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Reinforcement in Polybutadiene by Metal Oxides

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The effects of chemical characteristics of metal oxide fillers on mechanical and dynamic mechanical properties of polybutadiene are investigated.

KEY WORDS Dynamic properties modulus, particulate reinforcement, glass transition

INTRODUCTION

Influence of a particulate filler on deformability of a polymer was earlier considered to be purely hydrodynamic.¹ However, later it was proved that specific interaction between a filler and matrix is very important and hence qualitative gradation of fillers can be made.² In this paper we report the studies on chemical nature of a filler on mechanical and dynamic mechanical properties of filled polybutadiene. The fillers selected are zinc oxide and magnesium oxide.

EXPERIMENTAL

Materials—Polybutadiene rubber (Cisamer 1220) was obtained from Indian Petrochemicals Corporation Ltd., India. It was characterised by GPC and DSC. Table I gives the characteristics of the polymer obtained on GPC.

Fillers used were 99.9% chemically pure and manufactured by BDH Chemicals India. The fillers were ballmilled until the desired particle size (125–150 micrometers) was obtained.

Other chemicals such as sulphur, MBT, stearic acid and TMTD, manufactured by Bayer India Limited, were used in curing of composites.

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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	5.2
C)	Intrinsic viscosity	0.467

TABLE II
Recipe

Ingredient	Proportion (phr)
Rubber	100
Zinc oxide	5
Stearic acid	2
Sulphur	1
Mercaptobenzothiazole	1
Tetramethyl thiuram disulphide	0.6
Phenyl-naphthylamine	1
Curing temperature	140°C
Curing time	10 min

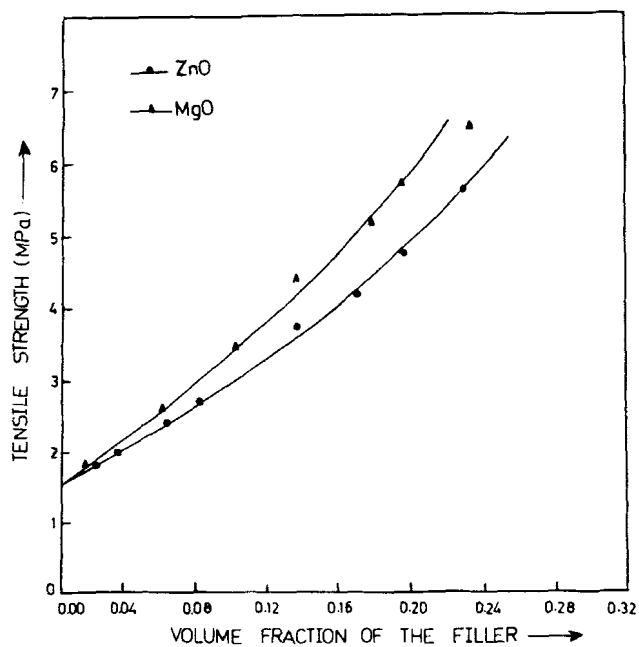


FIGURE 1 Tensile strength as a function of filler content.

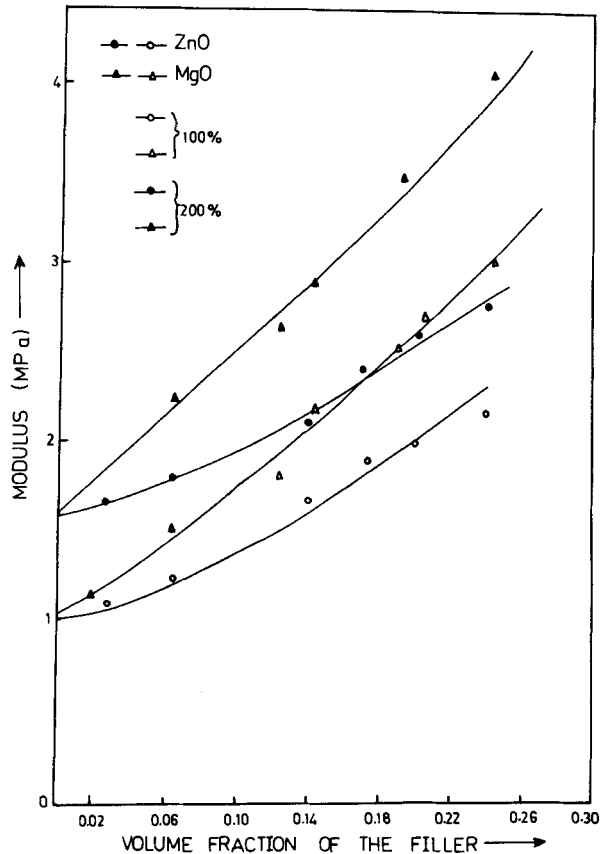


FIGURE 2 Modulus (100%, 200%) as a function of filler content.

