

# Effect of Fillers on Thermoplastic 1,2-Polybutadiene Rubber: Mechanical and Viscoelastic Properties

S. S. BHAGAWAN, D. K. TRIPATHY, and S. K. DE, *Rubber  
Technology Centre, Indian Institute of Technology, Kharagpur  
721302, India*

## Synopsis

The effects of silica, carbon black, and china clay on the mechanical properties of 1,2-polybutadiene have been investigated. They include stress-strain behavior, tensile strength, elongation, tear strength, tension set, impact strength, and hysteresis. The effect of silane coupling agent on these properties has also been studied. The stress-relaxation behavior of the filled and unfilled systems has also been compared. The rate of relaxation increases with temperature. The dynamic mechanical properties have been determined using a Rheovibron viscoelastometer at 35 Hz at different temperatures. The storage and loss moduli are enhanced by addition of fillers. Silane coupling agent increases storage modulus as well as  $\tan \delta_{\max}$  of the clay-filled polymer. The suitability of Voigt and Reuss models in predicting the composite moduli is examined.

## INTRODUCTION

Thermoplastic elastomers<sup>1,2</sup> have gained importance in recent years because they combine the processing advantages of plastics and the good physical properties of vulcanized rubbers. These materials may be block copolymers consisting of a hard thermoplastic segment and a soft rubbery segment, blends of a crystalline polyolefin and an elastomer or polymers which have a specified stereoregular structure with a controlled degree of crystallinity. 1,2-Polybutadiene (1,2-PBD) belongs to the last category. Due to its flexibility, reactivity, and good processing characteristics, 1,2-PBD has found application in areas such as thermoset resins, coatings, films, footwear, adhesives, and sponge. Some work on 1,2-PBD has been reported by Abe et al.<sup>3,4</sup> However, little information is available on the properties of filled 1,2-PBD, particularly the mechanical and viscoelastic behavior of such systems. Mechanical properties are important for quality control purposes as well as from the point of view of application. Stress-relaxation is a manifestation of the time-dependent behavior of polymer systems. The importance of dynamic mechanical testing as a powerful tool for obtaining structural and morphological information of unfilled and filled polymers is well known.<sup>5-8</sup> In this paper we report the results of our studies on the mechanical properties, stress-relaxation behavior, and dynamic mechanical properties of 1,2-PBD filled with silica, carbon black, and China clay.

## EXPERIMENTAL

The characteristics of the materials used in this study are described in Table I.

TABLE I  
Characteristics of Compounding Ingredients

1,2-Polybutadiene	JSR RB 820 manufactured by Japan Synthetic Rubber Co. Ltd., Tokyo. 92% 1,2 content; 25% crystallinity. (sp. gravity = 0.902).
Carbon black	HAF Black (N330) manufactured by Philips Carbon Black Ltd., Durgapur, India (sp. gravity = 1.81).
Silica	Precipitated silica (Vulcasil-S) manufactured by Bayer India Ltd. (sp. gravity = 2.0).
Clay	China clay (sp. gravity = 2.50).
Si 69	Bis(3-triethoxy silyl propyl)-tetrasulfide, gift sample from De Gussa, Federal Republic of Germany.

### Sample Preparation

Mixing of the ingredients was performed in a Brabender plasticorder Model PLE 330 equipped with a cam type mixer using a rotor speed of 80 rpm at a temperature of 140°C. Initially 1,2-PBD was mixed for 2 min followed by addition of required amount of filler, and the mixing was continued for another 4 min. By this time the torque attained an equilibrium value. The molten material was removed from the plasticorder and passed through a laboratory mill at a nip setting of 2 mm. The sheet thus obtained was fed into the plasticorder, mixed for one more minute for better dispersion, and finally sheeted out through the mill.

### Test Specimens

Sheets of 2 mm thickness were compression-molded at 150°C for 2 min in a hydraulic press. Dumbbell specimens conforming to ASTM D412 were punched out from these sheets and used for determining tensile strength, elongation, tension set, hysteresis, and stress-relaxation behavior. Standard test pieces (ASTM D624-Type C) were used for determining the tear strength. Hardness measurements were carried out according to ASTM D2240 using a Shore D durometer. Specimens measuring 50 × 10 × 2 mm were punched and used for measuring dynamic mechanical properties.

### Equipment

The tensile and tear specimens were tested using Instron universal tester Model 1195 at a crosshead speed of 500 mm/min. An electronic integrator attached to Instron was used for determining hysteresis loss. Tensile impact tests were performed according to DIN 53448, using a CEAST impact tester Model 6545/000 with a speed of 3.7 m/s.

The stress-relaxation measurements were also carried out on the Instron universal tester provided with a heating chamber. The samples were pulled to 100% extension at a strain rate of approximately 0.061 s<sup>-1</sup>, and the decay of

stress as a function of time was recorded on chart paper initially at high chart speed and later at a slow speed.

The dynamic mechanical properties were determined using Rheovibron Viscoelastometer DDV-III-C at 35 Hz over the temperature range of  $-80$ – $+100^{\circ}\text{C}$  with a heating rate of  $1^{\circ}\text{C}/\text{min}$ . This instrument uses the forced vibration technique (amplitude of vibration is 0.025 mm) and directly measures  $\tan \delta$  while the complex modulus is calculated<sup>9</sup> using the equation

$$E^* = \frac{L}{8AD \times S} \times 10^{11} \text{N/m}^2$$

where  $L$  is the length of the specimen,  $S$  is the sectional area, and  $A$  and  $D$  are instrument parameters. The storage and loss moduli were calculated using the following relations:

$$E' = E^* \cos \delta \quad \text{and} \quad E'' = E^* \sin \delta$$

## RESULTS AND DISCUSSION

### Mechanical Behavior

#### *Stress–Strain Properties*

The stress–strain curves of 1,2-PBD filled with three different fillers at equivalent volume loading are shown in Figure 1. It is interesting to note that each filler exhibits a characteristic stress–strain behavior. Also, filled and unfilled specimens exhibit crazing when stretched.

1,2-PBD shows an initial linear portion followed by a yield point and plastic deformation over a small region, after which the stress rises continuously till failure. The initial step and linear portion in the stress–strain curve is due to an elastic deformation of the crystalline–amorphous network. When the yield stress is reached, straightening of the chains starts. As the stretching is continued, further extension of the chains takes place resulting in very large stress. It may be remarked that the portion of the stress–strain curve at low strains resembles a partially crystalline polymer above its glass transition, and at higher strains it is similar to that of an elastomer.

Addition of clay to 1,2-PBD raises the yield point with a somewhat more extended plastic deformation region; the subsequent increase in stress is slower than for 1,2-PBD. In general, clay acts as an extender (inert filler) in many polymer systems. Hence addition of clay only slightly affects the stress–strain behavior of 1,2-PBD.

When carbon black is added to 1,2-PBD, it results in a high yield stress and greater stiffening after yield. This type of curve is similar to oriented partially crystalline polymers,<sup>10</sup> where the specimen extends uniformly without necking.

Silica-filled 1,2-PBD exhibits the highest yield stress, followed by a decrease in stress and a subsequent increase at higher strains. The curve is similar to

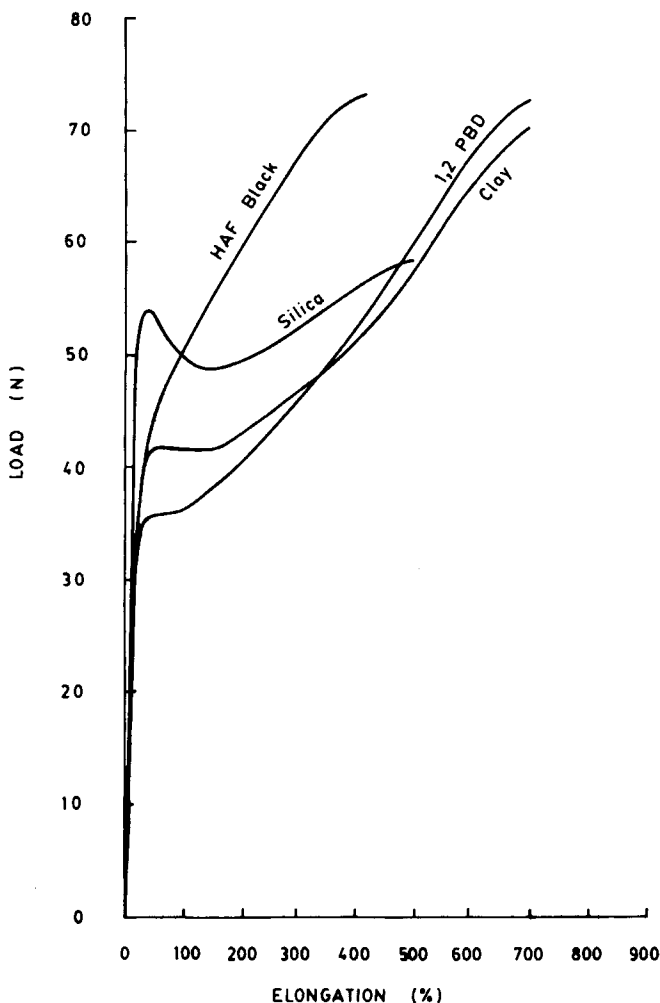


Fig. 1. Stress-strain curves of filled 1,2-polybutadiene.

that of unoriented crystalline polymers.<sup>11</sup> In such systems, after the initial elastic deformation, the material yields with a progressive reorganization of segments at both amorphous and crystalline regions. At higher strains, stress rises due to strain hardening and ultimately leads to failure. It is found that the nature of the stress-strain curve is not affected by increasing the filler loading.

