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Magnetic and processability studies on rubber ferrite composites based on natural rubber and mixed ferrite

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Polycrystalline single phasic mixed ferrites belonging to the series $Ni_{1-x}Zn_xFe_2O_4$ for various values of x have been prepared by conventional ceramic techniques. Pre-characterized nickel zinc ferrites were then incorporated into a natural rubber matrix according to a specific recipe for various loadings. The processability and cure parameters were then determined. The magnetic properties of the ceramic filler as well as the ferrite loaded rubber ferrite composites (RFC) were evaluated and compared. A general equation for predicting the magnetic properties was also formulated. The validity of these equations were then checked and correlated with the experimental data. The coercivity of the RFCs almost resemble that of the ceramic component in the RFC. Percolation threshold is not reached for a maximum loading of 120 phr (parts per hundred rubber by weight) of the filler. These studies indicate that flexible magnets can be made with appropriate magnetic properties namely saturation magnetisation (M_s) and magnetic field strength (H_c) by a judicious choice of x and a corresponding loading. These studies also suggest that there is no possible interaction between the filler and the matrix at least at the macroscopic level. The formulated equation will aid in synthesizing RFCs with predetermined magnetic properties.

1. Introduction

Ferrites find extensive applications in making useful devices like inductor cores, circulators, isolators, refrigerator door seals, EMI shields, storage media, etc. [1–4]. Polycrystalline ceramic ferrite powders can be incorporated into various elastomer matrixes to produce rubber ferrite composites (RFC) [5–9]. The incorporation of these ferrite powders can be carried out in various matrixes to produce RFCs, both in natural and synthetic rubber. This can not only bring in economy but also produce flexible magnets. They have the unique advantage of mouldability into complex shapes which is not easily possible by conventional ceramic magnets. The impregnation of magnetic fillers in the matrix imparts magnetic properties to the matrix and modifies the dielectric properties of the matrix. The microwave absorbing property of elastomers warrants an appropriate dielectric strength and a desirable magnetic property [10, 11]. This can be achieved by synthesizing RFC wherein appropriate amount of magnetic fillers are incorporated into the rubber matrix according to a specific recipe. Here the choice of compounding ingredients, compounding conditions and their processability also assumes significance. Also factors like percolation limit and nature of the matrix, like saturated/unsaturated/polar/nonpolar rubber, all influences the final properties of the composites. In principle, the macroscopic properties of the composites could be influenced by the interaction between the filler and the matrix, if any. The effect of fillers in modifying the properties is to be understood properly in explaining the physical properties of these composites. Knowledge of

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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 filler in the elstomer matrix.

In this paper we report the synthesis of ceramic Nickel zinc ferrite ($Ni_{1-x}Zn_xFe_2O_4$) with x varying from 0 to 1 in steps of 0.2 by using conventional ceramic techniques and their incorporation in a natural rubber matrix according to a suitable recipe. Natural rubber (NR) is selected because of its local availability and possible value addition to the naturally available raw material. Moreover, it can be compounded easily with any kind of filler since it is a nonpolar polymer.

Nickel zinc ferrites (NZF) belonging to the series $Ni_{1-x}Zn_xFe_2O_4$ were prepared by the ceramic technique. The formation of the respective compositions in single phase were confirmed by structural analysis. The structural parameters were evaluated. Particle size and surface area of the ceramic filler were also determined. These fillers were then incorporated in the NR matrix according to a specific recipe. The cure parameters namely the maximum torque, minimum torque and curetime were also evaluated. The variation in the cure parameters with loading is also studied. The results are correlated with the cure time and hardness of the corresponding RFC. The hysteresis loop parameters namely the saturation magnetization, and coercivity of the filler and the RFC were also determined.

In applications involving RFCs it is necessary to modify the magnetic and dielectric properties. This is true for RFCs intended for microwave applications where the composite warrants an appropriate permeability and permitivity. Normally simple mixture equations relate the total magnetic property of the composite with the weight fraction of the filler loaded and magnetization of the magnetic component in the RFC. This has an inherent draw back especially, when systems of the type $Ni_{1-x}Zn_xFe_2O_4$ for various x is incorporated to make RFCs. The tailoring of magnetic properties of RFC necessitates the knowledge of the saturation magnetization (M_s) of the filler corresponding to that particular composition x. The variations of M_s with composition were studied for ceramic as well as RFC for various loadings and a general relation connecting the magnetic property of the filler and the composites were formulated so as to predict the properties of the composites. This modified equation does not require the individual M_s values for various x values of the filler, but requires only the M_s corresponding to the composition at which it exhibits maximum M_s.

