Dielectric and mechanical properties of rubber ferrite composites

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Rubber ferrite composites (RFCs) containing powdered nickel zinc ferrite ($Ni_{1-x}Zn_xFe_2O_4$) in a natural rubber matrix have been prepared and their mechanical and dielectric properties have been evaluated. Variations in the relative permittivity of both the ferrite ceramics and RFCs have been studied over a range of frequencies, ceramic compositions, ceramic filler loadings, and temperatures, and the results have been correlated. Appropriate mixture equations have been formulated to calculate the dielectric permittivity of the composite from the dielectric permittivity of its constituents. Values calculated using these equations have been compared with experimental data on relative permittivity, and the two have been found to be in good agreement. In the present investigation it was also observed that for $x = 0{\cdot}4$ and for the maximum ferrite loading, the composite sample exhibits maximum magnetisation and optimum flexibility. PRC/1724

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INTRODUCTION

Magnetic materials find extensive applications in almost all realms of life. Composite magnetic materials have the unique advantage that their properties can be tailored to the requirements of specific applications. Rubber ferrite composites are ideal for applications where particular values of relative permittivity and magnetic permeability are among the criteria for materials selection. This is especially true for applications involving microwave absorption, which can be achieved by incorporating ferrites into rubber matrixes. These composites have the advantage of easy mouldability and flexibility.

Ferrites are a very well established family of magnetic materials. They are important because they are inexpensive, stable, and have a wide range of technological applications. Magnetic ceramics participate in virtually every relevant area of application, and in some areas there are no practical alternative materials.[1–5] Ferrites in the forms of ceramics and composites find many applications, in magnetic memories, flexible magnets, microwave absorbers, TV yokes, and many other useful devices.[1–9] Ceramic nickel zinc ferrites are used in devices such as high frequency transformers and inductors, especially because of their low eddy current losses and high resistivities.[1,5]

Rubber ferrite composites can be prepared by the incorporation of polycrystalline ferrite powders into elastomer matrixes. This not only reduces costs, but also produces flexible magnets. The use of rubber components often facilitates greater sophistication in engineering design and enables elastic compliance and flexibility to be introduced in a controlled and generally fail safe manner. The impregnation of the matrix with magnetic filler imparts magnetic properties and modifies the dielectric properties of the matrix.[10–14] The microwave absorbing properties of the filled elastomer provide appropriate values of relative permittivity and desirable magnetic properties, which are produced by synthesising RFCs with appropriate amounts of filler incorporated into the rubber matrix.

Natural rubber (NR) is particularly important to the rubber industry. The regularity of its chemical structure and its tendency to crystallise make it an irreplaceable material in many applications. Natural rubber is also an important commercial polymer. It is non-polar, easily processable, lightweight, and inexpensive.[15,16] The use of NR for functional technological applications offers the possibility of adding value to an abundant natural resource.

Modification of the dielectric properties of lossy dielectric materials by addition of magnetic fillers is of interest to various researchers who are seeking to understand the fundamental factors governing the properties of these materials. The frequency dispersion characteristics of polymer ferrite composites are particularly important because of their applications as electromagnetic wave absorbers and electromagnetic interference (EMI) shielding materials.[17,18] Rubber ferrite composites find applications in microwave absorbers, in response to the ever increasing problem of electromagnetic interference due to the immense growth in the use of electronic and electrical devices in industrial and other commercial applications. Gadgets based on RFCs can play a very crucial role. Studies of the microwave absorbing characteristics of these RFCs can develop more quantitative relationships between the magnetic and dielectric characteristics of these composites and their microwave absorbing properties. The literature already provides relationships for calculating surface impedance for the design of microwave absorbers, especially for single layer

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absorbers.[19,20] For a microwave absorbing layer the normalised input impedance at the absorber surface Z_{in} is given by

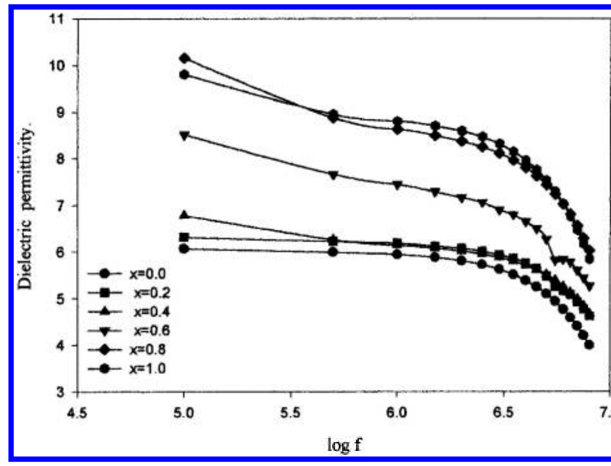
$$Z_{in} = \left(\frac{\mu^*}{\varepsilon^*}\right)^{1/2} \tanh\left[j\frac{2\pi d}{\lambda}(\mu^*\varepsilon^*)^{1/2}\right] \quad . \quad . \quad . \quad (1)$$

where $j = -1^{1/2}$, λ is the wavelength of the microwave in free space, and d is the thickness of the absorbing material; μ^* and ε^* are, respectively, the complex magnetic permeability and complex permittivity of the material and are given by $\mu^* = \mu_r^1 - j\mu_r^{11}$ and $\varepsilon^* = \varepsilon_r^1 - j\varepsilon_r^{11}$. The complex magnetic permeability and permittivity of the constituent materials of the microwave absorbers play a key role in determining the reflection or attenuation properties. They can be determined from the reflected and transmitted scattering parameters obtained from a network analyser. The reflection loss, which is a function of Z_{in}, is then expressed as

$$\text{Reflection loss (dB)} = 20 \log\left(\frac{Z_{in} - 1}{Z_{in} + 1}\right) \quad (2)$$

The absorbing properties of the sample can be calculated at a given λ and d. It is to be noted that the reflection loss depends sensitively on the absorber thickness, wavelength, complex permittivity, and complex magnetic permeability. The absorption performance can be improved by increasing the filler's magnetic permeability, the filler concentration, and the thickness of the absorbing material. The light weight, low cost, and flexibility of RFCs are added advantages. In addition, since any practical application involves some kind of mechanical loading, the evaluation of mechanical properties of these composites also assumes significance. Thus the present study is aimed at understanding the dielectric and mechanical properties of flexible magnets (RFCs) so as to make them useful from the application point of view.

