Processability, hardness, and magnetic properties of rubber ferrite composites containing manganese zinc ferrites

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Rubber ferrite composites have the unique advantage of mouldability, which is not easily obtainable using ceramic magnetic materials. The incorporation of mixed ferrites in appropriate weight ratios into the rubber matrix not only modifies the dielectric properties of the composite but also imparts magnetic properties to it. Mixed ferrites belonging to the series of $Mn_{(1-x)}Zn_xFe_2O_4$ have been synthesised with different values of x in steps of 0·2, using conventional ceramic processing techniques. Rubber ferrite composites were prepared by the incorporation of these pre-characterised polycrystalline $Mn_{(1-x)}Zn_xFe_2O_4$ ceramics into a natural rubber matrix at different loadings according to a specific recipe. The processability of these elastomers was determined by investigating their cure characteristics. The magnetic properties of the ceramic fillers as well as of the rubber ferrite composites were evaluated and the results were correlated. Studies of the magnetic properties of these rubber ferrite composites indicate that the magnetisation increases with loading of the filler without changing the coercive field. The hardness of these composites shows a steady increase with the loading of the magnetic fillers. The evaluation of hardness and magnetic characteristics indicates that composites with optimum magnetisation and almost minimum stiffness can be achieved with a maximum loading of 120 phr of the filler at $x = 0{\cdot}4$. From the data on the magnetisation of the composites, a simple relationship connecting the magnetisation of the rubber ferrite composite and the filler was formulated. This can be used to synthesise rubber ferrite composites with predetermined magnetic properties. PRC/1741

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INTRODUCTION

Progress in the use of ferrites and development of new ferrite composites has been rapid compared with other areas of research.[1-7] Ferrites can be divided into two groups, the magnetically soft and hard. They are also characterised by high resistivities and low eddy current losses,[8] which make them ideal for high frequency applications. Owing to their dielectric behaviour, they are sometimes called magnetic dielectrics. They are important commercially because they can be applied in many devices such as phase shifters, isolators, circulators, high frequency transformer cores, switches, resonators, refrigerator door seals, computer peripherals, television, and mobile phones.[9-11] The addition of these fillers to a polymer matrix such as natural or synthetic rubber alters its physical properties. The incorporation of ferrite fillers imparts magnetic properties to the composite and modifies its dielectric behaviour.

One application of these materials is in shielding against electromagnetic interference. The microwave absorbing properties of the rubber ferrite composites (RFCs) are determined by the surface impedance relationship, which is given by

$$Z_{in} = \left(\frac{\mu^*}{\varepsilon^*}\right)^{1/2} \tanh\left(j\frac{2\pi d}{\lambda}(\mu^*\varepsilon^*)^{1/2}\right) \quad . \quad . \quad . \quad (1)$$

where λ is the wavelength of the microwave in free space, d is the thickness of the absorber material, j is ≥ -1, and μ^* and ε^* are the complex magnetic permeability and complex dielectric permittivity of the material, respectively ($\mu^* = \mu_r' - j\mu_r''$ and $\varepsilon^* = \varepsilon_r' - j\varepsilon_r''$).[6,7,12,13] It can be seen from the above relationship that it is the permittivity and permeability, together with the thickness, that dictate the microwave absorption characteristics. Hence it is important that the permeability and permittivity are optimised for minimum thickness of the absorber. This is possible by using RFCs with appropriate magnetic and electric properties. This can be achieved by synthesising RFCs incorporating appropriate amounts of fillers into the matrix according to a specific recipe.[14] The choice of compounding ingredients, compounding conditions, and their processability also assume significance.

Knowledge of cure characteristics throws light on the processability of composites. Information regarding particle size and surface area are also valuable tools in explaining the surface activity with respect to the components, namely manganese zinc ferrite (MZF) in natural rubber (NR). The manganese zinc mixed ferrites are selected as fillers because of their high magnetic permeability and low eddy current loss. These ferrites are soft magnetic materials.

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The present work reports the synthesis of ceramic fillers, their structural characteristics, and the incorporation of these fillers into NR to yield RFCs. The magnetic properties of both ceramic MZF and RFCs are also studied. Natural rubber is selected as the matrix for the incorporation of the magnetic fillers because it is relatively inexpensive and easily processed. Moreover NR can be compounded easily with any kind of filler to a moderately high loading. The final properties of the composites depend not only on the properties of the filler but also on the properties of the matrix, for example, whether it is polar or non-polar, saturated or unsaturated. Several parameters, including lattice constant, particle size, porosity, and surface area of the ceramic filler were studied in detail as functions of the zinc content of the MZF. The results are correlated with the cure time, hardness, and magnetisation of the corresponding RFC. Variations in cure time and hardness with loading were also studied. Magnetisation measurements were carried out on RFCs with various values of x at different loadings. The results were analysed and correlated and a general equation connecting the saturation magnetisation σ_s of the RFC with that of the filler was formulated with the help of a semi-empirical curve fitting procedure proposed by Malini *et al.*[15] The validity of this equation was tested against the experimentally observed σ_s values.

