

# Nickel and iron nano-particles in natural rubber composites

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**Abstract** In this work, the mechanical, electrical, and magnetic properties of natural rubber (NR) composites containing iron or nickel nanoparticles at different percentage varying from 0 to 120 phr (part of magnetic particle per hundred rubber) have been investigated at room temperature. It was found that the optimum concentration of magnetic fillers in NR is 30 phr, which improve the rheometric characteristics and physico-mechanical properties. Magnetic properties of the rubber composites have been investigated using vibrating sample magnetometer (VSM) at room temperature. The magnetic measurements show superparamagnetic behavior for all Ni and Fe nanoparticles percentage. The electrical measurements show a strong dependency of the conductivity on the percentage of magnetic nanoparticles.

## Introduction

Polymer nanocomposites represent a new alternative to conventionally filled polymers due to their filler size and dispersion. Nanocomposites exhibit markedly improved properties compared to the pure polymers or their traditional composites. These include increased

modulus, strength and heat resistance, and decreased flammability [1]. Polymer nanocomposites using magnetic materials as fillers are important for many applications because the magnetic materials are widely used in various fields such as magnetic data storage media, magnetic field sensors and biomedical applications such as drug delivery. Magnets are usually blended with polymer materials such as rubber to obtain magnetic rubber composites, which has many applications [2–5].

Natural rubber (NR) is an unsaturated elastomer characterized by its crystallinity and has some good properties, such as high strength, outstanding resilience and high elongation at break [6, 7] and it is economically available [8, 9]. However, NR is very sensitive to heat and oxidation because of the double bonds in its chains [10]. Furthermore, NR is vulcanized with sulfur compounds, which can crosslink the chains because of the presence of the reactive double bonds. It has high strength in non black formulations, hot tear resistance, retention of strength at elevated temperature, excellent dynamic properties and general fatigue resistance, so it has accounted for its use in many applications [11, 12]. The incorporation of magnetic fillers with NR leads to the formation of a composite with improvement mechanical, magnetic and electrical properties.

The development of iron powder polymer composites was expected to broaden the application base for metal into high volume alternating current (AC) magnetic applications [13–15]. It is well known that ferromagnetic properties depend on the crystal size of the used materials [16–19]. Therefore, particular magnetic properties are expected for the nanometer-sized Ni-dispersed composites.

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In the present work composite magnetic materials were prepared by mixing different concentrations of magnetic nanoparticles of Fe (hard magnet) or Ni (soft magnet) with NR matrix to form composites with good mechanical, magnetic and electrical properties for different applications.

## Experimental

NR produced in Malaysia of type RSS-1, Ribbed Smoked Sheets with a specific gravity  $0.913 \pm 0.005$  and Mooney viscosity at  $100\text{ }^\circ\text{C} = 60\text{--}90r$  and glass transition temperature  $T_g = -75\text{ }^\circ\text{C}$ .

Other chemicals such as sulfur, zinc oxide, stearic acid, *n*-cyclohexyl-2-benzothiazole sulphenamide (CBS) and phenyl- $\beta$ -naphthyl amine (PBN) were of technical grade.

The fine grade of iron (Fe) with average particle size varying between 26 nm and 45 nm and nickel (Ni) with average particle size varying between 22 nm and 50 nm was supplied by VEB Laborchemie Apolda, Germany.

The formulations of the composites are given in Table 1. All rubber ingredients were blended on a two-roll mill (470 mm diameter and 300 mm working distance). The speed of the slow roll was 24 rpm with a gear ratio of 1:1.4. An oscillating disc rheometer model 100 from Monsanto, USA was used for measuring the curing characteristics of the rubber compounds according to ISO 289-1994. The compounded rubber was vulcanized in a hydraulic press under a pressure of about 4 MPa and temperature of  $142 \pm 1\text{ }^\circ\text{C}$  for their optimum cure time ( $T_{c90}$ ).

The tensile strength, elongation at break and Young's modulus were determined on dumbbell shaped specimens using a Zwick tensile machine (model 1425). This is carried out in accordance with ISO 37.

Hardness was measured using the Shore A durometer according to ISO 868. All tests were conducted at

room temperature ( $25\text{ }^\circ\text{C} \pm 1$ ). Average of 5 samples was taken for each measurements point.