2. Experimental

2.1. Preparation of $NiZnFe_2O_4$

NZF having the general formula $Ni_{1-x}Zn_xFe_2O_4$, for various $x = 0$ to 1 in steps of 0.2 was prepared by using conventional ceramic technique [12]. For the preparation of NZF appropriate amounts of precursors namely ferrous oxalate dihydrate, nickel oxide and zinc oxide were used. These were then mixed thoroughly in an agate mortar to produce a homogeneous mixture of fine particles. This homogeneous mixture was prefired at 500°C for several hours. Repeated sintering and mixing were continued till single phasic spinel compound was obtained. This pre sintered powder was then finally sintered at 1000 ± 15°C for several hours.

2.2. Structural evaluation

The X ray diffractograms of these powder samples were recorded on a X-ray diffractometer (Rigaku Dmax-C) using Cu K_α radiation ($\lambda = 1.5405$ Å). Lattice parameter was calculated [13] assuming cubic symmetry by employing the relation $d_{h,k,l} = \frac{a}{\sqrt{h^2+k^2+l^2}}$ and the average particle size was determined by Debye Scherrer [14] formula $D = \frac{0.9\lambda}{\beta \cos\theta}$. The surface area in m^2/g was evaluated from these data using the relation $6000/D\rho$ where 'D' is the diameter of the particle in nm and 'ρ' is the density of the particle in g/cc [15].

2.3. Incorporation of ferrites in natural rubber

Precharacterized NZF was then incorporated in a natural rubber matrix according to a specific recipe. The mixing was done in a Brabender Plasticorder (Torque Rheometer) model PL 3S. Rubber ferrite composites were prepared for loadings of 30 to 120 phr in steps of 30 phr. Further, it was homogenized using a two roll mill. After homogenization it was moulded into thin sheets at 150°C at their respective cure time in accordance with ASTM D 3188 using a hydraulic press [16].

2.4. Cure characteristics

The cure parameters of RFC for various loadings of NiZn Ferrite was studied by using Gottfert Elastograph model 67.85 at 150°C.

2.5. Hardness of elastomer

The hardness (shore A) of the moulded samples were tested by using Zwick 3114 hardness tester in accordance with ASTM D 2240–86. 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 seconds of indentation.

2.6. Magnetic measurements

Room temperature magnetic measurements were carried out by using a VSM (EG&G PAR 4500) and parameters like saturation magnetisation (M_s) and coercive force (H_c) were evaluated for both ceramic as well as RFCs.

3. Results and Discussion

3.1. Structural evaluation

From the X ray powder diffractograms recorded for NZF series, parameters namely, inter atomic spacing 'd', relative intensity ($I/I_0 \times 100$), lattice constant 'a' and particle size 'D' were determined. The evaluation of the structural parameters indicates that the compounds are monophasic without any detectable

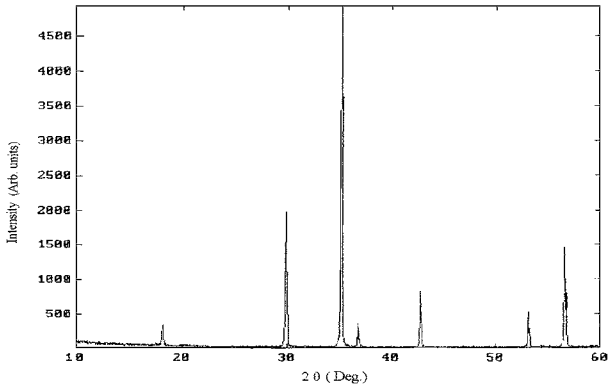


Figure 1 Representative XRD spectrum.

