Synthesis and DC Electrical Properties of Novel Lithium Ferrite Loaded Rubber Nano-Composites for Microwave Applications

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Abstract—**In this work, novel elastic rubber composites containing lithium ferrite ($Li_{0.5}Fe_{2.5}O_4$) have been prepared to be applied as microwave elements and in microwave shielding applications. Nano scale lithium ferrite powder was synthesized via citrate gel autocombustion route. It has been incorporated in nitrile butadiene rubber (NBR) in a concentration levels 10-100 phr. X-ray diffraction analysis revealed that the addition of LF to NBR matrix greatly enhanced the crystallinity of NBR.**

The DC electric properties of these LF loaded NBR composites have been studied. The DC conductivity of LF loaded NBR composites showed marked dependence on LF concentration. The addition of LF initially increased the DC conductivity up to a concentration level of 20 phr, then the conductivity decreases upon further addition of LF.

The dependence of current density on electric field intensity has been also studied. The behavior showed the non-Ohmic nature of the DC conduction process. Moreover, the possibility for space charge limited conduction was evident especially at high electric field limits. In order to investigate the mechanism governing the DC conduction, both Richardson- Schottcky and Poole-Frenkel relations have been plotted. LF loaded NBR composite samples were shown to follow the thermionic (Richardson-Schottcky) DC conduction mechanism. LF loaded NBR nano-composites are recommended to be used in various microwave engineering applications that require samples of specially designed structures. Making use of the elastic properties of the NBR matrix, they can be molded into various shapes as needed.

Keywords—Lithium Ferrite; NBR; microwave; shielding; nano-composites.

I. INTRODUCTION

In recent years, studies on the microwave shielding properties of polymer nano-composites have attracted much attention in view of their applications in both civilian and military fields [1]. Moreover, polymer nano-composites that can be used as microwave elements have great technological and industrial importance [1]. Ferrite rubber nano-composites have replaced the classical ferrite beads in the industry to suppress unwanted high-frequency electromagnetic noise [2]. The most important factor regarding this microwave shielding application is magnetic permeability losses (μ") at high frequencies [3]. Composites based on oriented ferromagnetic materials within an inert matrix have been developed for that purpose [1]. On the other side their electrical properties play a major role as well. This is because the high frequency behavior of ferrite rubber nano-composites is a function of their DC conductivity as well.

The study of electrical properties of polymer nano-composites aims to understand the nature of the charge transport prevalent in these materials in order to enhance their microwave properties. Electrical properties of polymer nano-composites can generally be modified by varying both the type and nature of the nanoscale filler. On the other hand, the advantages of rubbery materials, as a matrix, such as high elasticity, good moldability, and easy fabrication could be combined as an advantage with the great microwave properties of these inorganic nanoscale fillers [4].

The spinel magnetic ferrites have generated considerable interest among the researchers all across the world, due to their unique and versatile properties. Novel electrical and magnetic behaviors were observed for the nanosized ferrite particles when compared to that of their bulk counterparts [5].

Lithium ferrites and substituted lithium ferrites are indispensible materials for engineering microwave applications such as in circulators, isolators, and phase shifters. This is a direct result of their high resistivity, low dielectric losses, high Curie temperature, square hysteresis loop, and low cost [5]. Although lithium ferrite has been synthesized by different methods and studied by several authors [5], previous studies did not deal with the LF containing polymer composites. The most interesting point here is the effect of addition of lithium ferrite on the DC electrical properties of LF containing polymer composites which has not been dealt with so far.

The present study hopes to get a clear view about the effect of LF as ionic inorganic nanoscale filler on the DC electrical properties of lithium ferrite NBR composites. The probable DC conduction mechanism will be investigated as well.

Table (1): Composition of the LF loaded NBR composites.