Dielectric measurements permittivity  $\epsilon'$  and dielectric loss  $\epsilon''$  were carried out at 100 Hz and at room temperature using a LCR meter type AG-411 B (Ando electric Ltd. Japan). The capacitance  $C$ , loss tangent  $\tan \delta$  and AC resistance  $R$  were measured directly from the bridge from which the permittivity  $\epsilon'$ , dielectric loss  $\epsilon''$  and  $R_{dc}$  were calculated. The cell used for measuring the solid samples was a guard ring capacitor type NFM/5T [Wiss Tech. Werkstätten (WTW) GMBH, Germany]. The cell was calibrated using standard materials (trolitul, glass, and air) of different thickness ranging from 1 to 5 mm. For each sample, a relation between the thickness  $d$  and its capacitance  $CM$  was plotted as a standard curve. The capacitance  $CM$  for the standard materials obtained from the standard curves was plotted versus the known permittivity  $\epsilon'$  of each material ( $\epsilon' = 2.5, 7, 1$  for trolitul, glass and air respectively). The relation between  $CM$  and  $\epsilon'$  was found to be linear and thus the permittivity corresponding to any measured capacitance can be deduced. To check the standard curve, two Teflon samples ( $\epsilon' = 2.0$ ) [20] with different thicknesses were used. The experimental error in  $\epsilon'$  and  $\epsilon''$  was found to be  $\pm 3\%$  and  $5\%$ , respectively.

The magnetic properties, magnetization saturation ( $M_s$ ), permittivity ( $Br$ ), and coercive force,  $H_c$  were measured for the iron and nickel rubber composites by using a vibrating sample magnetometer (VSM) model (LDJ 9600-1).

## Results and discussion

Table 2 summarizes the rheometric characteristics of the NR composites. The minimum torque  $M_L$  is an indirect measure of the viscosity of the compound [21, 22]. The table shows that minimum torque is slightly increased with increasing Fe loading up to 30 phr then decreases. In the case of Ni composites no significant change in  $M_L$  was observed.

It is clear from Table 2 that the maximum torque  $M_H$  increases with Fe and Ni loading with the maximum values obtained at a concentration of 30 phr. The scorch time  $ts_2$  values in Table 2 indicate that the samples loaded with Fe and Ni exhibit longer scorch times than the unloaded rubber. It is observed that the scorch time increases up to 30 phr and then decreases with increasing filler content.  $T_{c90}$  is the optimum cure time for vulcanization and it is calculated as follows:

$$T_{c90} = (M_H - M_L) \times 0.9 + M_L$$

**Table 1** NR formulations containing different concentrations of Fe and Ni

Ingredients	Phr (part per hundred rubber)
NR	100
Stearic acid	1
ZnO	5
CBS	0.6
PBN	1
Sulfur	1.5
Iron (Fe)	0,10,30,60,90,120
Nickel (Ni)	0,10,30,60,90,120

**Table 2** Rheometric characteristics of NR composites

Filler content (phr)	$M_L$ (dNm)	$M_H$ (dNm)	$T_{c90}$ (min)	$ts_2$ (min)	CRI ( $\text{min}^{-1}$ )
<i>Fe</i>					
0	3.5	45	11	6	10
10	3	52	16	7	11
30	4.5	61	16.5	9	13.5
60	3.5	58	17	8	11.5
90	3	58	19	6.5	8
120	2.5	54	22	6.5	6.5
<i>Ni</i>					
0	3.5	45	11	6	10
10	2	58	13.5	6.5	14.5
30	3.5	65	14.5	9	18.5
60	3	63	14.5	8	15.5
90	2.5	60	15.5	7.5	12.5
120	2.5	56	16	7	11.5

$M_L$ —minimum torque;  
 $M_H$ —maximum torque;  
 $T_{c90}$ —optimum cure time;  
 $ts_2$ —scorch time; CRI—cure rate index

This is an important parameter as far as the vulcanization is concerned.

Evaluation of cure time is a prerequisite for molding the compounds. It is clear that  $T_{c90}$  values increase with the addition of magnetic filler.

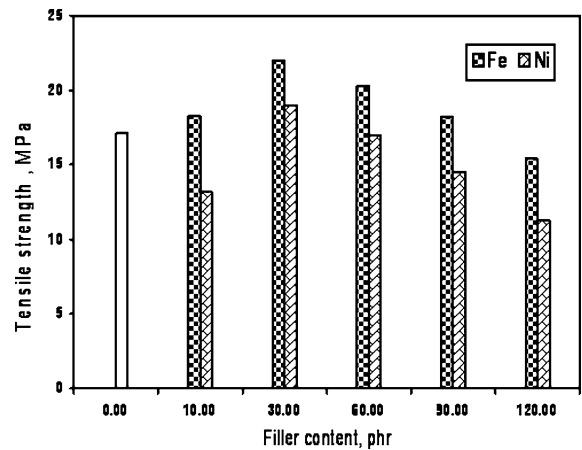
Cure rate index (CRI) is a direct measure of the fast curing nature of the rubber compounds and is calculated with the following relation:

