Cure Characteristics and Mechanical Properties of Rubber Ferrite Composites Based on Nano-Nickel Ferrites

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ABSTRACT: Ultra fine nickel ferrite have been synthesized by the sol-gel method. By heat treating different portions of the prepared powder separately at different temperatures, nano-sized particles of nickel ferrite with varying particle sizes were obtained. These powders were characterised by the X-ray diffraction and then incorporated in the nitrile rubber matrix according to a specific recipe for various loadings. The cure characteristics and the mechanical properties of these rubber ferrite composites (RFCs) were evaluated. The effect of loading and the grain size of the filler on the cure characteristics and tensile properties were also evaluated. It is found that the grain size and porosity of the filler plays a vital role in determining the mechanical properties of the RFCs. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 3019–3025, 2011

Key words: composites; crystal structures; gelation; magnetic polymers; rubber

INTRODUCTION

Ferrites can be incorporated in various elastomer matrixes to produce flexible magnets or rubber ferrite composites (RFCs).[1–8] RFCs are produced by the incorporation of these ferrite powders can be carried out in various matrixes such as natural and synthetic rubbers. RFCs have the unique advantage of mouldability into complex shapes, which makes them ideal for the application as flexible magnets. The addition of magnetic fillers in an elastomer matrix modifies the physical properties of the matrix considerably. They modify the dielectric properties and impart magnetic properties to the matrix.[9,10] In applications involving ferrites at high frequencies, it is essential that the material possess an appropriate dielectric permittivity and suitable magnetic permeability.[11–15] When preparing RFCs, the choice of compounding ingredients, compounding conditions and their processability are important. Also factors like percolation limit and nature of the matrix like saturated /unsaturated/polar/non polar rubber, all influence the final properties of the composites.

It has also been reported that the incorporation of ferrites in polymer matrix can lead to the development of magnetic nanocomposites with excellent performance characteristics.[16–19] Among the different ferrites, nanosized nickel ferrites possess attractive properties for application as soft magnets and low magnetic loss materials at high frequencies.[20] The preparation of RFCs and evaluation of various properties such as magnetic, dielectric, and mechanical assumes significance not only in tailor making compounds but also in understanding the fundamental aspects that govern these properties.

Knowledge of cure characteristics throws light on the processability and mechanical properties of composites.[4,20,21] Information regarding particle size, surface area, and porosity are also valuable tools in explaining the properties. By selecting appropriate matrix, magnetic fillers can be incorporated to form a composite of required mechanical, magnetic, and dielectric properties. Nitrile-rubber is selected as the elastomer for mixing the magnetic filler. Nitrile rubber, otherwise known by the generic name NBR, is a special purpose synthetic rubber. NBR shows no self-reinforcing effect, as there is no stress-induced crystallisation.[22] As it does not crystallise, reinforcing fillers are necessary to obtain optimum tensile strength, tear strength and abrasion resistance. Here the choice of compounding ingredients, compounding conditions and their processability are significant as far as the properties of RFCs are considered.

The mechanical properties like tensile strength, elongation at break and the modulus etc are important properties of polymeric materials because all applications involve some degree of mechanical loading.[23–27] A tensile test is the measurement of the

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ability of a material to withstand the forces that tend to pull it apart and to determine to what extent the material stretches before breaking. Different types of polymeric materials are often compared on the basis of their tensile strength, elongation at break and modulus. Hence the evaluation of these properties also assumes significance in making devices based on RFCs. The mechanical properties namely tensile strength, elongation at break, modulus at 100% elongation and 200% elongation of the prepared RFCs are evaluated and they are studied as a function of loadings and particle size of the fillers.

The parameters namely particle size, porosity and surface area of the ceramic filler plays a very important role in determining the mechanical properties of the composite. Since, after incorporation of fillers, RFCs are to be cured, their effects on the cure parameters are also to be determined.

The mechanical properties of the vulcanisate is also dependent on the amount of filler in the matrix and their porosity/particle size/surface area. Hence the evaluation of their cure characteristics and estimation of their mechanical properties is a prerequisite for further applications.

Here in our present investigation, ferrite fillers are incorporated in various loadings into nitrile rubber and their cure parameters are evaluated. Further after curing and moulding, their mechanical properties are investigated. Factors like tensile strength, modulus and elongations are determined as per ASTM. The results are correlated with loadings of the filler, particle size and porosity. The details of these findings are presented here.

