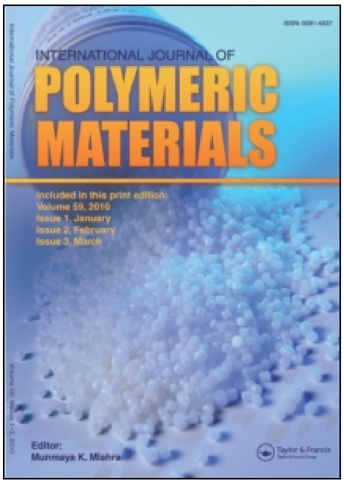

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Pandya, M. V. , Deshpande, D. D. , Hundiwale, D. G. and Kapadi, U. R.(1984) 'Reinforcement in Polybutadiene (PB) with Inorganic Fillers System I—Barium Chloride (Hydrate and Anhydrous) and Barium Fluoride', International Journal of Polymeric Materials, 10: 3, 189 — 197
To link to this Article: DOI: 10.1080/00914038408080269
URL: http://dx.doi.org/10.1080/00914038408080269

Intern. J. Polymeric Mater., 1984, Vol. 10, pp. 189–197
0091-4037/84/1003-0189 $18.50/0

Printed in the United Kingdom

Reinforcement in Polybutadiene (PB) with Inorganic Fillers System I—Barium Chloride (Hydrate and Anhydrous) and Barium Fluoride

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Polybutadiene (PB) elastomer is studied with barium chloride (hydrate), barium fluoride barium chloride (anhydrous) as filler. Properties like tensile strength, moduli at various elongation, Young's modulus, showed superior reinforcing nature of barium fluoride and insignificant improvement due to removal of water of hydration of barium chloride hydrate.

INTRODUCTION

Reinforcement of rubbers by incorporation of fillers is a very old phenomenon studied by many research workers. In spite of massive work done in the area, the phenomenon is not fully understood. Some important factors contributing to reinforcement are established such as, particle size, shape of the filler, surface characteris-

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tics and nature of polymer-filler interactions.[1] A number of elastomers have been studied mainly with different grades of carbon blacks[2] and silica.[3] It is generally agreed that Van der Waals forces are sufficient to give rise to reinforcing effects, but for superior reinforcement, high degree of adhesion between filler surface and the polymer, produced by chemical interaction is desirable.[4] Many equations have been put forth relating modulus of composite and volume fraction of the filler.[5,6]

To understand the reinforcement phenomenon, the study is undertaken in this laboratory with a variety of inorganic and organic fillers. Filler reinforcement of the system polybutadiene (PB) with zinc oxide is reported.[7] In this paper, properties like modulus at 100%, 200% and 300% elongation, tensile strength, elongation at break, hardness, Young's modulus, density etc. are reported for various filler composition for systems polybutadiene + barium fluoride, polybutadiene + barium chloride (hydrated).

EXPERIMENTAL

Materials

(a) Fillers—fillers used were of analytical grade and sieved to obtain particle size between 125–150 microns. Barium chloride anhydrous was prepared by heating barium chloride hydrate at 250°C for one week and then was cooled in a desiccator. The filler thus prepared was kept in the desiccator till used in compounding.
(b) Rubber—polybutadiene cisamer 1220 (cis – 97%) manufactured by Indian Petrochemicals Ltd. was used.
(c) Other chemicals—all other chemicals used were manufactured by Bayer (India) Ltd.

The following recipe was used:

Rubber—PB	100 parts by weight
Zinc oxide	5 phr
Filler	Variable
Sulphur	1 phr
Mercaptobenzothiazole (MBT)	1 phr
β-naphthyl phenyl amine	1 phr

Tetramethyl thiuram	0.6 phr
Curing temp.	140°
Curing time	10 minutes

RESULTS AND DISCUSSION

Tensile strength, modulus at 100%, 200% and 300% elongations, Young's modulus, elongation at break, hardness are given in Tables I, II and III for system $BaCl_2$ (hydrated) + polybutadiene (PB) BaF_2 + polybutadiene, and $BaCl_2$ (anhydrous) + polybutadiene respectively.