Silane coupling agents are known to improve the properties of filled polymers by modifying the filler surface. From Figure 2(a) it is seen that Si 69 modifies the stress-strain behavior of silica-filled 1,2-PBD. The drop in stress after yield which was observed in silica-filled 1,2-PBD disappears when coupling agent is added. This results in a higher value for M300 (Table II). In the case of clay-filled 1,2-PBD also [Fig. 2(b)], the coupling agent improves the polymer-filler adhesion as reflected in yield stress, M300, and storage modulus values (Fig. 12).

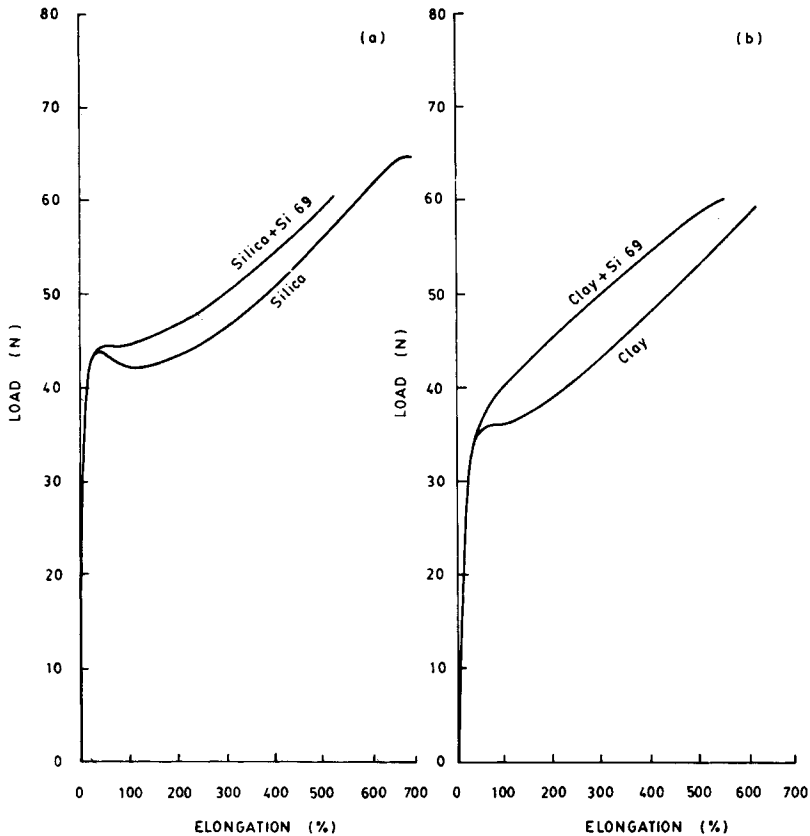


Fig. 2. Effect of Si 69 on stress-strain behavior of silica-filled 1,2-polybutadiene; (b) Effect of Si 69 on stress-strain behavior of clay-filled 1,2-polybutadiene.

### Mechanical Properties

From Table II it is seen that the tensile strength and tear strength are little affected by filler type and loading. Silica and clay systems exhibit lower values than the base polymer while carbon black shows a small increase in both tensile strength and tear strength. The elongation at break does not vary much with clay loading. Silica-filled 1,2-PBD shows a decrease of about 20% as loading increases from 20 to 40 phr (parts per hundred of rubber). The reduction in elongation by about 50% in the carbon black systems is due to stiffening of the matrix by higher degree of polymer-filler interaction, which is responsible for increase in tear strength of the black-filled system.

In rubbers, silica and carbon black act as reinforcing fillers. However, such fillers are not used in plastics since there is no increase in strength or rupture energy, because plastics derive strength from their ability to crystallize and orient themselves under stretching. It appears that filled 1,2-PBD exhibits mechanical behavior more similar to filled partially crystalline thermoplastics.

Stress at 300% elongation ( $M_{300}$ ) is commonly used in the rubber industry for quality control purpose. From Table II it is observed that carbon black exhibits higher value of  $M_{300}$  than silica. But the storage modulus values (Fig.

TABLE II  
Mechanical Properties of Filled 1,2-Polybutadiene

Sample no.	Composition	Tensile strength (MPa)	Elon-gation (%)	M300 stress at 300% (MPa)	Tear strength (kN/m)	Yield stress (MPa)	Hardness (Shore D)	Tension set (%)		Impact strength $(J/m) \times 10^{-3}$
								At 100% elongation	At break	
1	1,2-Polybutadiene	11.2	650	6.9	68.8	5.6	35	22	145	5.0
2	1,2-PBD + 20 phr silica	9.5	630	6.8	63.0	6.8	43	26	160	3.1
3	1,2-PBD + 30 phr silica	8.7	530	7.4	67.1	8.0	46	28	150	2.2
4	1,2-PBD + 40 phr silica	9.1	490	8.0	70.2	8.4	47	28	150	2.3
5	1,2-PBD + 20 phr silica									
6	+1 phr Si 69	9.7	600	7.0	67.5	6.8	40	26	127	1.8
7	1,2-PBD + 20 phr HAF Black	11.6	580	9.2	82.0	6.7 <sup>a</sup>	42	20	130	2.5
8	1,2-PBD + 30 phr HAF Black	11.3	450	10.4	77.0	7.2 <sup>a</sup>	45	26	107	2.8
9	1,2-PBD + 40 phr HAF Black	11.6	300	—	79.0	7.8 <sup>a</sup>	48	32	70	2.0 <sup>b</sup>
10	1,2-PBD + 30 phr China clay	9.5	625	6.5	62.6	5.5	38	28	158	3.7
11	1,2-PBD + 40 phr China clay	10.9	655	6.9	63.4	6.4	38	26	154	4.2
12	1,2-PBD + 50 phr China clay	9.0	595	6.5	55.6	6.0	40	28	150	1.9
	1,2-PBD + 30 phr China clay + 1 phr Si 69	9.3	590	7.6	64.4	5.9 <sup>a</sup>	37	26	120	3.7

<sup>a</sup> Offset yield values.

<sup>b</sup> Samples had blowholes.

6) indicate that silica has a higher value than black-filled 1,2-PBD. This apparent anomaly arises from their different stress-strain behavior (Fig. 1). In fact, up to the yield stress, silica exhibits a higher value than carbon black (see Table II); however, since it shows a fall in stress after yield, unlike carbon black, it has a lower  $M_{300}$  value than carbon black. Thus we find that  $M_{300}$  values could be misleading, especially when comparing different filler systems with different stress-strain behavior. Also it must be noted that the storage modulus, being a material property, is more appropriate for comparative purposes.

From the hardness values (Table II) it is seen that addition of silica and carbon black increases hardness depending on the filler loading, whereas in clay-filled 1,2-PBD the change is marginal since clay is a soft filler.

The tension set values at 100% elongation and at break are shown in Table II. It is seen that silica and clay do not improve the set at break while it is reduced with increase in loading of carbon black. This is due to the higher modulus and lower elongation obtained for carbon-black-filled samples. However, the set at 100% is not affected much by addition of fillers. The small increase in this value with HAF Black loading could possibly be due to stiffening of the matrix due to polymer-filler interaction.

Impact strength is found to reduce when fillers are added to 1,2-PBD (see Table II). This is due to the incorporation of rigid filler particles which reduce the flexibility of the specimen. This effect is more pronounced in the case of high modulus fillers like silica and carbon black than in case of clay.

