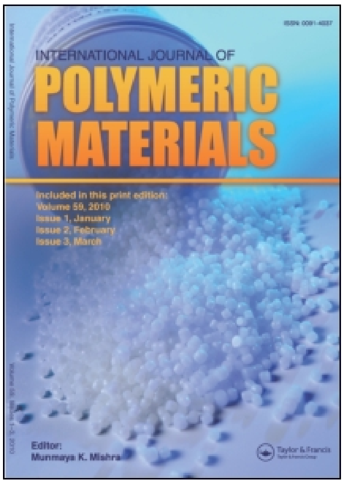

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Dynamic Mechanical Properties of Filled Polybutadiene

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INTRODUCTION

Dynamic mechanical tests measure the response of a material to a sinusoidal or other periodic stress. These tests provide the true picture of product performance. Such information may not otherwise be possible to obtain using a conventional technique of stress-strain measurement.[1] Dynamic tests over a wide temperature and frequency range are especially sensitive to the chemical and the physical structure of a material and can be carried out using various techniques such as free vibration technique, resonance vibration technique, etc.[2,3]

A study on mechanical properties of filled polybutadiene has been reported earlier.[4] In this paper dynamic mechanical properties of filled polybutadiene is discussed. The filler selected was barium chloride (hydrate), mechanical properties of the composites containing this filler have been reported earlier.[4] In the present investigation dynamic mechanical properties have been studied on using dynamic mechanical analyser and Torsion Pendulum. The former employs resonance vibration technique while the latter works on free vibration principle. Dynamic mechanical parameters such as mechanical loss factor (tan δ), storage modulus (E') loss modulus (E'') have been determined from −120° to 20°C.

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EXPERIMENTAL

Materials: Elastomer-Cisamer 1220 (manufactured by Indian Petrochemicals Corporation Limited) was used in the work. It was characterised by Gel Permeation Chromatography, and by differential scanning colorimetry. Table I gives the characteristics of the polymer determined from GPC.

Fillers: Barium chloride (hydrate) had the purity 99.0% (manufactured by BDH Chemicals India). It was ball milled till the desired particle size was obtained. The filler was sieved using standard size sieves to get a uniform particle size in the range of 125–150 μ.

Other Chemicals: Chemicals manufactured by Bayer India Limited were used in curing of the composites.

Recipe: Table II provides an idea about the composition. Optimum curing time for the recipe was determined using a Monsanto rheometer.

Compounding and Moulding: Compounding was carried out on a

TABLE I

Characteristics of polybutadiene

(A)	*Molecular Weight*:	
	Number Average	8.95×10^4
	Weight Average	4.68×10^5
	Viscosity Average	4.67×10^5
(B)	Dispersity	5.02
(C)	Intrinsic Viscosity	0.467
(D)	Microstructure	96% Cis.

TABLE II

Recipe of formulation

Ingredient	Phr
Polymer	100
Zinc Oxide	5
Stearic Acid	2
Sulphur	1
Mercaptobenzothiazole (MBT)	1
Tetramethyl Thiuram disulphide	0.6
Phenyl B-Naphthyl Amine	1

laboratory size two roll mill. The mill was provided with a cooling arrangement by circulation of water. The temperature of the mill was kept below 80° by circulation of water. A premasticated stock was used for all formulations so as to avoid any changes in Mooney viscosity.

The compounds were compression moulded at 140°C for 10 minutes to get composites in the form of sheets (15 cm × 15 cm × 0.2). These were then subjected to conditioning at 27°C and relative humidity of 65%, for 24 hours. Specimens for testing were cut using a punch and a cutting die (specimen for torsion pendulum).

Torsion Pendulum: Torsion pendulum is a standard technique for determination of dynamic shear modulus (G') and mechanical loss factor.[5,6] The torsion pendulum was fabricated in the laboratory.

