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Magnetic and processability studies of nitrile rubber vulcanisates containing barium ferrite and carbon black

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Fine particles of barium ferrite ($BaFe_{12}O_{19}$) belonging to the M-type hexagonal ferrites were prepared by the conventional ceramic techniques. They were incorporated into a nitrile rubber matrix according to a specific recipe for various loadings to produce rubber ferrite composites (RFC). The percolation threshold is not reached for a maximum loading of 130 phr (parts per hundred rubber). Here in this paper, the magnetic properties and processability of the nitrile rubber based RFCs containing barium ferrite (BaF) and HAF carbon black is reported. The magnetic properties of the ceramic ferrite and these rubber ferrite composites were evaluated and it was found that the coercivity values of RFCs were less than that of the ceramic BaF, but remained constant with the loading of both the ferrite filler and carbon black. However, other properties like saturation magnetization and magnetic remanence increased with the loading of ferrite filler.

Keywords: Magnetic materials, barium ferrite, rubber ferrite composites, nitrile rubber, carbon black

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Rubber ferrite composites (RFC) are magnetic polymer composites, which have a variety of high tech applications. They can be produced by the incorporation of ferrites in both natural and/or synthetic polymer matrices. Ferrites are a class of technologically important magnetic materials, which cannot be easily replaced by any other materials because of its stability, economy and wide-ranging applications[1-4]. Ferrites find extensive applications in making useful devices[5-7]. Ferrites are classified into two groups namely, magnetically soft and hard[8] and depending on its symmetry, it may be cubic, hexagonal or orthorhombic. Barium and strontium ferrites belong to the class of hexagonal ferrites. They are normally prepared by using the ceramic techniques apart from other techniques like sol-gel, ball milling and so on. The ceramic method is one of the cheapest of the methods employed for the preparation of the ferrites.

The incorporation of these hard ferrites into polymer matrices produces rubber ferrite composites[9,10], which are increasingly used as flexible permanent magnets, microwave absorbers and in other devices where flexibility and mouldability is an important criterion. Ferrites are normally used in the ceramic form and as they are not easily processable, it cannot be used to make complex shapes. However, RFC have the unique advantage of mouldability into intricate shapes. The addition of these magnetic fillers into the polymer matrix imparts magnetic properties and reinforces the matrix. It has earlier been reported that addition of carbon black to the matrix can enhance the microwave absorbing properties of the composites[11-13]. Thus, the effect of carbon black on the processability and magnetic properties has also been studied.

Experimental Procedure

Barium ferrite powders prepared by ceramic techniques are incorporated into the nitrile rubber matrix according to a specific recipe for various loadings to produce the RFC. From the RFC thus prepared, the one with 80 phr loading of BaF is selected as the control compound and carbon black (N330) were added stepwise to obtain carbon black containing RFC. Information about the cure characteristics gives an indication on the processability of the composites. The processability of these compounds was studied using a Goettfert

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Elastograph model 67.85. The magnetic properties were determined by using a vibrating sample magnetometer (VSM). The results of the investigation carried out on the ceramic barium ferrite and its incorporation in the nitrile rubber matrix (33 % acrylonitrile content) are presented here.

Preparation of barium ferrite

Barium ferrite was synthesized in large quantities (100 gram batch size) by the conventional ceramic techniques[14]. For this pure α-Fe_2O_3, prepared by the decomposition of freshly prepared ferrous oxalate dihydrate (FOD), is mixed with barium carbonate to produce a homogeneous mixture of fine particles. This homogenized mixture was pre-sintered at 500 °C for three hours.

$$BaCO_3 + 6\,Fe_2O_3 \longrightarrow BaFe_{12}O_{19} + CO_2$$

After three sets of homogenisations and pre-sintering, these powders were then fired at 1000 °C for 24 h.