EXPERIMENTAL

Preparation and characterisation of nickel ferrite

Analytical grades of $Fe(NO_3)_3.9H_2O$ and $Ni(NO_3)_2.6H_2O$ taken in a 2 : 1 ratio were dissolved in ethylene glycol at about 40°C. After heating the sol of the metal compounds to around 60°C a wet gel is obtained. The obtained gel when dried at about 100°C self ignites to give a highly voluminous and fluffy product. The powder obtained by the sol-gel method was kept as such and nanosized particles of $NiFe_2O_4$ with varying particle sizes were obtained by heat treating different portions of the prepared powder separately for 12 h at 300, 600, and 900°C.

Structural characterisation

The structural characterisation of all the four samples was carried out by the X-ray diffraction (XRD) technique on a Rigaku D_{max}/2C diffractometer with

nickel filter using Cu-Kα radiation (wavelength λ = 1.5418 Å).

The average particle size was determined from the measured width of their diffraction curves by using Debye Scherrer formula

$$D = \frac{0.9\lambda}{\beta \cos \theta} \tag{1}$$

Here λ is the wavelength of Cu K_α radiation (λ = 1.5406 Å), β is the angular width in radians which is equal to the full width at half maximum.

The X-ray density of the prepared ceramic samples were calculated using the relation

$$\rho_x = \frac{nM}{a^3N} \tag{2}$$

where n is the no. of molecules/unit cell, M is the molecular weight, a is the lattice parameter and N is the Avogadro number.

The apparent density is calculated by considering the cylindrical shape of the pellets and by using the relation

$$\rho_a = \frac{m}{V} = \frac{m}{\pi r^2 h} \tag{3}$$

where m is the mass r the radius and h the thickness of the pellet.

Porosity P of the ferrite samples were then determined by employing the relation

$$P = \frac{\rho_x - \rho_a}{\rho_x} \tag{4}$$

The surface area in m^2/g was obtained using the relation

$$S = \frac{6000}{D\rho} \tag{5}$$

where "D" is the diameter of the particle in nm and "ρ" the density of the particle in g/cc.[8,9]

Transmission electron microscopy

The synthesized samples were viewed under transmission electron microscope for the determination of particle size (Model-XGT-5700 WR EDXRF).

Incorporation of $NiFe_2O_4$ fillers in rubber matrix

The magnetic fillers synthesized by sol-gel method were incorporated in nitrile rubber matrix according to a specific recipe.[21,22] Compounds were prepared
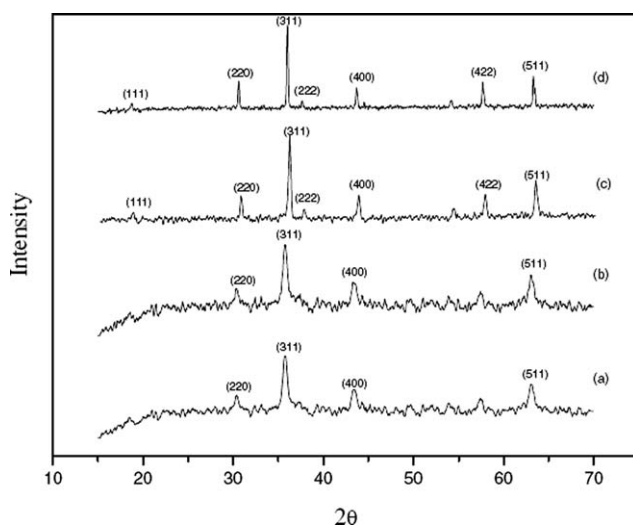
Figure 1 X-ray diffraction pattern of the (a) sol-gel prepared $NiFe_2O_4$ powder, (b) the $NiFe_2O_4$ powder heated at 300°C, (c) at 600°C, and (d) 900°C all for a duration of 12 h.

for various loadings of nickel ferrites; 20, 40, 80, and 120 phr with various grain sizes.

Cure characteristics

The cure characteristics of the composites were determined using a Goettfert elastograph model 67.85. Cure characteristics gives the minimum torque, scorch time, cure rate, maximum torque, and cure time of the composite. Cure temperature is fixed at 150°C. The time required for the optimum cure of the sample is determined from the respective cure characteristics.