### Hysteresis

(a) **At Low Strain.** Hysteresis curves for the different systems at 30% strain are shown in Figure 3(a). It is seen that the nature of the hysteresis

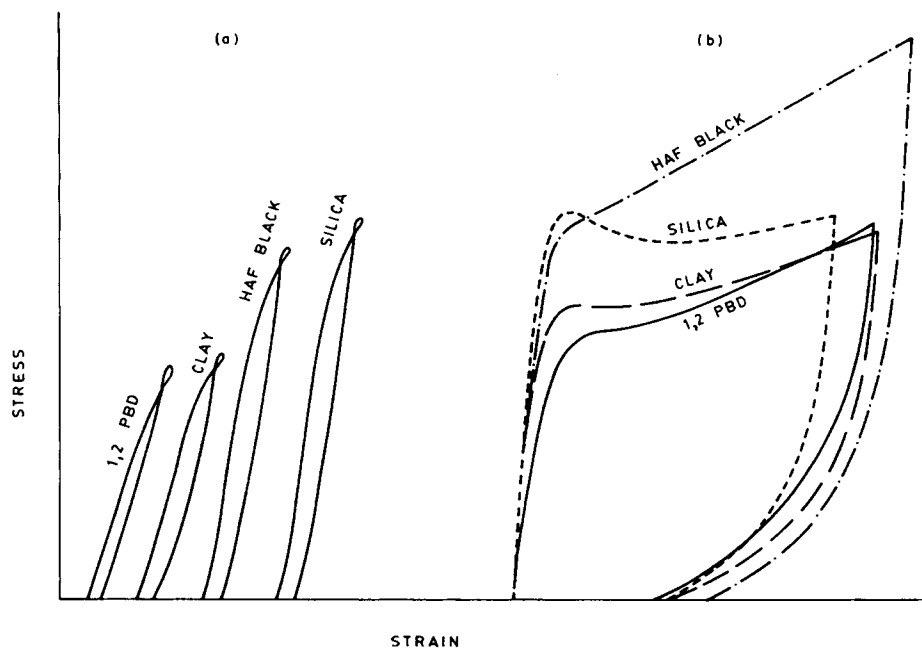


Fig. 3. Hysteresis curves of filled 1,2-polybutadiene at (a) 30% extension and (b) 300% extension.

TABLE III  
Hysteresis Behavior of Filled 1,2-PBD

System	Hysteresis loss at	
	30% strain	300% strain
1,2-PBD	0.177	0.772
1,2-PBD + 30 phr silica	0.339	0.852
1,2-PBD + 30 phr HAF Black	0.321	0.849
1,2-PBD + 40 phr clay	0.291	0.834

loop is not affected by the addition of filler. Unlike rubbers, on retraction, the stress reaches zero level at finite strain, indicating permanent deformation. Such a behavior is typical of thermoplastics.

**(b) At High Strain.** The hysteresis curves at 300% elongation are shown in Figure 3(b). This strain is far beyond the yield point. All the specimens exhibit high hysteresis and large irrecoverable plastic deformation as shown by the retraction curves. The area under the curve is apparently highest for black-filled 1,2-PBD. However, as shown in Table III, the hysteresis loss (ratio of energy loss to input energy) is highest for silica-filled 1,2-PBD and lowest for the clay-filled system when compared at equal volume loadings. All the filled systems show higher hysteresis than pure 1,2-PBD irrespective of strain level and the behavior is similar to that of thermoplastics. Increase in hysteresis on addition of fillers is due to the additional energy dissipation mechanisms, such as motion of filler particles, chain slippage or breakage, and dewetting at high strains.<sup>12</sup>

### Stress-Relaxation Behavior

Stress-relaxation is the decay of stress with time at constant strain. The stress-relaxation curves for the different filled systems at nearly equal volume fractions are shown in Figure 4. It is interesting to note that the rate of stress-relaxation is nearly the same for all the three filled systems. Moreover, the fillers do not appreciably affect the relaxation behavior of the polymer, because the relative stress  $\sigma/\sigma_0$  (where  $\sigma_0$  is stress at  $t = 0$  and  $\sigma$  is stress at any time  $t$ ), in filled 1,2-PBD is not much different from that of the raw polymer, particularly after about 100 s. By about  $10^4$  s all the data points merge. This effect is markedly different from that of fillers in conventional rubber vulcanizates, where the rate of stress-relaxation is greatly enhanced by addition of fillers.<sup>13</sup>

In gum vulcanizates stress-relaxation is determined by processes such as chain motion and orientation, rearrangement of broken chains, entanglements, crosslinks, etc. In filled vulcanizates weak physical interactions between elastomer chains and filler particles are broken during extension, resulting in a higher rate of stress relaxation.

In contrast, in 1,2-PBD which has no chemical crosslinks the stress-relaxation results from rearrangement of entanglements, chain motion, and orientation. Since the interaction between polymer and filler is less, as shown in the preceding sections, the contribution of fillers to stress-relaxation is quite small.



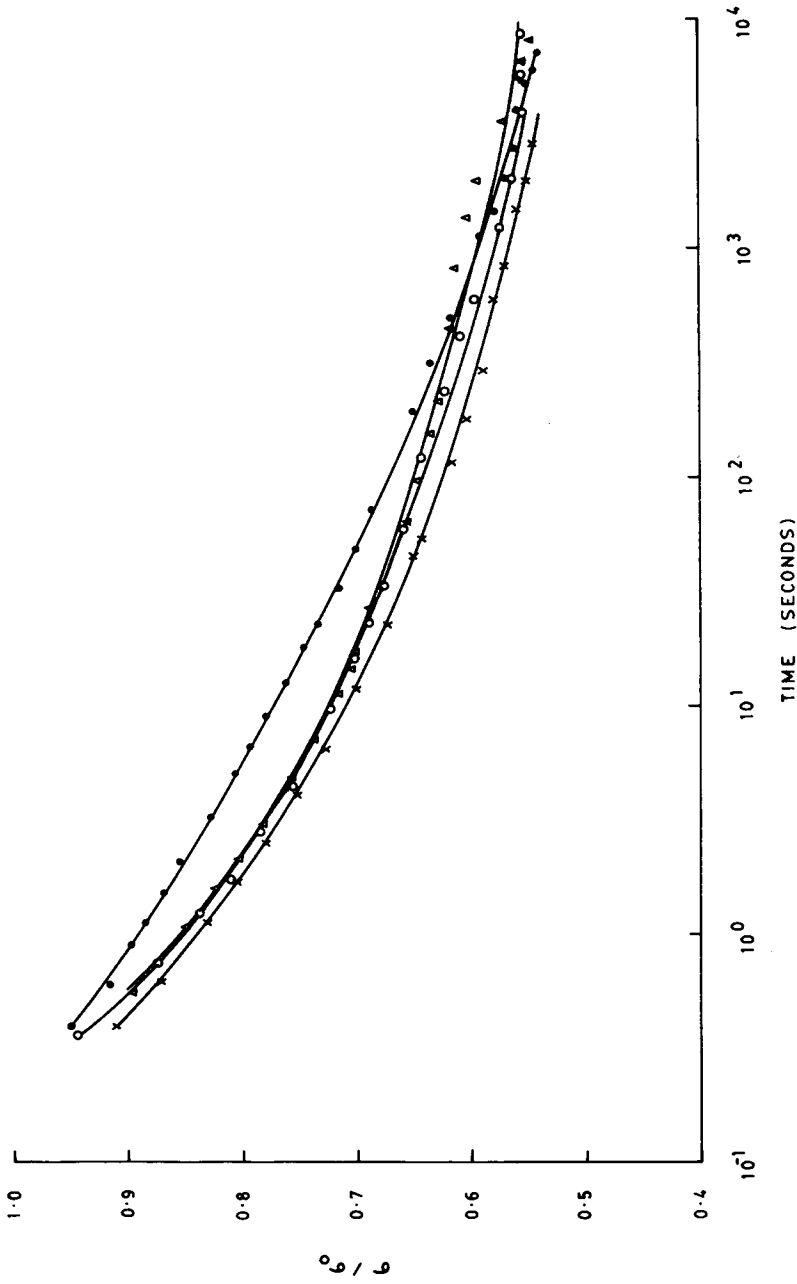


Fig. 4. Stress-relaxation behavior of 1,2-polybutadiene filled with silica, carbon black, and clay: (●) 1,2-PBD; (×) 1,2-PBD + 30 phr silica; (Δ) 1,2-PBD + 30 phr HAF Black; (○) 1,2-PBD + 40 phr clay.