Table II provides an idea about the recipe. Optimum cure time was determined on Monsanto Rheometer.

Compounding was carried out on a laboratory size two roll mill. Temperature of the mill was not allowed to exceed 80°C.

A premasticated stock of elastomer 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 sheets. The sheets were conditioned according to standard procedure.³

Low frequency relaxations were studied on Torsion Pendulum fabricated in the laboratory.

Dynamic Mechanical Analysis was carried out on DMA 981/TA 990 (DuPont). The temperature range was -100° to +10°C, under the heating rate of 5°/minute. The sample was exercised by a unique stress producing geometry with near zero hysteresis in horizontal direction and high rigidity in vertical direction in dynamic mechanical analysis.⁴

Results are presented in Figures 3-6. Results of mechanical tests are presented in Tables III and IV.

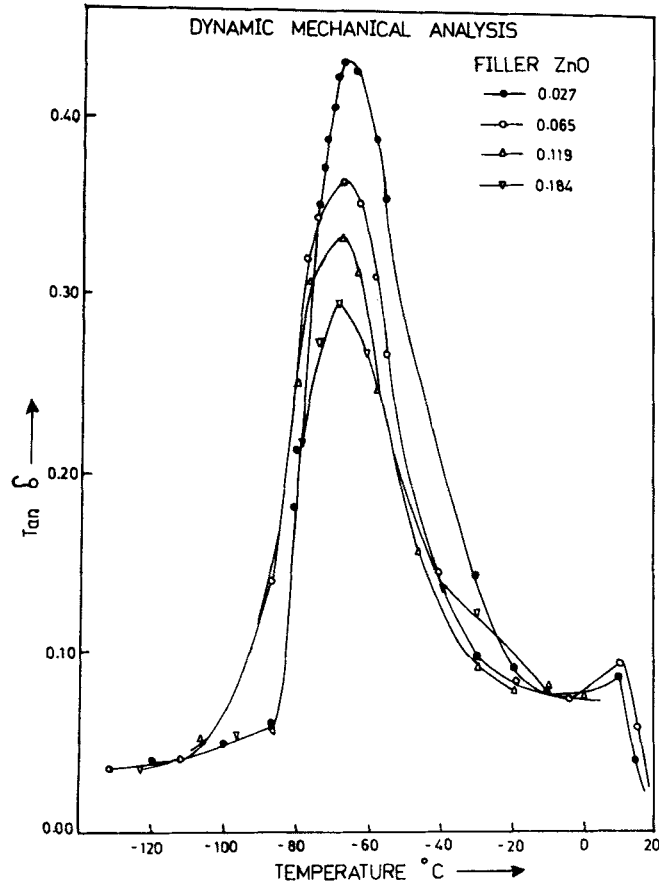


FIGURE 3 Tan δ as a function of filler content (BR-ZnO).

RESULTS AND DISCUSSION

Variation of tensile strength modulus as a function of filler content (Figures 1 and 2 respectively) imply that both the fillers caused an increase in the properties of the composites. Magnesium oxide imparted relatively large increase. The rate of increment in tensile strength was found to be higher at high filler loadings. Modulus (100%, 200%), data showed that the rate of improvement in the property was identical for both the systems and at any volume fraction of filler, the difference in moduli (200%), of composites filled with magnesium oxide and those filled with zinc oxide was greater than the similar comparison of modulus (100%). This implied that the interaction of magnesium oxide with matrix is considerably stronger than that of zinc oxide. Weaker interaction between matrix and zinc oxide was evidenced by the fact that the difference between magnitudes of modulus (200%) and modulus (100%) for any volume fraction of filler kept on increasing at higher filler loadings. Ultimate elongation data (Table III) also indicated that weak interaction between matrix and a filler is the cause of more elongation. Strong matrix-filler interaction for magnesium oxide filled composites was further supported by lower magnitudes