Dielectric properties in polycrystalline materials are explained by factors such as preparative conditions, cation distribution, grain size, the ratio of Fe^{3+}/Fe^{2+} ions, ac conductivity, and sintering temperature.[21] The dependence of these factors on the dielectric properties of the ceramic filler also has a profound influence on the overall physical properties of the composites containing the filler. Hence the evaluation of dielectric properties of the filler as well as the composites assumes significance in understanding the physical properties of these composites. Nickel zinc ferrites ($Ni_{1-x}Zn_xFe_2O_4$ where $0 \leq x \leq 1$ in steps of 0·2) prepared by ceramic techniques were incorporated into a natural rubber matrix according to a specific recipe to yield RFCs. The dielectric permittivity of ceramic $Ni_{1-x}Zn_xFe_2O_4$ and of rubber ferrite composites was studied as a function of frequency, ferrite composition, filler loading, and temperature. Appropriate mixture equations were formulated to predict the dielectric permittivity of the composites. The effects of temperature on the dielectric properties of both ceramic and RFC samples were also studied. The studies were carried out between room temperature and 120°C for all samples.



1 Variation of dielectric permittivity with frequency for ceramic NZF, where x is defined by $Ni_{1-x}Zn_xFe_2O_4$

The mechanical properties are most important for polymers because all applications involve some degree of mechanical loading. Different types of polymers are often compared on the basis of their tensile strength, elongation, and modulus.[22,23] Hence the evaluation of these properties assumes significance in making devices based on RFCs. The mechanical properties, namely tensile strength, elongation at break, and 100% modulus, of the prepared samples were also evaluated in this study.

