Effect of Carbon Black on the Mechanical and Dielectric Properties of Rubber Ferrite Composites Containing Barium Ferrite

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ABSTRACT: Fine particles of barium ferrite ($BaFe_{12}O_{19}$) were synthesized by the conventional ceramic technique. These materials were then characterized by the X-ray diffraction method and incorporated in the natural rubber matrix according to a specific receipe for various loadings of ferrite. The rubber ferrite composites (RFC) thus obtained have several applications, and have the advantage of molding into complex shapes. For applications such as microwave absorbers, these composites should have an appropriate dielectric strength with the required mechanical and magnetic properties. The N330 (HAF) carbon black has been added to these RFCs for various loadings to modify the dielectric and mechanical properties. In this article we report the effect of carbon black on the mechanical and dielectric properties of these RFCs. Both the mechanical and dielectric properties can be enhanced by the addition of an appropriate amount of carbon black. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 769–778, 2003

Key words: rubber; composites; fillers; mechanical properties; dielectric properties

INTRODUCTION

The hard ferrites are a major class among the ferrite materials due to their applications as permanent magnets and high-density magnetic recording media. The M-type hexaferrites, especially barium ferrite, find extensive use in plastic magnets, microwave devices, and as permanent magnets for various kinds of electric meters, loudspeakers and in other devices for which high coercivity, high remanence, and large hysteresis loss are desirable.[1–6] Low cost, excellent chemical stability and corrosion resistance are added advantages. Moreover, their magnetic properties can be tailored for various applications by a judicious choice of the constituents/doping with suitable metal ions and other appropriate techniques.[7,8]

The ferrites are usually employed in the ceramic form but they are not easily machinable to obtain complex shapes. Plastic magnets or elastomer magnets, on the other hand, have several advantages, as they are flexible, easily machinable, and moldable. Hence, rubber ferrite composites have the potential to replace conventional ceramic type of magnetic materials for applications where flexibility is an important criterion. Moreover, they are also important because of their microwave absorbing properties.

The incorporation of the ferrites into natural or synthetic rubber matrix produces rubber ferrite composites (RFC).[9–12] It is known that flexible magnets can be made with appropriate magnetic properties by a judicious choice of magnetic fillers.[13] The impregnation of hard ferrites in the elastomer matrix cannot only bring economy but also produce flexible permanent magnets that find extensive applications.[14,15] Furthermore, they modify the dielectric and mechanical properties and impart magnetic property to the elastomer. Rubber ferrite composites have a wide range of applications,[16–18] from the rudimentary application of the gasket on refrigerator doors to electromagnetic wave absorbers in the VHF and UHF bands.[19,20]

The incorporation of carbon black (CB) is known to reinforce the matrixes; moreover, recent studies have indicated that the addition of fillers like carbon black on rubber ferrite composites enhances the microwave absorbing properties of the composites.[21–25] So studies pertaining to the incorporation of carbon black along with magnetic fillers in elastomer matrixes are interesting and assume significance.

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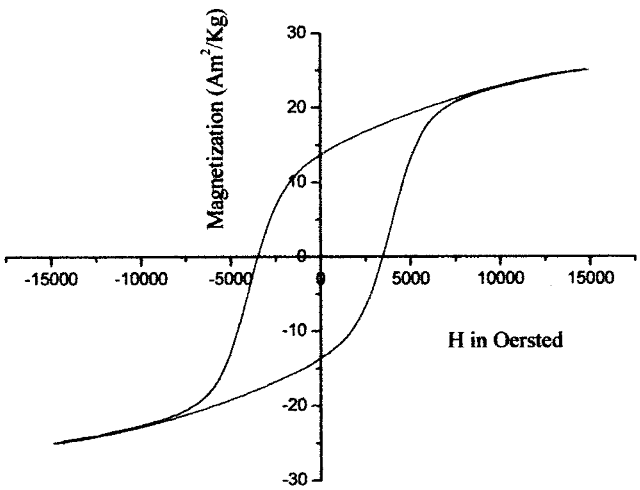


Figure 1 Representative hysteresis loop for RFC containing BaF.

In the present study, barium ferrite (BaF) prepared by the ceramic technique is incorporated into a natural rubber matrix according to a specific recipe for various loadings to produce RFCs. From this, an RFC having optimum loading of BaF is selected as the control compound and composites containing N 330 carbon black are prepared for various loadings. The mechanical and dielectric properties of these composites containing carbon black were determined and are presented here.

EXPERIMENTAL

Preparation of barium ferrite

Barium ferrite in large quantities were synthesized by the ceramic technique.[26] For this pure α-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 presintered at 500°C for 3 h. After three sets of homogenization and presintering, these were then fired at 1200°C for several hours.