EXPERIMENTAL

Preparation of $Mn_{(1-x)}Zn_x$ ferrites

Freshly prepared ferrous oxalate dihydrate precursors were used to synthesise the MZFs. Oxides of manganese and zinc were mixed with these ferrous oxalate dihydrate materials in the required weight proportions. They were then homogenised thoroughly using an agate mortar and pre-sintered at $\sim 500°C$ for several hours.[16] Repeated sintering and mixing were continued until a single spinel phase was obtained. Final firing was performed at $\sim 1000°C$ for several hours to yield ferrites belonging to the series $Mn_{(1-x)}Zn_xFe_2O_4$ with x varying from 0 to 1 in steps of 0·2.

Structural analysis

The MZF powders were analysed using X-ray powder diffraction techniques. The X-ray diffractograms of these powder samples were recorded on an X-ray diffractometer (Rigaku Dmax-C) using Cu K_α radiation ($\lambda = 1{\cdot}5405$ Å). Lattice parameters were calculated assuming cubic symmetry using[17]

$$d_{h,k,l} = \frac{a}{(h^2 + k^2 + l^2)^{1/2}}$$

and the average particle size was determined by the Debye–Scherrer formula.[18,19] The surface area of the powder in $m^2\,g^{-1}$ was evaluated from these data using the relationship[20] $6000/D\rho$, where D is the diameter of the particle in nm and ρ is the density of the particle in $g\,cm^{-3}$.

The porosity of each MZF powder was determined by pressing it into a 20 mm disc and comparing its density with the density of the perfect crystal calculated from the X-ray diffraction data.

Incorporation of ferrites into NR

The pre-characterised MZF ceramics were then incorporated into an NR matrix according to a specific recipe. The mixing was cariied out in a Brabender Plasticorder (torque rheometer) model PL 3S. Rubber ferrite composites were prepared with loadings of 30–120 phr in steps of 30 phr. They were then homogenised using a two roll mill. Details of the recipe are given in Table 1.[21] After homogenisation, the composites were moulded into thin sheets (thickness 0·5–2 mm) at 150°C for the recommended cure times, in accordance with ASTM D 3188, using a hydraulic press.[22,23]

Cure characteristics

The cure parameters of RFCs with various loadings of MZF were studied using a Gottfert Elastograph model 67·85.

Hardness of elastomer

The Shore A hardness of each moulded sample was tested using a Zwick 3114 hardness tester in accordance with ASTM D 2240 : 86.[23] The tests were carried out on a mechanically unstressed sample of 12 mm diameter and minimum 6 mm thickness. A load of 12·5 N was applied and, after ensuring firm contact with the specimen, the readings were taken after 10 s indentation.

Magnetisation measurements

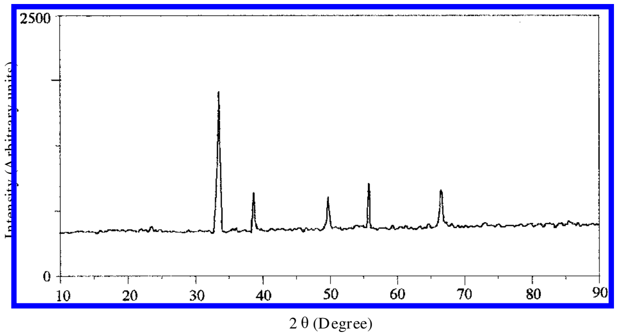
Magnetic measurements on the magnetic fillers and RFCs were carried out using a vibrating sample magnetometer (VSM EG&G PAR 4500). The hysteresis loop parameters saturation magnetisation σ_s, remanent magnetisation M_r, and coercivity H_c were determined.

RESULTS AND DISCUSSION

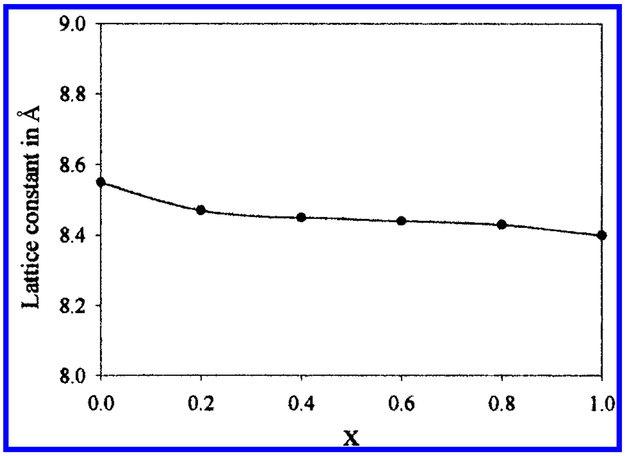
The structural parameters of the MZF ceramics, namely, interatomic spacing d, lattice constant a, and particle size D were determined from their X-ray diffractograms. These results indicate that the compounds are crystalline in nature, forming a single phase with no detectable impurities. A representative XRD spectrum of these ferrites is shown in Fig. 1. The lattice parameters for the $Mn_{(1-x)}Zn_x$ ferrite series lie in the range 8·4–8·55 Å and the results are shown in Fig. 2. These show that the lattice constants of the MZF series are slightly greater than the lattice constants of the same samples sintered at higher temperatures. Increasing the sintering temperature reduces the lattice constant and increases the particle size.[18,19,24] The relationship between the porosity of the ferrites and their zinc content is shown in Fig. 3.