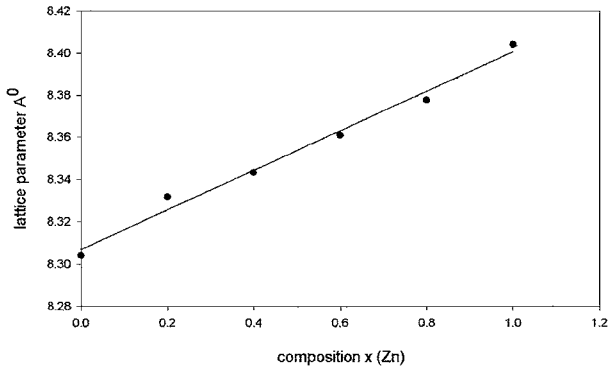


Figure 2 Variation of lattice parameter with composition for NZF.

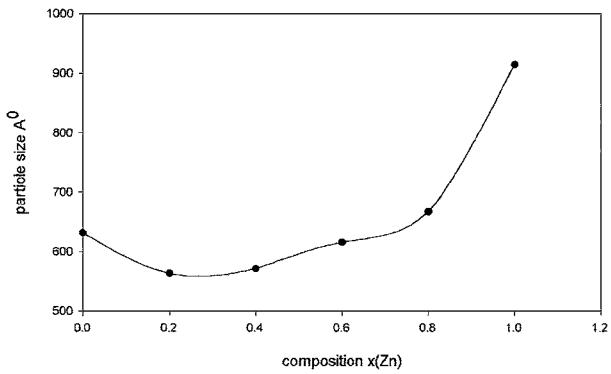


Figure 3 Variation of particle size with composition for NZF.

impurities and are crystalline in nature. A representative XRD spectrum of these ferrites is shown in Fig. 1. The lattice parameter corresponding to NZF series lies in the range 8.3 to 8.4 Å and the variation of lattice parameter with composition is in accordance with Vegards law [17, 18]. The results are depicted in Fig. 2. The average particle size was calculated for all these compositions. The variation in particle size is also plotted and shown in Fig. 3. The surface area of these powders were also evaluated using the relation $S = 6000/D\rho$. The variation of surface area with increasing zinc content is plotted and is shown in Fig. 4.

3.2. Cure characteristics

Graphs showing the variation of maximum torque, minimum torque with filler loading is also plotted and is shown in Figs 5 and 6. It is seen that the maximum

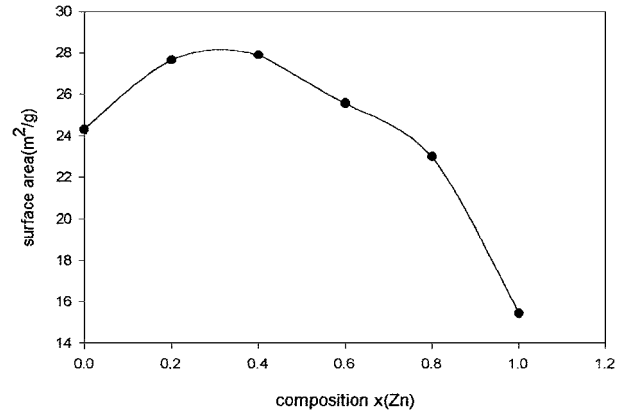


Figure 4 Variation of surface area with composition for NZF.

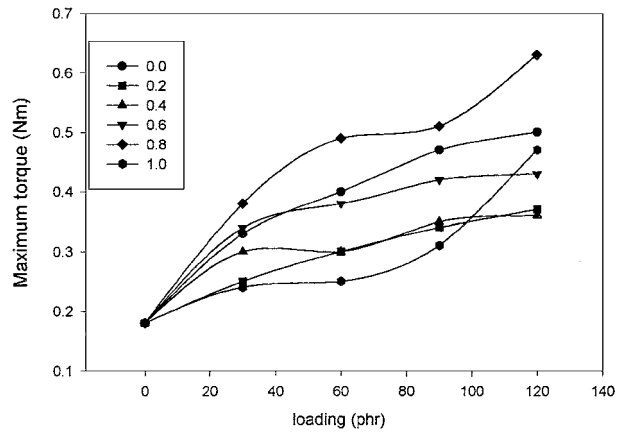


Figure 5 Variation of maximum torque with loading.

