Influence of Carbon Black on the Mechanical and Magnetic Properties of Nitrile Based Rubber Ferrite Composites

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Abstract

Barium ferrite ($BaFe_{12}O_{19}$) belonging to the M-type hexagonal ferrites was prepared by the ceramic technique. They were then characterised using X-ray diffraction technique and incorporated into a nitrile rubber matrix according to a specific recipe to produce rubber ferrite composites (RFC). These RFC have a wide range of applications as flexible magnets from the common refrigerator door seals to high tech sensors used in telecommunication and microwave absorbers. For most of the applications these composites requires suitable mechanical strength with the necessary magnetic properties, which can be achieved by in single step by synthesizing composites based on nitrile rubber and ferrites. The mechanical properties were studied using a universal testing machine (UTM) and the magnetic properties using a vibrating sample magnetometer (VSM). This study indicates that flexible magnets having appropriate mechanical strength and magnetic properties can be prepared by the incorporation of barium ferrite in elastomer matrixes.

Keywords: magnetic materials, hexagonal ferrites, rubber ferrite composites (RFC), nitrile rubber, barium ferrite, permanent magnets.

Introduction

Rubber ferrite composites (RFC) are magnetic polymer composites, which have a variety of high tech applications. They are produced by the incorporation of ferrites in both natural and/or synthetic polymer matrixes. Ferrites are a group of technologically important magnetic materials, which cannot be easily replaced by any other materials because they are stable, economical and possess a wide range of applications [1,2]. Ferrites are classified into two groups namely, magnetically soft and hard [3]. Further, 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. The incorporation of these ferrites into polymer matrixes produces rubber ferrite composites[4,5]. Some of these materials are used as electromagnetic wave absorbers in the VHF and UHF bands [6,7].

Ferrites are usually employed in the ceramic form and one of the drawbacks is that they are not flexible or mouldable to complex shapes. It has earlier been reported that plastic or elastic magnets with appropriate magnetic properties can be made by a well-judged choice of magnetic fillers [8,9]. The incorporation of ferrites in the elastomer matrix can not only bring economy but also produce flexible permanent magnets which find widespread applications[10].

These rubber magnets have the several advantages over the ceramic ferrites, as they are flexible, mouldable and easily machinable. The addition of ferrites into an elastomer matrix not only modifies the mechanical properties but also imparts magnetic property to the elastomer. Earlier studies [11, 12] have shown that the dielectric properties of these composites incorporated with ferrite fillers also increases with the filler loading and is useful as microwave absorbing materials.

Barium ferrite (BaF) is the most important among the hexagonal hard ferrites. This typical hexagonal ferromagnetic oxide, which are isomorphous with the mineral magnetoplumbite, is widely used as permanent magnet materials and is studied by various researchers due to its superior properties like large magnetisation values, high resistivity and low eddy current losses. In the present study the incorporation of barium ferrite into nitrile rubber matrix is carried out. The nitrile rubber has superior oil resistance to oils, greases, petroleum hydrocarbons and other non-polar solvents and hence can be used for the manufacture of RFCs with special properties.

Carbon black has the property of reinforcing the matrix. Moreover studies carried out earlier have shown that the addition of carbon black fillers into RFCs increases the microwave absorbing properties of the composites. Hence studies involving carbon black filled RFCs assume significance.

In the present study pre-characterised hexagonal BaF powder samples prepared by the ceramic techniques were incorporated into a nitrile rubber matrix according to a specific recipe to produce rubber ferrite composites. The mechanical and magnetic properties of these composites, both with and without carbon black were determined and are presented.

2. EXPERIMENTAL

2.1. Preparation of Barium Ferrite

Barium ferrite in large quantities were synthesised by the conventional ceramic techniques[13]. For the preparation of BaF, appropriate amount of the precursor namely α-Fe_2O_3, prepared by the decomposition of freshly prepared ferrous oxalate dihydrate (FOD) at 500 ^{0} C, is mixed with barium carbonate. They were then thoroughly mixed in an agate mortar to produce a homogeneous mixture of fine particles. This homogeneous mixture was pre-sintered at 500^0 C for three hours. After three sets of homogenisation and pre-sintering, these were then fired at 1200^0 C for twenty four hours.