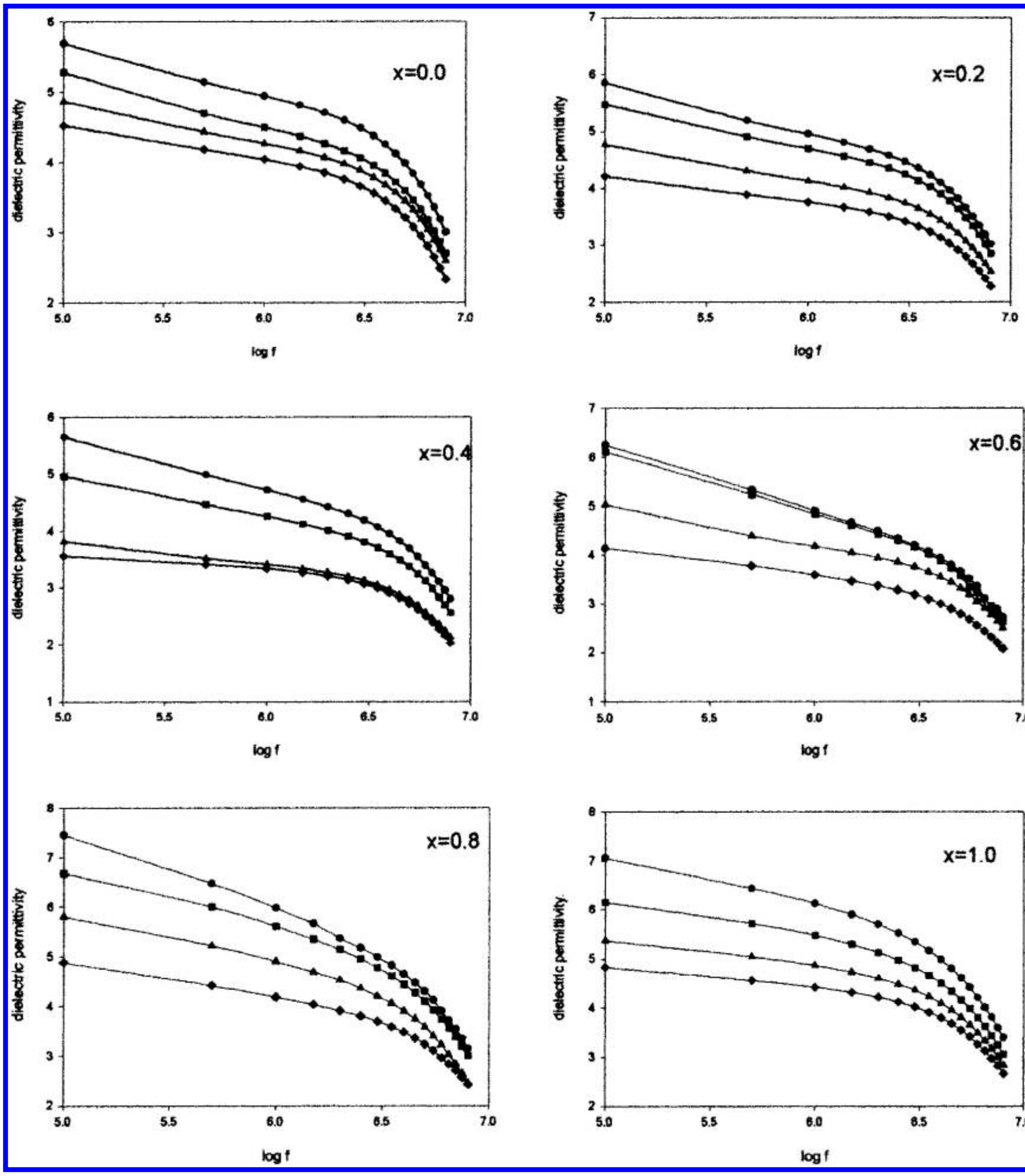
EXPERIMENTAL

Preparation of ceramic nickel zinc ferrite

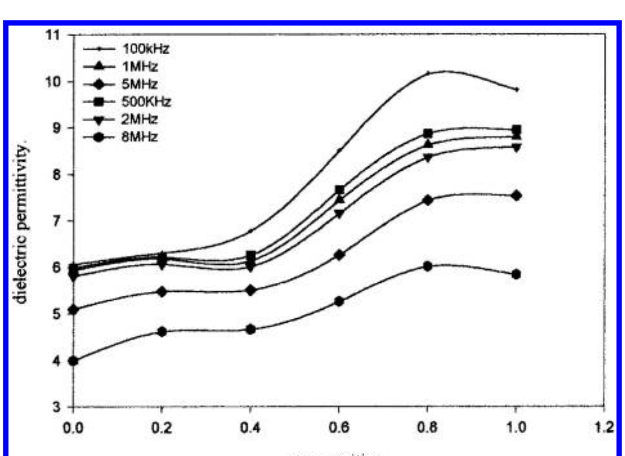
Nickel zinc ferrites (NZCs) having the general formula $Ni_{1-x}Zn_xFe_2O_4$, for various values of x ranging from 0 to 1 in steps of 0·2, were prepared using conventional ceramics techniques.[5] The process involved thoroughly mixing the precursors, namely ferrous oxalate dihydrate, nickel oxide, and zinc oxide, in appropriate ratios in an agate mortar to produce homogeneous mixtures of fine particles. Repeated sintering at 500°C and mixing of this powder were continued until an NZF with a single phase spinel structure was obtained. This pre-sintered powder was then finally sintered at 1000 ± 15°C for several hours.

Incorporation of ferrites into natural rubber

Pre-characterised NZF was then incorporated into a natural rubber matrix in accordance with a specific recipe. The blending was performed by mixing appropriate amounts of ZnO, stearic acid, tetramethyl thiuram disulphide (TMTD), mercaptobenzothiazyl disulphide (MBTS), and sulphur with the rubber, using a Brabender Plasticorder torque rheometer, model PL 3S. Rubber ferrite composites were prepared with ferrite loadings of 30 to 120 phr (parts per hundred parts of rubber by weight) in steps of 30 phr. Using a hydraulic press, the composites were moulded into thin sheets of about 2 mm thickness at 150°C for the recommended cure time in accordance with ASTM D 3188.



2 Variation of dielectric permittivity with frequency for RFC with ferrite content (◆) 30, (▲) 60, (■) 90, and (●) 120 phr; *x* indicates Zn content of ceramic



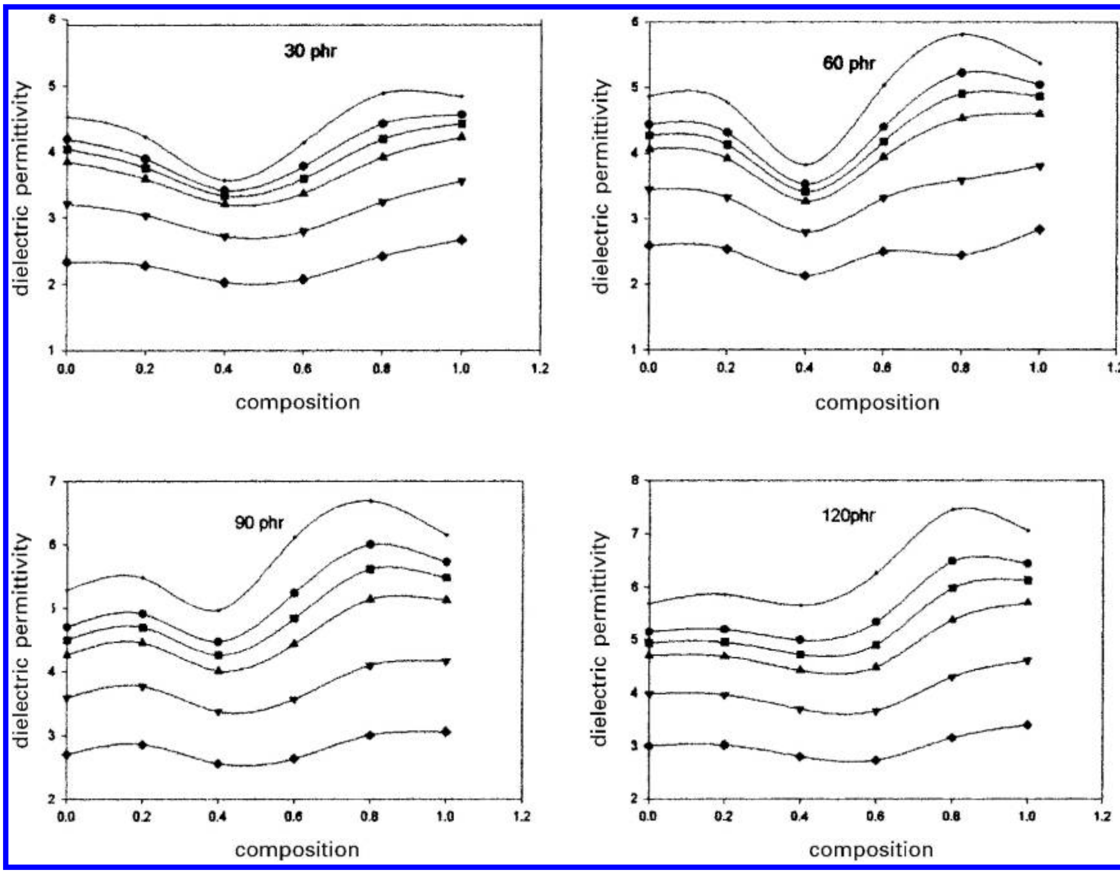
3 Variation of dielectric permittivity of RFC with zinc content *x*