Ingredients	Role	phr	Specific gravity
NBR	Matrix	100	0.98
Stearic acid	Plasticizer	2	0.940
Zinc oxide	Activator	5	5.58
Processing oil (DOP)*	Processing oil	50	0.98
Lithium ferrite (LF)	Ferromagnetic filler	0, 10, …100	1.3
MBTS*	accelerator	2	1.5
IPPD* 4020	antioxidant	1	0.995
Sulfur	Vulcanizing agent	2	2.05

*DOP Dioctyl phthalate   **IPPD**: N-Phenyl-N'-isopropyl-p-phenylenediamine
    MBTS: 2,2'-Dithiobenzothiazole   **phr** : Part per hundred parts of rubber by weight.

II. EXPERIMENTAL

a) Preparation of LF loaded NBR samples

Lithium ferrite $Li_{0.5}Fe_{2.5}O_4$ (LF) was prepared using the citrate-nitrate autocombustion method from ferric nitrate $Fe(NO_3)_3.9H_2O$ (BDH, England) and lithium carbonate Li_2CO_3 (BDH, England) precursors [6].

LF loaded NBR composites were prepared in accordance with ASTM D3182-07 using a two roll-mixing mill with outside diameter 470 mm, working distance 300 mm, speed of slow roll 24 rpm and fraction ratio of (1:1.4). The compounding ingredients were obtained from the Transport and Engineering Co., Alexandria, Egypt and are enlisted in table (1). Vulcanization was carried out using an electrically heated platen press at 155±2 °C and 4 MPa (150 bar) for the optimum cure time 30 minutes as previously determined from Monsanto Rheometer

b) X-Ray Diffraction analysis

X-ray diffraction was carried out at room temperature using Philips Pu 1390 diffractometer with a Cu-K$_\alpha$ target and a filter of wavelength (λ=1.791 A$^\circ$) operated at 50 kV and 150 A. X-ray diffraction data

were recorded from 10° to 80° (2θ) at a rate of 2° min^{-1}.

c) DC Electrical Measurements

The dc measurements were carried out using PASCO scientific model 1030A high voltage power supply and Keithly 614 electrometer. The circuit was constructed as shown in figure (1). The samples were molded into pellet shapes of 1cm thickness and 8 mm diameter. They were polished and covered with silver paste on both sides.
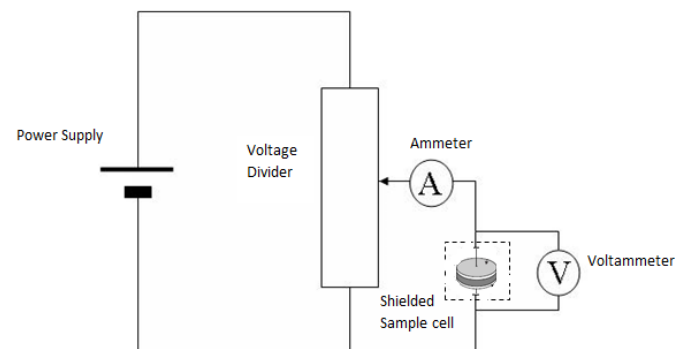

Figure (1): Schematic diagram of the circuit used for DC conductivity and I-V measurements.

The DC electric conductivity (σ) was calculated from:

$$\sigma = \frac{d}{AR} \quad (1)$$

Where d is sample thickness, A its area, and R is the measured resistance.

III. Results and discussion

a) X-ray diffraction analysis

Figure (2) shows the X-ray diffraction patterns of $Li_{0.5}Fe_{2.5}O_4$ sample. The pattern reveals single phase crystalline structure as compared with the ICCD card No. [00-049-0266]. Crystallite size was calculated using the well-known Scherrer's formula [7]: $a=d(h^2+k^2+l^2)^{1/2}$ assuming spherical shapes and was found to be 38 nm indicating that the sample is in the nanoscale. The maximum intensity in the $Li_{0.5}Fe_{2.5}O_4$ diffractogram i.e. the characteristic spike for $Li_{0.5}Fe_{2.5}O_4$ was at 2Ɵ = 35.718°.