Table 1 Recipe used for preparing RFCs

Ingredient	Amount, phr
Natural rubber	100
Zinc oxide	5
Stearic acid	3
MZF Filler	Yes
Mecapto bezothyazyl disulphide	0·8
Tetramethyl thiuram disulphide	0·2
Sulphur	2·5

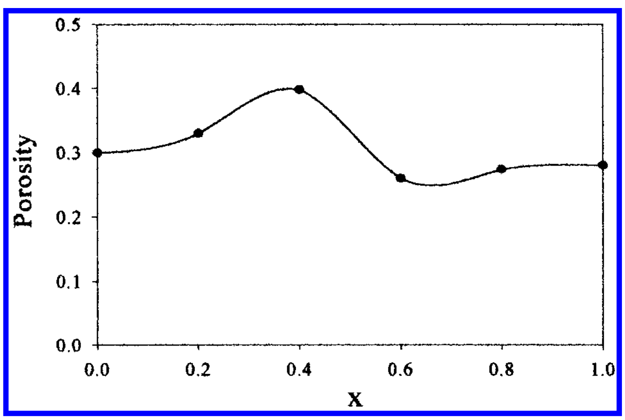


1 Representative X-ray scattering spectrum for MZF

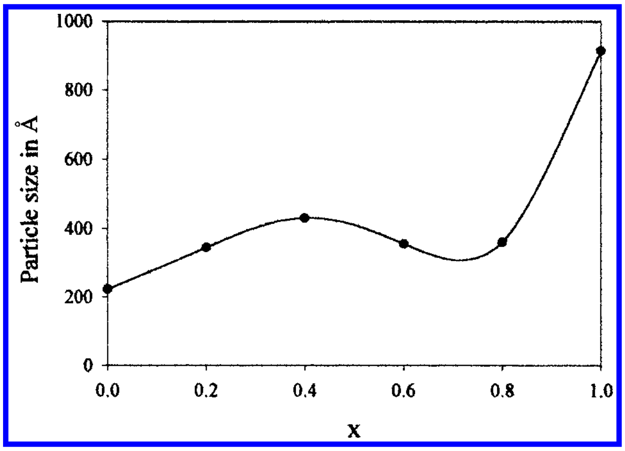


2 Lattice constant versus zinc content of MZF

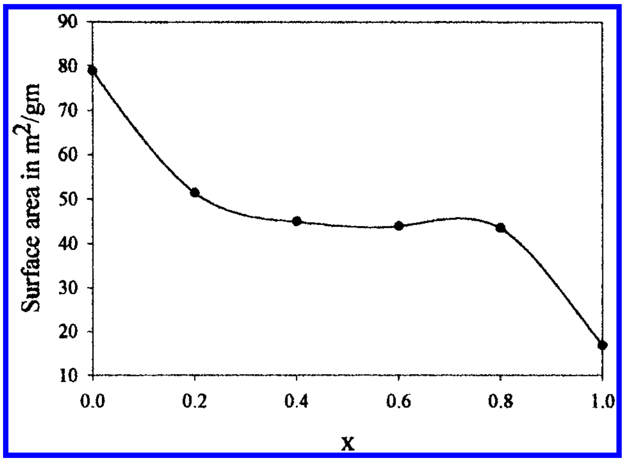
The sintering temperature was kept at 1000°C to inhibit the growth of particles. The average particle size was calculated for all compositions. The variation in particle size of MZF with zinc content is shown in Fig. 4. The surface area for each MZF was also evaluated using the relationship cited above. The variation of filler surface area with increasing zinc content is plotted in Fig. 5 for the RFCs containing MZF ceramics. However, it should be noted that the particle size D, which is calculated using the Debye–Scherrer formula, represents only an average value; hence the surface area calculated from the formula $6000/D\rho$ is only indicative, unlike that obtained from techniques such as the Branauer, Emmett and Teller (BET) method.[25]