Dielectric properties of $Ni_{1-x}Zn_xFe_2O_4$

The relative permittivity and dielectric loss of NZF samples were determined using a Hewlett Packard impedance analyser model HP 4285 A and a dielectric cell. The samples were made in the form of discs having a diameter of 12 mm and a thickness of $\sim$2 mm. The capacitances at room temperature were measured in the frequency range 0·1–8 MHz. The relative permittivity was calculated using the formula

$$C = \varepsilon_o \varepsilon_r A/d \quad (3)$$

where A is area of sample piece used, d is the thickness of the sample, ε_r is the relative permittivity of the medium, ε_o is the relative permittivity of air, and C is the observed capacitance of the sample. The complete measurement was automated with the help of the LabVIEW package. Data acquisition as well as the calculation of ε_r and tan δ for various frequencies



4 Variation of dielectric permittivity of RFC with zinc content *x* for various ferrite contents

and temperatures was carried out with this package, which is based on G-Programming. Appropriate modifications were incorporated into the software to enable automatic data acquisition and visual observation of the graphs on the computer screen. Relative permittivities at temperatures of 40, 60, 80, 100, and 120°C were also determined at different frequencies. Relative permittivities were also evaluated for RFCs containing these ferrites at various loadings.

Mechanical properties

The mechanical properties of representative samples of the RFCs were determined using an Instron universal testing machine model 4500. Dumbbell shaped samples were cut from the prepared RFCs containing $Ni_{1-x}Zn_xFe_2O_4$ (where $x = 0{\cdot}2$, 0·6, and 1·0) at loadings of 30, 60, 90, and 120 phr. Tensile strength, 100% modulus, and elongation at break were determined for these samples.