Evaluation of mechanical properties

Tensile properties of the RFCs are determined as per ASTM D 412 (1980) using dumb-bell shaped specimens on an Instron Universal Testing Machine, Model 4411 Test System. Specimens for the tests are punched out of compression moulded sheets along the mill grain direction using a standard die. The thickness of the narrow portion is measured by bench micrometer gauge. The sample is held

between the two grips on the UTM, the upper grip of which is fixed. The rate of separation of the power actuated lower grip is fixed at 500 mm/min. The tensile strength, elongation at break and modulus at different elongations which are some of the important indications of the strength of the material[4,15–20] are recorded and evaluated after each measurement by the microprocessor.

RESULTS AND DISCUSSIONS

The XRD pattern of the four samples of $NiFe_2O_4$ powders synthesized by the sol-gel technique is depicted in Figure 1(a). A sharp increase in the crystalline nature of the nickel ferrite powders is observed as the firing temperature was increased which is recorded as a decrease in the broadening of the peaks in the diffraction pattern. This clearly indicates that the grain size has increased with increase of firing temperature. The grain size of the four samples heated at different temperatures is calculated using eq (1) and the results are given in Table I.

XRD of the composite samples are provided as Figure 1(b). Typical transmission electron microscopic figure are also provided Figure 1(c). From the particle size analysis, it is found that the particle size analysis from the XRD and TEM are almost agreeable (Table I).
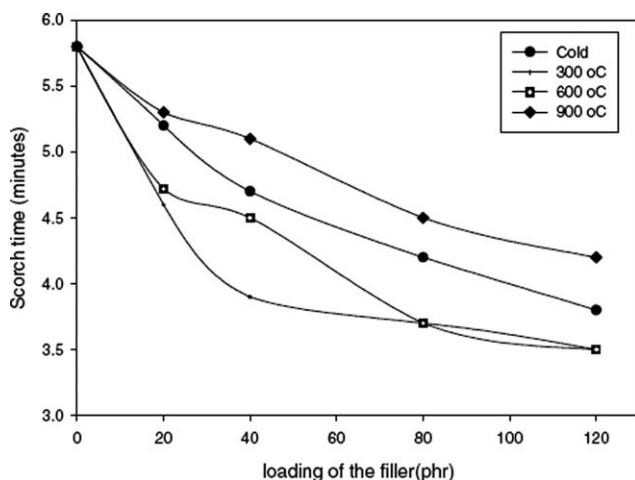
Cure characteristics of RFC

Figure 2 shows the variation of scorch time with loadings of nickel ferrite with varying particle sizes. The scorch time (t_{10}) decreases with the loadings of the fillers. All the samples show the same variation. The decrease in scorch time with increase in filler loading is due to the increase in the heat of mixing, with increase in filler loading.

Cure time is defined as the time required for optimum vulcanization of the samples. From Figure 3 it is seen that cure time sharply decreases for initial filler loadings (20 phr) and then increases for higher loadings. The high cure times at higher filler loading, is due to the adsorption of curatives by the filler particles.

RFCs based on nickel ferrites fired at low temperatures and having low grain sizes, the cure time

TABLE I
Structural Parameters of Sol-Gel Synthesized $NiFe_2O_4$

Firing temperature (°C)	Particle size (nm) (XRD)	Particle size (TEM)	Specific surface area (m²/g)	Theoretical density (g/cc)	Experimental density (g/cc)	Porosity (%)
As prepared powder	9.2	9.5	182.7	5.38	3.585	33.36
300	12.4	12.5	124.6	5.41	3.871	28.5
600	14.9	15	91.3	5.53	4.38	20.79
900	22	25	54.56	5.537	5.01	9.51