The specimen under consideration (in the form of a very thin strip) is suspended vertically from a rigid support and in suitable claws. It is subjected to a periodic stress. The frequency of oscillation of the specimen, depends on specimens dimensions and fabrications parameters. The oscillations of the specimen are recorded using a lamp and photocell arrangement along with an optical wedge. Thus the torsional oscillations of the pendulum can be converted into an electrical output of a photocell.[11,12]

Dynamic Mechanical Analysis: DMA 981/TA 990: Dynamic mechanical analysis was carried out using Du Pont-981-DMA module from −120° to +10°C under a heating rate of 5°C/min. DMA 981 module is coupled to 990 thermal analyser which comprises of a temperature programmer/controller and a recorder.

DMA operates on the compound resonance principle, in which the sample is exercised by a unique stress-producing geometry with near zero hysteresis in horizontal direction and high rigidity in the vertical direction.[7] If the sample is deformed and released, the system would oscillate at its resonance frequency with decreasing amplitude. The resonant frequency is related to the sample modulus (E') while the decaying amplitude envelope (damping) is a function of loss modulus (E''). DMA-981 gives direct a record of frequency signal, and damping signal versus temperature. From the values of the temperature at the maximum signal in temperature plane, the temperature of 'α' and 'β' relaxation processes can be read. From these graphs dynamic storage modulus (E') and loss factor ($\tan\delta$)

are calculated using following equations:

$$E' = \frac{(4\pi^2.f^2 J - K)(L/T)^3[1 + 0.71(2T/L)^2 - 0.1(2T/L)^3]}{2W[(1/2) + D]^2}$$

$$\tan = CVf^2$$

$$E'' = E' \tan \delta$$

Where E' = dynamic modulus (GPA), f = oscillation frequency (Hz) J = moment of inertia (k m^2), k = pivot spring constant (Nm), L = sample length (m), T = sample thickness (m), W = sample width (m), D = sample clamping distance (m), C = damping constant V = damping signal (mv).

Volume fraction of the filler in the composite was found by density measurement.

RESULTS AND DISCUSSIONS

Figure 1 represents the temperature dependence of mechanical loss factor ($\tan \delta$) measured using DMA. The volume fraction of the filler in the composite does not seem to influence the glass transition temperature of the base (matrix) polymer. Glass transition temperature (Tg) referred here is the temperature at which $\tan \delta$ attains the maximum magnitude. For all the composites irrespective of the filler content, Tg occurs at −68°C. The filler content however does influence the magnitude of $\tan \delta$ as evident from the figure, especially during and above the glass transition. During the glass transition region magnitudes of $\tan \delta$ were found to be suppressed significantly with increasing volume fraction of the filler in the composites. This indicated that the filler particles caused a change in the magnitude of dynamic storage modulus (E') as well as dynamic loss modulus (E'') and the latter could be less pronounced compared to the former, at the temperature of consideration.

At the higher temperature region (−30°C onwards), the onset of another transition seemed to occur. This transition could be due to the crystalline melting of the matrix and was confirmed by differential scanning colorimeter of pure polymer. An endotherum around 0°C confirms the occurrence of the transition (Figure 2). The influence exerted by the presence of filler on the magnitudes of

