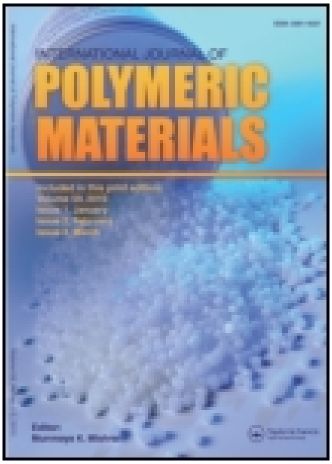


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# PROCESSABILITY AND MAGNETIC PROPERTIES OF RUBBER FERRITE COMPOSITES CONTAINING BARIUM FERRITE

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*Rubber ferrite composites (RFC) are magnetic polymer composites and have a variety of applications as flexible magnets, pressure/photo sensors, and microwave absorbers. The mouldability into complex shapes is one of the advantages of these magnetic elastomers. They have the potential of replacing the conventional ceramic materials, due to theire flexible nature. In the present study, the incorporation of pre-characterized hexagonal ferrites, namely barium ferrite ($BaFe_{12}O_{19}$), into natural rubber matrix is carried out according to a suitable recipe for various loadings of the filler. The processability of these compounds was determined by evaluating the cure characteristics: scorch time, cure time, and minimum and maximum torque. It has been found that the addition of magnetic fillers does not affect the processability of the composites, whereas the physical properties are modified. The magnetic properties of these composites containing various loadings of the magnetic filler were also investigated. The magnetic properties of RFC can be controlled by the addition of appropriate amount of the ferrite filler.*

**Keywords:** magnetic materials, ferrites, hexagonal ferrites, rubber ferrite composites, barium ferrite, natural rubber

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## INTRODUCTION

Ferrites are ferrimagnetic materials containing predominantly oxides of iron along with other oxides of barium, strontium, manganese, nickel, zinc, lithium, and cadmium. Ferrites are ideally suited for making devices like inductor cores, circulators, memory devices, and also for various microwave applications [1–5]. Although the saturation magnetization of ferrites is less than that of ferromagnetic alloys they have advantages such as applicability at higher frequency, lower price, and greater electrical resistance [6]. The practical applications of ferrites have been exploited by utilizing these advantages. Ferrites are classified into two groups, namely magnetically soft and hard [7]. Further, depending on their crystal symmetry, they may be cubic, hexagonal, or orthorhombic. Barium and strontium ferrites belong to the class of hexagonal ferrites. They are normally prepared by using ceramic techniques. The incorporation of these ferrites into rubber matrices produces rubber ferrite composites [8–9]. Some of these materials are used as electromagnetic wave absorbers in the VHF and UHF bands [10–11].

It has also been reported that flexible magnets can be made with appropriate magnetic properties by a judicious choice of magnetic fillers [12]. The incorporation of hard ferrites in the elastomer matrix can not only bring economy but also produce flexible permanent magnets that find extensive applications [13–14]. The addition of ferrites into an elastomer matrix modifies the dielectric properties and impart magnetic property to the elastomer.

Barium ferrite (BAF) in the nano meter regime is also being investigated by various researchers because of its superior properties compared to its micron size counterparts, for recording purposes [15]. In the persent study, barium ferrite, which resembles the magnetoplumbite structure [16], was prepared, characterized, and incorporated into a natural rubber matrix at different loadings, from 40 to 120, in steps of 20 parts per hundred parts of rubber (phr). The cure characteristics, mechanical and magnetic properties of these composites were determined and are presented here.

## EXPERIMENTAL

### Preparation of Barium Ferrite

Barium ferrite in large quantities were synthesized by ceramic techniques [17]. For this pure $\alpha$-$Fe_2O_3$ prepared by the decomposition of freshly prepared ferrous oxalate dihydrate (FOD) at 500°C, is mixed with barium carbonate. They were homogenized thoroughly and pre-sintered at 500°C for several hours. After three sets of homogenization and pre-sintering, these were then fired at 1200°C for several hours.

## X-Ray Powder Diffraction

The barium ferrite powder was analyzed by X-ray powder diffraction technique using X-ray diffractometer (Rigaku Dmax-C) with Cu $K_\alpha(\lambda = 1.5405\ A^0)$. The average particle size was determined by using the Debye Scherrer equation $t = \frac{0.9\lambda}{\beta\ \mathrm{Cos}\theta}$ where t is the particle size, $\lambda$ is the wave length, $\beta$ is the full width at half maximum and $\theta$ 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 $\rho$ is the density (g/cc).