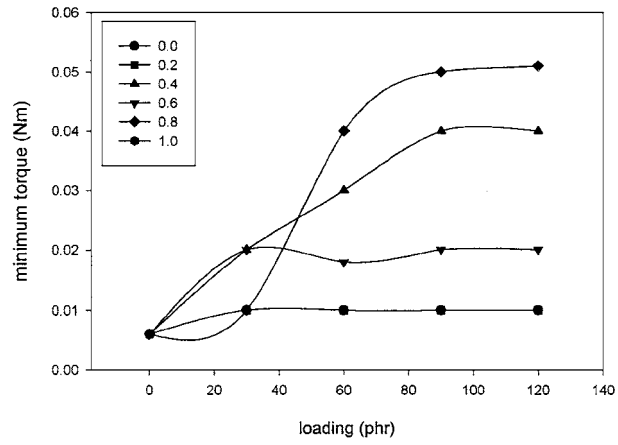


Figure 6 Variation of minimum torque with loading.

torque increases with loading for almost all compositions. Maximum torque gives an idea about the modulus of the compound. It shows an increasing trend with loading. Minimum torque is an indirect measure of the viscosity of the compound. Minimum torque also shows an increasing trend with loading without much variation at higher loadings. The variations in cure time for different loadings were studied for RFCs containing NZF in natural rubber matrix. They are shown in Fig. 7. From the figure it is seen that cure time sharply decreases for initial filler loadings (30 phr) and the change in cure time is only marginal for additional loadings of the filler. The above observations confirm that the filler addition does not affect the processability

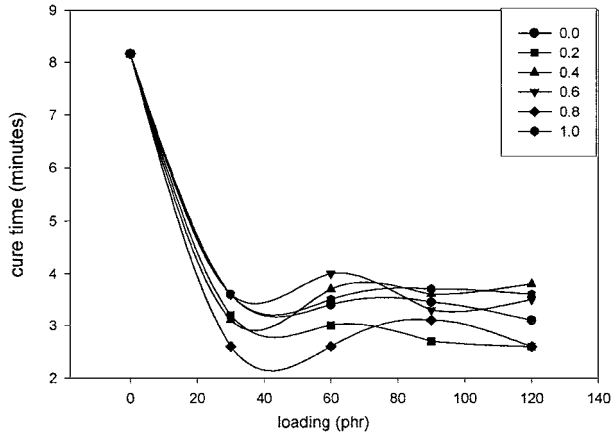


Figure 7 Variation of curetime with loading.

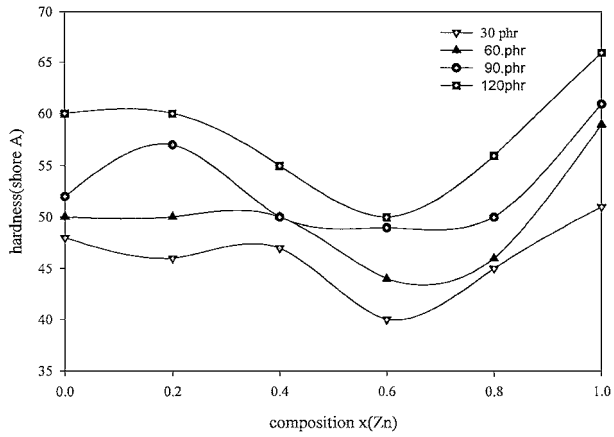
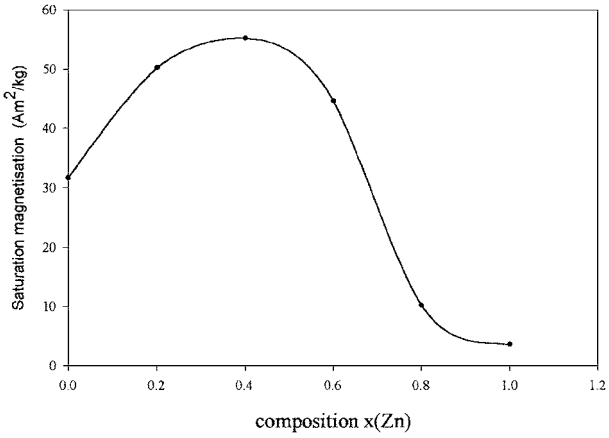
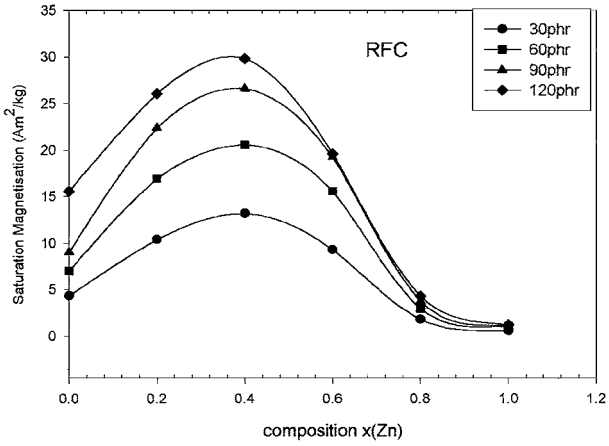


Figure 8 Variation of hardness with composition.