$$CRI = 100/T_{c90}ts_2$$

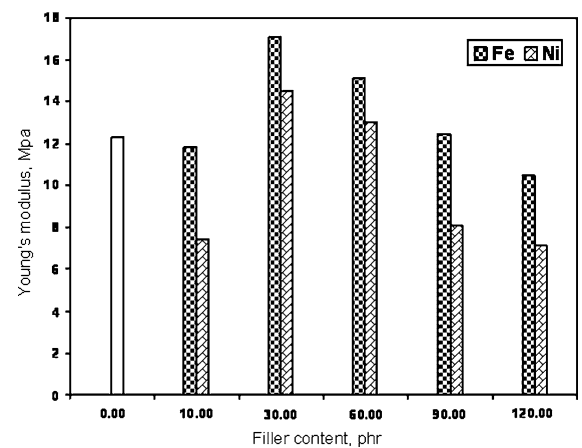
CRI increases with magnetic filler concentration and it supports the activation of the cure reaction up to 30 phr of the magnetic filler (Fe and Ni). At higher loading, there is a poor interfacial interaction between NR and the magnetic filler [23].

**Mechanical properties**

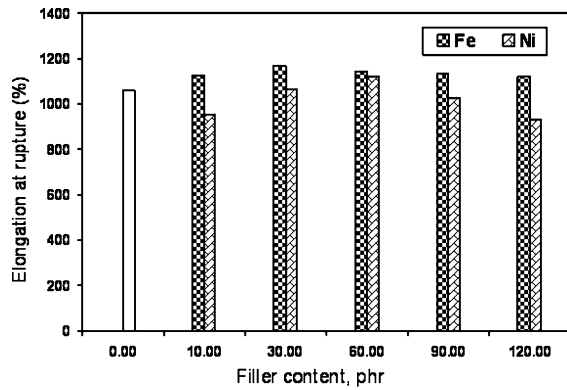
The variation of tensile strength, Young’s modulus and elongation at rupture with magnetic filler loading of Fe and Ni are presented in Figs. (1–3) respectively. The tensile strength of these composites increases with increasing the magnetic filler up to 30 phr and then it decreases with increasing the filler loading. Increasing of tensile strength at filler loading 30 phr was due to the good filler–rubber interaction as a result of better filler dispersion in the rubber matrix. Strong rubber–filler interaction would increase the effectiveness of the stress transferred from rubber matrix to filler particles dispersed in the rubber matrix [24]. However, the reduction in strength at filler loading (more than 30 phr) due to the reduction of the stress-induced crystallization of NR matrix by loading of magnetic filler [8].



**Fig. 1** Effect of filler content on the tensile strength of NR composites



**Fig. 2** Effect of filler content on the Young’s modulus of NR composites



**Fig. 3** Effect of filler content on the elongation at rupture of NR composites

The recorded Young's modulus also ensures the same behavior (Fig. 2). For the elongation at rupture (Fig. 3) no significant changes were observed.

The variation of hardness with loading magnetic filler is shown in Fig. (4). It shows that the hardness increases with increasing filler loading.

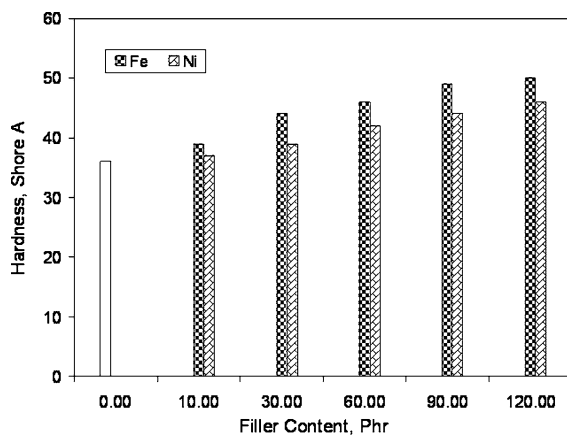
From these data, it is clear that the optimum concentration of magnetic fillers with NR is 30 phr, which improve the rheometric characteristics. It was observed that the Fe filler enhances the physico-mechanical properties more than Ni.