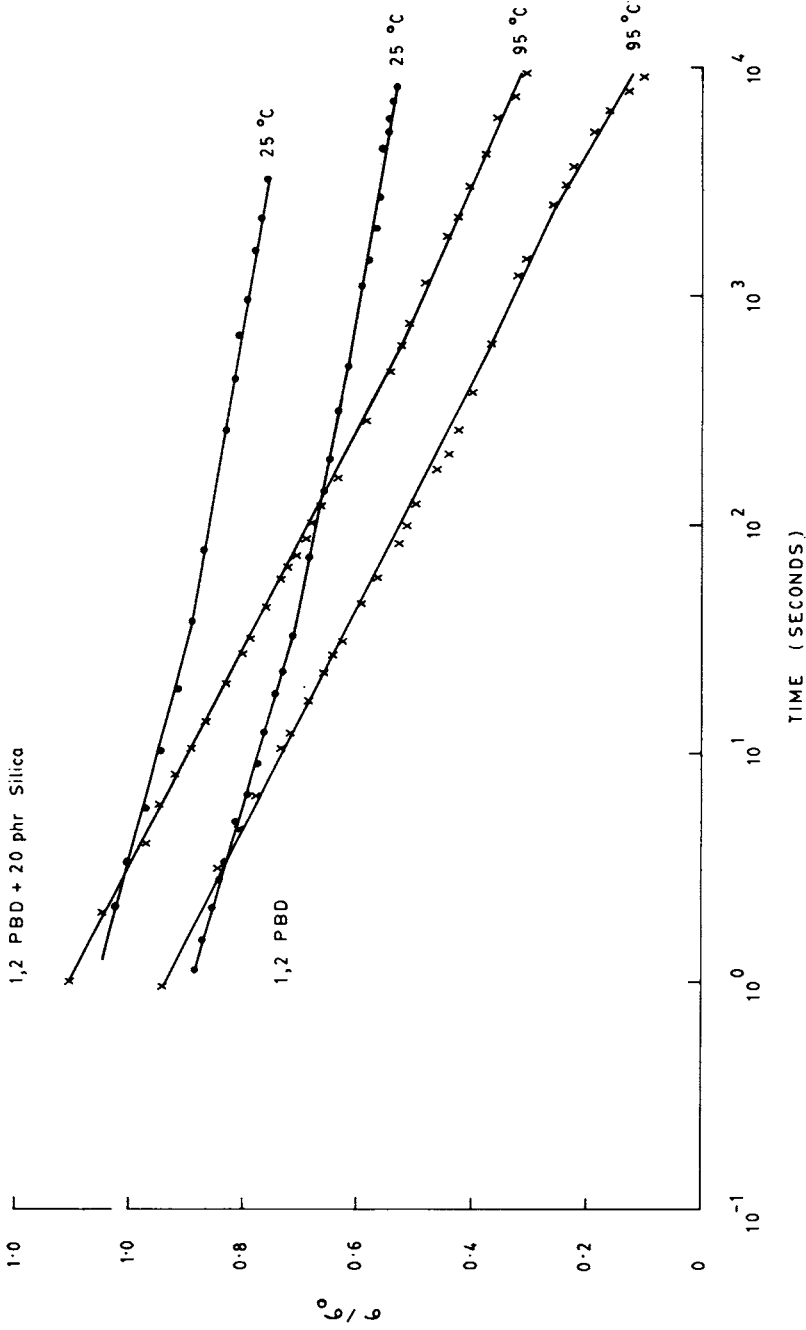


Fig. 5. Stress-relaxation behavior of 1,2-polybutadiene and 1,2-polybutadiene + 20 phr silica at 25°C (○) and 95°C (×). The curves for 1,2-polybutadiene + 20 phr silica have been shifted upward by 0.2. For this system, data at 25 and 95°C are at 30% strain level.

The largely physical nature of relaxation in 1,2-PBD systems is evident from Figure 5 where the relaxation behavior at 25 and 95 °C are compared. At 95 °C the silica-filled 1,2-PBD specimen failed at 100% strain level. Hence the data are reported at 30% strain. At higher temperature the rate of relaxation is faster, and the relative stress attains a low value ( $< 0.1$ ), indicating the large extent of stress relaxation ( $> 90\%$ ). This effect is observed in both raw and filled systems. It may be noted that extensive physical relaxation is also exhibited by styrene-butadiene-styrene (SBS), which is a thermoplastic elastomer.<sup>14</sup>

It has been found that silane coupling agent does not affect the stress-relaxation behavior. Also, the extent of relaxation at a given time marginally increases with filler loading.

### Dynamic Mechanical Behavior

#### *Effect of Filler Type*

The effect of different fillers on the storage modulus, damping factor and loss modulus are shown in Figures 6–8. The plots of storage modulus versus

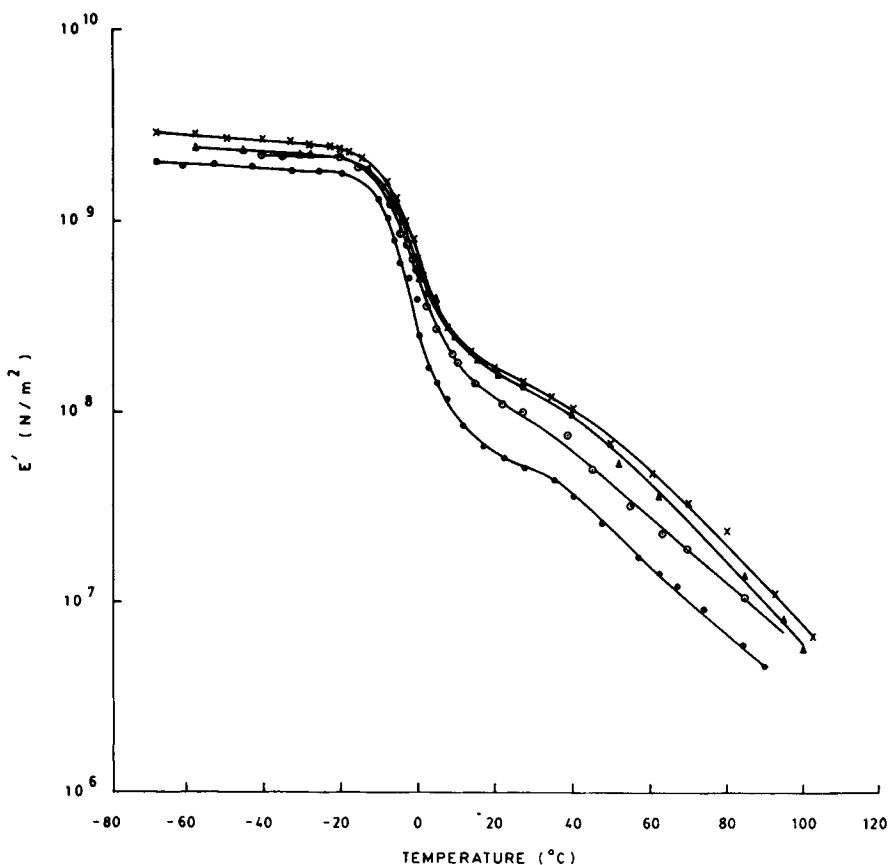


Fig. 6. Storage modulus as a function of temperature for 1,2-polybutadiene filled with clay, silica, and carbon black at 35 Hz: (●) 1,2-PBD; (×) 1,2-PBD + 30 phr silica; (▲) 1,2-PBD + 30 phr HAF Black; (○) 1,2-PBD + 40 phr clay.