(a)



(b)

Figure 9 (a) Variation of saturation magnetization with composition for ceramic NZF; (b) Variation of saturation magnetization with composition for RFC.

of the composites considerably. It is known from literature that the physico-chemical changes occurring during vulcanization is due to two factors namely, the specific surface activity and surface area [15]. Surface area variation with x (cf. Fig. 4) does not resemble the variation pattern observed for cure time versus x for the corresponding composites. This means that there is an interplay of surface activity and surface area which acts in tandem to nullify the effect mutually [19]. However earlier experiments conducted on RFCs containing hexagonal ferrites with and without carbon black indicates that the cure properties are dependent on particle size or surface area. That was for a different compound containing barium ferrite [20].

The hardness of these samples were also studied for different loadings of the filler and the results are shown in Fig. 8. From the graph of hardness versus 'x', for all loadings of filler, the hardness shows a minimum either at $x = 0.6$ or at $x = 0.4$. But the maximum hardness for both the samples are much below the maximum permitted limit for the elastomer even for 120 phr loading of the filler.

3.3. Magnetic measurements

Magnetic measurements on these ceramic and rubber ferrite composites were carried out and the parameters namely saturation magnetisation (M_s) and coercivity (H_c) were determined. The variation of M_s with composition is shown in Fig. 9a and b for ceramic and RFCs respectively. From these figures it can be seen that the same behaviour is obtained for both ceramic and RFC. The variation in magnetisation with composition is in accordance with those reported already by various researchers [1, 21, 22]. The saturation magnetisation increases first with increase in zinc content and reaches a maximum at $x = 0.4$ and then it decreases with increase in zinc content. This can be explained based on the canting of spins [12, 22–24]. As the zinc content increases the B-B interaction become predominant. At values of $x > 0.4$ a canted spin structure appears. At $x = 1.0$, B-B interaction is maximum such that spins at the B sites are antiparallel resulting in a minimum net magnetization. The magnetization shows a steady increase with loading (Fig. 10). The variation of coercivity is also plotted (Fig. 11a and b) and the same pattern is observed for both ceramic and RFCs. The similarity between the ceramic and composite samples implies that there is not much filler matrix interaction. The slight variations in coercivity of ceramic and composites may be attributed to the small particle size changes that has occurred during compounding/milling.

Attempts were also made to calculate the saturation magnetization value of the RFCs from the M_s values of the ceramic samples. These were calculated from the M_s values of the corresponding ceramic samples, using a simple mixture equation of the general form involving the weight fraction of the filler.

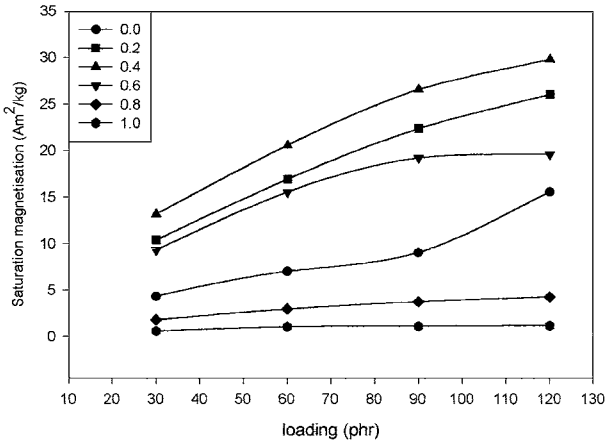


Figure 10 Variation of M_s with loading for RFC.