X-ray powder diffraction

X-ray powder diffraction technique was used to characterize the prepared barium ferrite powder, using X-ray diffractometer (Rigaku Dmax-C) with CuK_α (λ = 1.5405 Å). The average particle size was determined by using the Debye Scherrer equation[15] $t = \frac{0.9\lambda}{\beta \cos\theta}$ where t is the particle size (nm), λ is the wavelength, β is the full width half maximum and θ is the Bragg angle. The lattice parameter (a), the interatomic spacing (d) and their relative intensities ($I/I_o \times 100$) were also determined. The surface area A_s per gram (m^2/g) was evaluated using the equation $A_s = 6000/D\rho$ where D is the diameter of the particle (nm) and ρ is the density (g/cc).

Incorporation of barium ferrite in nitrile rubber matrix

BaF was incorporated in a nitrile rubber (Aparene-N 553 with 33 % acrylonitrile content) matrix according to the recipe as shown in Table 1. The RFC were prepared for various loadings of BaF, ranging from 40 to 120 parts per hundred grams of rubber (phr) in steps of 20. The mixing was first carried out in a Brabender Plasticorder (Torque Rheometer) model PL 3S at 70 °C for 10 min at a speed of 50 rpm. This was then homogenised by using a two roll mixing mill (15 × 33 cm) as per ASTM D 3182-89.

Table 1—Recipe used for compounding of nitrile rubber with barium ferrite

Ingredients	Weight (g)					
	A	B	C	D	E	F
Nitrile rubber	100.0	100.0	100.0	100.0	100.0	100.0
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5
CBS	1.5	1.5	1.5	1.5	1.5	1.5
Antioxidant (SP)	1.0	1.0	1.0	1.0	1.0	1.0
BaF	0	40	60	80	100	120

Studies carried out earlier[16] on RFC based on natural rubber have shown that the percolation threshold was not reached even at a loading of 120 phr of magnetic fillers. Hence RFC containing 80 phr loading of BaF was taken as the control compound for further loadings of carbon black. RFCs containing carbon black were prepared for various loadings namely 10 to 50 phr, in steps of 10. The carbon black employed for the study was N330 (HAF).

Determination of cure characteristics of rubber ferrite composites

Goettfert elastograph model 67.85 was used for the determination of cure characteristics of the RFC. The cure parameters of the composites, both with and without carbon black were determined at 150 °C.

Preparation of test specimen

The specimens with 2 mm thickness for studying the magnetic properties were prepared by compression moulding on an electrically heated hydraulic press having 45 × 45 cm platens at a pressure of 140 kg cm^{-2} in a standard mould. The rubber compounds were vulcanised up to their respective cure time at 150 ^{o}C. The samples for magnetic studies were then cut from the vulcanised sheet using standard dies.

Evaluation of magnetic properties

The room temperature magnetic measurements of these rubber ferrite composites were carried out using vibrating sample magnetometer (VSM), model: EG & G PARC 4500. Magnetic properties of the rubber ferrite composites for different loadings of the BaF filler with and without carbon black were carried out. The magnetic parameters like Saturation magnetization (M_s), Magnetic remanence (M_r) and Coercivity (H_c) were evaluated from the hysteresis loops obtained at room temperature.

Results and Discussion

Structural studies

Analysis of the X-ray diffractograms of the barium ferrite shows that they are monophasic and highly crystalline in nature without any detectable impurities. The data from the X-ray diffractograms is given in Table 2. The interatomic spacing (*d*) and their relative intensities ($I/I_o \times 100$) matches well with that of the reported values in the literature[17]. The XRD spectrum of the ceramic barium ferrite prepared is shown in Fig. 1.

The particle size determination by the Debye Scherrer equation have shown that the average particle size of BaF has been found to be in the range 60-70 nm and had a surface area of 20-25 m^2/g. However, it may be noted that the particle size determined by the Debye Scherrer equation represents only the average distribution of the particles.

