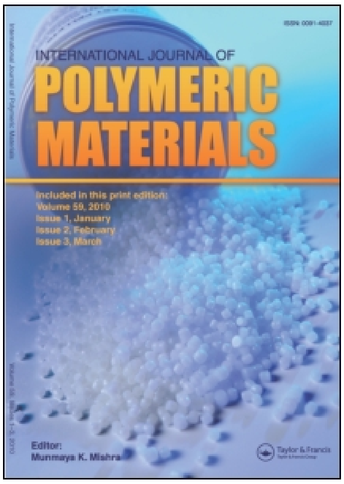

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Dynamic Mechanical Properties of Filled Polybutadiene

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The effect of filler on dynamic mechanical properties of polybutadiene-barium fluoride composites are investigated. The properties studied are; glass transition temperature, storage modulus and loss modulus.

KEY WORDS Dynamic mechanical properties, polybutadiene, barium fluoride.

INTRODUCTION

Dynamic mechanical properties of elastomeric composites can conveniently be studied by measuring the response of the material when subjected to resonance or forced oscillations, in frequency or temperature plane. The study of these properties gives a lot of useful information regarding product performance.[1-3]

In the earlier communications, dynamic mechanical properties of polybutadiene filled with barium chloride has been reported.[4,5] A report on filler effects on dynamic mechanical properties of polybutadiene-barium fluoride composites is presented here. The properties studied are glass transition temperature, storage modulus, loss modulus etc.

EXPERIMENTAL

Materials

a) Polymer. Polybutadiene rubber (Cisamer 1220, Indian Petrochemicals Corporation Ltd.) having high cis content (96%) was utilized in the work. The polymer was characterized by GPC and DSC[5] (Table I).

b) Filler. Barium fluoride was prepared by precipitation technique. Dilute solution of barium chloride was added to a concentrated solution of sodium fluoride

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TABLE I

Characterization of polybutadiene by GPC

i) Molecular Weight	
$\bar{M}n$	8.95×10^4
$\bar{M}w$	4.68×10^5
$\bar{M}v$	4.67×10^5
ii) Dispersity	5.02
iii) Intrinsic Viscosity	0.467

TABLE II

Recipe of formulation

Ingredient	Phr.
Polymer	100
ZnO	5
Filler (BaF_2)	Variable
Stearic Acid	2
Sulphur	1
MBT	1
TMTD	0.6
Phenyl B-Naphthyl amine	1

till the precipitate ceased to form. The precipitate was filtered, washed with water to remove any traces of barium chloride. The precipitate thus obtained was subsequently dried in an oven at 80°C for 72 hours. The filler in the desired particle size range (150 μ) was then obtained by ballmilling and sieving. The average particle size of the filler was determined on an Image Analyzing System (IAS, Leitz TAS-PLUS).

Recipe. Recipe formulation has been shown in Table II. Optimum cure time for this formulation was determined on Monsanto Rheometer.[6]

Compounding and Molding

The process has been carried out as described earlier.[4] Composites containing various volume fractions of BaF_2 (0.034, 0.096, 0.152, 0.237) were prepared.

Characterization of the Composites

The volume fraction of the filler was determined by incineration method as well as by density measurements.

Dynamic mechanical properties were studied on DMA 981-TA 990 (DuPont) and a freely oscillating torsion pendulum (TP).

RESULTS AND DISCUSSIONS

The temperature dependence of mechanical loss factor (tan δ) for composites of varying volume fractions of the filler has been shown in Figure 1. The glass transition temperature (Tg) of the composites did not show a variation with the concentration of the filler in the composites. Thus the concentration of the filler does not seem to have an influence on the mobility of the polymeric chains. However, it suppresses