X-ray powder diffraction

The structural parameters of BaF were evaluated by employing the X-ray powder diffractometer (Rigaku Dmax-C) with Cu K_α (λ = 1.5405 Å) and the monophasic nature of the sample were ascertained. The average particle size was determined by using the Debye Scherrer equation,

$$\delta = \frac{0.9\lambda}{\beta \operatorname{Cos}\theta} \quad (1)$$

where δ is the particle size, λ is the wavelength of the X-ray, β is the full-width half maximum in radians, 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,

$$A_s = 6000/D\rho \quad (2)$$

where D is the diameter of the particle (nm) and ρ is the density (g/cc).[27]

Incorporation of fillers in natural rubber matrix

These precharacterized BaF were then incorporated in a natural rubber (ISNR 5 grade) matrix according to a specific recipe. The details are cited elsewhere.[15] The RFC were prepared for various loadings of BAF, ranging from 40 to 120 parts per hundred parts of rubber (phr) in steps of 20. Studies carried out earlier[28] on RFC 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. RFC containing carbon black was prepared for various loadings namely 10 to 50 phr, in steps of 10. The carbon black employed for the study was N330 (HAF), supplied by M/S Philips Carbon Ltd., Cochin Unit, Cochin, India.

The mixing was first carried out in a Brabender Plasticorder model PL 3S at 70°C for 10 min at a speed of 50 rpm. This was then homogenized using a two roll mixing mill (15 × 33 cm) as per ASTM D 3182-89.

Determination of cure characteristics of rubber ferrite composites

Goettfert elastograph model 67.85 was utilized for the determination of cure characteristics of the RFC. The

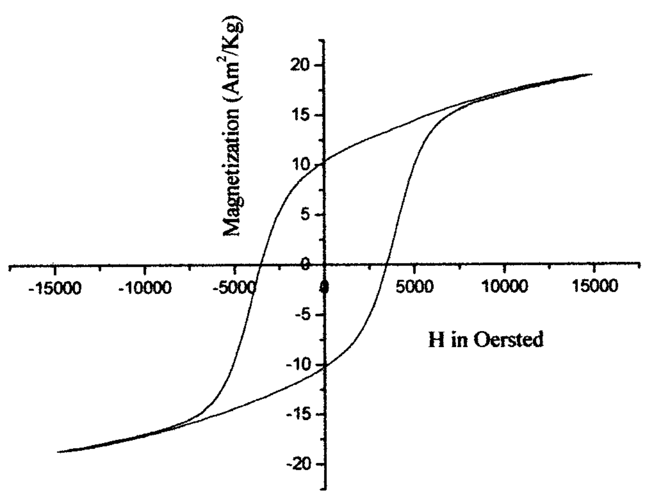


Figure 2 Representative hysteresis loop for RFC containing 80 phr BaF and carbon black.

TABLE I
Magnetic Properties of Ceramic BaF and NR-Based RFC Containing Various Loading of BaF

Barium ferrite loading (phr)	Coercivity, H_c (A/m)	Magnetic remanence, M_r (Am^2/kg)	Saturation magnetization, M_s (Am^2/kg)	M_r/M_s
40	3458	8.10	14.94	0.54
60	3468	11.57	21.01	0.55
80	3468	13.68	24.81	0.55
100	3468	15.49	28.25	0.55
120	3468	17.44	31.71	0.55
Ceramic BaF	3468	30.52	58.83	0.52

TABLE II
Magnetic Properties of NR-Based RFC Containing 80 phr of BaF and Various Loading of Carbon Black

Carbon black loading (phr)	Coercivity, H_c (A/m)	Magnetic remanence, M_r (Am^2/kg)	Saturation magnetization, M_s (Am^2/kg)	M_r/M_s
0	3468	13.68	24.81	0.55
10	3509	13.08	23.98	0.55
20	3509	12.48	22.79	0.55
30	3509	11.65	21.56	0.54
40	3509	11.07	20.18	0.55
50	3509	10.41	18.76	0.56

TABLE III
The Tensile Parameters and the Hardness of the Rubber ferrite Composites Containing Carbon Black

Carbon black loading (phr)	Tensile strength (M Pa)	Elongation at break (%)	200% modulus (M Pa)	300% modulus (M Pa)	Hardness (Shore A)
0	18.70	504.86	5.49	8.59	47
10	19.78	515.30	6.17	9.48	48
20	20.63	619.22	6.52	10.42	51
30	21.29	624.15	8.51	12.75	54
40	19.89	495.13	7.89	12.39	61
50	18.84	483.69	9.43	13.96	65

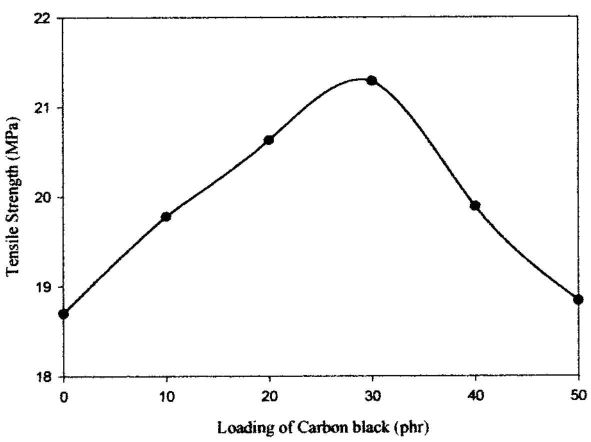


Figure 3 Variation of tensile strength vs. loading of carbon black.

cure parameters of the composites, both with and without carbon black, were determined at 150°C.