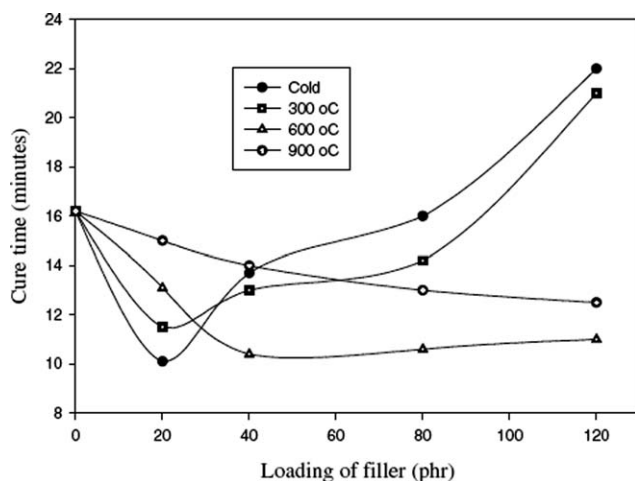**Figure 2** Variation of scorch time with loading of the filler.
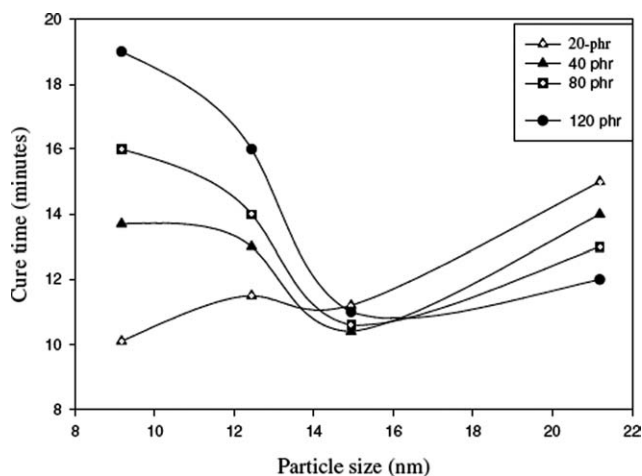
Figure 4 Variation of cure time with grain size of the filler.

increases for higher loadings of fillers. But the change in cure time is only marginal for additional loadings of fillers for higher grain sizes. These observations confirm that fillers of low grain sizes affect the processability of the composite into a certain extent while that of larger grains do not affect the processability of the composites.

Cure time is studied as a function of grain size of nickel ferrite filler and their variation is shown in Figure 4. From the curve it is evident that for fillers having less than 14 nm; the cure time decreases with particle sizes Also for fillers of small grains and for higher loadings, there will be an increasing tendency for agglomeration and this will retard the action of the accelerator and hence the cure time increases.

Figure 5 shows the variation of maximum torque with loadings of the fillers fired at various temperatures. It is observed that the maximum torque increases with loading for almost all composites.

Maximum torque gives an indication about the modulus of the compound. It shows an increasing trend with loading. Solomon et al.[21] obtained the same variation in case of hexagonal ferrites incorporated in nitrile rubber. From Figure 5, it is clear that, for nickel ferrite filler fired at low temperatures, the maximum torque shows an increasing trend.

Minimum torque is an indirect measure of the viscosity of the compound, or it can be generally treated as the measure of the stiffness of the unvulcanised rubber compound at the lowest point of the curve. Variations of minimum torque with loadings of the fillers against varying particle sizes are shown in Figure 6. Minimum torque increases with loadings of the filler.

Variation of minimum torque with grain size of the nickel ferrite is shown in Figure 7. These observations confirm that the addition of nano ferrite in nitrile rubber affect the processability of the

Figure 3 Variation of cure time with loading of filler.
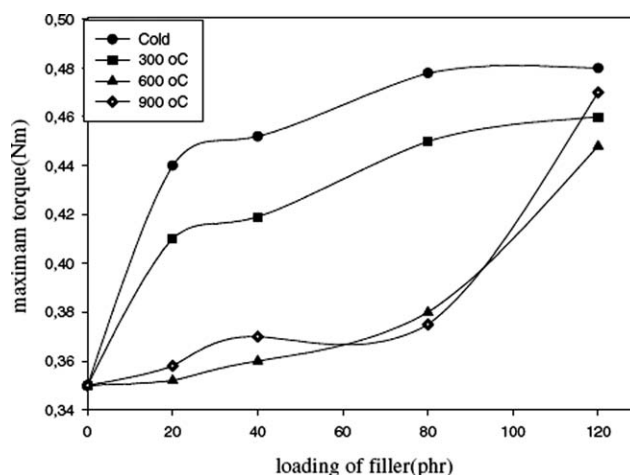
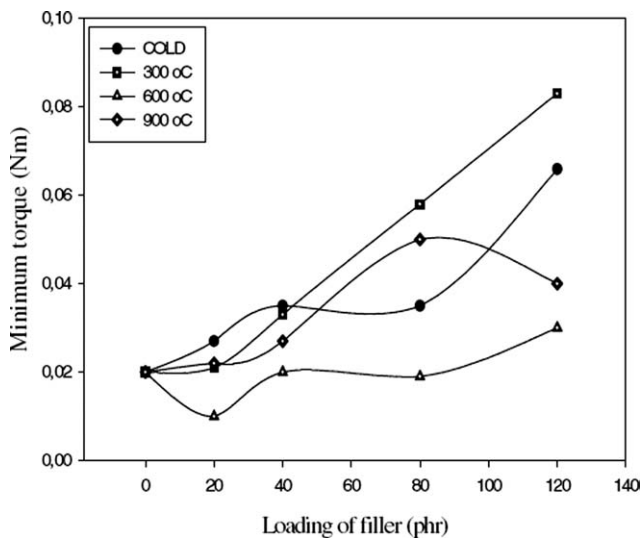**Figure 5** Variation of maximum torque with loading.