Processability studies

The processability studies of the polymer are important since the final vulcanized product is to be moulded. The processability of the composites was determined by evaluating the cure characteristics such as minimum torque M_L, maximum torque M_H, scorch time t_{10}, and optimum cure time t_{90} using the Goettfert elastograph. Evaluation of the cure time is a prerequisite for moulding the compounds. The variations in cure time for different loadings were studied for RFCs containing BaF and carbon black in nitrile rubber matrix. Graphs showing the variation of scorch time and cure time with the loading of BaF and carbon black in NBR are shown in Figs 2 and 3 respectively. Both the Scorch time (t_{10}) and optimum cure time (t_{90}) of these composites, decreases with the addition of ferrite fillers. The addition of carbon black reduces both the scorch time and cure time. The

Table 2—Wide angle X-ray diffraction data for barium ferrite

Inter atomic spacing d(Å)	Relative intensity $I/I_0 \times 100$
2.757	100
2.605	97
2.920	55
1.619	52
1.468	51
2.406	47
2.223	47
1.659	42
1.625	37
1.468	32
2.460	29

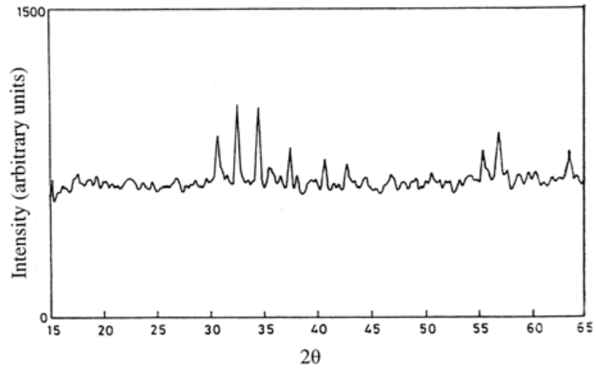


Fig. 1—Wide angle X-ray diffraction spectrum of ceramic barium ferrite.

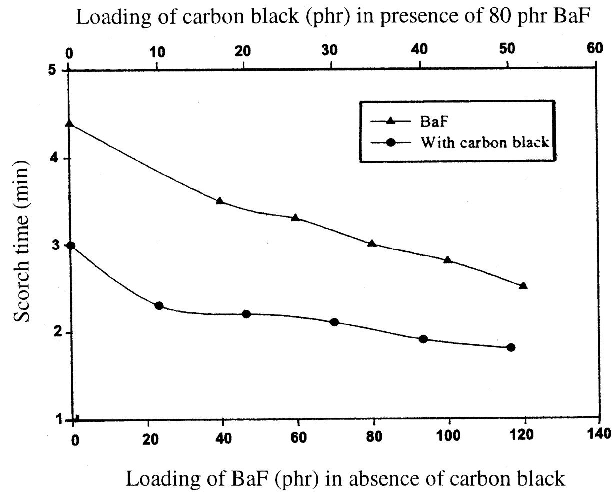


Fig. 2—Variation in scorch time with the loading of barium ferrite in absence of carbon black and carbon black in presence of 80 phr BaF in NBR.

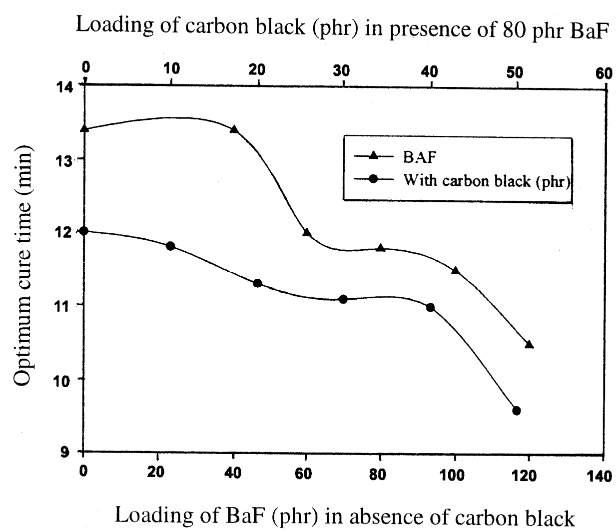


Fig. 3—Variation in cure time with the loading of barium ferrite in absence of carbon black and carbon black in presence of 80 phr BaF in NBR.

scorch time decreases with the filler loading because the heat of mixing increases as the filler loading increases. This is because of the greater amount of shearing that occurs between filler and polymer matrix. The cure time also decreased with the addition of fillers. The addition of carbon black in the compound containing 80 phr BaF decreased the time of cure. Evaluation of the cure parameters indicated that RFCs containing BaF, with and without carbon black reduced both the scorch time and cure time. This showed that cure reaction is accelerated due to addition of these fillers and even though the scorch time decreased with the addition of these materials the composites were still processable.