Tensile strength

As observed in Figure 1, tensile strength, for the system $BaCl_2$(h) + PB slightly increases with filler concentration; it passes through a maximum and decreases slightly. For the system with BaF_2 as a filler, tensile strength increases considerably with concentration of the filler and passes through a maximum. To ensure that the low tensile strength with $BaCl_2$ (hydrate) as a filler is not due to water of crystallisation, a few measurements are taken with anhydrous $BaCl_2$ as filler (Table III) and it is found that the significant increase in tensile strength is not observed.

Modulus

Modulus increases with elongation as expected because due to stretching, orientation of elastomer matrix takes place and interaction with filler increases. This is observed in both systems (Figure 2).

Elongation at break

It is observed that in both the systems percent elongation at break increases with filler content. Increase is much more in the system with BaF_2 as a filler. Normally rigid fillers cause a dramatic decrease in elongation because all the elongation comes from elastomer

TABLE I

System PB + $BaCl_2$ (hydrate): variation of tensile strength, moduli, elongation at break (%) Young's modulus, hardness, and relative modulus with filler content

Filler phr	vol. fraction	Density g/cc	Tensile strength MPa	Modulus (MPa) 100%	Modulus (MPa) 200%	Modulus (MPa) 300%	Elongation at break %	Young's modulus MPa	Hardness shore A	Relative modulus exptl.	Relative modulus theoretical
0	0	0.955	13.83	11.73	—	—	149 ± 25	23.54	35	1.00	1.00
10	0.030	1.020	12.51	10.55	—	—	144 ± 13	20.46	44	0.87	1.09
20	0.054	1.072	13.41	10.53	—	—	184 ± 08	24.90	46	1.06	1.18
30	0.079	1.125	13.87	10.32	13.31	—	208 ± 15	23.48	47	1.00	1.29
40	0.104	1.176	13.23	10.05	12.66	—	208 ± 15	26.34	47	1.12	1.41
80	0.179	1.331	14.83	10.00	12.66	—	266 ± 20	32.32	55	1.37	1.87
110	0.220	1.426	14.40	9.40	12.35	—	282 ± 11	29.77	53	1.27	2.23
130	0.297	1.590	14.37	8.50	11.50	—	266	31.21	53	1.33	2.99
160	0.318	1.900	12.74	9.93	11.28	—	278	29.76	60	1.26	3.22

TABLE II

System PB + BaF_2: variation of tensile strength, moduli, elongation at break (%) Young's modulus, hardness, and relative modulus with filler content

Filler content phr	Filler content vol. fraction	Density g/cc	Tensile strength MPa	Modulus (MPa) 100%	Modulus (MPa) 200%	Modulus (MPa) 300%	Elongation at break %	Young's modulus MPa	Hardness shore A	Relative modulus exptl.	Relative modulus theoretical
20	0.034	1.089	23.20	12.30	18.60	—	282 ± 37	25.39	46	1.08	1.10
30	0.051	1.157	22.10	12.50	18.27	—	267 ± 37	25.00	46	1.06	1.16
40	0.072	1.236	21.50	13.50	18.23	—	270 ± 12	27.30	47	1.16	1.25
60	0.096	1.333	29.50	14.70	20.74	25.19	358 ± 54	30.57	53	1.30	1.37
100	0.152	1.551	41.60	18.60	27.63	37.20	334 ± 10	44.40	59	1.89	1.71
140	0.199	1.740	47.00	20.83	30.40	40.40	368	41.55	63	1.77	2.06
180	0.237	1.887	41.00	19.00	26.43	35.22	368	47.98	65	2.04	2.38
220	0.272	2.028	41.77	20.35	27.28	35.46	370	53.71	68	2.28	2.72

TABLE III

System PB + $BaCl_2$ (anhydrous): variation of tensile strength, moduli, elongation at break (%) Young's modulus, Hardness, and relative modulus with filler content

Filler content phr	Filler content vol. fraction	Density g/cc	Tensile strength (MPa)	Modulus (MPa) 100%	Modulus (MPa) 200%	Modulus (MPa) 300%	Elongation at break %	Young's modulus (MPa)	Hardness shore A	Relative modulus exptl.	Relative modulus theoretical
10	0.024	1.025	16.11	11.66	—	—	206 ± 26	25.00	36	1.06	1.06
40	0.080	1.187	14.40	11.50	13.94	—	237 ± 29	28.57	45	1.21	1.28
80	0.162	1.425	16.05	11.68	13.66	15.70	300 ± 18	39.58	55	1.68	1.75