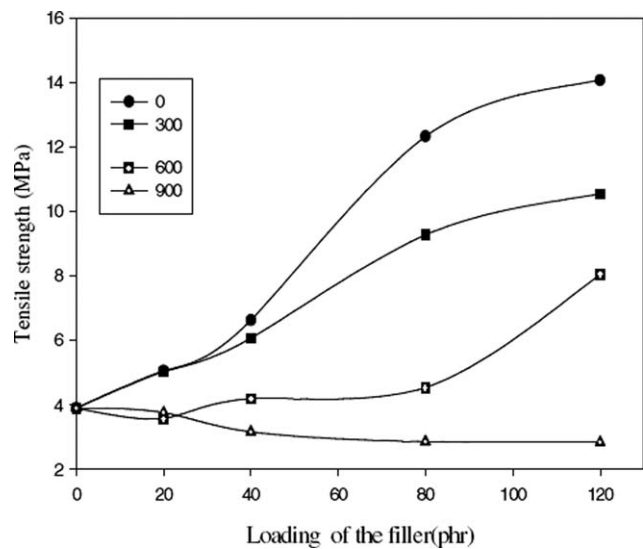**Figure 6** Variation of minimum torque with loading of filler.

Figure 8 Variation of tensile strength with loading of the filler.

composite and thus nano ferrite act as a reinforcement agent for the matrix.

Mechanical properties

The mechanical properties of the RFCs were determined using an Instron Universal Testing Machine, Model 4500 Test System. Dumbbell shaped specimens were cut from the prepared RFCs containing nickel ferrites of different particle sizes, at loadings of 20, 40, 80, and 120 phr as per ASTM procedure. Parameters namely tensile strength, modulus at different percentages, and elongations at break, which are some of the most important indications of the strength of the material[21,28,29] were determined and

their variation with loading and with grain size were studied.

Variation of tensile strength with loading of nickel ferrite is shown in Figure 8. The tensile strength increases with the loading of Nickel ferrite. The addition of nickel ferrite filler greatly reinforces the nitrile rubber matrixes and showed a maximum reinforcement for the nickel ferrites of small grain size. NBR gum vulcanisate has relatively low tensile strength due to lack of stress induced crystallization, which increases with increasing filler loading. The addition of ferrite filler reinforces the NBR matrix and showed maximum reinforcement for samples fired at low temperature or samples with low grain
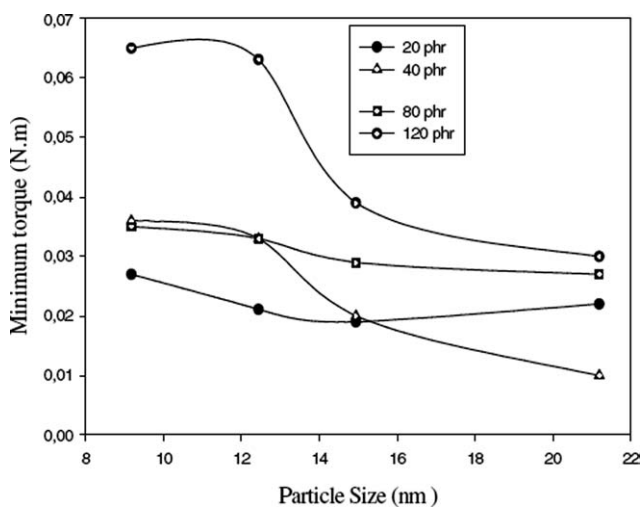