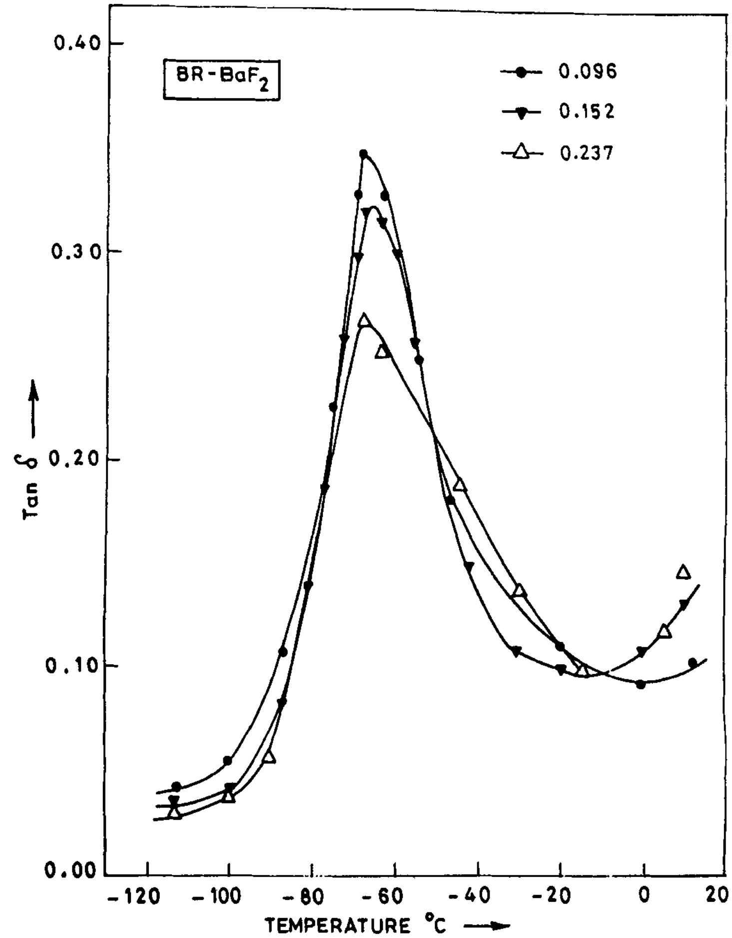

FIGURE 1 Tan δ as a function of temperature (determined on DMA).

the magnitude of tan δ generally, and particularly during the Tg region. The trend was observed in barium chloride filled composites also. Those however exhibited much greater magnitudes of tan δ and damping compared to those of the composites filled with barium fluoride. The dependence of tan δ_{max} on the volume fractions of the filler has been shown in Figure 2. The curves show negative slope indicating that the magnitudes of tan δ_{max} decrease with an increase in the concentration of the filler. The slope of both the curves is nearly identical, implying that the effect of filler content on the property being identical for both the fillers, and chemical nature of the filler being an important factor in addition to its concentration. The graph also represents the nature of the interaction of the polymer with the filler at Tg. Barium fluoride was found to interact strongly with the matrix since the magnitudes of the tan δ_{max} were found to be low. Though the magnitudes of the tan δ were low for the barium fluoride filled composites compared to those of barium chloride filled composites, determined on DMA, the measurements on TP did not show a similar effect. This is presumably due to inherent drawback of TP in measurement of high damping materials. For accurate determination of tan δ