3 Porosity versus zinc content of MZF

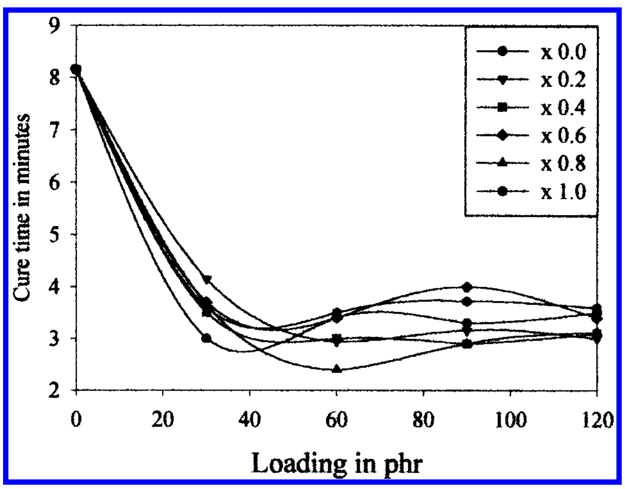


4 Particle size versus zinc content of MZF

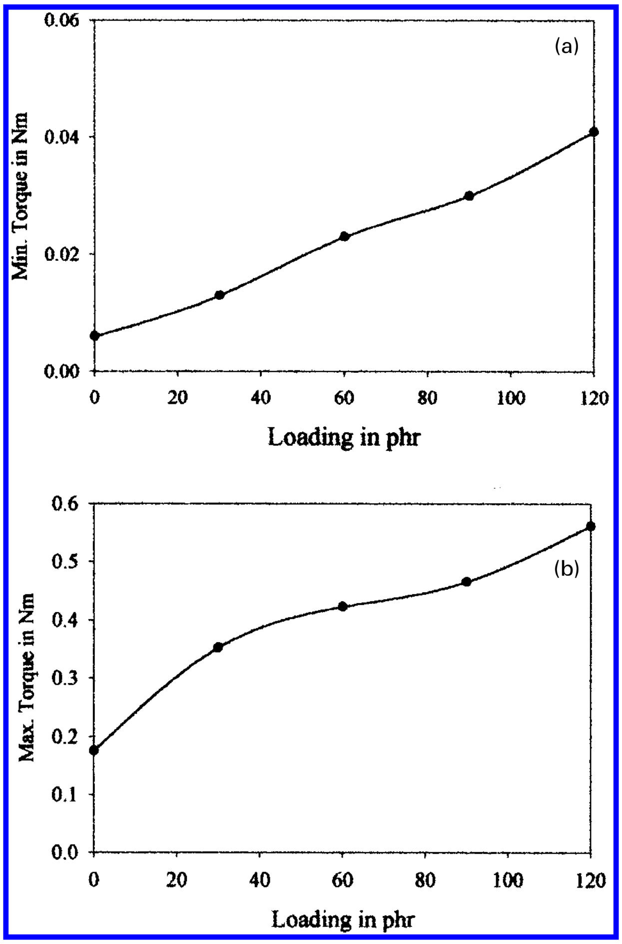


5 Surface area versus zinc content of MZF

The variations in cure time for RFCs containing different loadings of MZF are represented in Fig. 6. Graphs showing variations of maximum and minimum torque for various loadings of ferrite are presented in Fig. 7. For RFCs containing MZF, the cure times are much shorter than that of the unfilled rubber, but the changes in cure time with filler content are relatively unimportant as the ferrite loadings are increased from 30 to 120 phr in steps of 30 phr. The viscosity of the curing system remains well within

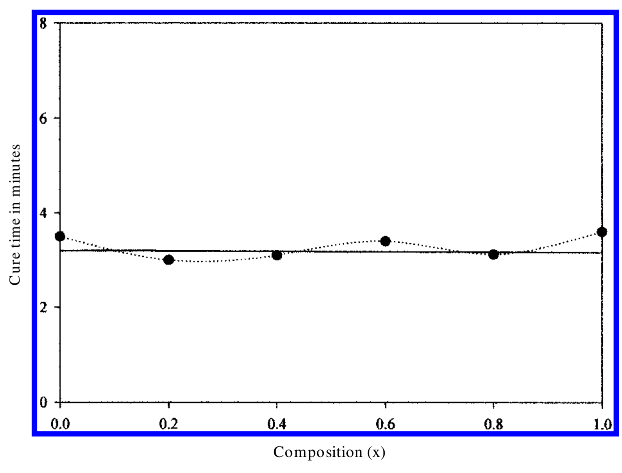


6 Cure time versus loading of RFC, with *x* varying from 0 to 1

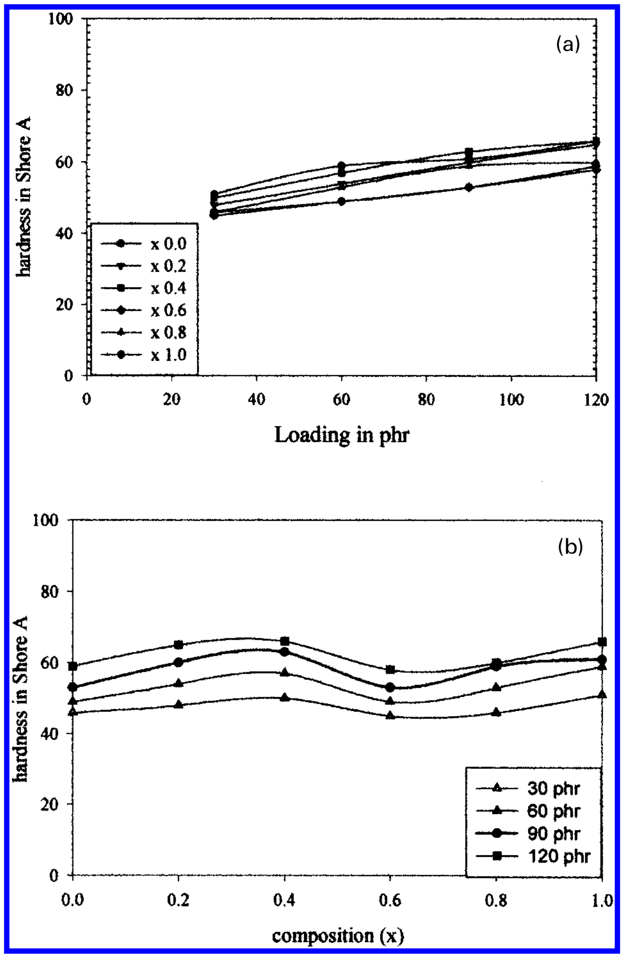


7 Representative curves of *a* minimum and *b* maximum torque versus filler loading in RFCs

processable limits. Graphs for cure time versus x for the MZF series are shown in Fig. 8; it can be seen that the cure time is not significantly dependent upon the zinc content of the ferrite. The straight line in Fig. 8 represents the typical cure time for NR containing a mixed ferrite system. It is known from the literature[20] that the total contribution of a filler to physicochemical changes during vulcanisation is mainly due to two factors, i.e. the specific surface activity and the surface area. The variation in surface area with x shown in Fig. 5 does not resemble the pattern