## Incorporation of Barium Ferrite in Natural Rubber Matrix

The barium ferrite thus prepared was characterized and then incorporated in a natural rubber (ISNR 5 grade) matrix according to a specific recipe. The rubber ferrite composites were prepared for various loadings of BAF, ranging from 40 to 120 parts per hundred parts (phr) in steps of 20. Studies carried out earlier [18] on RFC have shown that the percolation threshold was not reached even at a loading of 120 phr of magnetic fillers.

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 homogenized by using a two roll mixing mill ($15 \times 33$ cm) as per ASTM D 3182-89.

## 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 characteristics of the composites, namely scorch time, cure time, and minimum and maximum torques were determined.

## Preparation of Test Specimen

The specimens for testing the physical properties were prepared by compression molding on an electrically heated hydraulic press having $45 \times 45$ cm platens at a pressure of 140 Kg $cm^{-2}$ in a standard mold.

The rubber compounds were vulcanized up to their respective cure time at 150°C. Dumb-bell specimens for the tensile test were then cut from the vulcanized sheet using a standard die.

## Evaluation of Mechanical Properties

The tensile properties of the composites were determined on a Zwick Universal Testing Machine (UTM), model 1445, using a crosshead speed of 500 mm $min^{-1}$ as per ASTM D 412-87. The tensile strength, elongation at break, and modulus at 300% elongation were evaluated.

## Hardness

The hardness (shore A) of the molded samples were ‘tested using a Zwick 3114 hardness tester in accordance with ASTM D 2240-86. The tests were carried out on mechanically unstressed samples of 12 mm diameter and minimum 6 mm thickness. A load of 12.5 N was applied to ensure firm contact with the specimens and readings were taken after 10 s of indentation.

## Evaluation of Magnetic Properties

The magnetic parameters, namely saturation magnetization, retentivity, and coercivity of these rubber ferrite composites were evaluated by using a vibrating sample magnetometer (VSM), model EG & G PARC 4500.

# RESULTS AND DISCUSSION

X-ray diffractograms of BAF and subsequent evaluation of structural parameters indicate that the compounds are monophasic and highly crystalline in nature, without any detectable impurities. The interatomic spacing (d) and their relative intensities $[(I/I_o) \times 100]$ matches well with the reported values in the literature [19] and are shown in Table 1.

The variation of scorch time and cure time with loading of ferrite are shown in Figure 1. The Scorch time ($t_{10}$) and cure time ($t_{90}$) of these composites decrease marginally with the addition of ferrite fillers. The scorch time decreases with the filler loading because the heat of mixing increases as the filler loading increases. The optimum cure time also decrease with the addition of fillers. These results show that the processability of the compounds is not apparently affected by the

**TABLE 1** X-Ray Diffraction Data for Barium Ferrite

| Inter atomic spacing $d(A^0)$ | 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 |

filler loading. The variation of minimum torque and maximum torque of the compounds are shown in Figure 2. From the cure characteristics of the comopsites, it can be observed that the minimum torque ($M_L$), which is a measure of the viscosity of the compound, increases with