Preparation of test specimen

The specimens for testing the mechanical and dielectric properties were prepared by compression molding on an electrically heated hydraulic press having 45 × 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. Dumbbell specimens for the tensile test and disc shaped samples for dielectric studies were then cut from the vulcanized sheet using standard dies.

Evaluation of mechanical properties

The tensile properties of the composites were determined on an Instron Universal Testing Machine,

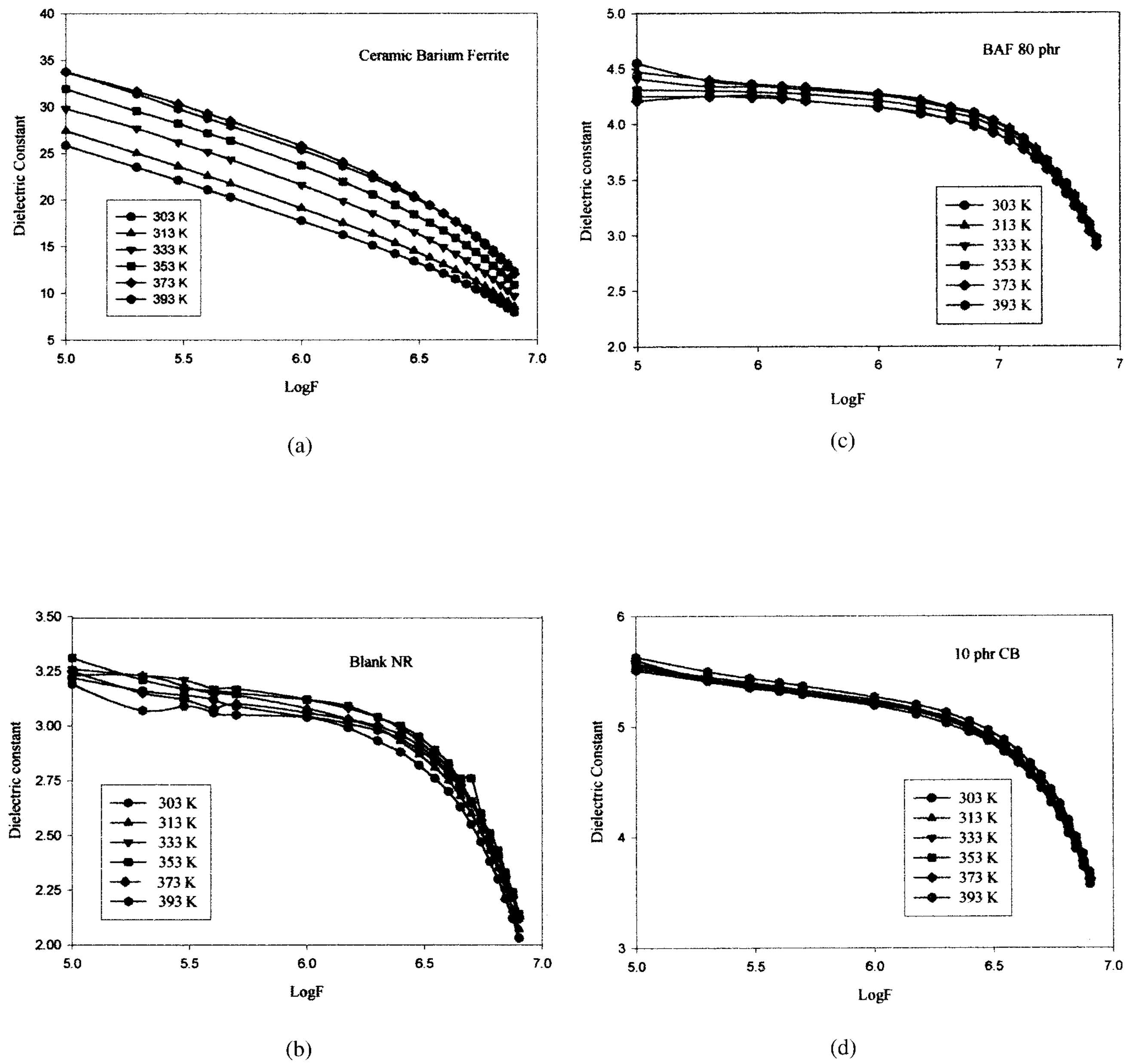


Figure 4 (a–h) Dielectric constant vs. frequency at different temperatures.