8 Cure time versus composition of RFC



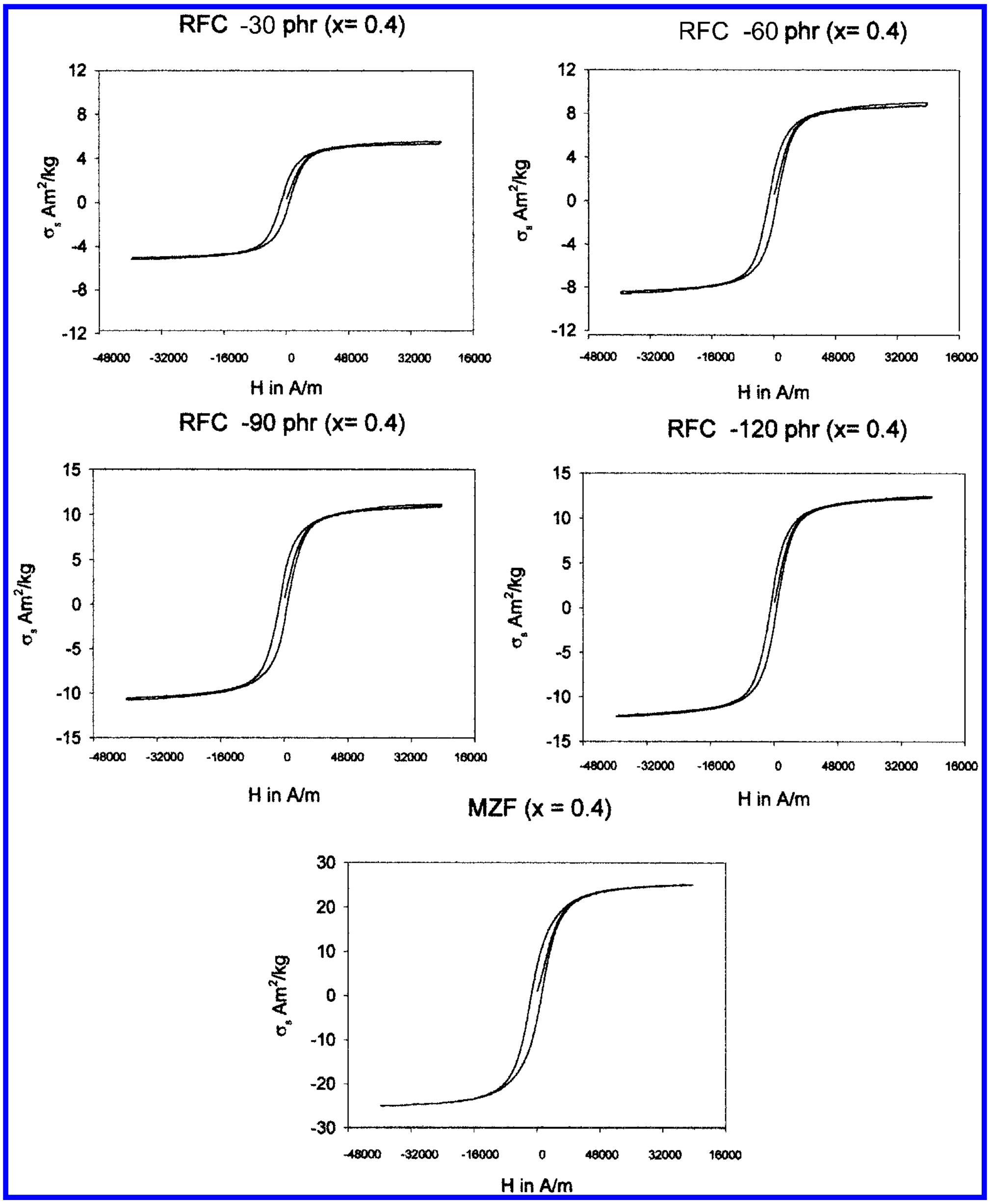
9 *a* Hardness versus loading of RFC, with *x* varying from 0 to 1; *b* hardness of RFCs versus zinc concentration in ceramic filler, at filler loadings 30–120 phr

observed for the cure time of the corresponding composites. There may be a small effect on cure time due to the surface activity of the MZF filler.[26] However, more confirmatory tests are required to determine whether this effect is real.