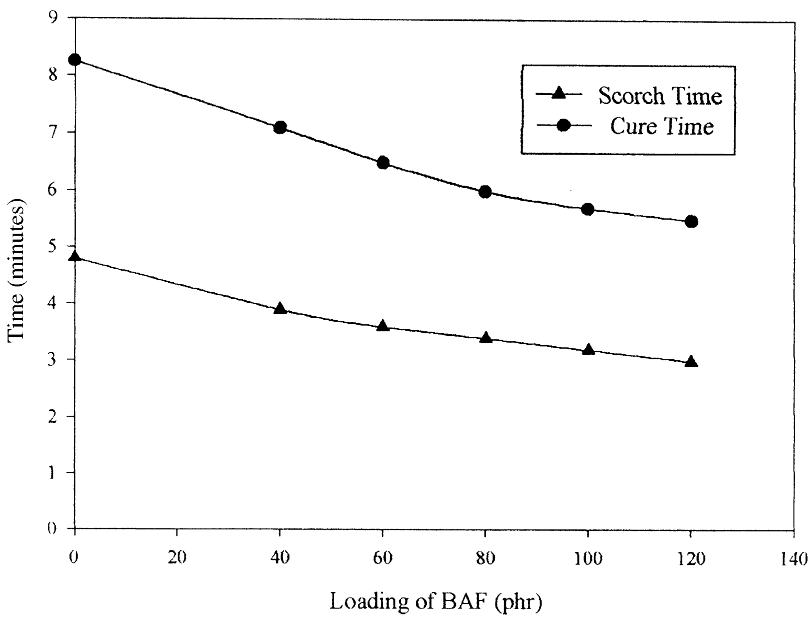


**FIGURE 1** Scorch time and cure time versus loading of fillers.

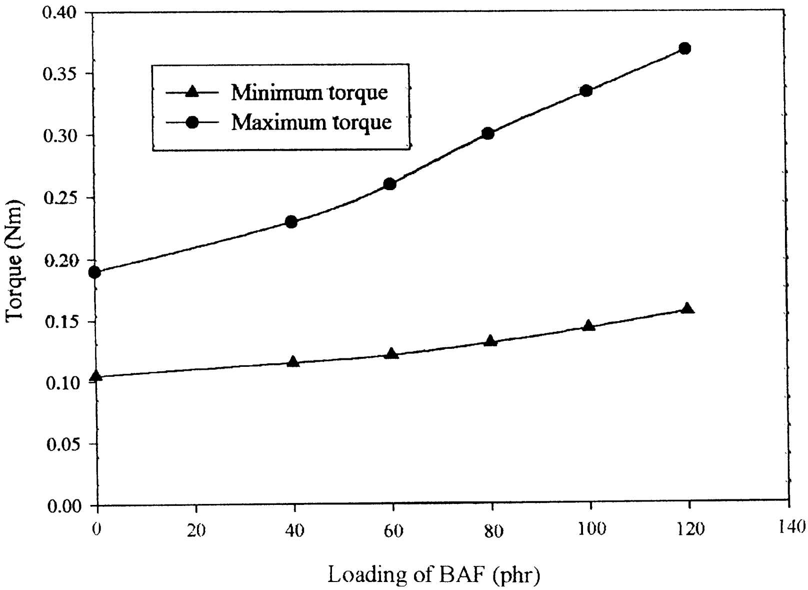


**FIGURE 2** Minimum torque and maximum torque versus loading of fillers.

the loading of filler, as expected. The maximum torque, ($M_H$), which is an indication of the modulus of the vulcanizates, increases with filler loading.

The tensile properties and hardness of the vulcanizates containing BAF are shown in Table 2. Tensile strength decreases with the additional of ferrites. This is due to the poor interfacial adhesion between the ferrite filler and natural rubber. The mechanical properties have also reduced at higher loadings because of the dilution

**TABLE 2** Tensile Parameters and Hardness Values of Natural Rubber Containing Barium Ferrite

| Loading of barium ferrite (phr) | Tensile strength (M Pa) | Elongation at break (%) | 200% modulus (M Pa) | 300% modulus (M Pa) | Hardness (ShoreA) |
|---|---|---|---|---|---|
| NR Blank | 23.95 | 691.15 | 3.14 | 4.88 | 40 |
| 40 | 20.97 | 623.30 | 4.37 | 7.12 | 42 |
| 60 | 19.85 | 516.22 | 5.35 | 8.74 | 45 |
| 80 | 18.70 | 504.86 | 5.49 | 5.49 | 47 |
| 100 | 17.85 | 485.15 | 5.83 | 9.26 | 49 |
| 120 | 16.72 | 482.95 | 6.32 | 9.68 | 52 |

effect, which is due to the diminishing volume fraction of polymer in the composite.

The modules of the composites increases, which is characteristic of a reinforcing filler. The modulus at 300% of these rubber ferrite composites showed a steady increase with addition of BAF.

The hardness of these magnetic materials showed a steady increase with the filler loadings. This is expected. But the maximum hardness for the samples is for below the maximum permitted limit for the elastomer even for a loading of 120 phr of the filler. This property can be exploited to make RFC with optimum magnetic properties and flexibility.

The magnetic parameters of BAF and the RFCs obtained have shown that they are magnetic. The values obtained from the VSM measurements are shown in Table 3. Representative hysteresis loops for rubber ferrite composites are shown in Figure 3.

The variation of saturation magnetization of the composites loaded with barium ferrite has studied. Figure 4 shows the variation of magnetization, both experimental and calculated, with loading. The magnetization shows a steady increase with loading.