2.2 X-Ray Powder Diffraction

The barium ferrite powder was analysed by x-ray powder diffraction technique using X-ray diffractometer (Rigaku Dmax-C) with Cu K_α ($\lambda = 1.5405$ A^0). The average particle size was determined by using the Debye Scherrer equation $t = \frac{0.9\lambda}{\beta \cos\theta}$ where t is the particle size, 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)[16].

2.3 Incorporation of barium ferrite in natural rubber matrix.

The barium ferrite thus prepared were characterised and then incorporated in nitrile rubber (Aparene- N 553) 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 on RFC have shown that the percolation threshold was not reached even at a loading of 120 phr of magnetic fillers. Hence the 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 mixing was first carried out in a Brabender Plasticorder (Torque Rheometer) model PL 3S at 70^0 C for ten minutes at a speed of 50 rpm. This was then homogenized using a two roll mixing mill (15 X 33 cm) as per ASTM D 3182-89.

2.4 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 RFCs, at 150^0 were determined.

2.5 Preparation of test specimen.

The specimens for testing the mechanical and magnetic properties were prepared by compression moulding on an electrically heated hydraulic press having 45 X 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. Dumb-bell specimens for the tensile test and the samples for magnetic studies were then cut from the vulcanised sheet using standard dies.

2.6 Evaluation of mechanical properties

The tensile properties of the composites were determined on an Instron Universal Testing Machine, Model 4411 Test System, 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.

2.7 Hardness

The hardness (shore A) of the moulded samples were tested using 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 6mm thickness. A load of 12.5 N was applied to ensure firm contact with the specimens and readings were taken after 10 seconds of indentation.

2.8 Abrasion Resistance

The abrasion resistance of the samples was determined using a DIN abrader (DIN 53516). Cylindrical samples of 15 mm diameter and 20 mm length was kept on a rotating sample holder and 10 N load was applied. Initially a pre run was given for the sample and its weight taken. The weight after the final run was also noted. The difference in weight is the weight loss on abrasion. It is expressed as the volume of the test piece abraded by its travel through 42 m on a standard abrasive surface. The volume loss on abrasion was calculated as follows:

$$V = \Delta M / \rho$$

Where V = volume loss, ΔM = mass loss, and ρ = density of the sample.

Abrasion resistance is the reciprocal of volume loss on abrasion.

2.9 Magnetic measurements

The room temperature magnetic measurements of these rubber ferrite composites were carried out by using vibrating sample magnetometer (VSM), model: EG & G PARC 4500. The magnetic parameters namely saturation magnetization(M_s), magnetic remanence(M_r) and coercivity (H_c) were obtained from these measurements.

3. RESULTS AND DISCUSSION

Structural studies

Analysis of the X-Ray Diffractograms of BaF indicated that the compounds are monophasic and highly crystalline in nature, without any detectable impurities. The interatomic spacing (d) and their relative intensities ($I/I_o \times 100$) matched well with that of the reported values in the literature[14] and is shown in table 1. The average particle size of BaF lies in the range 60-70 nm and had a surface area of 20-25 m^2/g. It may be noted that the particle size determined by the Debye Scherrer equation represents only the average distribution of the particles and hence the surface area calculated by employing the relation $A_S = \frac{6000}{D\rho}$ is only indicative and this cannot be compared with the surface area as determined by techniques like BET (Branauer, Emmett and Teller).

Table I. X-ray diffraction data for barium ferrite

Inter atomic spacing, d (A°)	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
1.467	32
2.460	29

Mechanical Properties

The tensile properties and hardness of the rubber ferrite composites containing various loadings of barium ferrite in nitrile rubber are shown in table 2. Figure 1 shows the variation in tensile strength of RFC with the loading of BaF and its effect with the addition of carbon black.

