Parts of Carbon Black Filler, Ultimate Elongation 50%

Type of Process	Temp (K)	Mass Parts of Filler											
		0			20			40			60		
	τ (s)	B (s)	U (kJ/mol)	τ (s)	B (s)	U (kJ/mol)	τ (s)	B (s)	U (kJ/mol)	τ (s)	B (s)	U (kJ/mol)	
λ_1	293	150		55	130		128		54	140		53	
	303	92	$2.85 \cdot 10^{-8}$	55	85	$3.85 \cdot 10^{-8}$	84	$3.26 \cdot 10^{-8}$	54	80	$5.16 \cdot 10^{-8}$	53	
	313	70		56	56		60		60	60			
	323	18		17	17		16		16	19			
λ_2	293	740		54	720		712		54	720		53	
	303	501		54	210		209		54	215		53	
	313	281	$2.17 \cdot 10^{-7}$	54	161	$1.38 \cdot 10^{-7}$	192	$1.95 \cdot 10^{-7}$	54	192	$1.95 \cdot 10^{-7}$	53	
	323	170		72	72		75		75	86			
λ_3	333	83		43	43		48		48	52			
	343	25		23	23		21		21	22			
	293	10882		9601	9601		9521		9480	9480			
	303	5741		5502	5502		5700		5530	5530			
Φ	313	2582		2301	2301		2382		2375	2375			
	323	2000	$2.82 \cdot 10^{-6}$	54	1280	$1.02 \cdot 10^{-6}$	1325	$1.55 \cdot 10^{-6}$	54	1330	$2.01 \cdot 10^{-6}$	54	
	333	977		751	751		742		742	391			
	343	309		370	370		381		381	181			
Φ	353	245		153	153		172		172	181			
	293			$2.51 \cdot 10^6$	$2.51 \cdot 10^6$		$2.43 \cdot 10^5$		$2.43 \cdot 10^5$	$2.57 \cdot 10^6$			
	303			$1.00 \cdot 10^6$	$1.00 \cdot 10^6$		$9.89 \cdot 10^4$		$9.89 \cdot 10^4$	$9.77 \cdot 10^4$			
	313			$7.94 \cdot 10^4$	$7.94 \cdot 10^4$		$7.90 \cdot 10^4$		$7.90 \cdot 10^4$	$7.70 \cdot 10^4$			
Φ	323			$3.23 \cdot 10^4$	$3.23 \cdot 10^4$		$3.12 \cdot 10^4$		$3.12 \cdot 10^4$	$3.09 \cdot 10^4$			
	333			$7.94 \cdot 10^3$	$7.94 \cdot 10^3$		$7.16 \cdot 10^3$		$7.16 \cdot 10^3$	$7.07 \cdot 10^3$			
	343			$3.98 \cdot 10^3$	$3.98 \cdot 10^3$		$4.25 \cdot 10^3$		$4.25 \cdot 10^3$	$4.17 \cdot 10^3$			
	353			$1.41 \cdot 10^3$	$1.41 \cdot 10^3$		$1.70 \cdot 10^3$		$1.70 \cdot 10^3$	$1.90 \cdot 10^3$			

Table V Parameters of Relaxation Processes of Vulcanized Rubber Based on SBR 1500 with 60 Parts of Vulkasil C or Kaolin BG Filler at an Ultimate Elongation of 50%