When RFC for specific applications are required, synthesis of RFC with pre-determined properties are mandatory. Thus, attempts were made to tailor the magnetic properties of the composites from the known values of the saturation magnetization (Ms) of the ceramic fillers. If the Ms values of the ceramic fillers are known, a simple mixture equation of the general form (Eq. 1) involving the weight fractions of the filler may be employed to estimate the Ms of the composite samples.

$$M_{rfc} = W_1 M_1 + W_2 M_2 \tag{1}$$

**TABLE 3** Hysterisis loop Parameters of Natural Rubber containing Barium Ferrite

| Loading of barium ferrite (phr) | Coercivity (A/m) | Retentivity ($Am^2/Kg$) | Saturation magnetization ($Am^2/Kg$) | $M_T/M_S$ |
|---|---|---|---|---|
| 40 | 3458.007 | 8.096 | 14.940 | 0.542 |
| 60 | 3468.011 | 11.565 | 21.011 | 0.551 |
| 80 | 3468.030 | 13.679 | 24.814 | 0.551 |
| 100 | 3468.030 | 15.493 | 28.252 | 0.548 |
| 120 | 3468.030 | 17.440 | 31.712 | 0.550 |
| Ceramic BAF | 3468.030 | 30.521 | 58.831 | 0.519 |

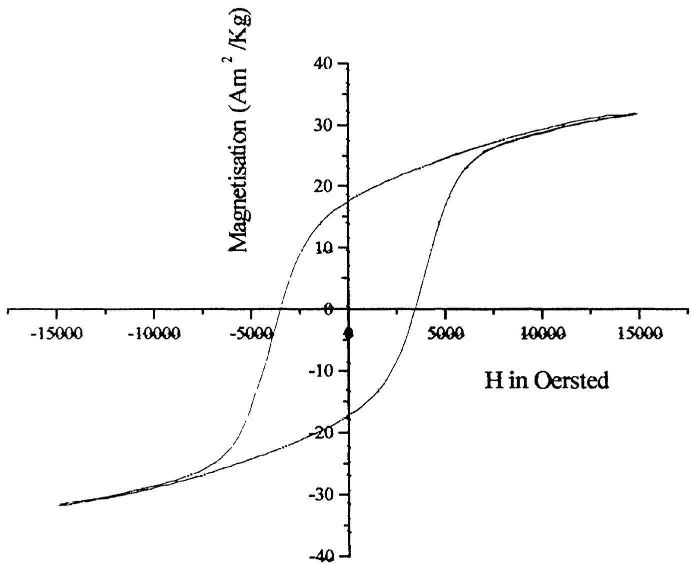


**FIGURE 3** Representative hysteresis loop for RFC containing BAF (120 phr).

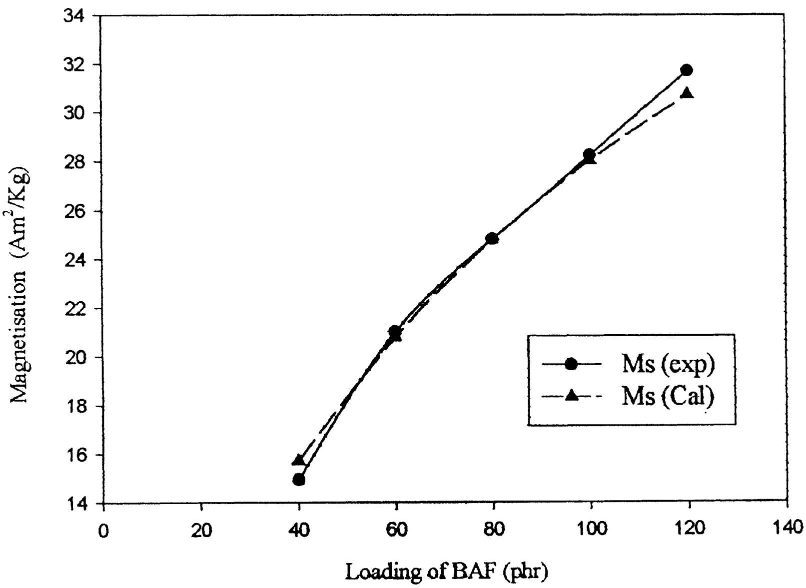


**FIGURE 4** Saturation magnetization versus loading of filler, experimental and calculated.

where $W_1$ is the weight fraction of filler, $M_1$ is the magnetization of the filler, $W_2$ is the weight fraction of matrix, $M_2$ is the magnetization of the matrix. Because the matrix, namely NR, is nonmagnetic this equation can be reduced to the following from

$$M_{rfc} = W_1 M_1 \tag{2}$$

The Ms values were calculated using Eq. 2 and the measured and calculated values of Ms are shown in Figure 4.