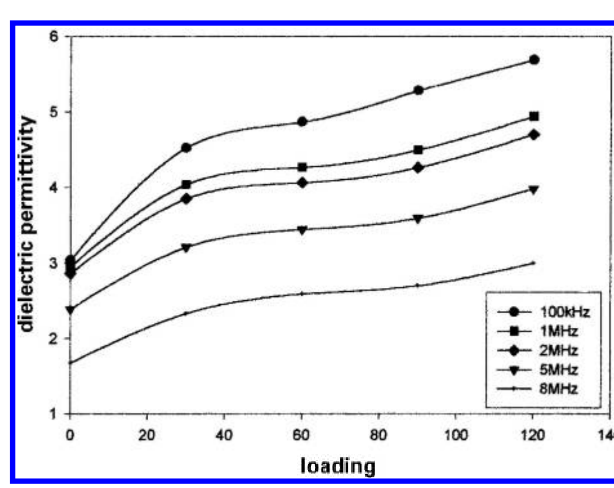
RESULTS AND DISCUSSION

Dielectric measurements

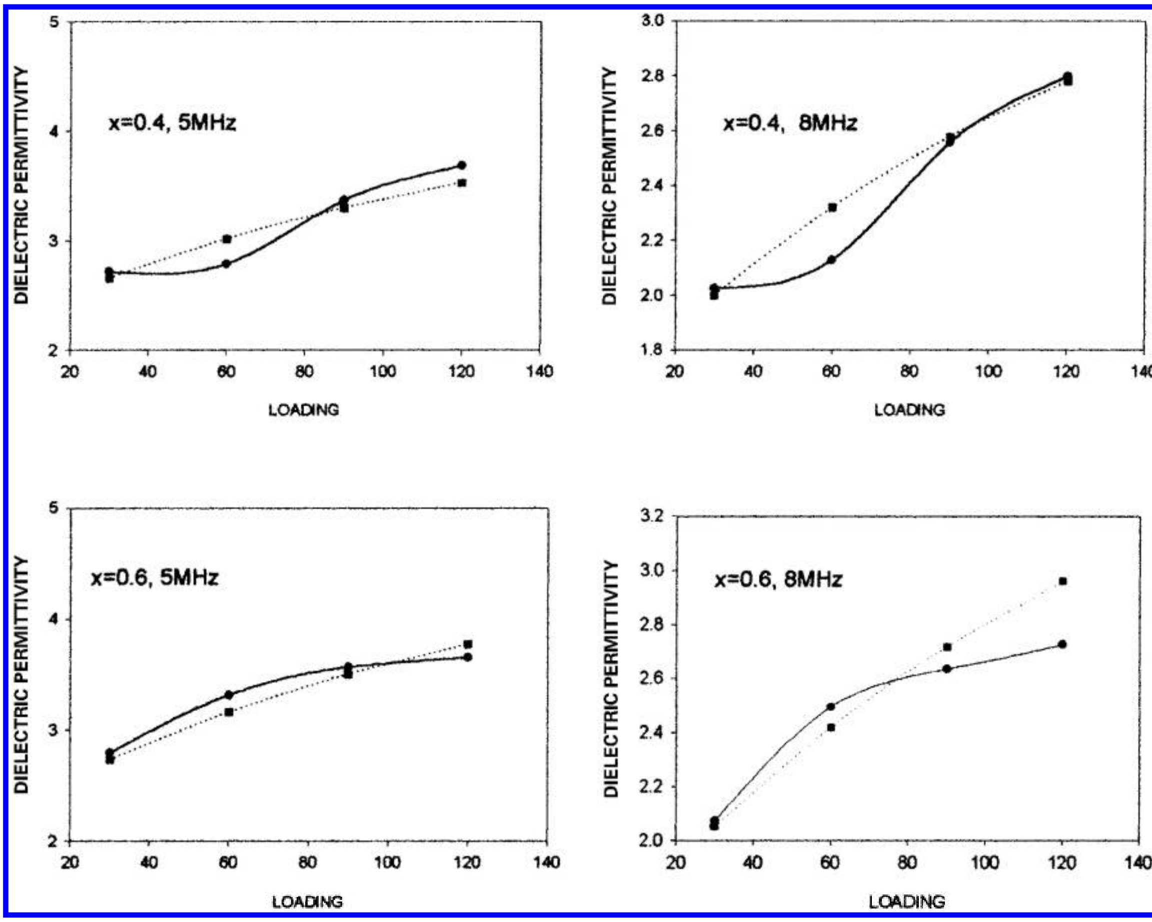
Frequency dependence

The frequency dependence of relative permittivity for all ceramic samples (with $x = 0$ to 1 in steps of 0·2) is shown in Fig. 1. The relative permittivity decreases with increasing frequency. The decrease occurs relatively slowly at the lower frequencies (i.e. up to 2 MHz) and more rapidly at higher frequencies. The general pattern of variation remains the same for all compositions.

The time required for electronic or ionic polarisation to occur is very small (10^{-12} to 10^{-15} s) compared with the period of the voltage oscillations, even at the highest signal frequency used in this work.[24] Thus it can be concluded that the contributions of ionic and electronic polarisation to the observed changes in dielectric response are negligible. But dipolar polarisation does have an effect; as the frequency of the applied voltage increases, the value of the relative permittivity at first remains unaltered and thereafter shows a decrease. This is because at higher frequencies the relaxation times of the dipoles are longer than the period of oscillation of the electric field, resulting in a decreased relative permittivity. The same behaviour is observed in composite samples, as shown in Fig. 2.



5 Representative graph of variation of dielectric permittivity with phr ferrite for $NiFe_2O_4$



6 Measured (●) and calculated according to equation (5) (■) values of dielectric permittivity with phr ferrite for various values of zinc content *x*

Composition dependence

The variation of relative permittivity with ferrite composition is shown in Fig. 3. It can be seen that the relative permittivity increases with increasing zinc content. The pattern of variation remains the same for all frequencies. It is well known that the mechanism of dielectric polarisation in ferrites is similar to the conduction mechanism,[23,24] which involves electron hopping between ferrous and ferric ions on the octahedral sites in n-type semiconductor ferrites, and hole hopping in p-type ferrites (Verwey type of conduction).[23–26] In $NiFe_2O_4$ (i.e. $Ni_{1-x}Zn_xFe_2O_4$ with $x =$ zero), hole hopping ($Ni^{2+} \leftrightarrow Ni^{3+}$) at B sites is the dominant mechanism. As the zinc content increases, the Ni content at the B sites decreases and hence hole hopping decreases. However, at the same time the Fe content at the B sites increases, which in turn will increase the conductivity due to electron hopping ($Fe^{3+} \leftrightarrow Fe^{2+}$). It is also known that in NZF systems the ($Fe^{3+} \leftrightarrow Fe^{2+}$) conversion is relatively less effective up to $x = 0{\cdot}4$ and hence a slight decrease in relative permittivity is observed at $x = 0{\cdot}4$. Beyond $x = 0{\cdot}4$, electron hopping is more active, and as the zinc content increases electron hopping increases as a result of the increased numbers of Fe^{3+} and Fe^{2+} ions on B sites. At higher sintering temperatures, the evaporation of zinc contributes to an increase in the numbers of Fe^{2+} ions on the B sites, which localises the hopping electrons and decreases the Fe^{3+}/Fe^{2+} ratio, which in turn results in a decrease in relative permittivity.[25–30] This is confirmed by ac conductivity measurements.[31]

The pattern of variation in the relative permittivity of RFCs with ferrite composition is shown in Fig. 4. The pattern of variation is almost the same as in the ceramic samples and remains the same for all filler loadings. From the graph it can be noted that the relative permittivity increases with increasing zinc content except for a small decrease at $x = 0{\cdot}4$. At lower loadings of filler, the behaviour resembles that of the matrix and at higher loadings it is predominantly dictated by the ceramic filler's dielectric properties. These results suggest that the dielectric properties of the blend can be suitably modified by an appropriate choice of composition and filler loading.

Filler loading

Figure 5 shows the dependence of the relative permittivity of RFCs on magnetic filler loading. The relative permittivity increases with increasing weight fraction of ferrite. The highest value of relative permittivity is observed at a loading of 120 phr. The pattern of variation is the same for all compositions at different frequencies.

Attempts were also made to calculate the relative permittivity of the composite samples from those of the ceramic filler and unfilled NR, using several mixture equations.[24,32,33] Composite dielectrics can be considered as mixtures of several components. For example, for a mixture of m components the relative permittivity ε^* is given by

$$\log \varepsilon^* = \sum_{i=1}^{m} y_i \log \varepsilon_i \quad (4)$$

where ε^* is the relative permittivity of the mixture and y is the weight fraction of the component.[24] For a two component system the relationship can be written as

$$\log \varepsilon^* = y_1 \log \varepsilon_1 + y_2 \log \varepsilon_2 \quad (5)$$

where ε^* is the relative permittivity of the composite; ε_1, y_1 and ε_2, y_2 are the relative permittivity and weight fractions of the matrix and the filler component, respectively. Figure 6 compares the measured values of relative permittivity with those calculated using equation (5).