Table 2. Mechanical Properties of nitrile rubber based RFCs containing barium ferrite

Barium ferrite loading (phr)	Tensile strength (MPa)	Elongation at break (%)	200 % Modulus (MPa)	300% Modulus (MPa)	Hardness (Shore A)
0	2.13	465.9	1.74	2.09	55
40	2.93	456.0	1.78	2.10	58
60	3.12	445.0	1.79	2.11	62
80	3.29	439.9	1.83	2.14	65
100	3.44	394.0	1.87	2.14	67
120	3.26	304.7	1.90	2.24	69

NBR gum vulcanisate has relatively low tensile strength compared to NR gum vulcanisate (23.95 MPa) due to lack of stress induced crystallization. The gum NBR vulcanisate showed low tensile strength (2.13 MPa), which increased with increasing filler loading. The addition of ferrite filler reinforce the NBR matrix and showed a maximum reinforcement in the presence of carbon black. The addition of the carbon black along with ferrite filler increased the tensile strength greatly (around 20 MPa), since it act as a good reinforcing filler. Carbon black is a good reinforcing filler and it forms a reinforcing BaF-Carbon black aggregate, which explains the increase in the tensile strength. The tensile strength reduced at higher filler loadings because of the dilution effect, which is due to the diminishing volume fraction of polymer in the composite.

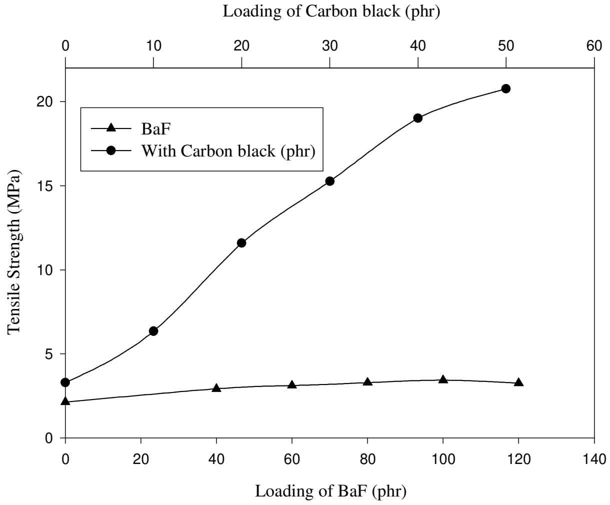

Fig 1 Variation in tensile strength of RFC versus loading of BaF and carbon black in NBR

Figure 2 represents the variation in modulus at 300 % elongation with the loading of BaF filler and carbon black in nitrile rubber. The modulus increased slightly with the addition ferrite fillers, but the increase was more with the loading of carbon black. The modulus of the composites increased with the incorporation of both ferrite filler and carbon black, which is characteristic of reinforcing filler.

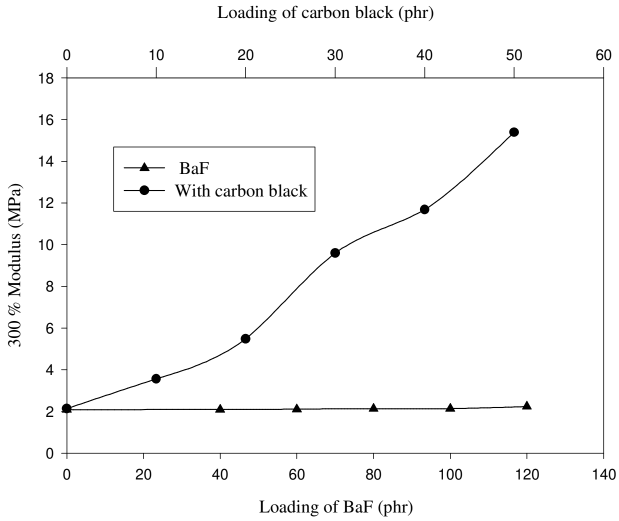

Fig 2 Variation in 300 % modulus with the loading of BaF and carbon black in NBR.

The elongation at break of the RFC based on NBR containing BaF with and without carbon black is shown in figure 3. The elongation at break showed a steady decrease with increasing loading of ferrite fillers and carbon black in the case RFCs based on nitrile rubber.

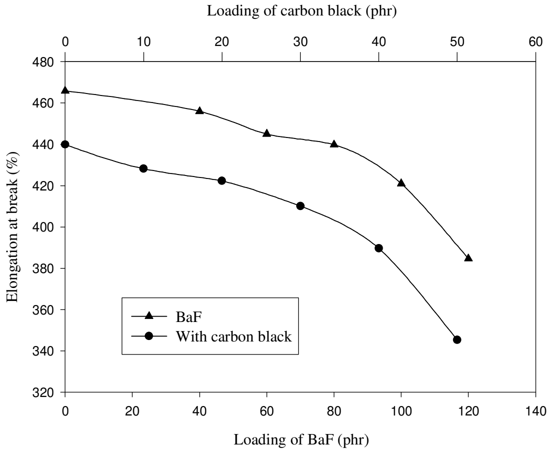

Fig 3 Variation in elongation at break versus loading of BaF and carbon black.