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.

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 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 dielectric properties

The dielectric studies of both ceramic and rubber ferrite composites were carried out using a dielectric cell and an impedance analyzer model: HP 4285 A. The details of these measurements are cited elsewhere.[18] Disc-shaped samples were used for the evaluation dielectric constant. The capacitance and dielectric loss in the frequency range 100 kHz–8 MHz were found out. Dielectric constant or relative permittivity were calculated using the formula

$$\varepsilon_r = \frac{C \times t}{\varepsilon_0 A} \qquad (3)$$

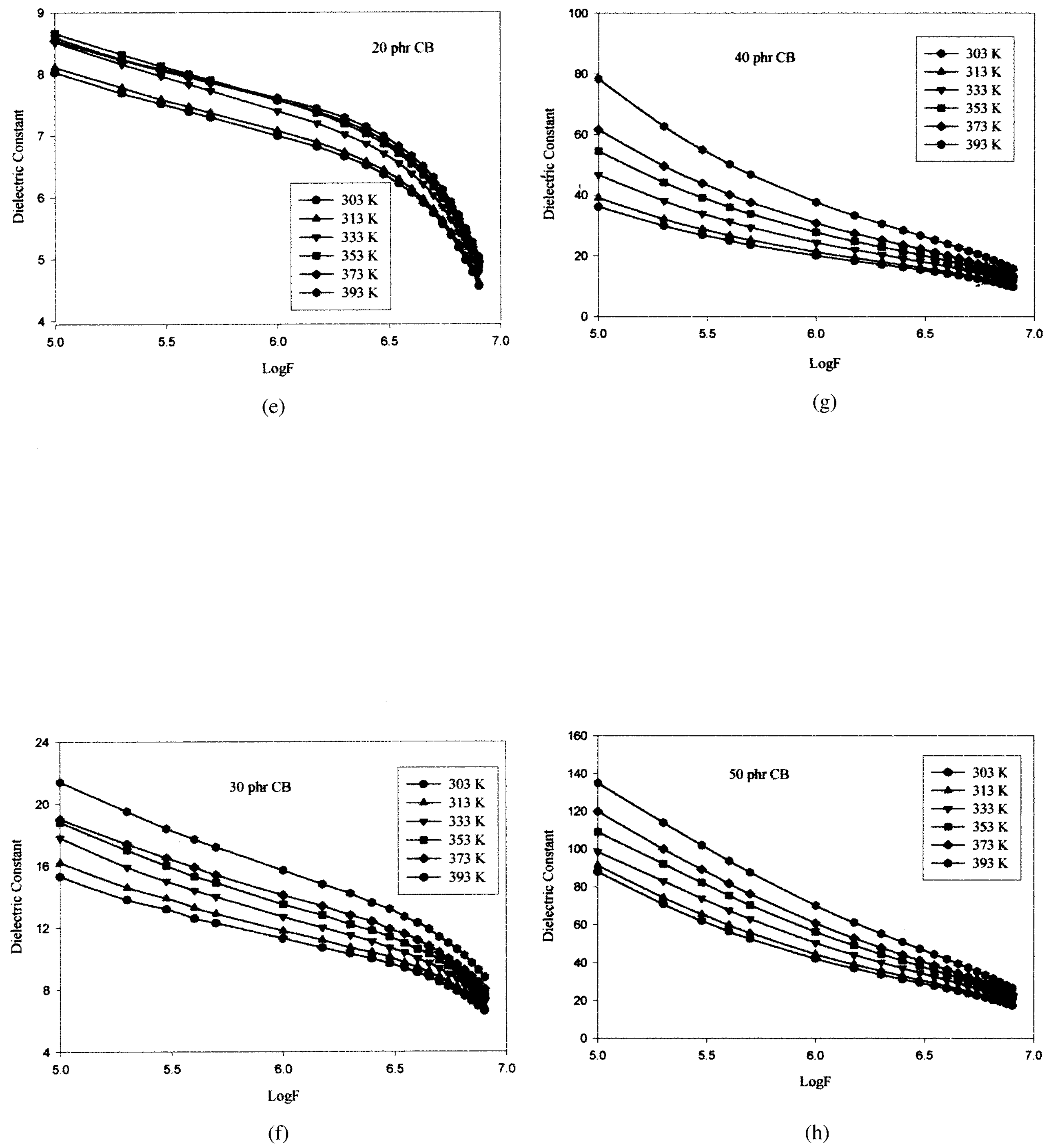


Figure 4 (*Continued from the previous page*)

where t is the thickness of the sample, C the capacitance, A the area of cross-section of the sample, and ϵ_0 is the permitivity of free space. ϵ_r is the relative permittivity of the material, which is a dimensionless quantity. From these measurements ϵ_r and tan δ for both ceramic and RFC were determined.