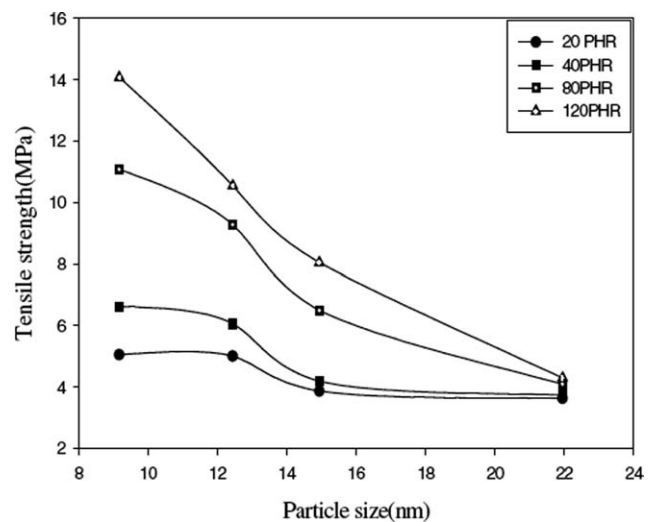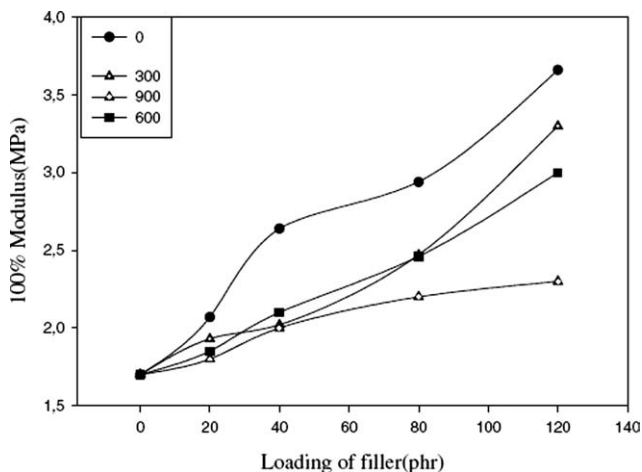**Figure 7** Variation of minimum torque with grain size of the filler.

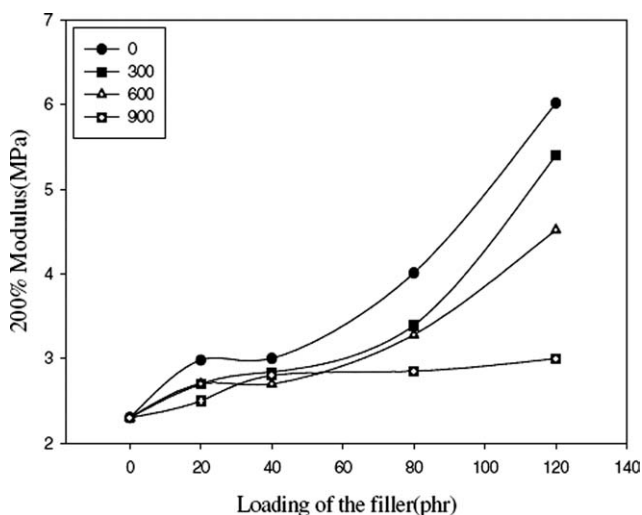**Figure 9** Variation of tensile strength with grain size of the filler.

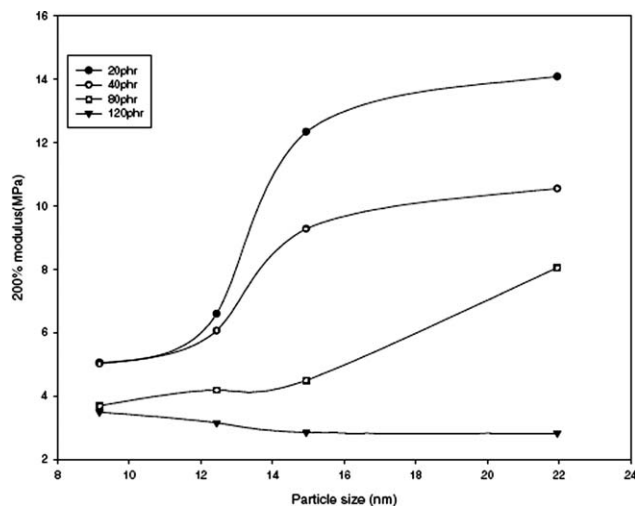**Figure 10** Variation of 100% modulus with loadings of the filler.

size. For higher loadings of nickel ferrite (120 phr) the change in tensile strength is only marginal, which is due to the diminishing volume fraction of the polymer available for wetting the filler particles.