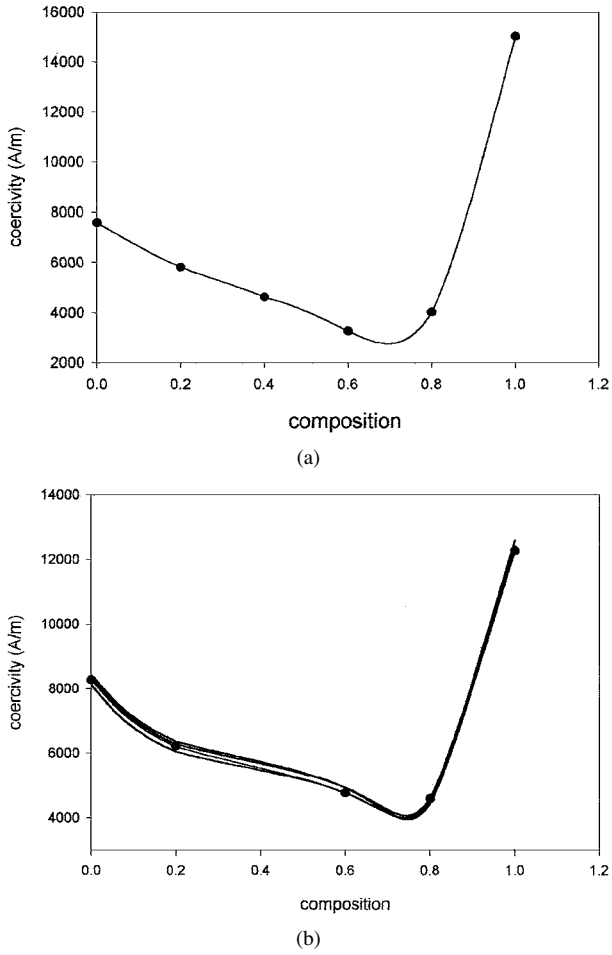


Figure 11 (a) Variation of coercivity with composition for ceramic NZF; (b) Variation of coercivity with composition for RFC.

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

where $\boldsymbol{W}_1$ is the weight fraction of filler, $\boldsymbol{M}_1$ is the magnetisation of the filler, $\boldsymbol{W}_2$ is the weight fraction of matrix, $\boldsymbol{M}_2$ is the magnetisation of the matrix.

Since the matrix namely NR is nonmagnetic this equation can be reduced to the following form

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

The M_s values were calculated using Equation 2 and the measured and calculated values of M_s are shown in (Fig. 12).

This mixture equation requires the magnetization corresponding to all x values of the filler in order to predetermine the saturation magnetization (M_s) of the corresponding composites. However, an inspection of the behaviour of M_s vs x reveals that it follows a Gaussian profile and can be represented by a general formula

$$M = A \exp\left(-0.5\left(\frac{x - x_0}{b}\right)^2\right) \tag{3}$$

where A and b are constants.

This was first formulated by fitting the experimental data of M_s for different x and for different loadings. This was then modified to the final form (Equation 4) by giving appropriate meanings to the coefficients obtained. The final equation is of the form

$$M_{\text{rfc}} = (1 + 0.2x) M_{\text{cermax}} W_1 \exp\left(-0.5\left(\frac{x - x_m}{0.26}\right)^2\right) \tag{4}$$

M_{cermax} is the magnetisation corresponding to maximum M_s of the ceramic filler; W_1 is the weight fraction of the filler; x is the composition; x_m is the composition corresponding to the maximum M_s of the filler.

The validity of the modified equation (Equation 4) was checked by comparing the calculated and measured values of M_s for different loading and compositions in RFC. The variation of calculated and measured values of M_s with composition is shown in (Fig. 13). From the graph it can be noticed that they are in excellent agreement. The formulated equation can also be applied to other systems with different matrix and fillers [25, 26]. This equation requires only the maximum M_s value of the filler and the corresponding composition (Fig. 9a and b). It may also be noted that this equation can be modified for predicting the saturation magnetization of ceramic samples in systems showing similar behaviour with composition as well.

By synthesizing RFC we have the unique advantage of modifying M_s and H_c according to the requirement. It may also be noted that the desired M_s can be imparted by appropriate choice of composition and loading. The H_c of the composite will be that of the ceramic component without much change. However, it is to be noted that the H_c is dependent on various parameters like particle size and heat treatment. These results indicate that the magnetic property can be suitably modified by the appropriate loading of the filler with a particular composition. The calculated values tally well with the measured values of the saturation magnetization, which indicate that it is possible to tailor materials with definite magnetization values by appropriate loading of the proper filler in a NR matrix.