Another mixture equation[24] of the form

$$\varepsilon^* = \frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 y_2 + \varepsilon_2 y_1} \quad (6)$$

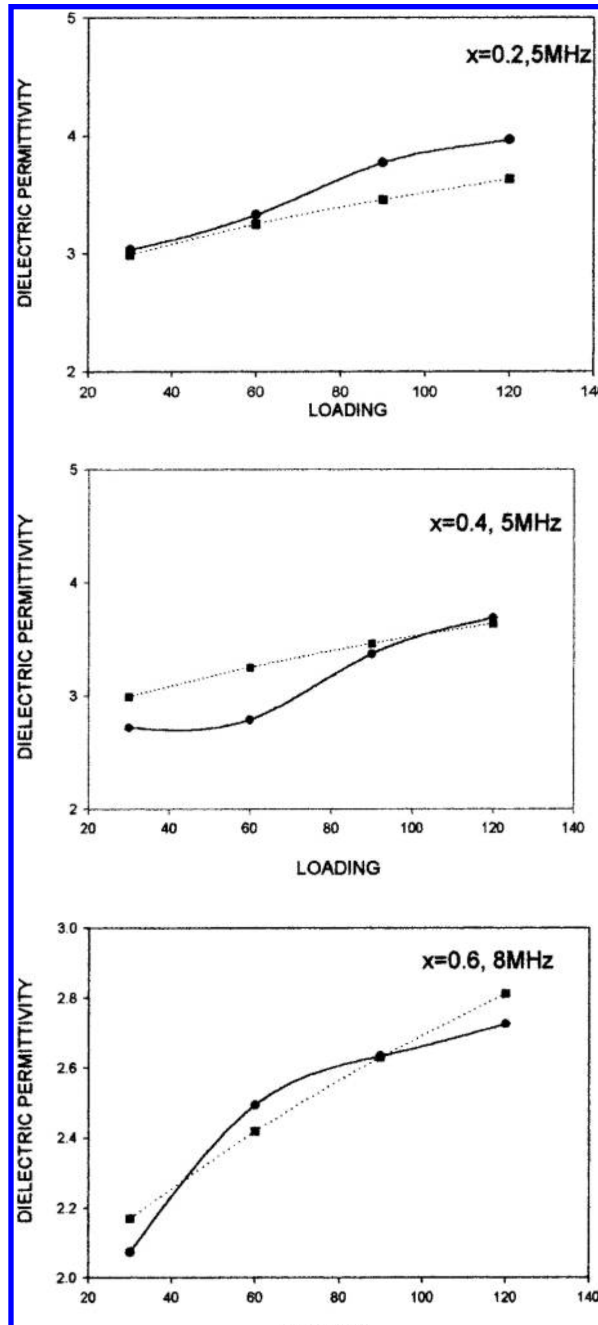
is also useful for calculating the dependence of relative permittivity of the RFC on filler loading. Representative graphs showing measured values of relative permittivity and calculated values obtained using equation (6) are given in Fig. 7.

Comparisons of the measured and calculated values of relative permittivity using the above mentioned equations for various loadings and frequencies were made for all compositions. They indicate that equation (5) is suited for all frequencies, but at higher loadings equation (6) gives better fits to experimental data. It can also be seen that equation (6) is not suitable for predicting the relative permittivity at lower frequencies.

Temperature dependence

The temperature dependence of the relative permittivity of the ceramic samples and their rubber composites was also studied between 303 and 423 K. The dependence of relative permittivity upon temperature for ceramic NZFs is shown in Fig. 8; it increases with increasing temperature. In most cases, the atoms or molecules in the samples cannot orient themselves rapidly enough in the low temperature region. When the temperature rises, orientation of dipoles in the applied electric field is facilitated, and this increases the dielectric polarisation. However, at very high temperatures the chaotic thermal oscillations of the molecules are intensified and the degree of orderliness of their orientation is diminished; consequently, the permittivity passes through a maximum value. In the present study the maximum temperature of measurement was only 423 K and hence no decrease in relative permittivity was observed. The variation of relative permittivity with temperature at low frequencies (100 kHz) is much more pronounced than at higher frequencies. For all compositions, the dependence of permittivity on temperature appears to obey the relationship