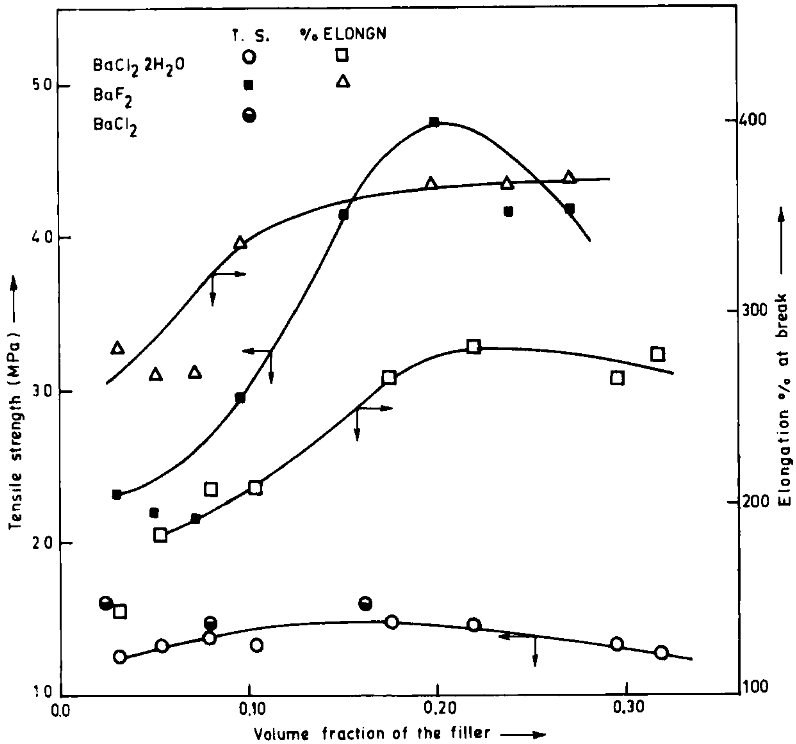

FIGURE 1 Tensile strength and elongation at break (%) as a function of volume fraction of fillers.

matrix if the filler is rigid. But according to Nielsen[8] when fillers introduce additional crazing and perhaps at the same time act as stoppers to crack growth do polymers filled with rigid fillers have elongation at break which is equal to or greater than that of unfilled polymer?

Young's modulus

Young's modulus values (Figure 3) are calculated from initial values of stress strain curve. Here it is observed that for the system with BaF_2 as filler, it increases considerably with filler concentration and for the chloride filler system a maximum is obtained and remains more or less steady.

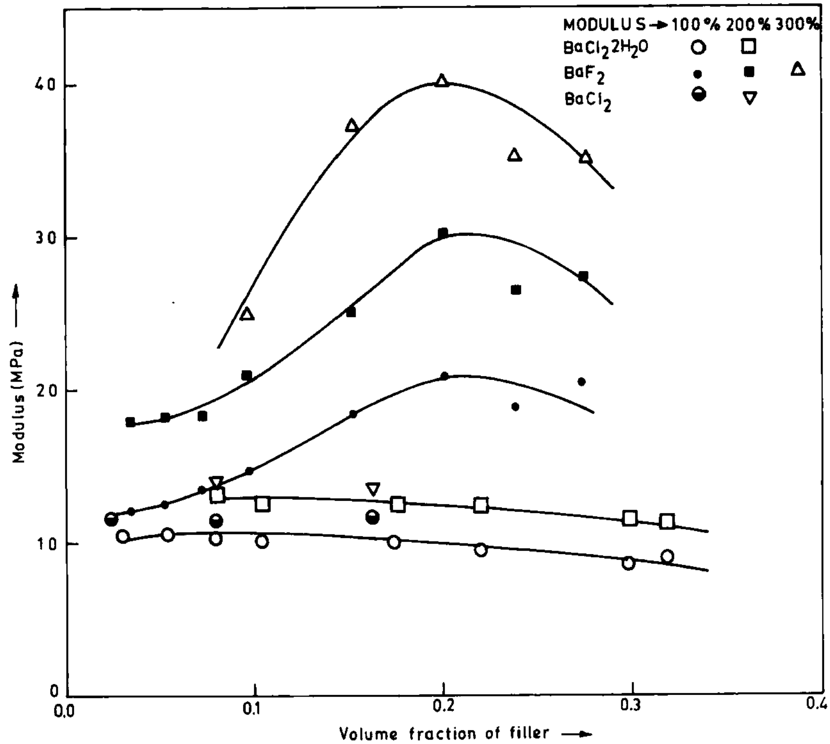

FIGURE 2 Modulus at 100%, 200%, and 300% elongation as a function of volume fraction of fillers.