The variation of minimum torque and maximum torque with the loading of barium ferrite and carbon black is shown in Figs 4 and 5 respectively. The minimum torque (M_L) and maximum torque (M_H) of these composites roughly increase with BaF loading and with carbon black. From the cure characteristics of the composites, it can be observed that the minimum torque, which is a measure of the viscosity of the compound prior to onset of curing increases with the loading of filler as expected. The maximum torque, which gives an idea about the shear modulus of the fully vulcanised rubber at the vulcanization temperature, also more or less increases with filler loading.

Magnetic properties

It is well known that the addition of ferrites, both soft and hard, into the rubber matrix imparts magnetic properties and modifies the mechanical and dielectric properties. This was evident from the earlier studies of RFCs containing soft ferrites, like mixed ferrites namely $Ni_{1-x}Zn_xFe_2O_4$, $Mn_{1-x}Zn_xFe_2O_4$ in butyl/natural rubber[18-20] and hard ferrite like barium ferrite in natural rubber[11]. Moreover, the addition of carbon black in the natural rubber matrix appreciably increases the mechanical and dielectric properties[21], even though it slightly reduces its magnetic character. Tailoring the magnetic properties like saturation magnetization of the composites by varying the amount of magnetic filler is an added advantage of the RFC. The study of the rubber ferrite composites in a nitrile rubber matrix, which is polar and having the oil resistant property, thus, assumes importance. The magnetic parameters of BaF and the nitrile based RFCs obtained have shown that they are magnetic.

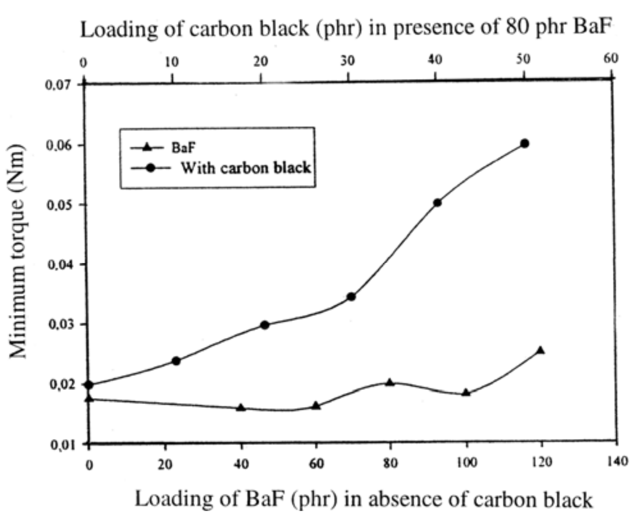


Fig. 4—Variation in minimum torque with the loading of BaF in absence of carbon black and carbon black in presence of 80 phr BaF in NBR.

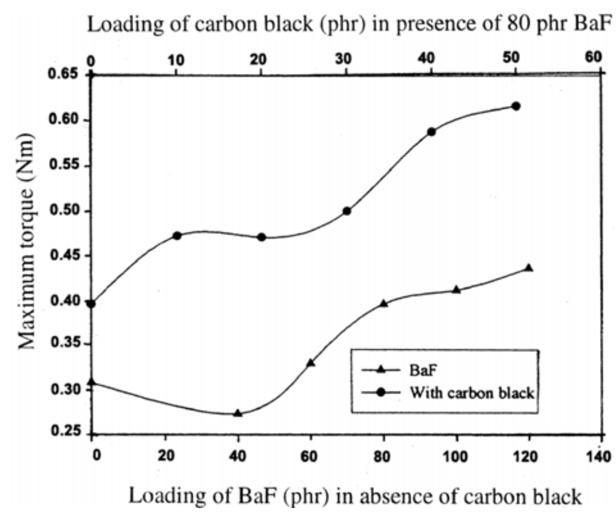


Fig. 5—Variation in maximum torque with the loading of BaF in absence of carbon black and carbon black in presence of 80 phr BaF in NBR.