The entire data acquisition and evaluation of the dielectric constant were automated by using a package called LabVIEW, based on G programming. This was carried out with the aid of a base package supplied by M/S National Instruments. The characteristic feature of this automatic data acquisition is that 20,000 data points or more can be acquired in a

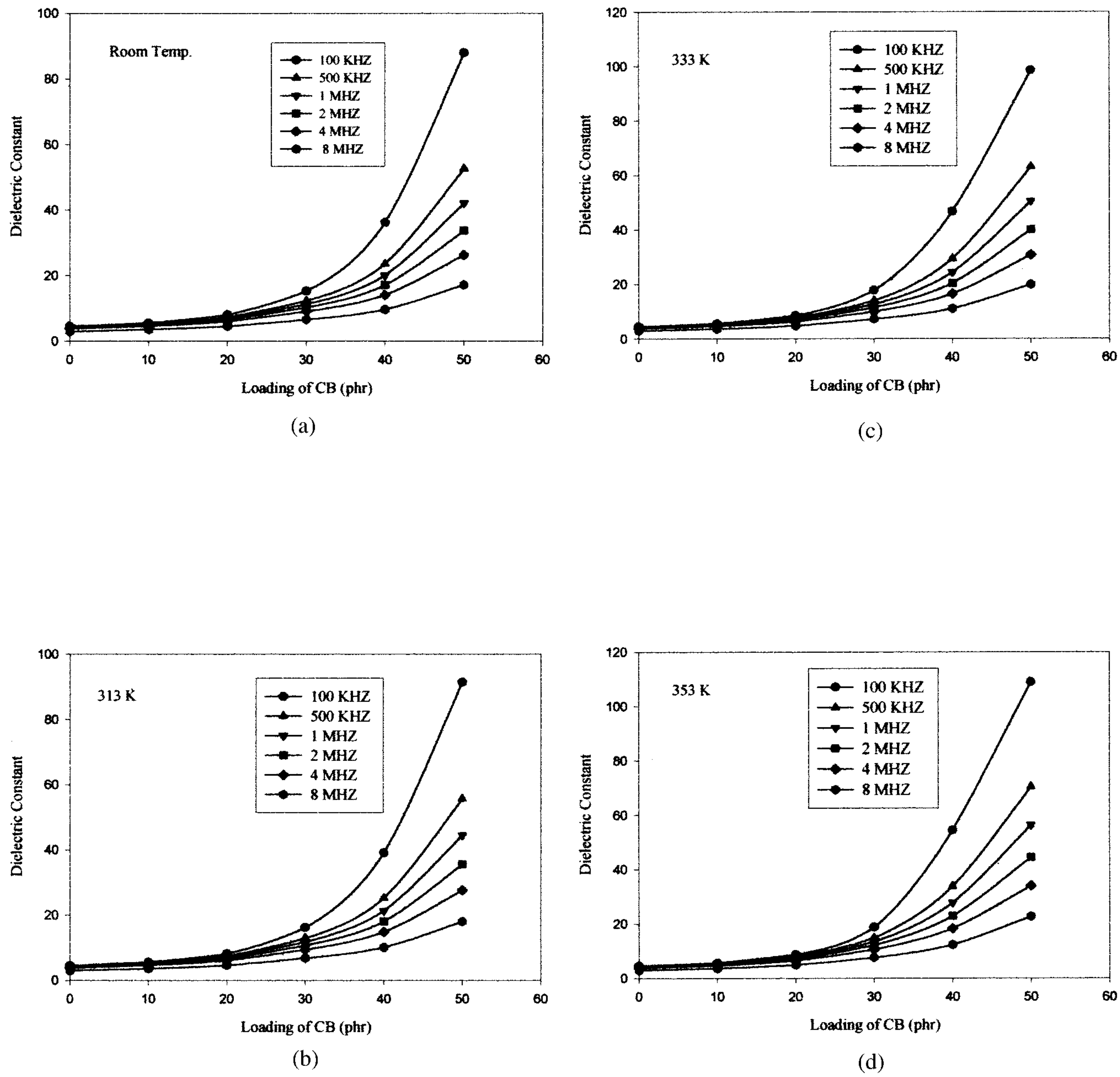


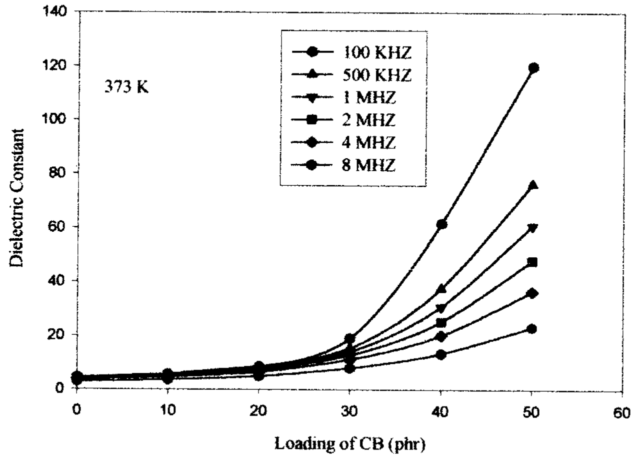
Figure 5 (a–f) Dielectric constant vs. loading of carbon black at different frequencies and various temperatures.

matter of minutes and the data can be plotted and analyzed.