Hardness

Hardness increases with increase in volume fraction of rigid filler. In the present study hardness of composites increases more with BaF_2 as filler compared with that in identical volume fraction, of other fillers.

Relative modulus

Einstein Guth Gold equation[9]

$$\frac{E_c}{E_0} = 1 + 2.5c + 14.1c^2$$

is used to calculate relative modulus. It is found that experimental

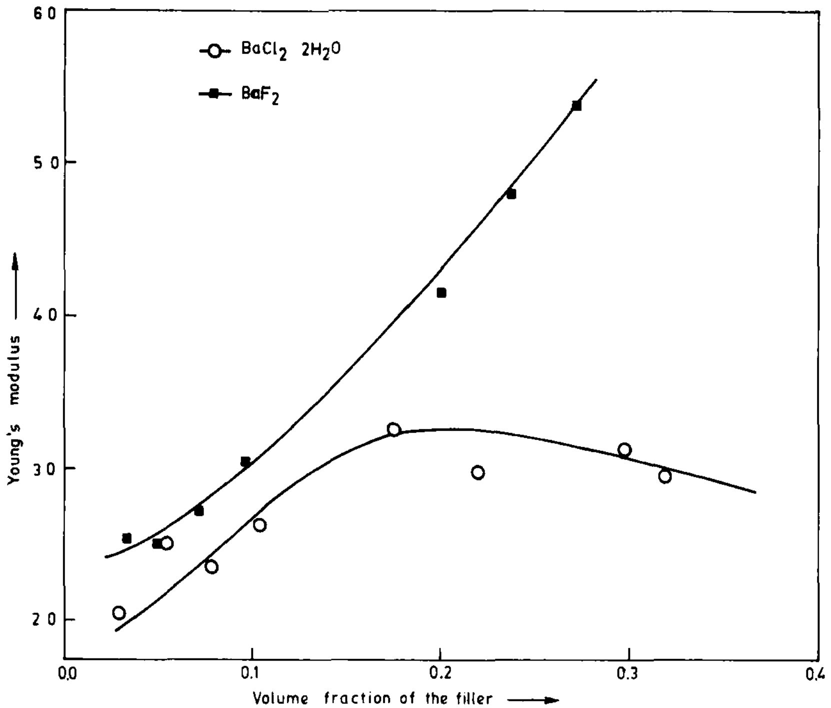

FIGURE 3 Young's modulus as a function of volume fraction of fillers.

results BaF_2 are fairly in good agreement with the calculated values for polybutadiene BaF_2 system.

CONCLUSION

Barium fluoride as a filler has more reinforcing properties compared to barium chloride as a filler. Most of the moduli increase by 100% with BaF_2 as filler. From the results of elongation at break and moduli it is clear that fluoride ion interacts strongly with elastomer matrix compared to chloride ion.

References

1. G. Kraus, *Reinforcement of Elastomers,* Interscience Publishers, New York, pp. 125
2. W. Hess, *ibid,* pp. 187
3. J. Sellers and F. Toodner, *ibid,* pp. 405
4. J. Bachmann *et al. Rubber Chem. Technol.* **38,** 1070 (1965).
5. E. Guth, *J. Appl. Phys.* **16,** 20 (1945).
6. H. Eilers, *Kolloid Z.* **97,** 313 (1941).
7. M. V. Pandya, *et al., J. Compos. Mat.* (communicated).
8. (a) L. Nielsen, *Mechanical Properties of Polymers,* Marcel Dekker Inc., New York, 1974, vol. 2, pp. 408. (b) L. Nicolais and M. Narkis, *Polym. Eng. Sci.* **10,** 97 (1966).
9. E. Guth, *J. Appl. Phys.* **15,** 758 (1944).