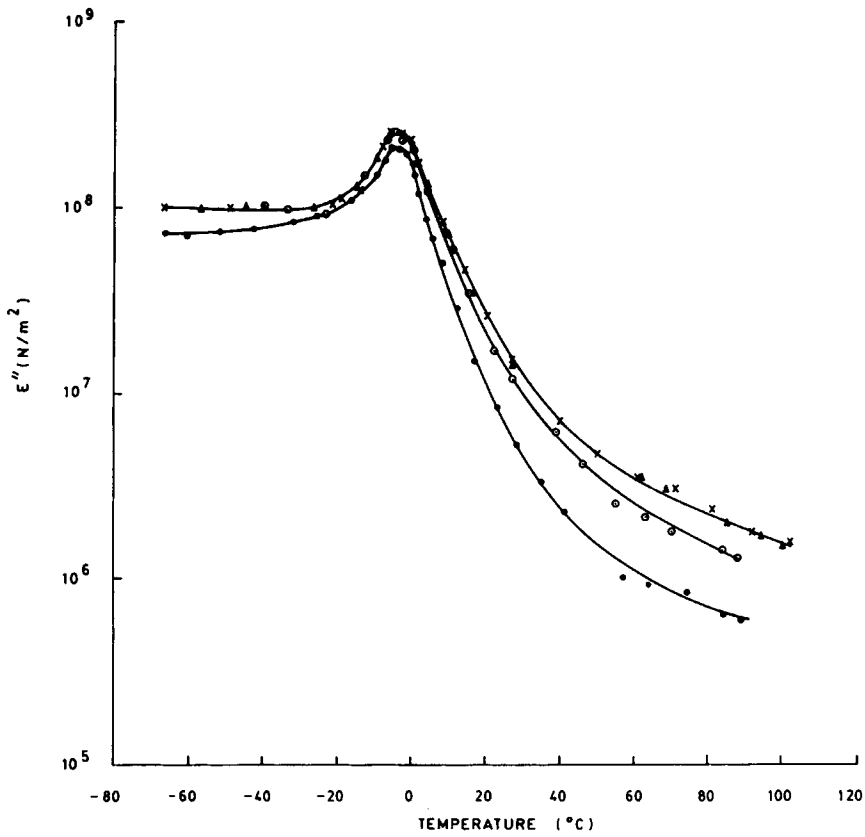


Fig. 7. Loss modulus versus temperature plots for 1,2-PBD filled with clay, silica, and carbon black at 35 Hz: (●) 1,2-PBD; (×) 1,2-PBD + 30 phr silica; (Δ) 1,2-PBD + 30 phr HAF Black; (○) 1,2-PBD + 40 phr clay.

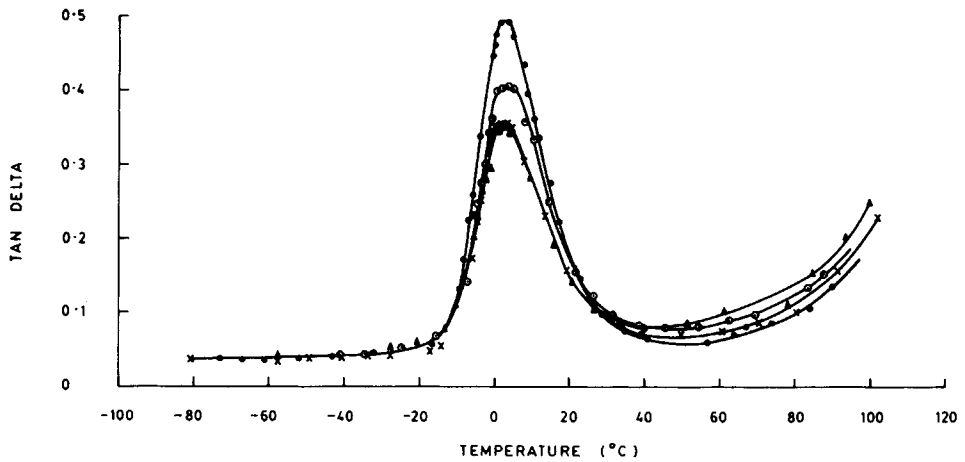


Fig. 8. Loss tangent as a function of temperature for filled 1,2-PBD systems: (●) 1,2-PBD; (×) 1,2-PBD + 30 phr silica; (Δ) 1,2-PBD + 40 phr HAF Black; (○) 1,2-PBD + 40 phr clay.

temperature exhibit a sharp drop in the modulus in the temperature range of  $-10$  to  $+10^{\circ}\text{C}$ . This corresponds to the transition from the glassy to the rubber state. Since 1,2-PBD is uncrosslinked, the rubbery plateau resulting from entanglements occurs over a small temperature range. Above  $40^{\circ}\text{C}$ , as  $T_m$  (melting point of crystallites) is approached, changes in crystalline structure and degree of crystallinity result in a rapid decrease of modulus.<sup>15</sup>

In all cases the filled polymer systems exhibit higher storage moduli than the raw polymer at all temperatures. Interestingly, at nearly equal volume loading the moduli in the transition region are nearly the same for the three filled systems. Below  $T_g$  (glass transition temperature), silica imparts a somewhat higher modulus than clay and carbon black. Above  $T_g$  the differences become more pronounced. Silica and carbon black exhibit nearly equal moduli but higher than clay filled and unfilled samples.

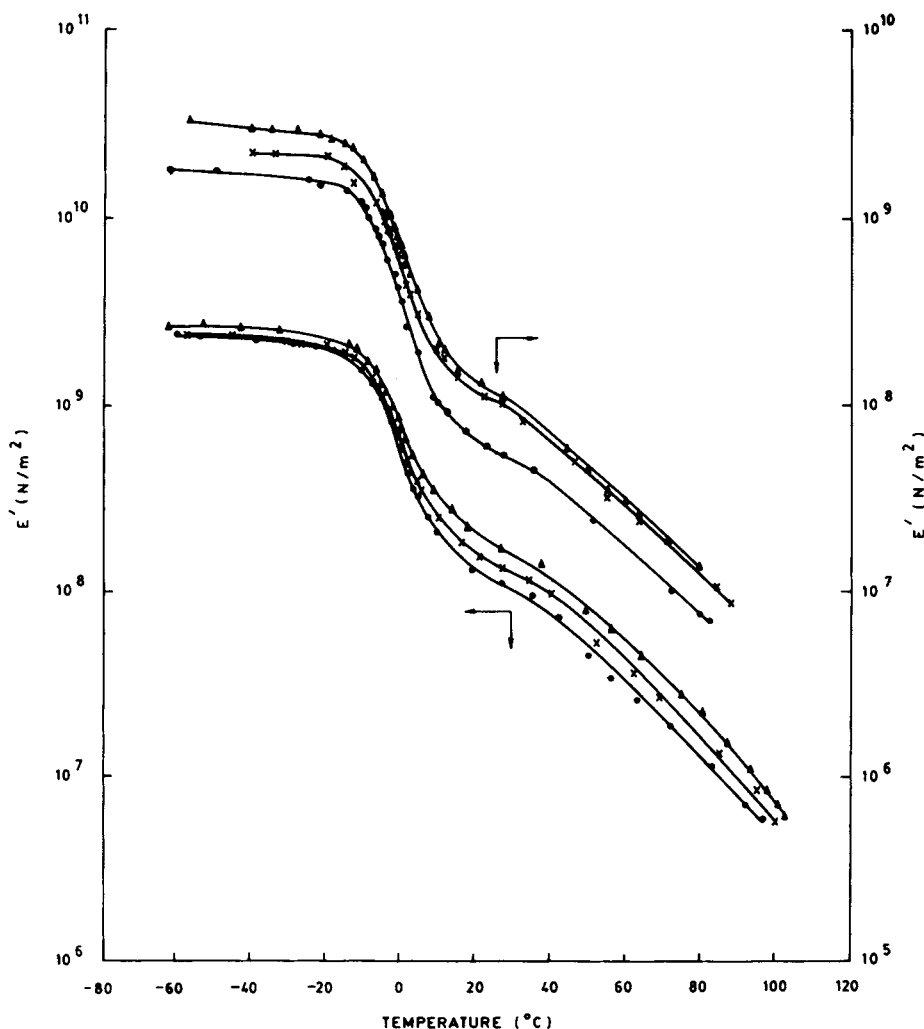


Fig. 9. Effect of loading on storage modulus versus temperature plots for clay and HAF-black-filled 1,2-PBD. Top: (●) 1 phr clay; (×) 40 phr clay; (Δ) 50 phr clay. Bottom: (●) 20 phr HAF Black; (×) 30 phr HAF black; (Δ) 40 phr HAF Black.

The loss modulus (Fig. 7) of the filled samples is greater than that of the unfilled polymer at all temperatures. This is because of additional mechanisms of energy dissipation operating in the presence of filler.<sup>12</sup> Among the filled systems, clay exhibits lowest  $E''$  while silica- and carbon-black-filled systems have nearly same loss moduli. The energy loss per cycle is directly related to loss modulus. Thus, the energy loss or heat buildup as a function of temperature is less in clay-filled 1,2-PBD than silica- or carbon-black-filled systems. The loss modulus data of the filled systems are in agreement with results obtained from hysteresis measurements.

From the loss tangent curves, it is seen that the neat polymer exhibits highest  $\tan \phi_{\max}$  followed by clay; silica and carbon black show nearly identical behavior. Also the temperature at which  $\tan \delta_{\max}$  occurs is only slightly affected by addition of fillers.