This also confirms the finding on RFCs prepared with synthetic rubber matrix of butyl rubber [21, 26]. These investigations reveal that the required magnetic properties to these matrices can be imparted without compromising on the processability, flexibility and mechanical properties.

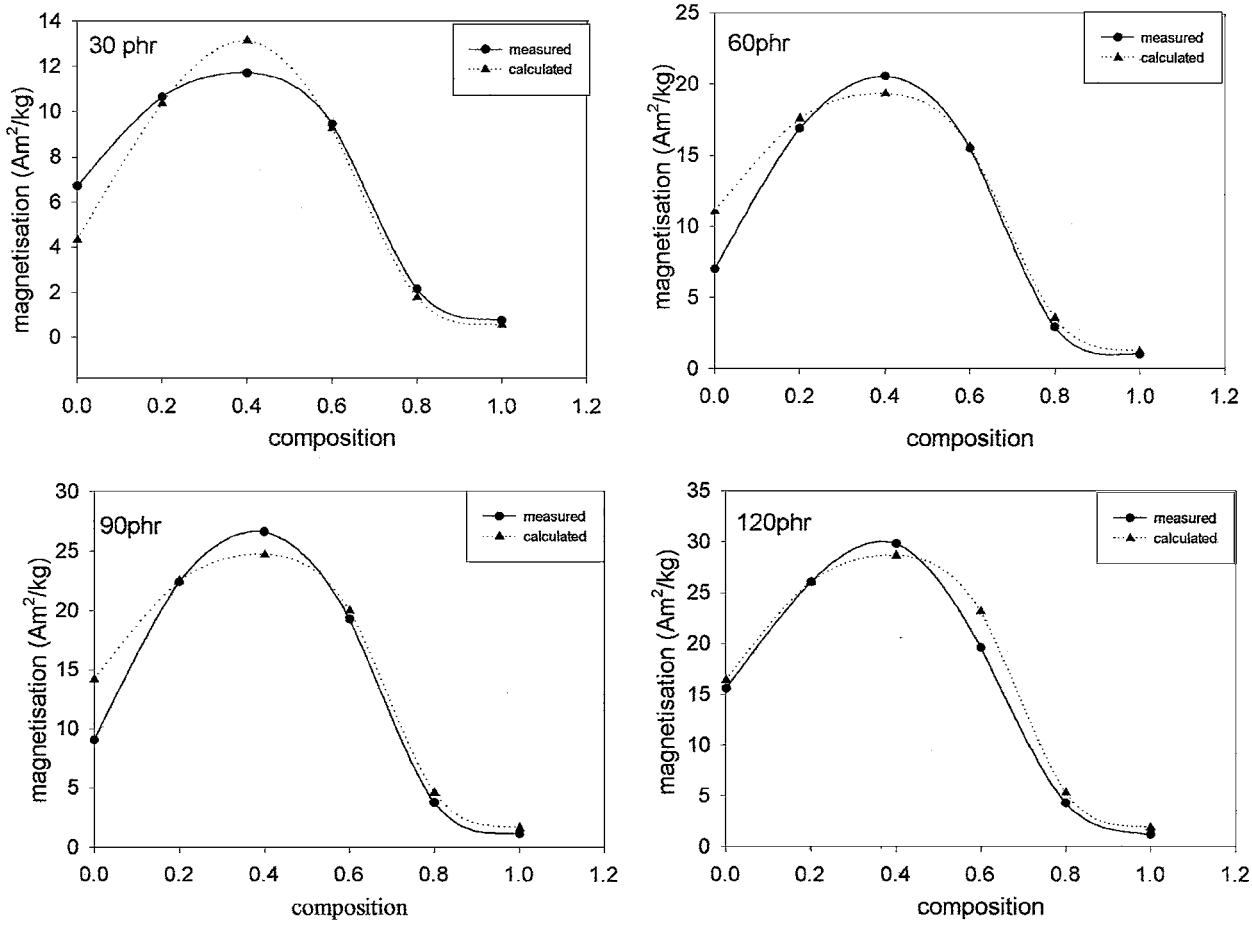


Figure 12 Measured and calculated values of M_s (Equation 2).