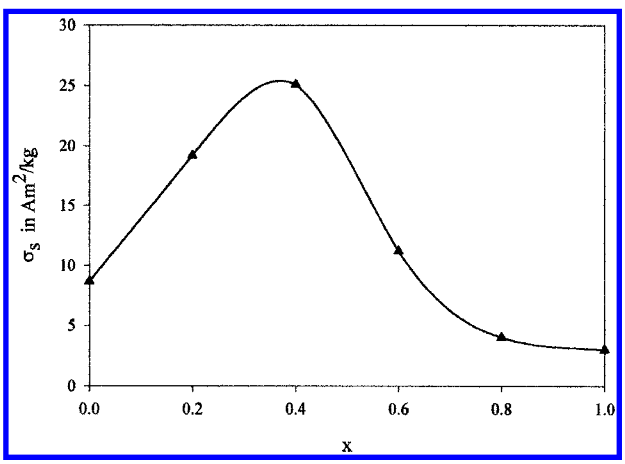
The hardness of the RFC samples was also studied for different loadings and zinc contents of the MZF fillers, and the results are shown in Fig. 9. The Shore A hardness shows a minimum at $x = 0{\cdot}6$. The porosity of the filler also shows a similar type of the same variation, giving a minimum at $x = 0{\cdot}6$ (*see* Fig. 3). However, the maximum hardness for the samples is well below the maximum design limit for the elastomer even for a filler loading of 120 phr.[20] This result can be exploited to make RFCs with optimum magnetic properties and maximum flexibility.

Representative hysteresis loops for both MZF and a series of MZF loaded RFCs are shown in Fig. 10. The hysteresis loops of both MZF and RFC samples show minimum losses and the coercivity has almost the same value in the ceramic and composite samples. A comparison of Figs. 11 and 12 shows that the variations of saturation magnetisation with zinc content are identical in the ceramics and the RFCs.

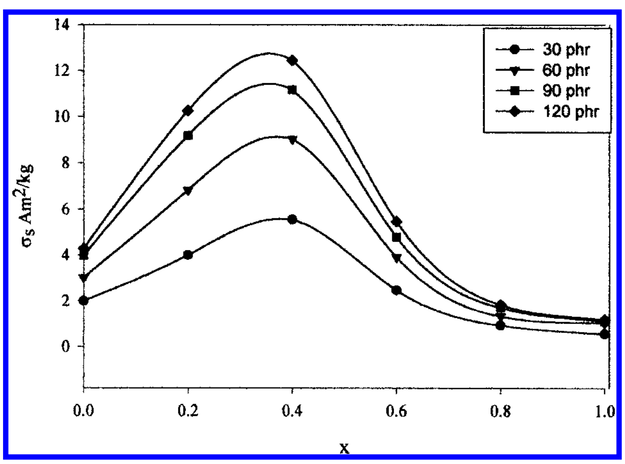
The saturation magnetisation of $MnFe_2O_4$ fired at lower temperatures ($-1000°C$) is less than that of $MnFe_2O_4$ fired at higher temperatures ($>1000°C$). The



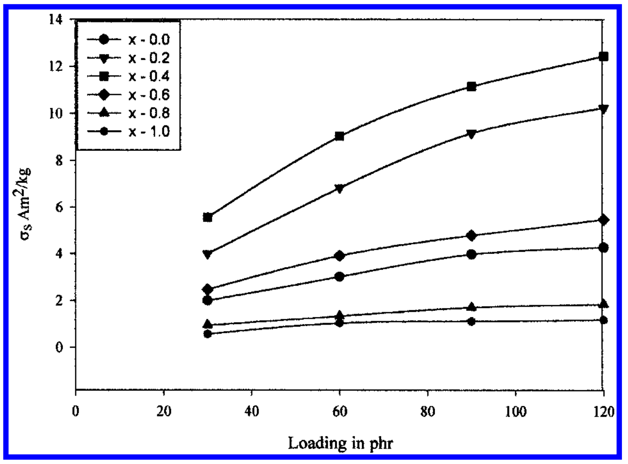
10 Representative hysteresis loops for MZF with x 0·4 and RFCs containing MZF at various loadings



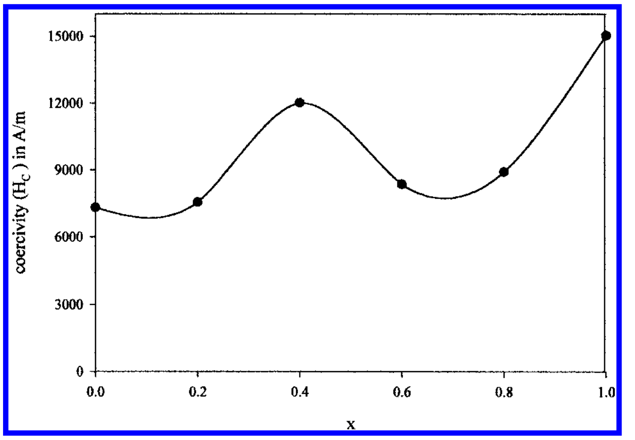
11 Saturation magnetisation as function of zinc content of MZF