### *Effect of Filler Loading*

Figures 9–11 show the variation of dynamic properties with temperature for three loadings of filler in case of clay and carbon black. As expected, the

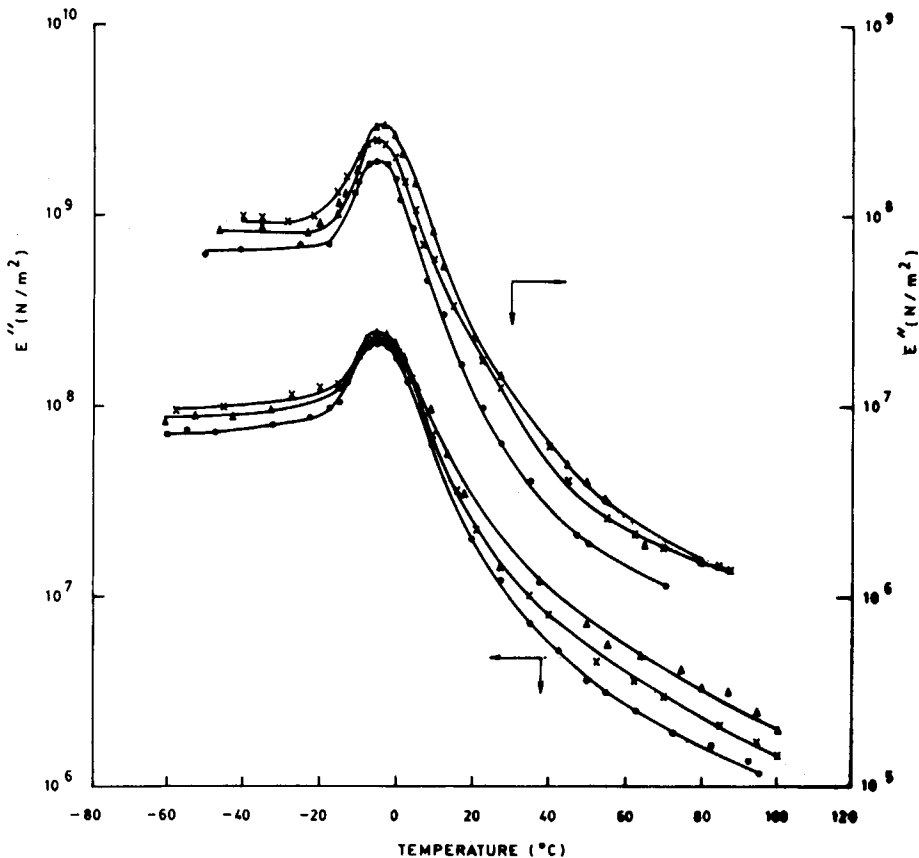


Fig. 10. Loss modulus as a function of temperature for 1,2-PBD containing different loadings of clay and HAF Black. Top: (●) phr clay; (×) 40 phr clay; (▲) 50 phr clay. Bottom: (●) 20 phr HAF Black; (×) 30 phr HAF black; (▲) 40 phr HAF Black.

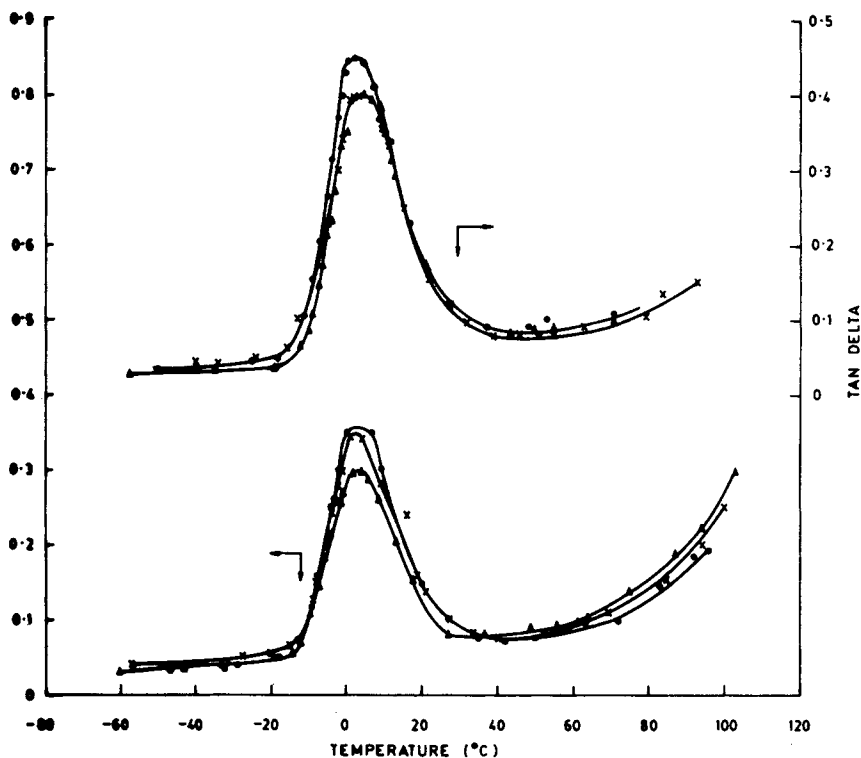


Fig. 11. Effect of loading on loss tangent vs. temperature curves for clay- and HAF Black-filled 1,2-PBD. Top: (●) 30 phr clay; (×) 40 phr clay; (Δ) 50 phr clay. Bottom: (●) 20 phr HAF black; (×) 30 phr HAF black; (Δ) 40 phr HAF Black.

storage and loss moduli increase, and  $\tan \delta_{\max}$  decreases with filler loading. The effects are more prominent in the clay-filled system than in the carbon black samples. When clay is the filler, the differences in  $E'$  are large in the glassy state as well as after  $T_g$ , whereas in carbon black they are prominent after  $T_g$ . When clay is used,  $E''_{\max}$  increases and  $\tan \delta_{\max}$  decreases with loading. In case of carbon black,  $\tan \delta_{\max}$  decreases with loading, but the effect of loading on  $E''$  is prominent above 30°C. Since energy dissipation is favored at polymer-filler interface, increase in filler loading would lead to large polymer-filler interface and correspondingly an increase in loss modulus.

Thus from the preceding sections we find that the mechanical properties, stress-relaxation behavior, and dynamic properties of clay are not markedly different from silica- and black-filled 1,2-PBD. Thus considering composite properties and cost, clay emerges as a more useful filler for 1,2-PBD than a conventional reinforcing filler like silica and carbon black.

#### *Effects of Silane Coupling Agent*

The dynamic properties of 1,2-PBD filled with clay and silica and treated with Si 69 have been studied. The results are shown in Figures 12–14.

In silica-filled 1,2-PBD the increase in  $E'$  due to the addition of Si 69 is quite pronounced after  $T_g$ . However,  $\tan \delta_{\max}$  and loss moduli are not affected.

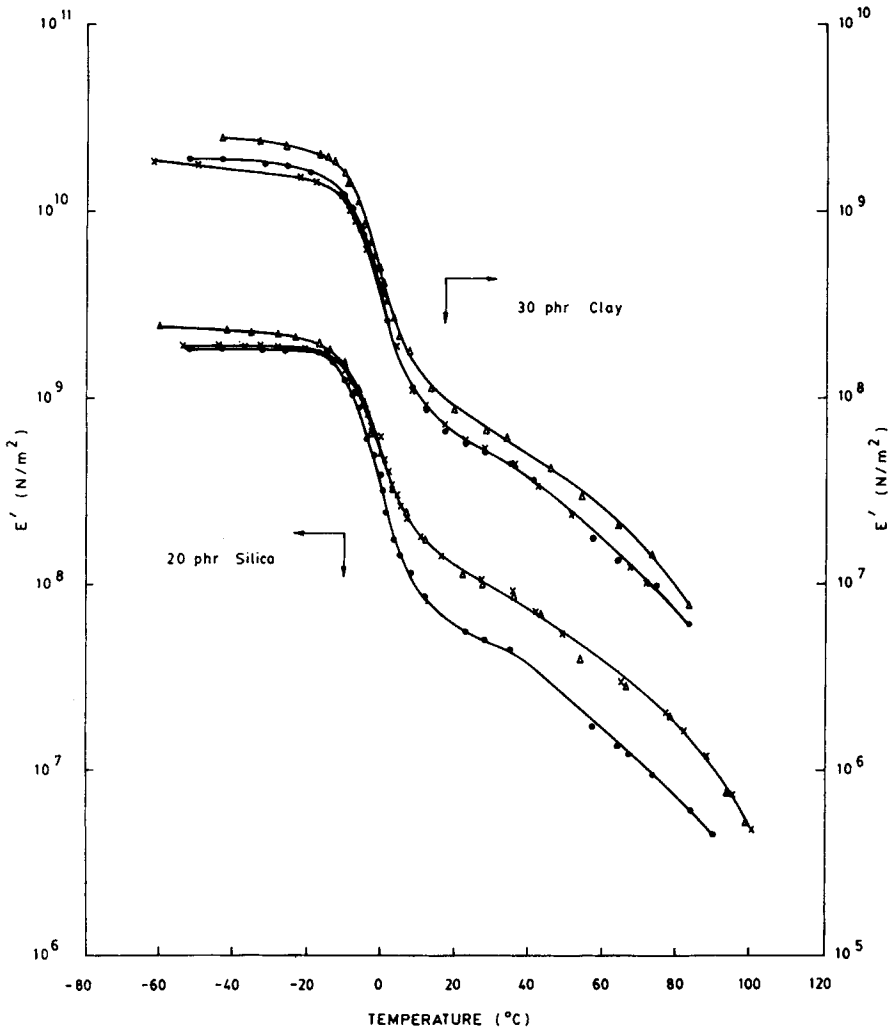


Fig. 12. Effect of silane coupling agent on storage modulus vs. temperature curves of 1,2-PBD filled with clay and silica: (●) 1,2-PBD; (×) 1,2-PBD + filler; (Δ) 1,2-PBD + filler + Si 69 (1 phr).