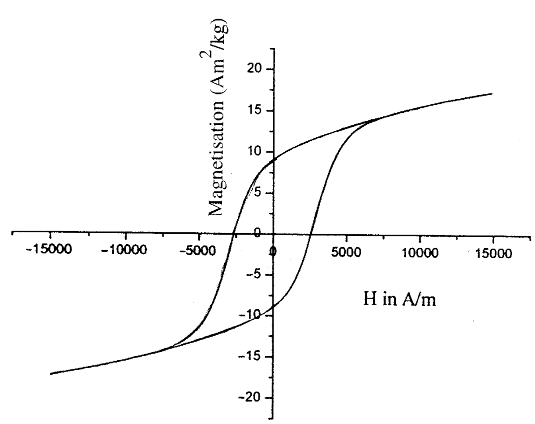


Fig. 6—Representative hysteresis loop of NBR based RFC containing 40 phr of BaF without carbon black.

Table 3—The magnetization parameters of ceramic BaF and NBR based RFC containing various loading of BaF

Loading of barium ferrite (phr)	Coercivity, H_z (A/m)	Magnetic remanence, M_r (Am^2/kg)	Saturation magnetization, M_s (Am^2/kg)	M_r/M_s
40	2533	8.75	16.89	0.52
60	2533	11.45	23.15	0.50
80	2533	14.74	28.22	0.52
100	2533	15.55	30.31	0.51
120	2533	16.56	33.08	0.50
Ceramic BaF	3059	32.17	58.04	0.55

Hysteresis loop of the NBR based rubber ferrite composites containing 40 phr of BaF in the absence of carbon black is shown in Fig. 6. The values obtained from the VSM measurements are shown in Table 3 and it indicated that the magnetic properties of the RFCs, namely the saturation magnetization (M_s) and the magnetic remanence (M_r) increased steadily with the loading of BaF filler. The variation of M_r for different loadings of BaF is shown in Fig. 7. The coercivity values of RFCs were less than that of the ceramic BaF, but did not vary with the different loading of BaF. The variations in coercivity of ceramic and composites, which occur, may be attributed to the small particle size that can occur during mixing[22]. Thus, it can be concluded that the addition of ferrite loading has no effect on coercivity.

Effect of carbon black on the magnetic properties of RFCs containing barium ferrite

The RFCs containing 80 phr of BaF and various loading of carbon black in NBR was prepared and the magnetic properties were studied. The Table 4 shows the hysteresis loop parameters of these RFCs, which indicated that, the saturation magnetization and the magnetic remanence values decreased with the loading of carbon black. Fig. 8 depicts the variation in saturation magnetization with loading of carbon black in NBR based RFCs containing 80 phr BaF, whereas the Fig. 9 shows the variation in magnetic remanence with loading of carbon black. However, the coercivity values remained the same for these composite as well. Even though the RFCs containing carbon black shows lower magnetization values, they are useful in making devices, which requires good mechanical and dielectric properties. Fig. 10 depicts the hysteresis loop for NBR based RFC containing 80 phr BaF and 50 phr of carbon black. Thus by the proper loading of the barium ferrite and carbon black into the rubber matrix, the RFCs with required magnetic properties for specific applications can be tailored.

Table 4—The magnetization parameters of NBR based RFC containing 80 phr of BaF and various loading of carbon black

Loading of carbon black (phr)	Coercivity, H_z (A/m)	Magnetic remanence, M_r (Am^2/kg)	Saturation magnetization, M_s (Am^2/kg)	M_r/M_s
0	2533	14.74	28.22	0.52
10	2533	13.85	26.12	0.53
20	2533	12.08	24.19	0.50
30	2533	11.66	23.15	0.50
40	2533	11.45	22.39	0.51
50	2533	11.23	22.16	0.51