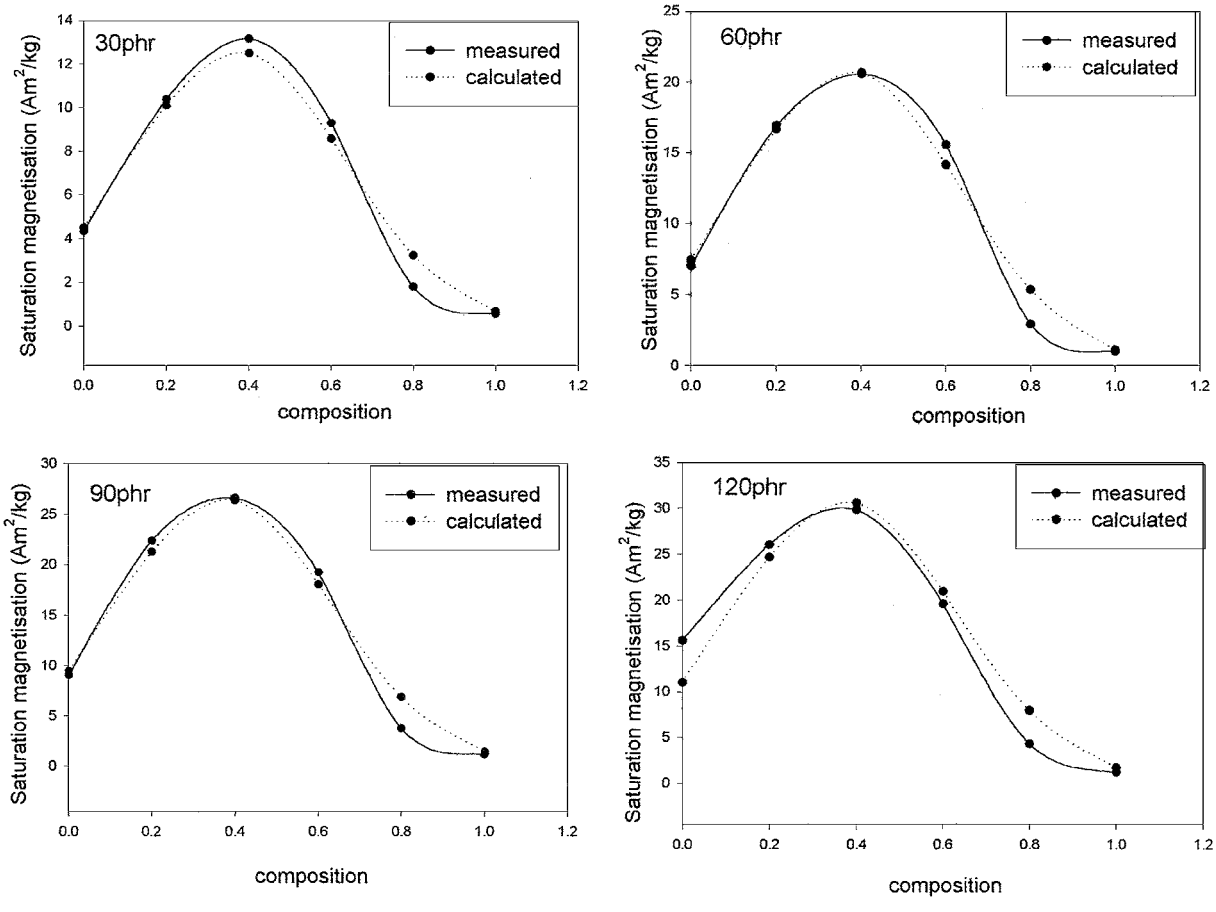


Figure 13 Measured and calculated values of M_s (Equation 3).

4. Conclusion

Rubber ferrite composites (RFCs) containing $Ni_{1-x}Zn_xFe_2O_4$ in natural rubber matrix have been prepared. The cure characteristics reveal that the processability and flexibility of the matrix is not much affected even upto a maximum loading of 120 phr of the filler in our set of experiments. It also indicate that the percolation threshold is not yet reached. Magnetic parameters of the ceramic as well as RFCs were studied and a general equation for predicting the saturation magnetization (M_s) of the ceramic as well as the composite samples is formulated. It is found that the measured and calculated values are in very good agreement. The coercivity variation with loading is found to be minimal. This indirectly shows that there is not much matrix filler interaction at least at the macroscopic level. The formulated equation will aid in predicting the properties and tailoring materials for various applications. This methods of preparation can be adopted for preparing RFCs for microwave applications.

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