In clay-filled 1,2-PBD addition of Si 69 increases storage and loss moduli below and above  $T_g$ . Also, the damping factor is increased. This is in contrast to the observation by Chacko et al.,<sup>16</sup> who found that the damping marginally reduces when a coupling agent is added to polyethylene. Saini et al.<sup>17</sup> reported a reduction in  $E'$  and  $\tan \delta_{\max}$  when a silane coupling agent is added to ferrite-filled styrene-isoprene-styrene, a thermoplastic rubber. Perhaps the silane is a better coupling agent for clay-filled systems since it increases  $E'$  as well as the damping behavior. This is due to improved polymer-filler adhesion as shown by the stress-strain curves [Fig. 2(b)] and also due to improved dispersion of filler.<sup>18</sup>

#### *Comparison with Model Composites*

It is useful to compare the dynamic mechanical behavior of the filled 1,2-PBD systems with model composites. The commonly used models are the



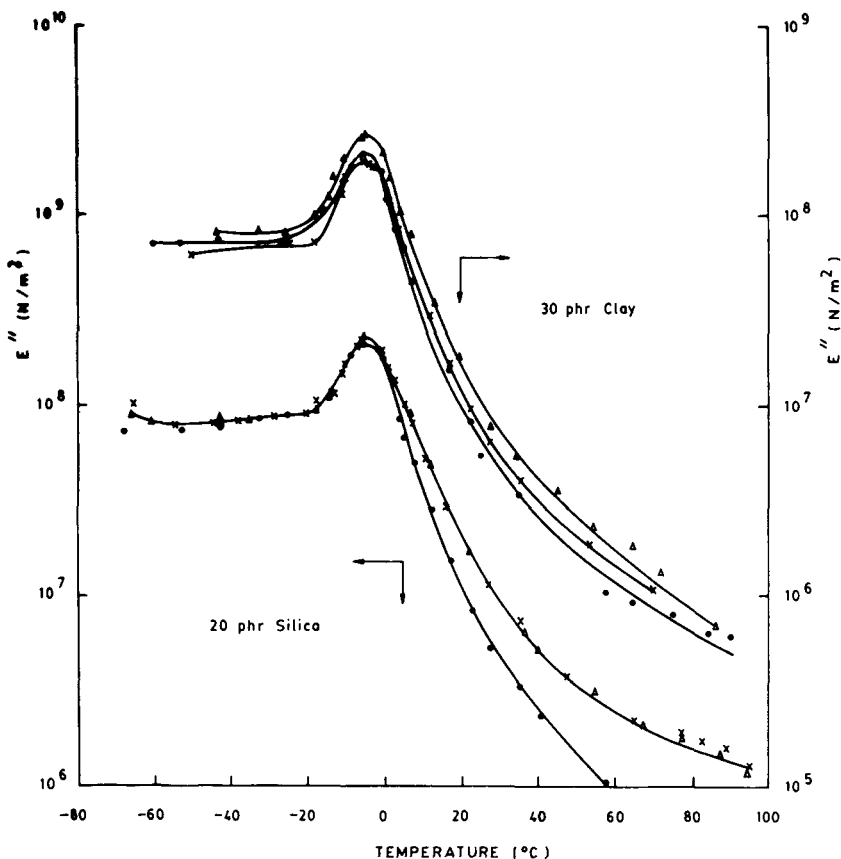


Fig. 13. Effect of silane coupling agent on loss modulus vs. temperature plots of 1,2-PBD filled with clay and silica: (●) 1,2-PBD; (×) 1,2-PBD + filler; (Δ) 1,2-PBD + filler + Si 69 (1 phr).

#### Voigt and Reuss models.<sup>19-21</sup>

The Voigt model is the theoretical lower bound for a composite modulus while the Reuss model is the theoretical upper boundary. The expressions for composite modulus  $E'_c$  can be written as

$$\text{Voigt model: } \frac{E'_p}{E'_c} = 1 + \left( \frac{E'_p}{E'_f} - 1 \right) \phi$$

$$\text{Reuss model: } \frac{E'_c}{E'_p} = 1 - \left( \frac{E'_f}{E'_p} - 1 \right) \phi$$

where  $E'$  is the storage modulus,  $\phi$  is the volume concentration of filler and the subscripts  $c$ ,  $f$ , and  $p$  refer to composite, filler, and polymer, respectively. In Figure 15 the relative composite moduli are plotted at different filler loadings with  $E_f/E'_p = 6.4$  (at  $T = -5^\circ\text{C}$ ). Figures 16(a) and 16(b) are corresponding plots for silica and carbon black with  $E_f/E'_p = 26$  and 10.45, respectively (at  $T = 82^\circ\text{C}$ ). It is seen from these figures that the Reuss model satisfactorily predicts the viscoelastic behavior of composites containing silica

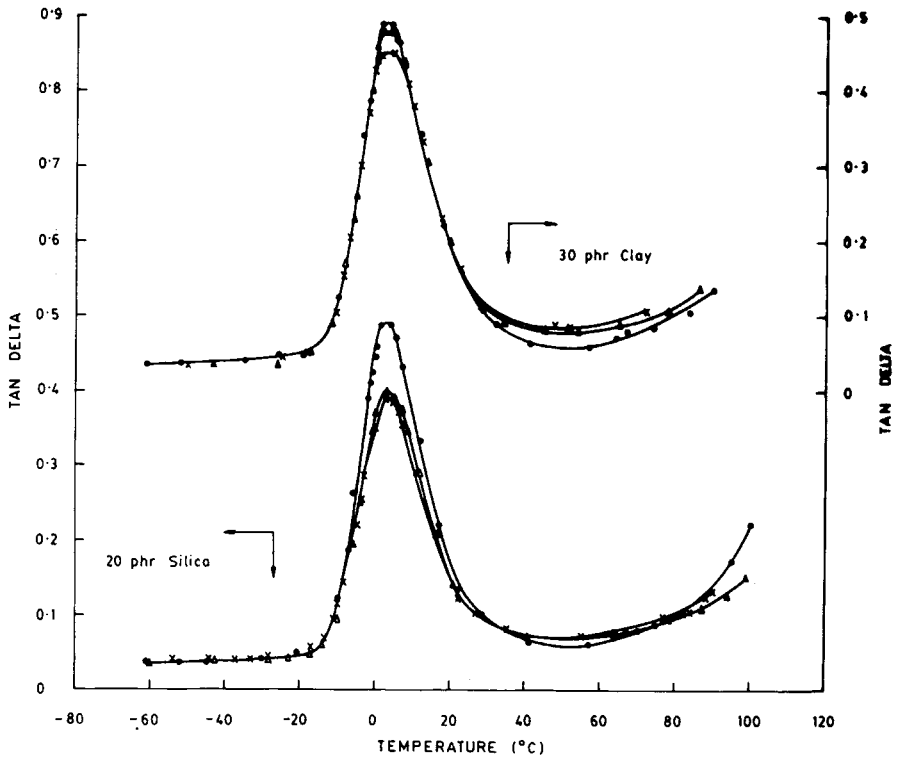


Fig. 14. Effect of silane coupling agent on loss tangent vs. temperature curves of 1,2-PBD filled with clay and silica: (●) 1,2-PBD; (×) 1,2-PBD + filler; (Δ) 1,2-PBD + filler + Si 69 (1 phr).