The hardness of these magnetic composites showed a steady increase with the filler loadings as expected. However the maximum hardness for the sample is much below than the maximum permiited limit for the elastomer even for higher loading of the filler. Thus RFCs of suitable flexiblity with required mechanical and magnetic properties can be designed. Figure 4 shows the variation in hardness for RFC containing BaF and carbon black in NBR.

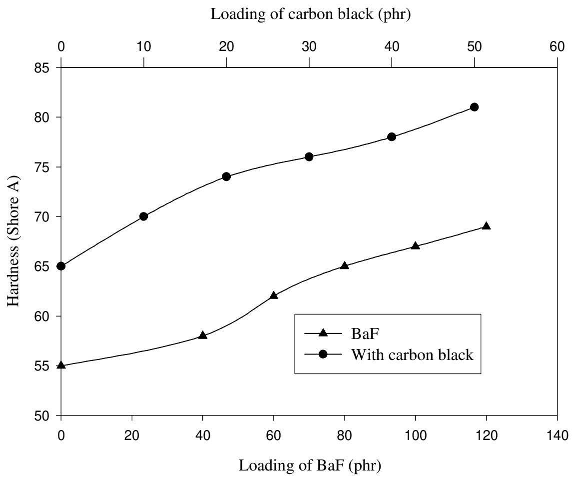

Fig 4 Variation in hardness for RFC containing BaF and carbon black in NBR.

Abrasion Resistance

The abrasion resistance of the samples was determined using a DIN abrader (DIN 53516). Figure 5 shows volume loss on abrasion of the rubber ferrite composites containing barium ferrite in nitrile rubber. The abrasion loss showed an increasing trend with the loading of ferrite fillers whereas in the case of rubber ferrite composites' containing various loading of carbon black it was less. This is because the particle size of carbon black is finer than that of ferrite fillers. Thus it is possible to produce flexible magnets for various applications, which requires high abrasion resistance by the incorporation of different loading of carbon black.

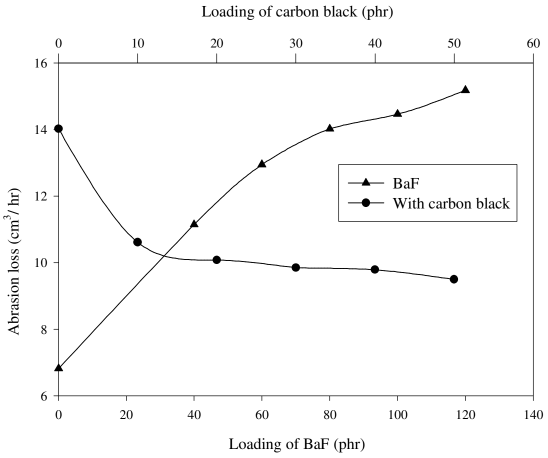

Fig 5 Variation in volume loss on abrasion versus loading of BaF and carbon black in NBR

Magnetic studies

The magnetic properties were determined using a Vibrating Sample Magnetometer (VSM) and the magnetic parameters of BaF and the RFC obtained have shown that they are magnetic. Representative hysteresis loops for rubber ferrite composites are shown in figure 6 .