It was also observed that the magnetic remnance (Mr) increases with loading. The variation of Mr for different loadings is shown in Figure 5. The variation of coercivity with loading of fillers for RFCs is shown in Figure 6. It shows almost similar behavior as that of the ceramic component. Light variations in coercivity of ceramic composites may occur and be attributed to the small particle size changes that may occur during compounding/mixing. However, this variation is negligible. From this observation it can be concluded that loading has no effect on coercivity or there is no interaction between the filler and the matrix.



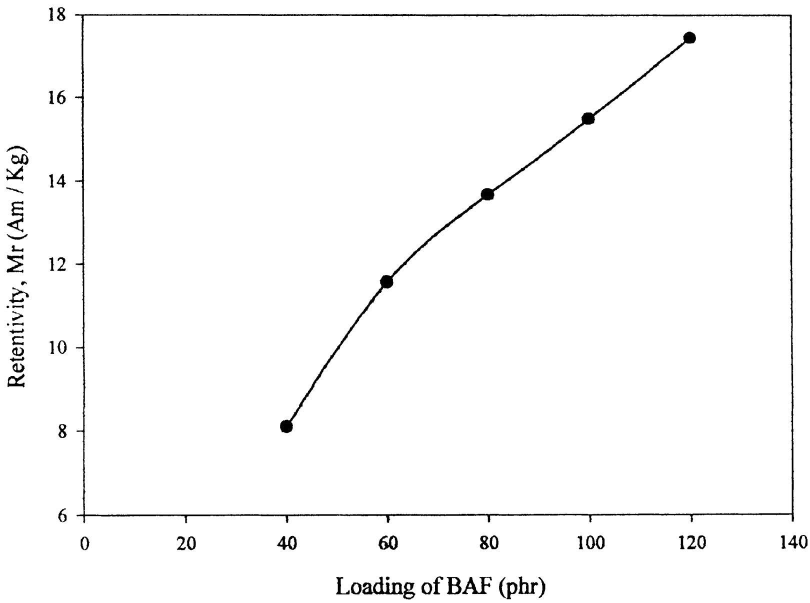


**FIGURE 5** Retentivity versus loading of fillers.

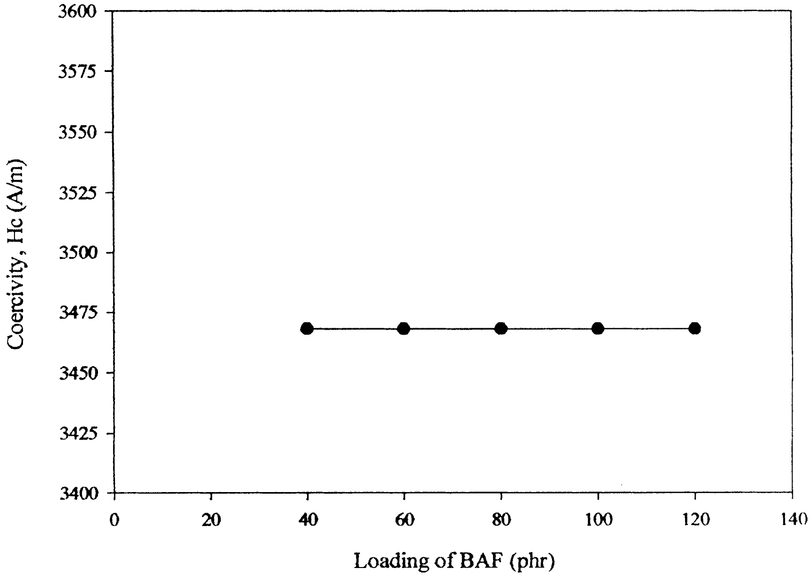


**FIGURE 6** Coercivity versus loading of fillers.

## CONCLUSION

Precharacterized barium ferrite was incorporated into natural rubber. It was found that the processability was not much affected by filler incorporation. Analysis of the physical properties indicated that the addition of magnetic fillers increased the modules and hardness, with marginal decrease in the tensile strength. Evaluation of the cure parameters and mechanical properties indicated that BAF act as a semi-reinforcing filler, and even after the addition of these materials the composites were processable. Study of the magnetic properties indicated the formation of elastomer magnets with suitable value of saturation magnetization and retentivity. The production of these magnetic polymers assumes importance due to their wide range of applications.

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