12 Saturation magnetisation of RFCs containing 30–120 phr filler, as functions of zinc content of filler



13 Saturation magnetisation of RFCs as functions of filler loading, with *x* varying from 0 to 1



14 Coercivity of MZF as function of zinc content

sintering temperature and the method of preparation have a profound influence on the final properties of $MnFe_2O_4$ samples. It is known from the literature[3] that the distribution of cations between the tetrahedral A and octahedral B sites in a ferrite depends on various factors, including cation size, ionic charge, and heat treatment. In $MnFe_2O_4$ samples sintered at temperatures below 1000°C, there are fewer Mn^{2+} ions occupying the tetrahedral A sites than when the ceramic is fired at higher temperatures. At higher sintering temperatures, electron hopping can change Mn^{3+} ions into Mn^{2+} and force Fe^{2+} ions to convert to Fe^{3+}. The Mn^{2+} ions migrate from octahedral B sites to tetrahedral A sites, forcing Fe^{3+} ions from tetrahedral A sites to octahedral B sites. At lower sintering temperatures the simultaneous presence of Mn^{3+} and Fe^{2+} ions can reduce the magnetic moment of the ceramic, as explained by Harrison *et al.*[27] This is more probable in the case of the MZF samples chosen for the present investigation and is one reason for the reduced saturation magnetisation of MZF samples baked at lower temperatures. The concentrations of Mn^{3+} ions are relatively greater in samples fired at lower temperatures. However, the presence of Mn^{3+} in the MZF series has not been confirmed by any other studies and remains speculative. The oxygen parameter u (which is a measure of the distance between the oxygen ion and a face of the cubic unit cell) also changes the spin alignment to reduce the saturation magnetisation.[1,4]

The observed variations in magnetisation with composition are in agreement with those reported by other researchers.[1,3] The saturation magnetisation initially increases with increasing zinc content and reaches a maximum at $x = 0{\cdot}4$, after which it decreases. This can be explained by the canting of spins.[1,28–31] As the zinc content increases, B–B interactions become predominant. At values of $x > 0{\cdot}4$, a canted spin structure appears. At $x = 1{\cdot}0$, the B–B interactions reach a maximum, and the spins at the B sites are antiparallel, resulting in a minimum net magnetisation. The details are well established and are described elsewhere.[1,4]

The increase in ferrite loading produces a steady increase in saturation magnetisation, as shown in Fig. 13. The variation in coercivity with zinc content for ceramic and composite samples is shown in Figs. 14 and 15. The pattern is the same for ceramics and RFCs and has the same form as the variation of coercivity with porosity shown in Fig. 3. These similarities reveal that the incorporation of a ferrite filler into the rubber does not introduce any significant change or modification to the structure of the filler or matrix as a result of milling.

The synthesis of RFCs with predetermined properties is essential when RFCs are required for specific applications. The measured saturation magnetisations of RFCs were fitted to a simple equation of the form

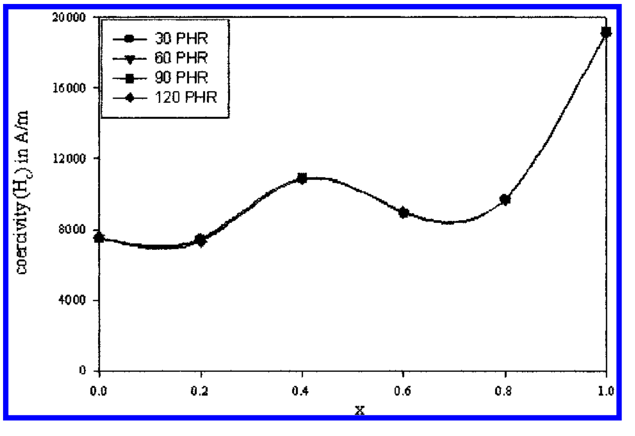
$$M_{rfc} = W_f M_f + W_m M_m \quad \quad (2)$$

where W_f, W_m, and M_f, M_m are the weight fractions and saturation magnetisations of the filler and matrix, respectively.[15]

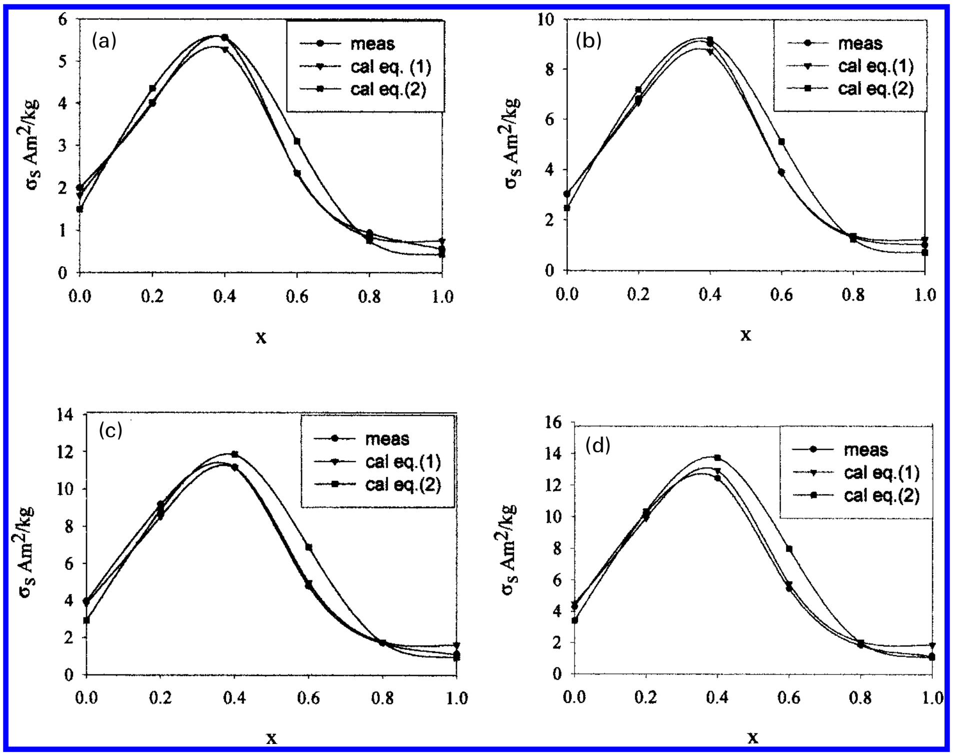
This simple rule of mixtures equation relates the magnetisation of RFCs to the magnetisation of the filler component and the matrix. It should be noted that for NR, which is non-polar and non-magnetic, the value of M_m is zero. Hence equation (2) reduces to the final form