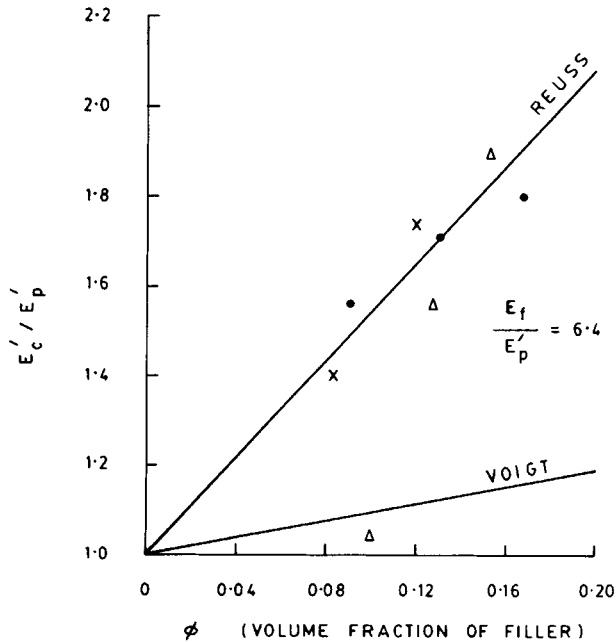


Fig. 15. Comparison of predicted dynamic modulus by Reuss and Voigt models with experiment at  $-5^{\circ}\text{C}$ : (●) HAF Black; (×) silica; (Δ) clay.

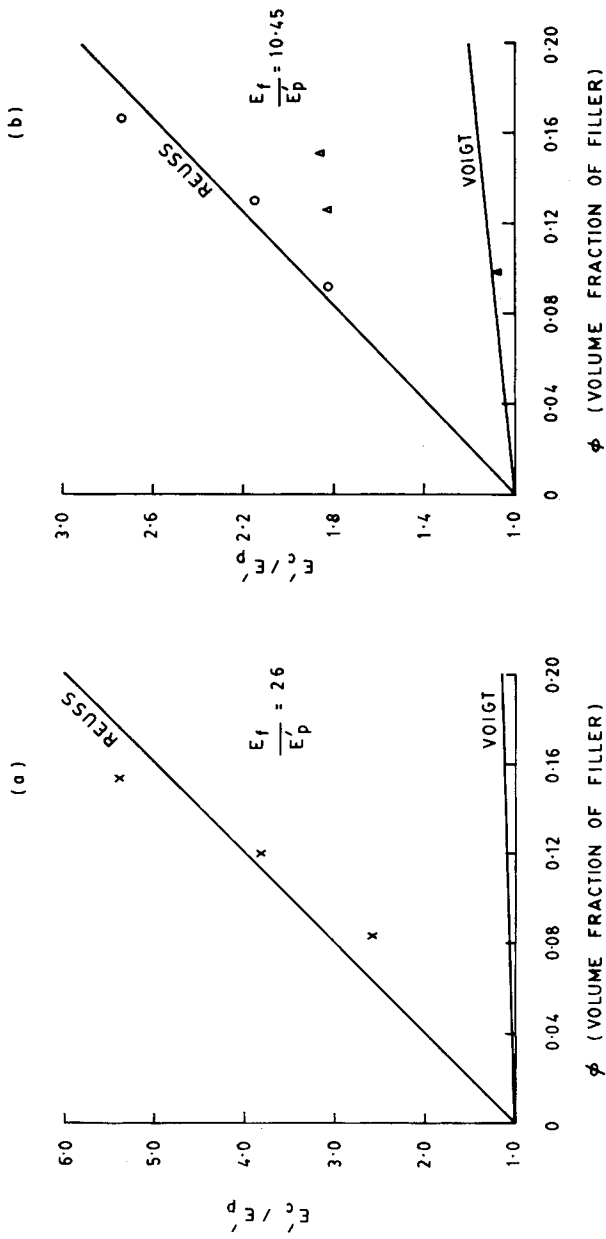


Fig. 16. Comparison of predicted dynamic modulus by two models with experiment: (a) (x) silica-filled 1,2-PBD at 82°C; (b) (o) carbon-black- and ( $\Delta$ ) clay-filled 1,2-PBD at 85°C.

and carbon black. However, the fit is very poor in case of clay. It is believed that lack of correspondence between models and real materials<sup>16</sup> can be due to various reasons such as agglomeration of filler phase because of the vastly different chemical nature of the matrix, lack of adhesion at the polymer–filler interphase, or thermal effects due to different coefficients of thermal expansion of the two phases. In case of semicrystalline polymers like 1,2-PBD the fillers influence the overall crystallinity as well as the morphological character of the matrix.

### CONCLUSIONS

The tensile strength, elongation, and tear strength of 1,2-PBD are marginally affected by addition of silica, clay, or carbon black. Filler loading has a similar effect. However, the stress–strain behavior depends on the type of filler. Silane coupling agent modifies the stress–strain curve for silica- and clay-filled 1,2-PBD systems.

The tension set at 100% elongation and at break are marginally increased while the impact strength is reduced when fillers are added. This is due to reduction in the flexibility of the polymer in presence of rigid inclusions. Hysteresis loss is increased on addition of filler.

Increase in the rate of stress–relaxation due to filler addition is not so marked as in the case of conventional rubber vulcanizates because in 1,2-PBD (both filled and unfilled) the relaxation is predominantly physical in nature.

All the three fillers enhance storage and loss moduli of 1,2-PBD. The increase is more prominent at higher temperature. Among the fillers, clay exhibits the lowest moduli and highest  $\tan \delta_{\max}$  values. Carbon-black- and silica-loaded systems do not differ much in their dynamic mechanical behavior. The effect of loading is more prominent in clay-filled systems. Si 69 increases the storage modulus and loss modulus, particularly in clay-filled 1,2-PBD.

With the proper choice of  $E_f/E_p'$ , the Reuss model appears to predict the composite moduli satisfactorily for silica- and carbon-black-filled systems.

### References

1. B. M. Walker, *Handbook of Thermoplastic Elastomers*, Van Nostrand Reinhold, New York, 1979.
2. A. Wheelan and K. S. Lee, Eds., *Developments in Rubber Technology*–3, Applied Science, London, 1982.
3. S. Kumura, N. Shiraishi, S. Yanagisara, and M. Abe, *Polym. Plast. Technol. Eng.*, 5(1), 83 (1975).
4. Y. Takeuchi, A. Sekimoto, and M. Abe, *Am. Chem. Soc. Ser. 4 (New Ind. Polym. Symp.)*, 15 (1974).
5. T. Murayama, *Dynamic Mechanical Analysis of Polymeric Material*, Elsevier, Amsterdam, New York, 1978.
6. J. Heijboer, *Static and Dynamic Properties of the Polymeric Solid State*, R. A. Pethrick and R. W. Richards, Eds., Reidel, London, 1982.
7. L. E. Nielsen, *Mechanical Properties of Polymers and Composites*, Dekker, New York, 1974.
8. B. E. Read and G. D. Dean, *The Determination of Dynamic Properties of Polymers and Composites*, Wiley, New York, 1978.
9. *Rheovibron Viscoelastomer Manual*, Tokyo Baldwin, Tokyo.
10. *Mechanical Properties of Polymers*, N. M. Bikales, Ed., Wiley, New York (1971).

11. J. W. S. Hearle, *Polymers and Their Properties*, Ellis Harwood, Chichester, U. K., 1982, Vol. 1.
12. G. Kraus, in *Science and Technology of Rubbers*, F. R. Eirich, Ed., Academic, New York, 1978.
13. A. N. Gent, *Rubber Chem. Technol.*, **36**, 397, 697 (1963).
14. Ging Ho Hsiue and Guro Wen Wo, *J. Appl. Polym. Sci.*, **25**, 2119 (1980).
15. J. J. Aklonis and W. J. Macknight, *Introduction to Polymer Viscoelasticity*, Wiley, New York, 1983.
16. V. P. Chacko, F. E. Karasz, and R. J. Farris, *Polym. Eng. Sci.*, **22**, 968 (1982).
17. D. R. Saini, A. V. Shenoy, and V. M. Nadkarni, *J. Appl. Polym. Sci.*, **29**, 4123 (1984).
18. C. D. Han, C. Sandford, and H. J. Yoo, *Polym. Eng. Sci.*, **18**(11), 849 (1978).
19. J. A. Manson and L. H. Sperling, *Polymer Blends and Composites*, Plenum, New York, 1976.
20. Z. Hashin, *Appl. Mech. Rev.*, **17**, 1 (1964).
21. R. M. Christensen, *Mechanics of Composite Materials*, Wiley-Interscience, New York, 1979.

Received July 3, 1986

Accepted January 5, 1987