#### Electrical properties

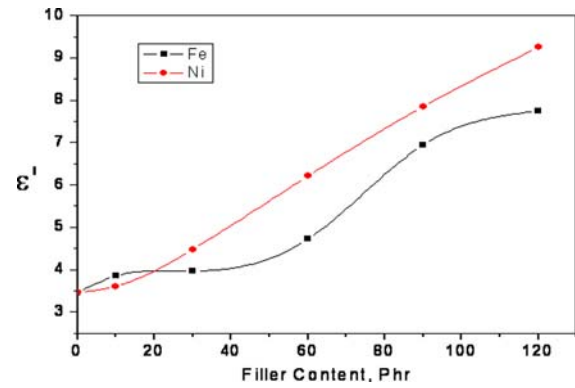
It was interesting to study the electrical properties of magnetic rubber composites prepared in the present work.

Results of permittivity  $\epsilon'$  and dielectric loss  $\epsilon''$  of various rubber/iron and nickel composites are shown in Figs. 5 and 6.

Figures 5 and 6 represent the variation of both  $\epsilon'$  and  $\epsilon''$  versus filler content at room temperature and at



**Fig. 4** Effect of filler content on the hardness

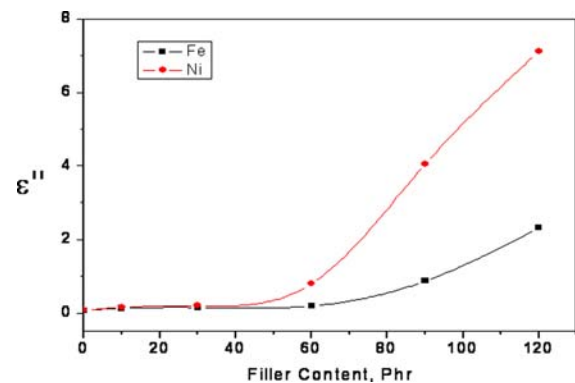


**Fig. 5** Variation of permittivity against filler content

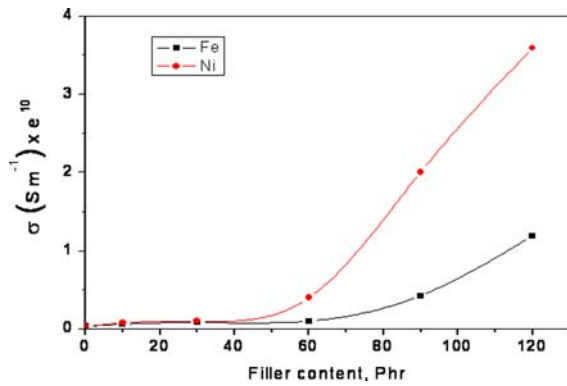
constant frequency  $f = 100$  Hz. From these figures it is notable that both  $\epsilon'$  and  $\epsilon''$  increase by increasing both filler content. Although the values of  $\epsilon'$  are higher in case of Ni-composites, these higher values are accompanied by higher loss values when compared to Fe-composites. This might be due to the formation of some oxide layer on the Fe particles during processing the samples that could reduce its conductivity.

From the above investigation it is clear that iron composites possess more preferable insulating properties when compared with those of Ni.

The conductivity ( $\sigma$ ) was calculated from the measured resistance  $R$  using the equation  $\sigma = L/RA$  where  $A$  is the area of the sample in  $\text{cm}^2$  and  $L$  its thickness in cm. The variation in conductivity with respect to filler concentrations is shown in Fig. 7. From this figure it is clear that,  $\sigma$  increases by increasing filler content. The conductivity data  $\sigma$  are found to be  $0.59 - 11.9 \times 10^{-11} \Omega^{-1} \text{cm}^{-1}$  for the samples containing different concentrations of iron, while it ranges from  $0.76$  to  $35.9 \times 10^{-11} \Omega^{-1} \text{cm}^{-1}$  for the different concentration of nickel. These results could lead to the conclusion that



**Fig. 6** Variation of dielectric constant against filler content



**Fig. 7** Variation of conductivity against Filler content

the investigated systems are considered to be insulating materials as their conductivity values are in the order of those found in literature ( $10^{-8}$ – $10^{-12} \Omega^{-1} \text{ cm}^{-1}$ ) [25].