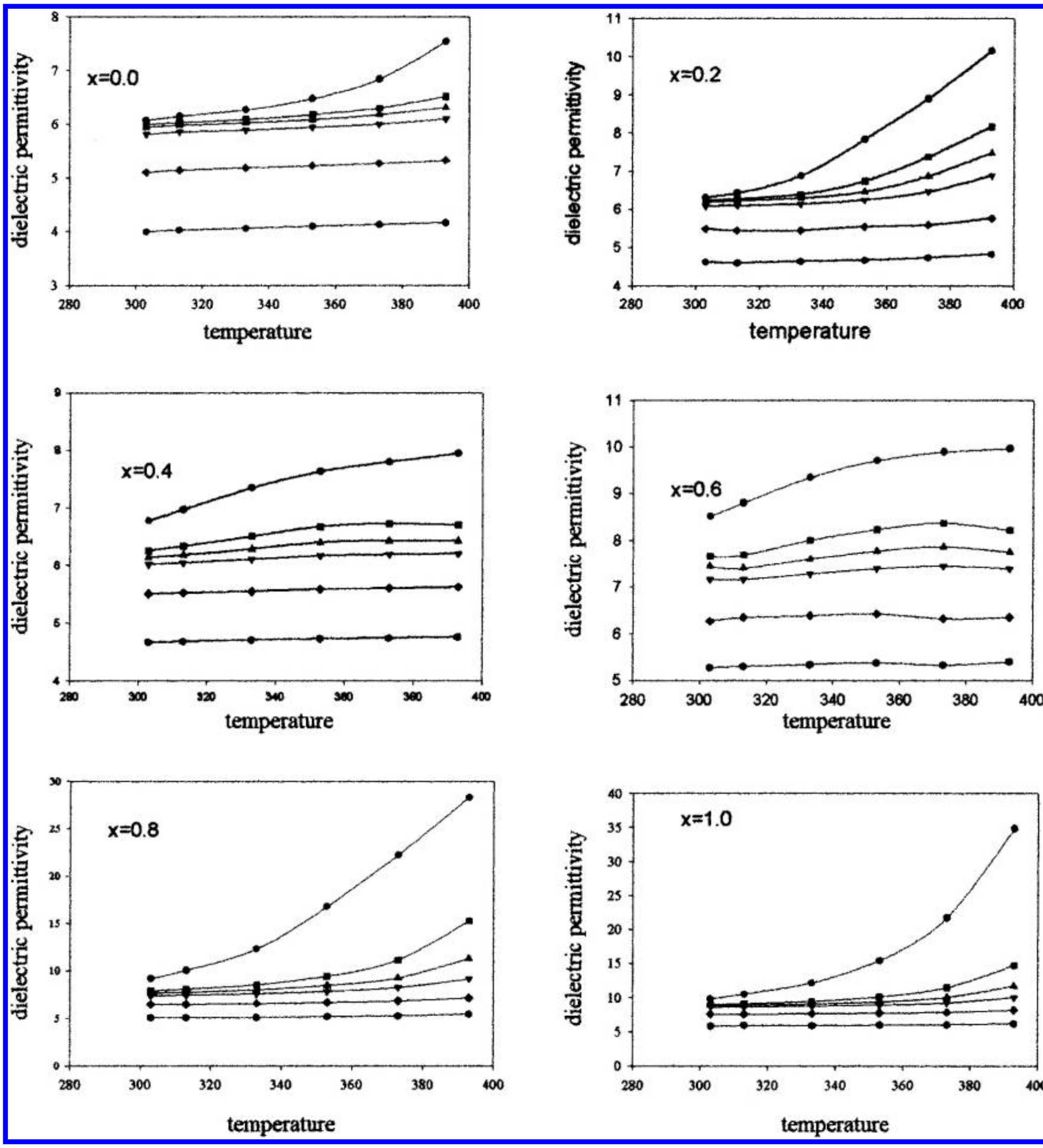
$$y = y_0 + A \exp(BT)$$



7 Measured (●) and calculated according to equation (6) (■) values of dielectric permittivity with phr ferrite for various values of zinc content *x*

where A and B are constants. At higher frequencies the effect of temperature on relative permittivity is minimal.

The relative permittivity of rubber ferrite composites increases with increasing temperature. Representative graphs showing this variation are given in Fig. 9. The relative permittivity of unfilled NR was also evaluated over a range of temperatures. As shown in Fig. 10, the relative permittivity decreases with increasing temperature. This is because the polymer density is reduced as the temperature increases, which causes a decrease in relative permittivity. Thermal expansion reduces the number of molecules in a given length of the dielectric, thereby reducing the permittivity.



(●) 100 kHz; (■) 500 kHz; (▲) 1 MHz; (▼) 2 MHz; (◆) 5 MHz; (●) 8 MHz

8 Variation of dielectric permittivity with temperature for RFCs with varying values of zinc content *x*

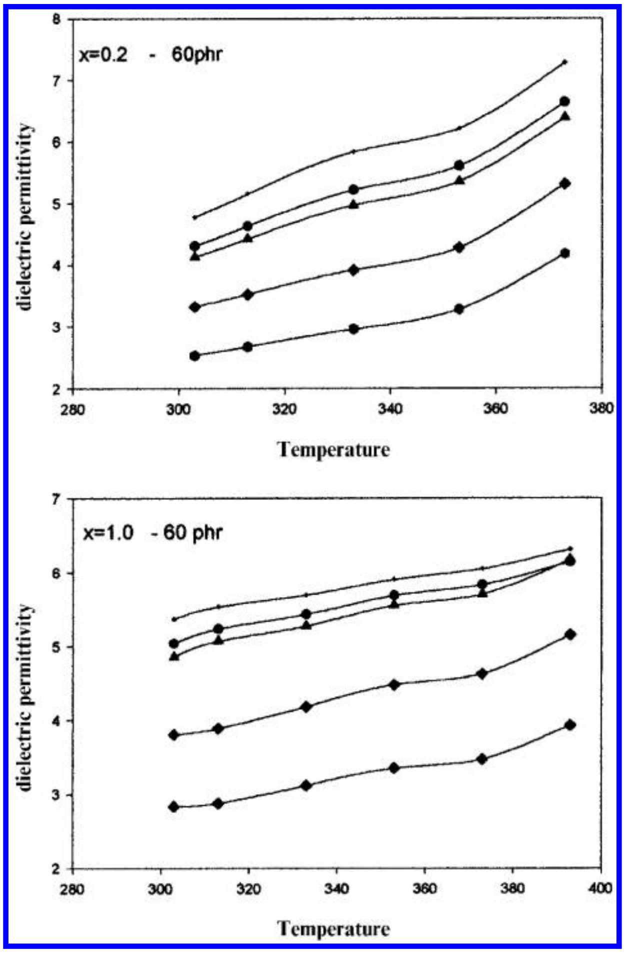
Mechanical properties

The mechanical properties of the RFCs, namely the tensile strength, elongation at break, and 100% modulus, were determined for all filler loadings. The variation of tensile strength with loading is shown in Fig. 11. The tensile strength first decreases for loadings up to 30 phr; thereafter it increases with loading. It is known that stress induced crystallisation increases the tensile strength and hence the blank NR has a high tensile strength. The addition of filler inhibits stress induced crystallisation, which in turn results in a decreased tensile strength for the initial filler loading of 30 phr.[23] With further loading of filler the tensile strength shows an increasing trend. This means that the NZF filler is acting as a semireinforcing filler. In some cases a slight decrease in tensile strength is observed at higher loadings, which may be due to dilution effects. Elongation at break shows a similar decrease for the initial loading and remains approximately constant for higher loadings (*see* Fig. 12). This can also be explained by the decrease in stress induced crystallisation. The 100% modulus shows an increasing trend with increasing filler loading (Fig. 13). This is also evident from the cure characteristics.[34] It may also be noted that the addition of filler reduces the molecular weight between crosslinks slightly and this also causes a small decrease in both tensile strength and modulus.