RESULTS AND DISCUSSION

From the X-ray powder diffractograms of BaF, and subsequent evaluation of structural parameters indicates that the compounds are monophasic and crystalline in nature, without any detectable impurities. The interatomic spacing (d) and their relative intensities ($I/I_o \times 100$) match well with that of the reported values in the literature.[29]

The magnetization measurements were carried out using a Vibrating Sample Magnetometer (VSM) and the hysteresis loop of some typical composites are shown in Figures 1 and 2. Figure 1 depicts the hysteresis loop of RFC containing 80 phr of BaF, whereas the Figure 2 depicts that of the same RFC with 50 phr of carbon black. From the hysteresis loop, loop parameters, namely saturation magnetization (M_s), magnetic remanence (M_r), coercivity (H_c), and M_r/M_s were evaluated. Reported value of M_s for barium ferrite is 72 emu/g at 20°C while that of the barium ferrite filler used in this particular study exhibit a M_s of $\approx$60 emu/g at 30°C, and this compares very well. The details of these magnetic measurements for the RFC are shown in Tables 1 and 2. It can be seen that the saturation magnetization value increases linearly with the incorporation of the magnetic filler. The saturation magnetization (M_{rfc}) value of the composites contain-



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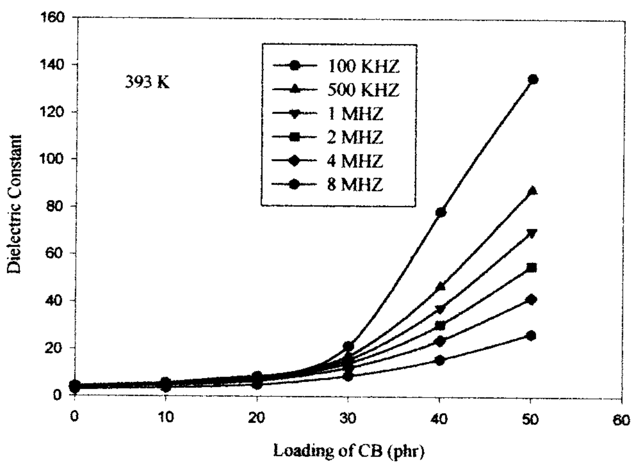


(f)

Figure 5 (*Continued from the previous page*)

ing filler can be related to the loading of the filler by a simple relation,

$$M_{rfc} = W_1 M_1 \qquad (4)$$

where W_1 is the weight fraction of filler and M_1 is the saturation magnetization of the filler. The coercivity of the composites with loading of fillers remains the same as that of BaF and does not undergo any appreciable change with filler loading. Apart for a small drop in coercivity when compared to a composite without carbon black, the H_c of composites with carbon black also have almost identical values. The magnetic saturation of the composites with carbon black decreases with the increasing loading of carbon black, which is on predicted lines.

Barium ferrite-filled NR vulcanizates shows a lower tensile strength when compared to the gum vulcanisate. This is because of the poor interfacial adhesion between the ferrite filler and natural rubber. The average particle size determination by employing the Debye-Scherrer equation have shown that the particle size of these hexagonal ferrites are greater than that of reinforcing fillers like carbon black. The average particle size of BaF lie in the range of 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 $A_s = 600/D\rho$ is only indicative, and this cannot be compared with the surface area as determined by techniques like BET (Branauer, Emmett, and Teller). The total interface area between the filler and the elastomer depends on the surface area of the filler and the amount of filler in the compound. Because the surface area of BaF is smaller, the extent of interface between the polymer and ferrite filler is also less; thereby decreasing the tensile strength.

The tensile properties and hardness of the vulcanizates containing BaF and carbon black are shown in Table II. Figure 3 depicts the variation of tensile strength of RFC with the loading of carbon black. Tensile strength increases with the addition of carbon black up to a loading of 30 phr and decreases thereafter. This is due to the fact that the carbon black is a well-known reinforcing filler. The tensile strength decreases at higher loading of carbon black because of the dilution effect, which is due to the diminishing volume fraction of polymer in the composite.

The modulus of the composites increases, which is characteristic of reinforcing fillers. The modulus at 300% of these rubber ferrite composites showed a steady increase with addition of carbon black. The hardness of these composites also showed a steady increase with the loading of carbon black, which is on expected lines.