The tensile strength of the RFCs, were studied as a function of grain size of the ferrite filler and their variation is given in Figure 9. Tensile strength of the RFCs, were found to increase with decreasing particle size. As the grain size of the filler decreases, the specific surface area available for wetting with rubber molecules increases; and as a result the reinforcement increases.

As the firing temperature increases, the grain size of the particles increases and the porosity decreases. For samples prepared at low temperatures the porosity is maximum. As the porosity increases the chance of bound rubber formation increases due to the flow of the macro molecules (rubber molecules), and as a result the tensile strength increases.


Figure 12 Variation of 200% modulus with grain size of the filler.

The modulus of the composites increases with increase in the loading of the filler, which is characteristic of reinforcing filler. Figures 10 and 11 depict the variation of 100% and 200% modulus with loading of the filler. The variation of 200% modulus with particle size is shown in Figure 12.

For fillers fired at low temperatures the elongation at break increases with loadings. But for samples fired at 900°C, the elongation at break decreases with loadings. The variation is given in Figure 13. The coarser particles generally decrease the elongation at break.

Elongation at break increases with loadings of the fillers in case of ferrite samples fired at low temperature or fillers having lower particle sizes. For smaller particles, the polymer filler interface will be stress bearing and this will lead to the increase in elongation at break.

Figure 11 Variation of 200% modulus with loading of the filler.
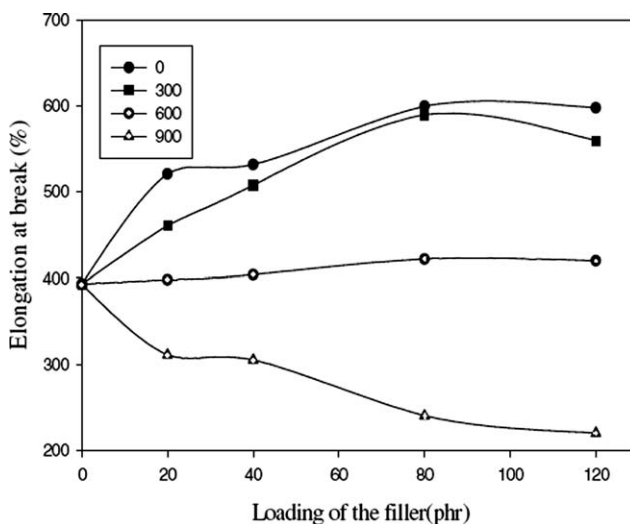
Figure 13 Variation of elongation at break with loading of the filler.
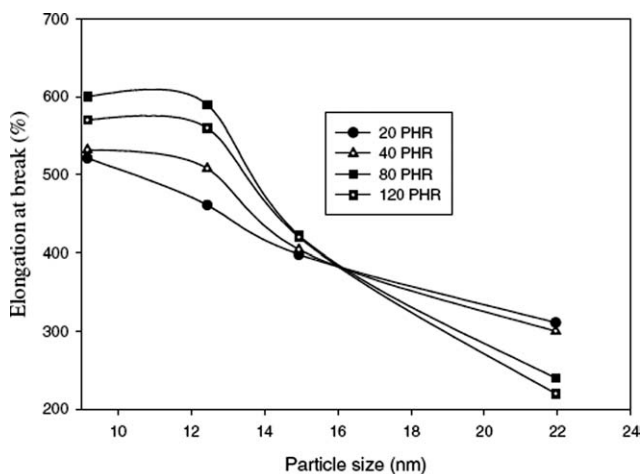
Figure 14 Variation of elongation at break with particle size.

The variation of elongation at break with the size of the filler is shown in Figure 14.

CONCLUSION

The cure characteristics reveal that if the particle size of the filler is below 15 nm, the cure time increased with the loading of the filler. The minimum and maximum torque values increases with increase in loading of the filler. The addition of ferrite fillers can enhance the mechanical properties of the nitrile rubber matrix. Thus the nanoparticles of nickel ferrite act as a reinforcing agent for nitrile rubber matrix. The grain size and the porosity of the filler play a vital role in determining the mechanical properties. As the porosity increases, the chance for bound rubber formation increases due to the flow of the rubber molecules, and as a result the tensile strength increases. The rubber ferrite composites have the unique advantage of mouldability and incorporation of nano-ferrites in the appropriate ratios in to the nitrile rubber not only modifies the mechanical and dielectric properties but also imparts magnetic properties to it. These RFCs are powerful tools for the absorption of electromagnetic waves.

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