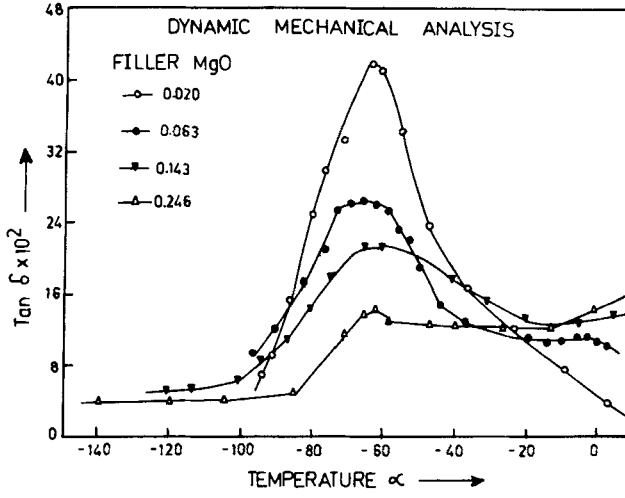


FIGURE 4 Tan δ as a function of filler content (BR-MgO).

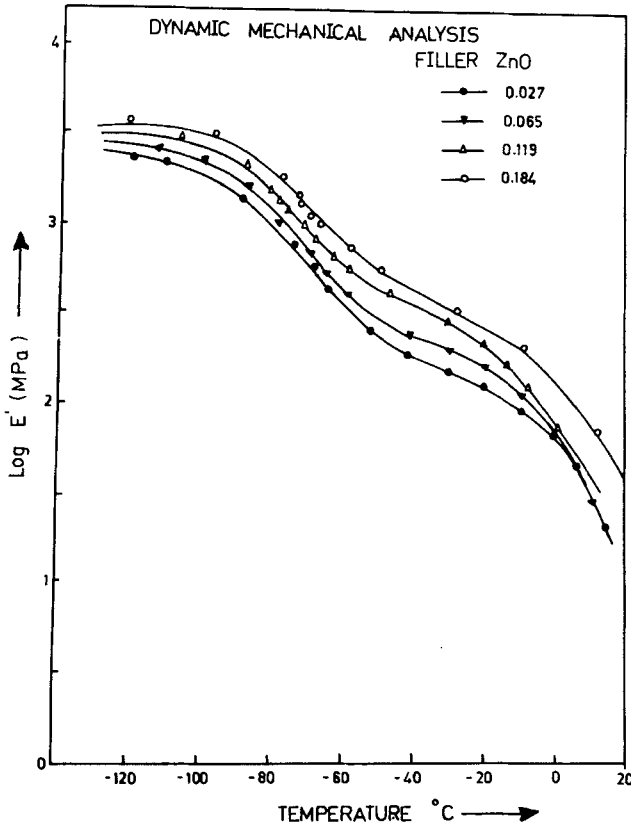


FIGURE 5 Log E' as a function of temperature (BR-ZnO).

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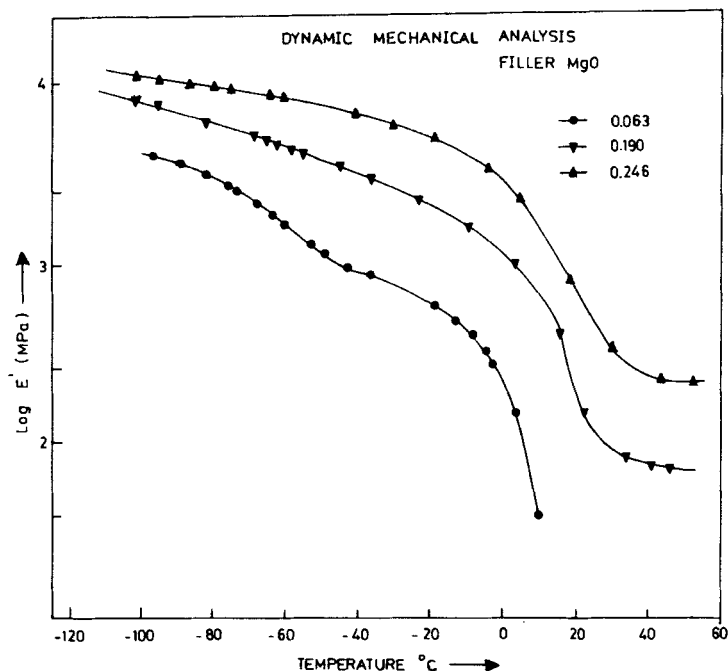


FIGURE 6 Log E' as a function of temperature (BR-MgO).

of ultimate elongation, high tensile strength and high Young's modulus. Thus the contribution of magnesium oxide in reinforcement was more than that of zinc oxide. This can be explained on the basis of high ability of magnesium oxide in curing the composite, owing to its role as an acid acceptor and also curator. As the concentration of magnesium oxide is increased final cure is more complete.⁵ The higher moduli shown by magnesium oxide filled composites may be due to high hardness of magnesium oxide (5.6 Mohs) compared to that of zinc oxide (3.6 Mohs), since modulus of a filler is directly proportional to its hardness.