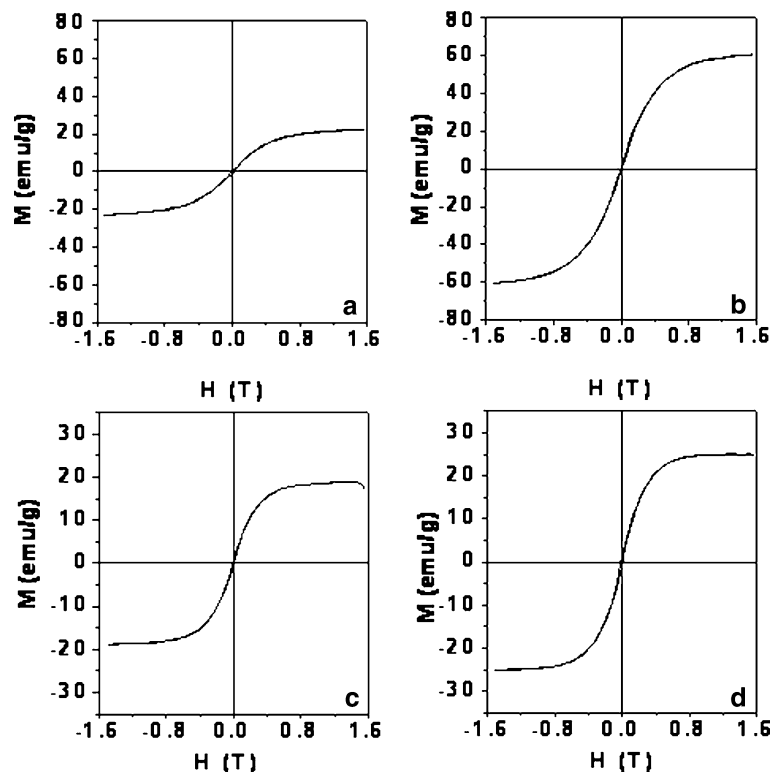
**Magnetic properties**

Figure 8 shows the hysteresis loops measured using vibrating sample magnetometer (VSM) at room temperature. Figure 8a, b show the hysteresis loops for rubber samples contain 30 phr and 120 phr of iron respectively. It is clearly shown that the hysteresis loops of the magnetic nanoparticles which are distributed in the rubber (which is a nonmagnetic medium) have a superparamagnetic behavior. The magnetic

nanoparticles Fe 30 phr show a switching field ( $H_s$ ) of 0.007728 T and the magnetization saturation ( $M_s$ ) is 22.75 emu/g. While for Fe 120 phr the switching field is 0.005049 T and  $M_s$  is 60.67 emu/g. It is clearly shown that by increasing the Fe nanoparticles in the rubber samples, the magnetization (emu/g) increases while the switching field ( $H_s$ ) decreases. Increasing the magnetic nanoparticles in the rubber medium, leads to decrease the distance between the magnetic nanoparticles. Decreasing the distance leads to magnetic coupling between the nanoparticles. This coupling decrease the switching field because once one particle switched, the other particles started to switch earlier due to the magnetic coupling. This leads to decrease the switching field and increase the magnetization in the rubber medium. Fig. 8c, d shows the hysteresis loops for rubber samples with 30 phr and 120 phr Ni nanoparticles respectively. In Ni samples, the switching field ( $H_s$ ) for 30 phr Ni is 0.00438 T and  $M_s$  is 18.96 emu/g while the  $H_s$  for 120 phr is 0.003620 T and  $M_s$  is 25.03 emu/g.

From Fig. 8a–d, it is clearly shown that, the Ni samples show the same behavior as Fe samples except the switching field which is higher at Fe nanoparticles (hard magnet) compared with Ni nanoparticles (soft magnet). Increasing the magnetic particles has an influence on the magnetic properties (due to the coupling between the magnetic nanoparticles which affect on the switching field) rather than the electrical properties.

**Fig. 8** Hysteresis loops of Ni and Fe NR composites



## Conclusion

Magnetic filler of Fe and Ni were incorporated into NR with different loading levels up to 120 phr to obtain rubber composites.

The cure characteristic and the physico-mechanical properties of rubber composites depend mainly on both concentration and type of magnetic filler.

The optimum concentration of magnetic filler of Fe and Ni is 30 phr of NR. Iron (Fe) enhances the rheometric characteristics and physico-mechanical properties more than Ni.

The electrical measurements show a strong dependency of the conductivity on the magnetic particles concentration. Ni samples show more conductivity than Fe samples which may be due to the formation of some oxide layer on the Fe particles during processing the samples that could reduced its conductivity.

From the magnetic measurements, it is clear that the samples show a superparamagnetic behavior for the all samples. The hysteresis loops show a switching dependence on the particles percentage and on the type of the magnetic particles.

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