The dielectric constant of pure BaF and natural rubber vulcanizates with and without carbon black at various frequencies and at different temperatures were evaluated and are shown in Figure 4(a)–(h). It can be seen that the dielectric constant decreases with increasing frequency for composites containing BaF and different loadings of carbon black. This behavior is in accordance with the Maxwell Wagner theory of interfacial polarization[30] and they obey the relation,

$$\varepsilon^{11} = (r - r^1)(\varepsilon^1 \times \omega) \qquad (5)$$

where ϵ^1 and ϵ^{11} are the real and imaginary parts of the dielectric constant, r and r^1 are the AC and DC conductivity, respectively, and ω is the frequency.

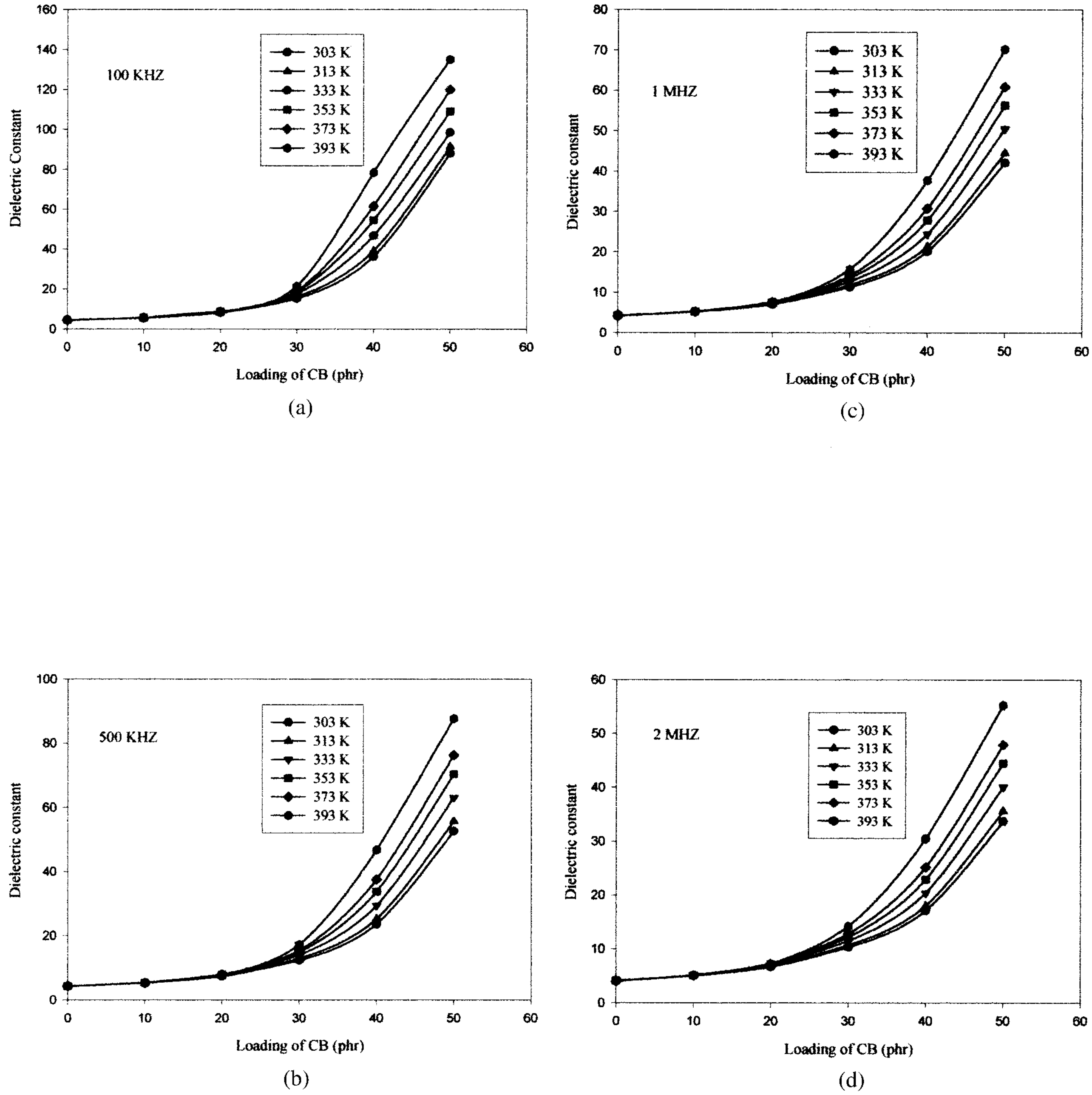


Figure 6 (a–f) Dielectric constant vs. loading of carbon black at different temperatures and various frequencies.