It is worth noting that the magnetisation measurements also showed a maximum[34] at around $x = 0{\cdot}4$ or 0·6 and the mechanical properties were also optimum for these compositions. This is useful for selecting RFCs with optimum properties.

CONCLUSIONS

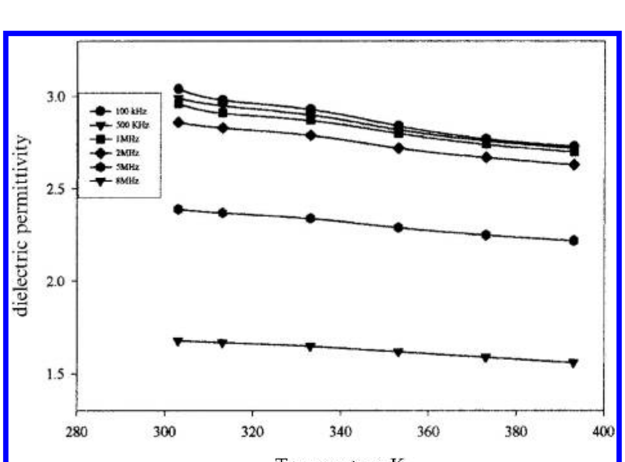
Rubber ferrite composites consisting of NZF in an NR matrix have been prepared at various loadings,



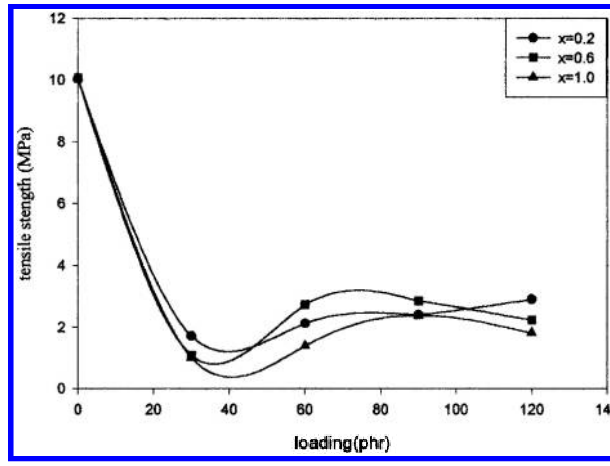
('') 100 kHz; (●) 500 kHz; (▲) 1 MHz; (▼) 2 MHz; (◆) 5 MHz; (●) 8 MHz

9 Representative graphs of variation of dielectric permittivity with temperature for RFC with $x = 0{\cdot}2$ and 1

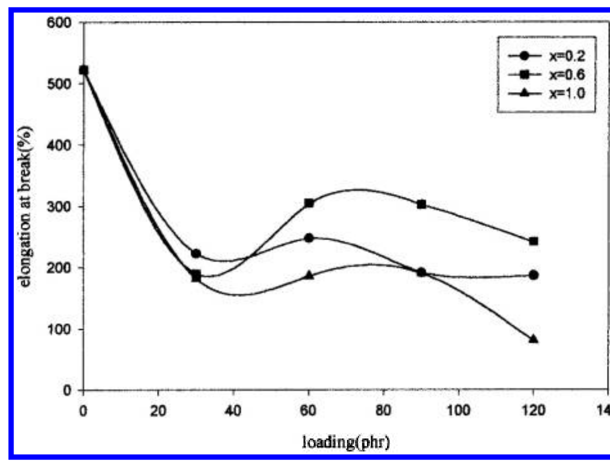
and their dielectric properties have been evaluated. The dependence of relative permittivity upon temperature, ferrite loading, frequency, and ferrite composition have been studied and correlated. Mixture equations for predicting the relative permittivity at various loadings were also formulated. The validity of these mixture equations was checked, and their predictions were found to be in good agreement



10 Variation of dielectric permittivity with temperature for neat NR

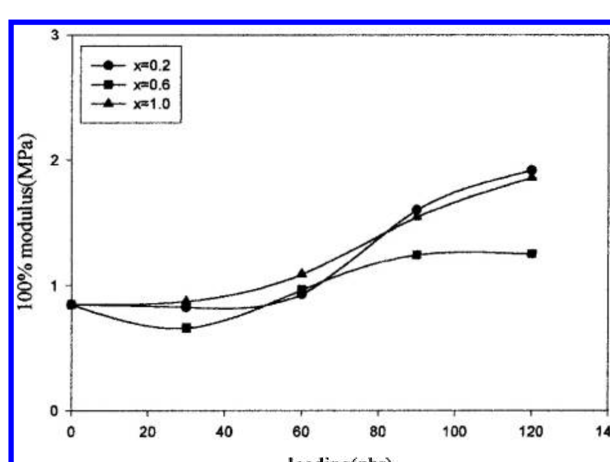


11 Variation of tensile strength with phr ferrite for various values of zinc content *x*



12 Variation of elongation at break with phr ferrite for various values of zinc content *x*

with the observed values. These results suggest that with appropriate loading and a judicious choice of the filler it is possible to optimise the dielectric properties of rubber ferrite composites. The mechanical properties of representative samples were studied and it was found that the filler modifies the mechanical properties. It is also noted that NZF compositions corresponding to $x = 0{\cdot}4$ and $0{\cdot}6$ give optimum



13 Variation of 100% modulus with phr ferrite for various values of zinc content *x*

strength and magnetisation with minimum hardness. The modification of these properties will aid in the design of composite materials for possible applications.

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