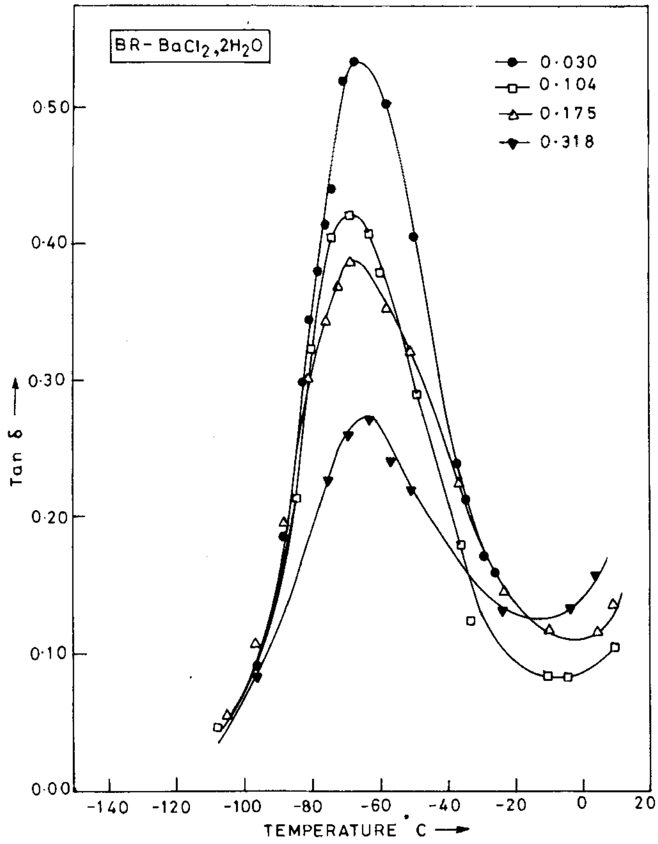

FIGURE 1 Tan δ as a function of temperature.

tan δ during the transition however is totally opposite to that observed during the glass transition.

The possible explanation for this apparently absurd effect lies in the physical state of the composite. When crystallites start melting, the flow properties (liquid like behaviour) show a marked increase and hence the filler particles act as if they are suspended in a fluid of finite but very high viscosity. At this stage the viscosity, and damping increase greatly while rigidity of the composite does not increase with increasing volume fraction of the filler, since matrix rigidity is very poor.

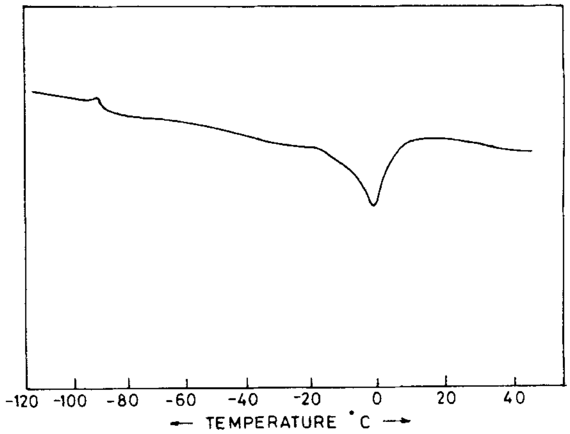

FIGURE 2 DSC thermogram of polybutadiene (BR).

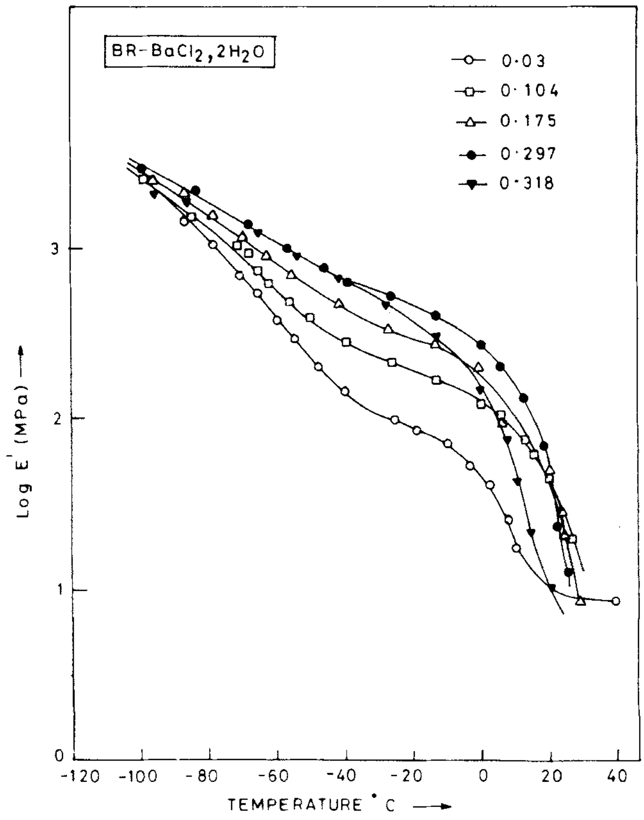

FIGURE 3 Log E' as a function of temperature.