It is known that the addition of carbon black fillers in rubber ferrite composites enhances the bandwidth of absorption.[31,32] The microwave absorption of the composite is dictated by the surface impedence,

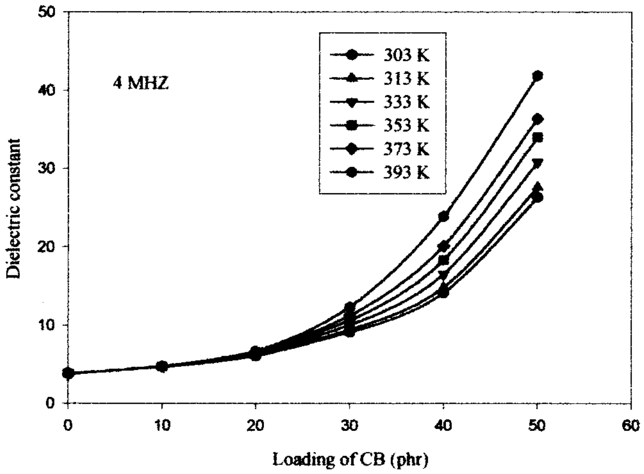
$$Z_{\text{in}} = (\mu_r/\in_r)^{1/2}\tanh\left|j(2\pi d/\lambda)(\mu_r/\in_r)^{1/2}\right| \quad (6)$$

where λ is the wavelength of the microwave in free space and d is the thickness of the absorber. According to the transmission line theory, the reflection coefficient of electro magnetic radiation, R (dB), under normal wave incidence at the surface of a single-layer material backed by a perfect conductor can be defined by[33]

$$R = 20\log\left[\frac{Z_{\text{in}} - Z_o}{Z_{\text{in}} + Z_o}\right] \quad (7)$$

where Z_o is the characteristic impedence of free space, $Z_o = \sqrt{(\mu_0/\epsilon_0)}$.

In RFC, the addition of magnetic fillers modify the permeability and the incorporation of carbon black in RFC increases the dielectric permittivity of the composite. Thus, a judicious choice of magnetic filler with



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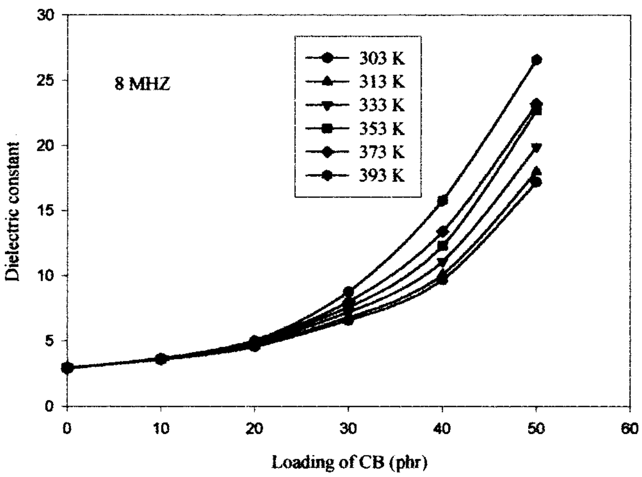

(f)

Figure 6 (*Continued from the previous page*)

an appropriate reinforcing filler enhances the microwave absorbing characteristics of a composite apart from modifying the mechanical properties of the composite. The increase of permittivity is evidenced by our results, which are shown in Figure 5(a)–(f). From Figure 5(a)–(f), it can be seen that the dielectric constant increases substantially after a loading of 20 phr of carbon black. It may be noted that dielectric constant of 4.3 increases to 135 (at 100 kHz at 393 K) for a loading of 50 phr of carbon black on a base RFC containing 80 phr of BaF. This result is significant because devices based on natural rubber and ferrites with the required mechanical strength and dielectric constant can be prepared by the incorporation of carbon black into the RFC.

The effect of loading of carbon black on the dielectric permittivity at different temperatures and various frequencies has also been studied and is represented in Figure 6(a)—(f). The dielectric permittivity increases with the loading of carbon black. The dielectric constant also increases with temperature. This is because in dielectrics, ionic polarization increases the dielectric constant with increase in temperature. Moreover, the increase in dielectric constant is prominent at lower frequencies than the one at a higher frequency. Thus, by an appropriate loading of barium ferrite and carbon black in natural rubber, rubber ferrite composites with the required dielectric properties and optimum mechanical and magnetic properties can be prepared.

CONCLUSION

Rubber Ferrite Composites (RFC) based on natural rubber and barium ferrite containing carbon black can be synthesized according to a specific recipe. It was found that the processability was not much affected by filler incorporation, and the percolation threshold was not reached even at 130 phr of the filler. Studies on magnetic properties indicated that these composites posses suitable magnetization values. The coercivity of the composites remained almost the same as that of the ceramic barium ferrite. Analysis of mechanical properties indicated that the addition of N 330 (HAF) carbon black enhanced the tensile strength and modulus. The dielectric constant increases appreciably with the incorporation of carbon black. Hence, the mechanical, dielectric, and magnetic properties of these composites can be tailored for various applications, particularly for designing the microwave absorbers by the judicious choice of barium ferrite and carbon black.

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