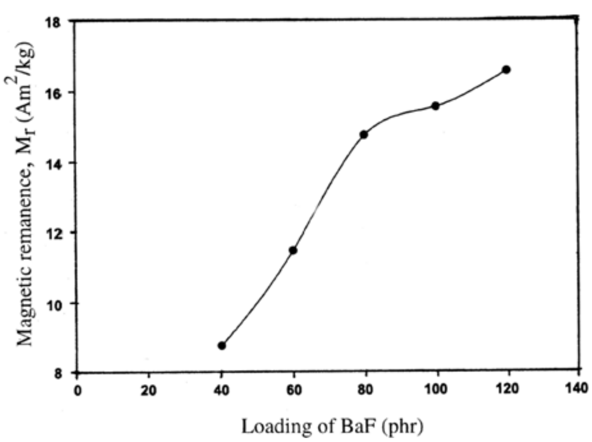
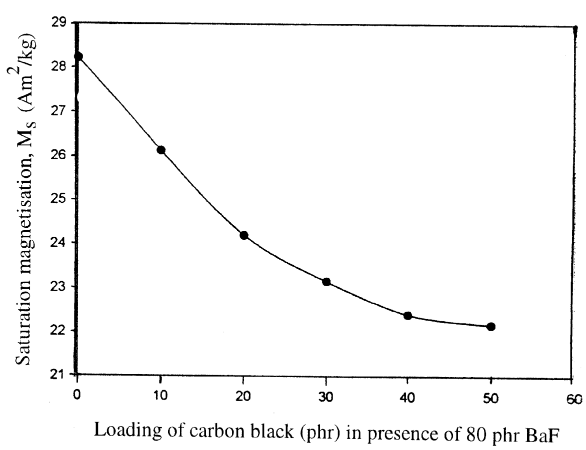


Fig. 7—Variation in magnetic remanence with loading of carbon black in NBR based RFCs containing 80 phr BaF.



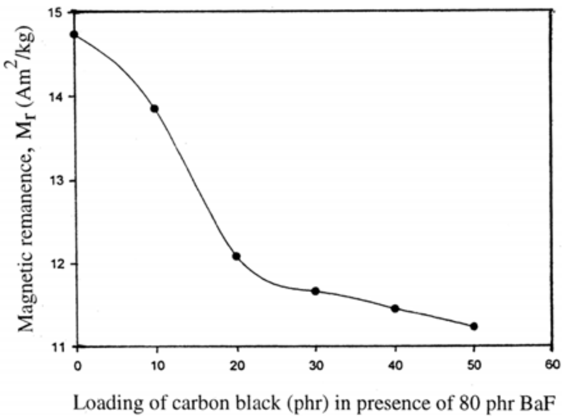


Fig. 9—Variation in magnetic remanence with the loading of BaF in NBR.

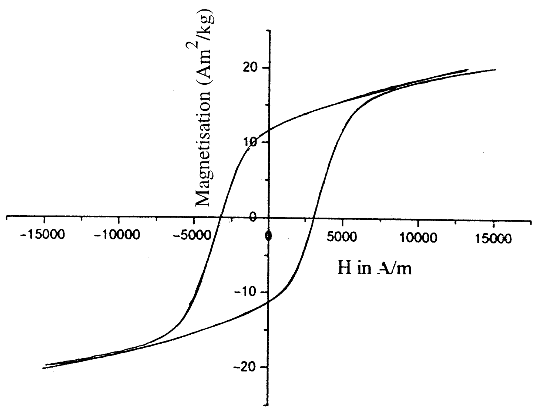


Fig. 10—Representative hysteresis loop of NBR based RFCs containing 80 phr BaF and 50 phr of carbon black.

Fig. 8—Variation in saturation magnetisation with loading of carbon black in NBR based RFCs containing 80 phr BaF.

Conclusion

Rubber ferrite composites (RFCs) containing barium ferrite and carbon black in nitrile rubber matrix have been prepared. The magnetic studies indicated that flexible magnets having suitable magnetic properties could be prepared by the incorporation of barium ferrite. From the magnetic measurements it has been found that the coercivity values of RFCs were less than that of the ceramic BaF, but did not vary with the different loading of BaF as well as carbon black, whereas other properties like saturation magnetization and magnetic remanence increased with the loading of ferrite filler.

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