$$M_{rfc} = W_f M_f \quad \quad (3)$$

The saturation magnetisations of RFCs of differing zinc contents and at various loadings have been calculated using equation (3) and are compared with the measured values in Fig. 16. It should be noted that the σ_s values for the individual ceramic compositions x must be known in advance in order to



15 Coercivity of RFC as function of zinc content of filler and filler loading of RFC



RFC = *a* 30, *b* 60, *c* 90, and *d* 120 phr

16 Calculated and measured values of saturation magnetisation for RFCs containing various loadings of filler, as functions of zinc content of filler

calculate the magnetic properties. A close examination of the data on magnetisation (σ_s) versus x for the MZF series shows that they can be correlated using a curve fitting procedure based on the Gaussian equation, as follows

$$\sigma_s = A \exp\{-0{\cdot}5[(x - x_m)/b]^2\} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

This expression was first formulated by Malini *et al.*[15] Appropriate meanings were assigned to the coefficients from observations on the experimental values and a modified equation was formulated to relate the saturation magnetisations σ_{rfc} of RFCs with those σ_s of the ceramic filler component. The fit produced a general equation from the Gaussian relation shown in equation (4) and is of the form

$$\sigma_{rfc} = (1 + 0{\cdot}2x)\sigma_{f0} W_f \exp\{-0{\cdot}5[(x - x_m)/b]^2\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where σ_{f0} and x_m are the maximum saturation magnetisation of the ceramic filler and its zinc content respectively, x is the zinc content of the ceramic filler used in the composite, and W_f is its weight fraction; b is a constant ($\sim$0·26) for the MZF series. It should be noted that in tailoring of the magnetic properties of RFCs, only the magnetisation of the ceramic with an x value that gives the maximum magnetisation need be determined. Equation (4) was used to obtain the calculated values. These are compared with measured values in Fig. 16. The observed and calculated values are in good agreement.

Malini *et al.*[15] and Anantharaman *et al.*[32] have previously used similar equations in two different systems, namely $Ni_{(1-x)}Zn_xFe_2O_4$ (NZF) in an NR matrix and NZF in a butyl rubber matrix, respectively. When magnetic elastomers are used for magnetic applications the coercive field H_c is also an important factor. If the particle size of the filler is reduced during milling, this can modify the H_c of the composite. From Figs. 14 and 15, it can be noted that the H_c values of RFCs containing MZF and the ceramic MZF itself are almost the same, as expected. This means that the saturation magnetisation of RFCs can be improved by selecting an appropriate loading of the filler without changing the H_c significantly. Using equation (5), the saturation magnetisation can be predetermined. The coercive field H_c can be modified by heat treatment of the filler.

The results presented in this paper indicate that the magnetic properties of RFCs can be suitably modified by using an appropriate loading of a filler with a particular composition. This also confirms the findings on the RFCs prepared with $Ni_{(1-x)}Zn_xFe_2O_4$ in both synthetic and NR matrixes.[32] These investigations reveal that appropriate magnetic properties can be imparted to these matrixes without affecting the processability of the rubber compound and without too much stiffening of the matrix.[32]

It should be noted that where magnetic properties and hardness are the decisive factors in the selection of a composite for a specific application, the optimum magnetic properties can be achieved by selecting an MZF with $x = 0{\cdot}4$.

CONCLUSIONS

Composites made by blending NR with ceramics selected from the $Mn_{(1-x)}Zn_x$ ferrite series show almost the same cure characteristics as NR itself. The cure time, minimum torque, and maximum torque are only marginally affected by different loadings of the ceramic filler. This indicates that processability is not significantly affected by the addition of MZF. The hardness of the RFCs shows a minimum at $\sim x = 0{\cdot}6$ for $Mn_{(1-x)}Zn_x$ ferrite fillers. The hardnesses of the samples are well below the maximum design limit (85 Shore A) for the elastomer even at a filler loading of 120 phr. This property can be exploited to make an RFC with optimum magnetic properties and maximum flexibility. The maximum value for saturation magnetisation for both ceramic and rubber composite samples is obtained at $x = 0{\cdot}4$. The coercive field of the RFCs does not vary with magnetic filler loading. The direct relationship between the saturisation magnetisation of RFC and the magnetisation of the respective fillers can be used to tailor magnetic properties.

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