Type of Process	Temp (K)	Vulkasil C			Kaolin BG		
		τ (s)	B (s)	U (kJ/mol)	τ (s)	B (s)	U (kJ/mol)
λ_1	293	108			87		
	303	75			43		
	313	55	$4.09 \cdot 10^{-8}$	55	33	$2.48 \cdot 10^{-8}$	54
	323	14			11		
λ_2	293	650			603		
	303	180			158		
	313	160	$1.70 \cdot 10^{-7}$	53	140	$1.59 \cdot 10^{-7}$	53
	323	72			60		
	333	44			38		
	343	20			19		
λ_3	293	8002			7031		
	303	5101			4732		
	313	2010	$1.87 \cdot 10^{-6}$	54	1751	$1.35 \cdot 10^{-6}$	55
	323	1096			839		
	333	690			632		
	343	342			291		
	353	155			135		
Φ	293	$1.20 \cdot 10^5$			$7.76 \cdot 10^4$		
	303	$8.11 \cdot 10^4$			$6.17 \cdot 10^4$		
	313	$6.91 \cdot 10^4$			$5.01 \cdot 10^4$		
	323	$1.95 \cdot 10^4$	$1.26 \cdot 10^{-6}$	62	$1.58 \cdot 10^4$	$4.45 \cdot 10^{-6}$	59
	333	$6.12 \cdot 10^3$			$5.37 \cdot 10^3$		
	343	$3.85 \cdot 10^3$			$3.24 \cdot 10^3$		
	353	$1.81 \cdot 10^3$			$1.60 \cdot 10^3$		

probably be traced back to the fact that rubber covers the filler particles in layers, which are, due to adsorptive forces resulting from the particle surface, strongly interconnected, and the adsorptive bonds between the particle surface and rubber layer exceed in strength the cohesive forces within the rubber phase.

The B coefficients of the ϕ -process for SBR 1500-based vulcanizates filled with carbon black vary from 1.10^{-7} to 1.10^{-8} s. The values of these coefficients can be explained by assuming that the relaxation phenomena in this case involve not only polymer segments but also larger structural elements, i.e., filler particles. Their regrouping in the relaxation process is slow. B is similar in magnitude to B_1 and B_2 ; therefore, it can be assumed that the filler particles and ordered rubber blocks are similar in size to each other.¹¹ If one compares the relaxation times of λ -processes in mixtures with 60 mass parts of Vulkasil C and kaolin BG with those of unfilled mixtures, it can be seen that the mixtures without

fillers had higher relaxation times (Tables IV and V).

The B coefficients increase and the corresponding relaxation times for all three λ -processes decrease with incorporation of the filler and with decreasing filler activity (Tables IV and V). This is probably a consequence of the decrease of the part of the filler bound to the polymer and the decrease of the adsorptive rubber/filler bond strength.

The energy of activation of the ϕ -process decreased with decreasing filler activity, i.e., when carbon black was replaced by the less active kaolin (Tables IV and V). The energy of activation of the ϕ -process can thus serve as a measure of the rubber/filler adhesive bond strength. As all λ -processes based on SBR 1500 have the same energy of activation (54 kJ/mol), which is a result of intermolecular forces inherent to the pure polymer, the filler activity is proportional to $\Delta U = U\phi - U\lambda$. It can easily be shown that for carbon black $\Delta U = 16$ kJ/mol, and for kaolin BG, only 5 kJ/mol. This is re-

Table VI Parameters of Relaxation Processes of Vulcanized Rubber Based on SBR 1712 Rubber Without Filler and With 60 Mass Parts of Carbon Black

Type of Process	Temp (K)	SBR 1712 Without Filler			Rubber SBR 1712 with 60 mp Carbon Black		
		(s)	<i>B</i> (s)	<i>U</i> (kJ/mol)	(s)	<i>B</i> (s)	<i>U</i> (kJ/mol)
λ_1	293	138			1084		
	303	88			83		
	313	63	$9.1 \cdot 10^{-8}$	51	53	$8.90 \cdot 10^{-8}$	51
	323	17			16		
λ_2	293	643			521		
	303	298			172		
	313	178			141		
	323	79	$3.01 \cdot 10^{-7}$	50	65	$3.23 \cdot 10^{-7}$	51
	333	58			41		
	343	21			19		
λ_3	293	6891			5471		
	303	4732			4431		
	313	2328			2188		
	323	1433	$6.93 \cdot 10^{-6}$	51	1202	$7.63 \cdot 10^{-6}$	50
	333	746			692		
	343	371			351		
	353	171			151		
Φ	293				$1.27 \cdot 10^5$		
	303				$8.40 \cdot 10^4$		
	313				$7.28 \cdot 10^4$	$1.22 \cdot 10^{-6}$	63
	323				$2.41 \cdot 10^4$		
	333				$6.61 \cdot 10^3$		
	343				$4.05 \cdot 10^3$		
	353				$1.80 \cdot 10^3$		

flected in eq. (6) where B_i increases when an active filler is replaced by an inactive one, but at the same time, $\exp(-U/kT)$ changes in the opposite direction.