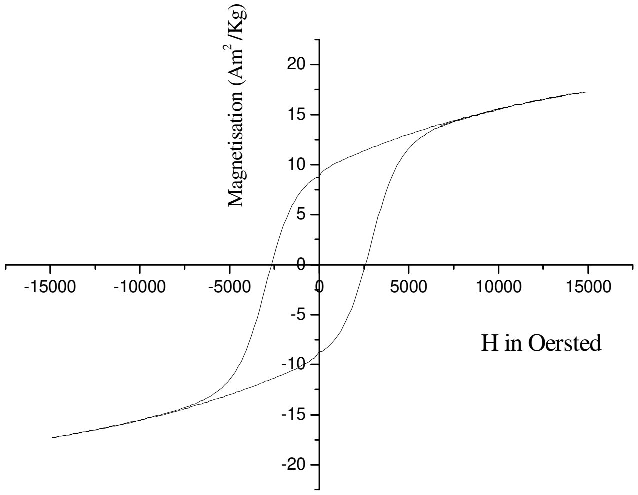

Fig 6 Hysteresis loop of the NBR based RFC containing 40 phr of BaF

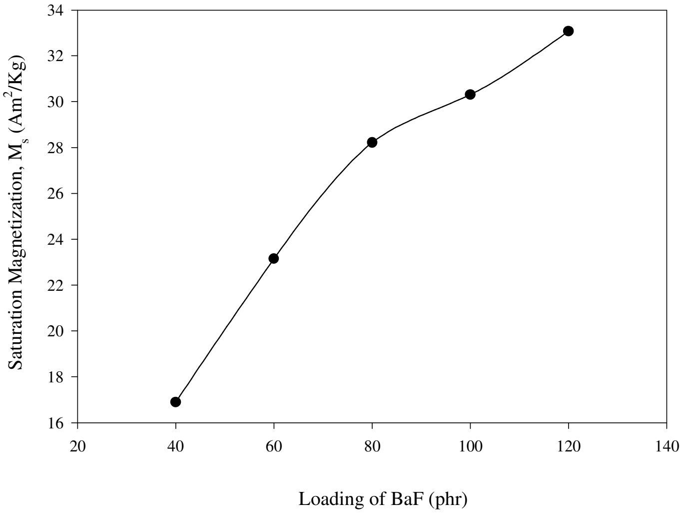

Fig 7 Variation in saturation magnetisation with the loading of BaF in NBR

The measured values of saturation magnetisation of the ceramic BaF matched well with that of the reported values. The saturation magnetization of the RFC shows that it increases with the loading of BaF (Fig 7). The variation of magnetic remanence of the composites with the loading of the barium ferrite (Fig 8) is studied and the values increased steadily with the loading of BaF. The coercivity of the composites remained the same as that of the ceramic component. The little variation in the coercivity values can occur, which may be due to the small particle size changes that can occur during compounding or milling. However the variation is negligible. Thus it can be concluded that the loading has no effect on coercivity or there is no interaction between the filler and the matrix.

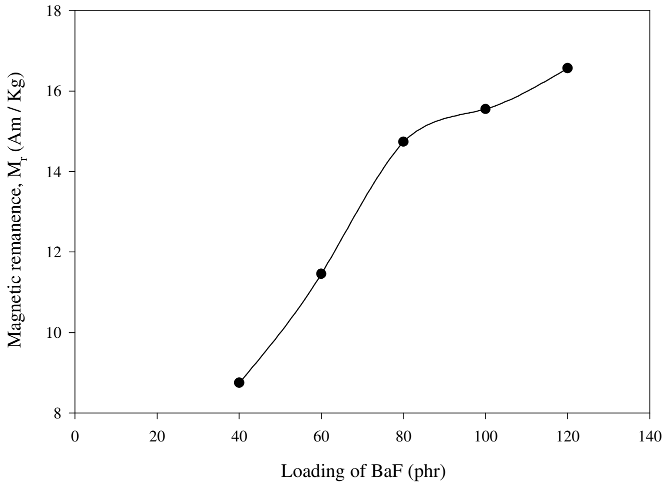

Fig 8 Variation in magnetic remanence with the loading of BaF in NBR

CONCLUSION

Rubber ferrite composites containing barium ferrite in nitrile rubber matrix were prepared. Magnetic parameters of the ceramic ferrites as well as that of the RFCs were studied. Study of the magnetic properties indicated the formation of elastomer magnets with suitable saturation magnetisation and magnetic remanence. The saturation magnetisation and the magnetic remanence increased with increase in the loading of barium ferrite. The coercivity of the RFCs remained almost same as that of the ceramic component. The evaluation of mechanical properties revealed that the flexibility of the matrix was not much affected even up to a loading of 120 phr of ferrite fillers and the mechanical strength increased with the loading of ferrite filler and carbon black.

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