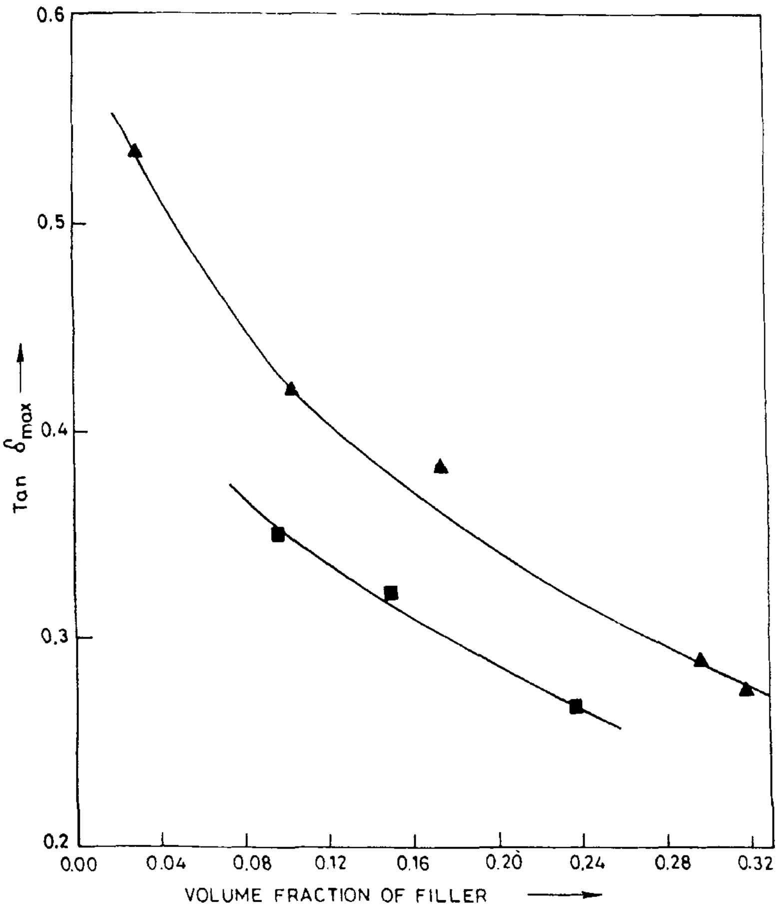

FIGURE 2 Tan δ as a function of volume fraction of the fillers.

on TP, damping train corresponding to 5–10 oscillations should be considered, while for a specimen with a high damping material it is not possible to get such a damping train. The damping in such material is so large that after 1–2 oscillations only, the damping train dies out. Hence, tan δ_{max} could not be obtained accurately on TP. The Tg as determined from tan δ_{max} value obtained on TP is identical for both the systems and occurred at −86°C manifesting the effect of frequency of measurement on dynamic mechanical parameters (Figure 3).

Dynamic storage modulus (E′) for various composites has been shown as a function of temperature in Figure 4. The glass transition region is associated with an inflection in the storage modulus at −68°C. The other inflection occurring around 10°C is ascribed to melting of crystallite which reduce the rigidity of the polymer matrix to the minimum. The phenomenon can be explained considering the crystallites acting as filler particles, reinforcing the material.[7] The filler concentration shows a positive effect on E′ in the entire temperature range of consideration. The increase in E′ during the glass transition is more compared to the