DYNAMIC MECHANICAL ANALYSIS

Dependence of mechanical loss factor ($\tan \delta$) on temperature is graphically shown in Figures 3 and 4. In both the cases two transitions are found to occur at -68°C and around 10°C . These can be ascribed of α (transition from glassy to rubbery) and α_c (crystallite melting).^{6,7} It is further observed that $\tan \delta_{\max}$ (the maximum magnitude of $\tan \delta$) undergoes a suppression with increase in filler loading, indicating that filler particles influence E' (dynamic storage modulus) and/or E'' (dynamic loss modulus). Further the influence on E'' is less pronounced compared to that in E' . The filler zinc oxide did not show any influence on segmental mobility of the polymeric matrix as the transition occurred at -68°C while magnesium oxide caused slight increase in the temperature as filler loading increased (Figure 4). In the glassy state filler loading causes insignificant reinforcement for zinc oxide filled

TABLE III
Mechanical properties of system BR-ZnO

Volume fraction of the filler	Tensile strength, MPa	Young modulus, MPa	Modulus MPa		Elongation %	Hardness share A	Density, g/cc	Relative Young's modulus
			100%	200%				
0.027	1.75	31.9	1.10	—	190	45	1.0754	1.60
0.038	2.00	36.6	1.14	1.65	200	46	1.1270	1.83
0.065	2.40	45.0	1.23	1.80	280	48	1.2536	2.25
0.085	2.68	55.8	1.40	1.78	330	50	1.3460	2.79
0.141	3.70	82.0	1.62	2.10	500	57	1.6060	4.10
0.174	4.20	103.0	1.90	2.40	540	63	1.7591	5.15
0.200	4.75	123.7	2.00	2.64	580	66	1.8802	6.19
0.240	5.60	140.4	2.14	3.00	600	71	2.0658	7.02

TABLE IV
Mechanical properties of system BR-Mgo

Volume fraction of the filler	Tensile strength, MPa	Young modulus, MPa	Modulus		Elongation %	Hardness share A	Density, g/cc	Relative Young's modulus
			100%	200%				
0.020	1.77	31.3	1.14	—	180	45	1.0200	1.57
0.063	2.63	69.4	1.50	2.25	200	50	1.1410	3.47
0.106	3.89	126.3	1.80	2.60	230	56	1.2540	6.32
0.143	4.40	183.2	2.20	2.90	250	61	1.3511	9.16
0.190	5.30	200.0	2.50	3.50	270	68	1.4720	10.00
0.246	6.50	220.0	3.00	4.10	300	75	1.6031	11.00

composite (Figure 5) presumably because of substantial increase in the modulus of the matrix (due to freezing of segmental motion) and poor wettability of the matrix at low temperatures.⁸

Magnesium oxide as a filler showed substantial increase in E' in glassy as well as rubbery state (Figure 6). Also the inflection point indicative of transition is observed to go weaker as the filler concentration increased. This indicates stronger interaction between matrix and the filler. The other transition (α_c) remained unaffected for both the systems. However magnesium oxide filled composites showed higher magnitudes of $\log E'$ after the occurrence of transition.

Dynamic mechanical analysis on a free oscillating torsion pendulum showed glass transition to occur at lower temperature. The difference was not unexpected as frequency of operation for DMA and torsion pendulum was different.⁹ Magnitudes of $\tan \delta$, measured on the torsion pendulum were rather low as compared to those measured on DMA. This was due to the inherent limitation of torsion pendulum in measuring high magnitudes of $\tan \delta$.¹⁰

CONCLUSIONS

Magnesium oxide imparts higher reinforcement in the composite compared to that imparted by zinc oxide. The strong interaction of the filler with matrix is evidenced by high tensile strength, high Young's low ultimate elongation, high hardness high E' . The interaction which imparts reinforcement does influence segmental mobilities of the matrix, as the glass transition temperature for the filler system (magnesium oxide) slightly shifted to higher temperatures. Dewetting of the filler from matrix occurs in the case of zinc oxide filled composites at higher filler loading. Crystallite melting temperature is observed to occur at 0°C.

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