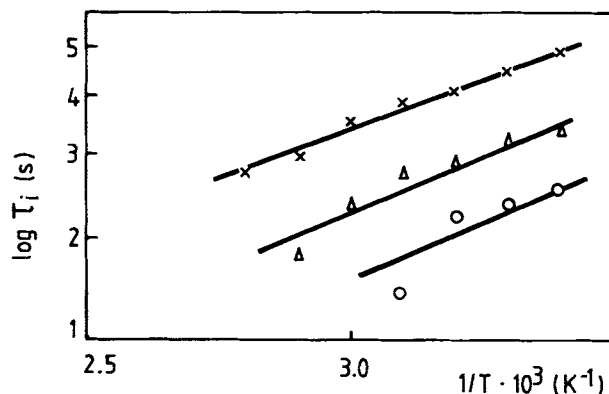


Figure 3 The logarithm of the relaxation times τ_i plotted against $1/T$ for the vulcanizate based on SBR 1500 without filler, representing the (○) λ_1 , (△) λ_2 , and (x) λ_3 processes.

The numerical values of the relaxation parameters for vulcanized samples based on SBR 1712 are presented in Table VI. It can be seen that in this case also the λ -relaxation times increased when the filler was present, but that the energies of activation of 51 kJ/mol remained unchanged in all cases.

By comparing the results from Tables IV and VI, it can also be seen that SBR 1500-based vulcanizates had higher relaxation times than those based on SBR 1712. This can be explained by the effect of the oil component in SBR 1712 that acts as a diluent to the matrix. For the same reason, the activation energies of both λ - and λ -processes are higher for samples based on SBR 1500 than for those based on SBR 1712.

CONCLUSIONS

From the results obtained, it can be concluded that the slow stadium of relaxation of vulcanized styrene/

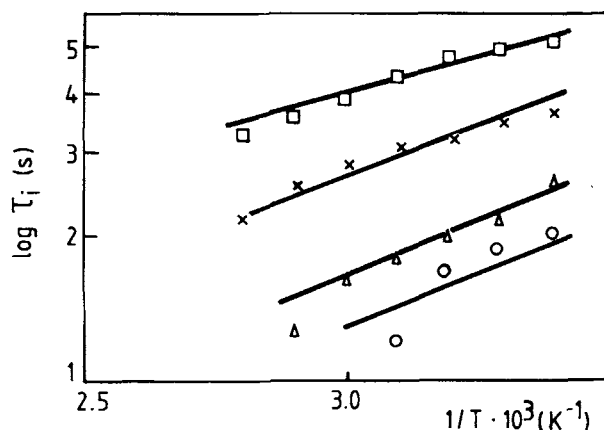


Figure 4 The logarithm of the relaxation times τ_i plotted against $1/T$ for the vulcanized based on SBR 1712 with 60 mass parts of carbon black filler, representing the (○) λ_1 , (Δ) λ_2 , (x) λ_3 , and (□) ϕ processes.

butadiene rubbers involves three λ -processes characterized by the same energy of activation that does not depend on the type and content of filler and can be linked to the mobility of the segment as the kinetic unit. The relaxation times are, however, different, probably due to the different sizes of the microblocks involved in the relaxations. The relaxation times τ_i for all three processes increase with decreasing filler activity.

A ϕ -process, present only in filled rubbers, was detected, with longer relaxation times and a higher activation energy. In vulcanized samples based on oil-extended SBR 1712, the relaxation times and activation energies are lower compared to those obtained for SBR 1500.

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