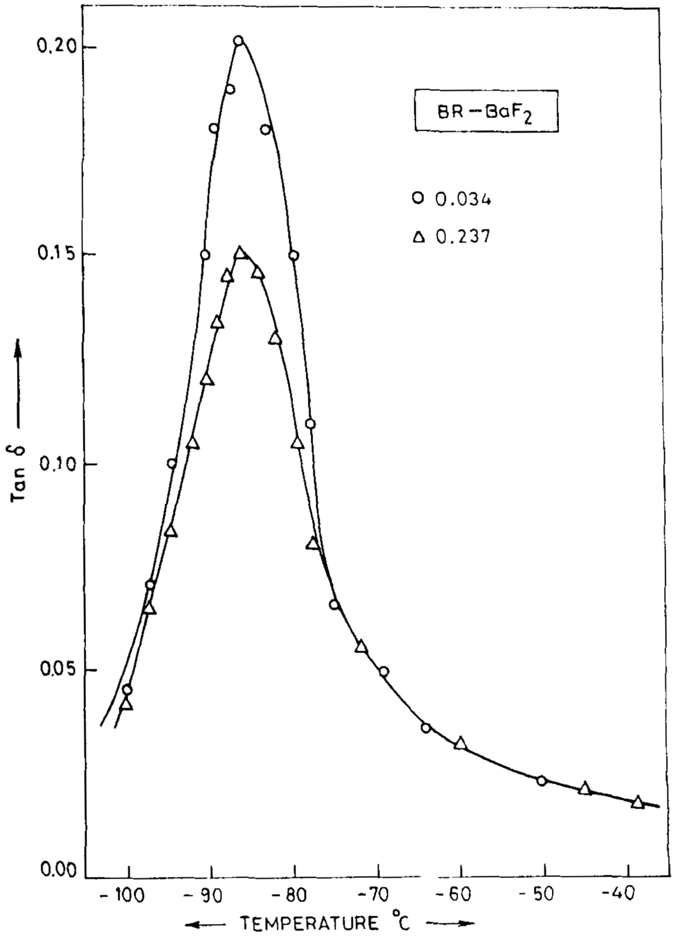

FIGURE 3 Tan δ as a function of temperature (determined on torsion pendulum).

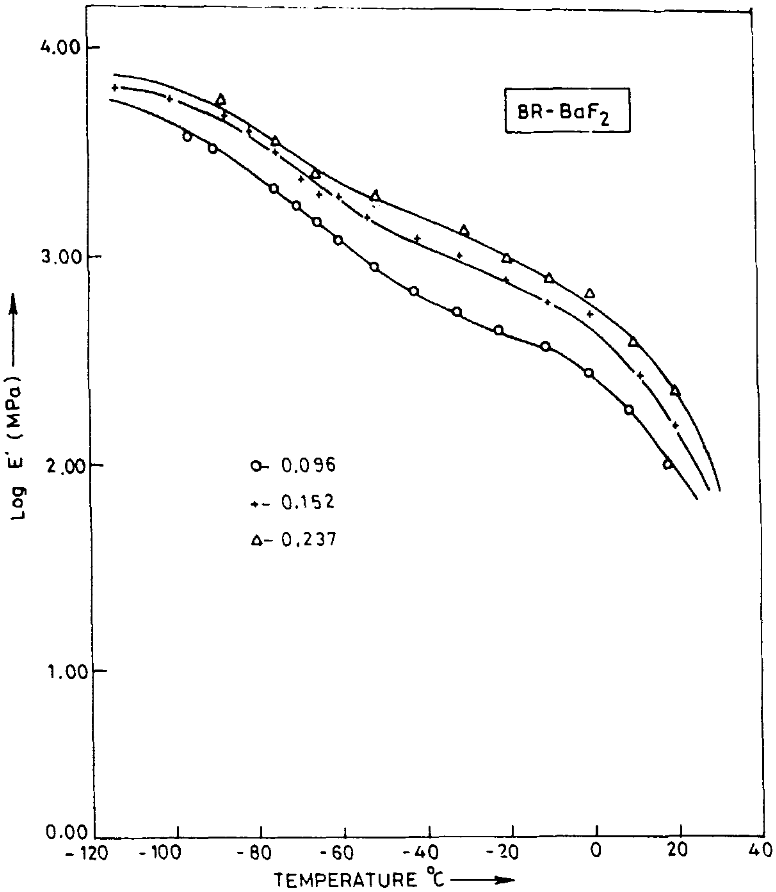

FIGURE 4 Log E' as a function of temperature.

increase in the pre-transition and post-transition temperature regions. Careful observation of the pre-transition region reveals that the filler concentration does not increase the modulus of the composites significantly. This may be presumably due to two factors. First is decreased relative contribution of the filler toward the modulus of the composites. Since the polymeric chains stiffen at temperatures lower to Tg, the modulus of the matrix (polymer) attains very high magnitude of modulus, at the same time, the modulus of the filler does not show any increase in modulus due to lowering of temperature. Secondly, wettability of a matrix at lower temperatures is quite poor and hence the filler polymer adhesion bond is weakened reducing the efficiency of the reinforcement.

CONCLUSION

Barium fluoride was found to react with strongly polybutadiene matrix as compared to barium chloride. This is substantiated by the fact that the former exhibited lower magnitudes of mechanical loss factor (tan δ_{max}) values. The suppression of tan δ_{max} values with increasing filler content indicated that the filler particles caused a change in dynamic storage as well as dynamic loss modulus and the change in the latter is less pronounced compared to that in the former at a common temperature. The amount of filler in the composites did not influence the chain mobilities (Tg).

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