Effect of temperature on dynamic storage modulus of the composites is shown in Figure 3. The two transistors mentioned above can be confirmed by occurrence of inflections on the corresponding temperature regions. The effect of filler concentration on E' below the glass transition is insignificant. This possibly is due to relatively small contribution of the filler at the temperature, of consideration, (at this temperature, the polymer is glassy and hence itself offers a very high modulus thereby reducing the relative contribution of the filler in the property of the composites.[8] Polymer

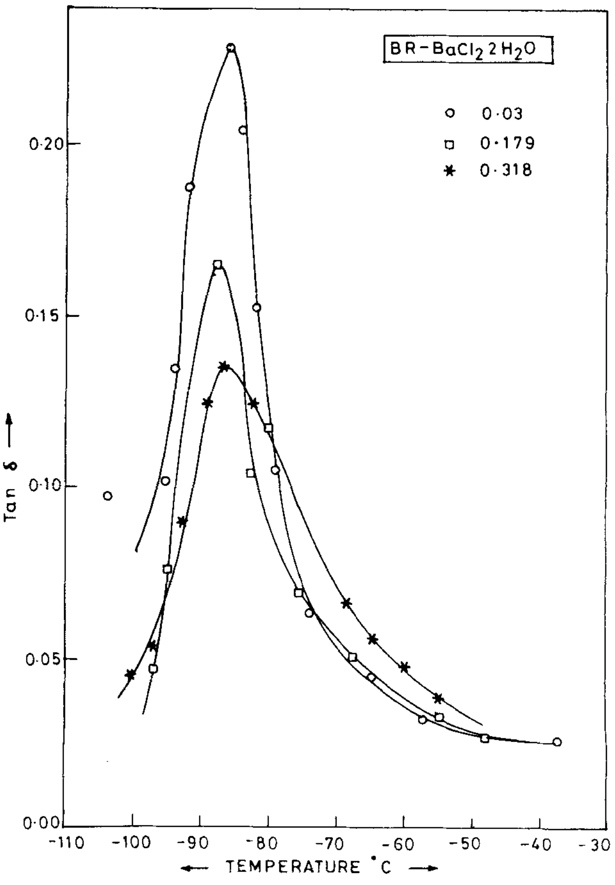

FIGURE 4 Tan δ as a function of temperature.

filler interaction (wetting of filler particles) also drastically cuts at such low temperatures, due to an infinite increase in the viscosity of the matrix.

Measurements on Torsion Pendulum helped in confirming validity of the data obtained on DMA. Figure 4 depicts the dependence of tan δ on temperature. The temperature at which tan δ passed through the maximum was found to be at lower side (−96°C).

The difference can be explained on the basis of technique of and frequency of measuring instrument.[9] Transition in Polymers occur at low temperature if low frequency is used in measurement. The magnitudes of tan δ determined using TP are subjected to an error if they exceed 0.2.[10] (tan δ is calculated considering an average of 5–10 oscillations and high damping in the specimen offers only 1 or 2 oscillations.)

During the glass transition region the concentration of the filler shows a significant effect. The effect is more pronounced above Tg compared to that below Tg. This is due to the enhanced wettability of the matrix, which comes from an increase in temperature. However at further high temperatures the filler fails to influence E'. This is due to occurrence of crystalline melting in the matrix, which manifests itself in liquidlike behaviour and thus the rigidity is lost totally in the polymer.

CONCLUSIONS

Dynamic mechanical parameters such as tan δ, E', E'', of composites show effect of concentration of the filler. Mechanical loss factor (tan δ) suppressed with increasing filler concentration in the composites. This is due to presence of multiple relaxation times caused by increased matrix-filler interaction. Presence of such interaction during glass transition, causes higher increases in rigidity compared to corresponding increase in damping characteristics (Because during the transition segmental mobility is permitted and not the flow properties.) Transition occurring due to crystalline melting of the matrix shows the opposite effect since flow properties become predominant at that temperature. Thus an increase in the filler concentration increases tan δ. The occurrence of the transition is confirmed on DSC.

Storage modulus does not show an influence of the filler concentration below Tg, presumably due to very high rigidity of the matrix itself and poor wettability of the matrix. At higher temperatures the wettability increases and the filler increases E' however when crystalline melting occurs the filler does not impart any improvement, owing to predominance of flow properties.

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