The addition of lithium ferrite to NBR in a 100 phr loading level has resulted in an appreciable increase in NBR crystallinity. This is clearly evidenced from the appearance of lithium ferrite characteristic spike at 2Ɵ = 35.718°. Other peaks belonging to LF appear also within the amorphous NBR background at 53.871°, 57.433°, and 63.079°.
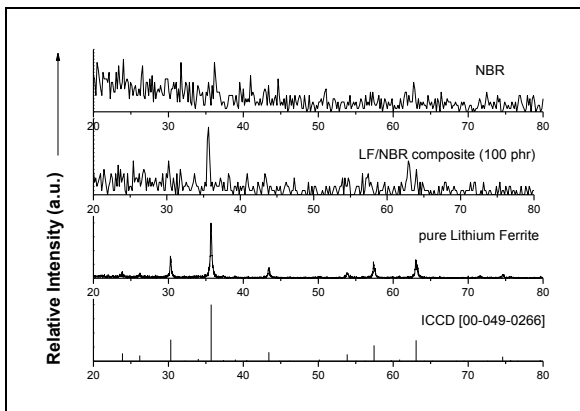

Figure (2): XRD pattern of lithium ferrite powder, NBR, LF/NBR composite (100phr) as compared with ICDD [00-049-0266] at 300 K.

b) DC conductivity of LF loaded NBR composites

Figure (3) shows the evolution of DC conductivity for lithium ferrite loaded NBR composites as a function of loading level of $Li_{0.5}Fe_{2.5}O_4$ (LF). The DC conductivity of LF loaded NBR composites initially increased linearly with an increase in filler content and reached a maximum value at 20 phr. This is clearly explained by the introduction of the ionic LF nanoparticles which enhance the conductivity. However, for LF loading level above 20 phr, the bulk

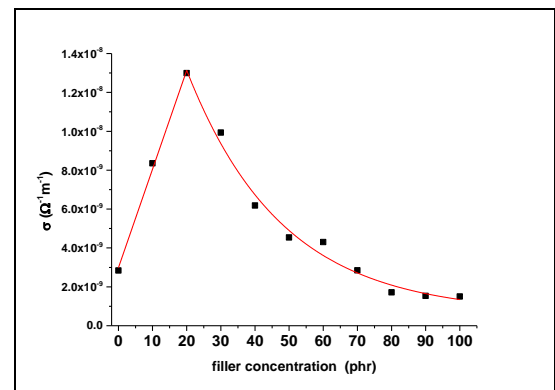conductivity of the non-composites was found to decrease exponentially.

Figure (3): Variation of DC conductivity (σ) with filler content (phr) for LF loaded NBR composites at 300 K.

The process can be viewed as if on further addition of LF, a continuous non-conductive phase builds up in the form of an electrically inert component. The latter would block up charge carrier transport, resulting in an increase in total resistance of the rubber nano-composite.

Generarlly speaking, the bulk resistivity of nanoparticle filled polymer nanocomposites depends on the interfacial polymer nano-layer close to the nanoparticles resulting from the interaction between polymer chains and the highly charged nanoparticles surface [8]. The interfacial nano-layer can be considered to consist of two sub-layers. The first nanolayer is the one tightly bound to the nanoparticles surface which causes the polymer chains to be highly immobile. The second nano-layer around the first layer contains polymer chains which are loosely bound. At lower filler loading, the fraction of the extended loose polymer layer is high, which would probably allow the existence of free ions and their unhindered transport through the bulk of the material, causing the initial rise in the electrical conductivity. At slightly higher filler loading, i.e. > 20 phr for LF/NBR composites, any increase in filler concentration results in a subsequent increase in the fraction of immobile nanolayers in polymer matrix. These immobile nano-layers probably act as ion traps. Subsequently ion mobility is inhibited resulting in a decrease in the DC electrical conductivity of LF/NBR nanocomposites.

b) Current- Voltage characteristics of LF loaded NBR composites

Current density (J, A/m^2) vs electric field (E, V/m) curves for LF loaded NBR composites at 300 K are shown in figure (4) plotted on a log-log scale. They all show linear behavior indicating the clear dependence of current density on the intensity of the applied

electric field. However, they are non-Ohmic as revealed for the slopes representing the non-Ohmicity factors. The mean value of the slopes was found to be 0.9.
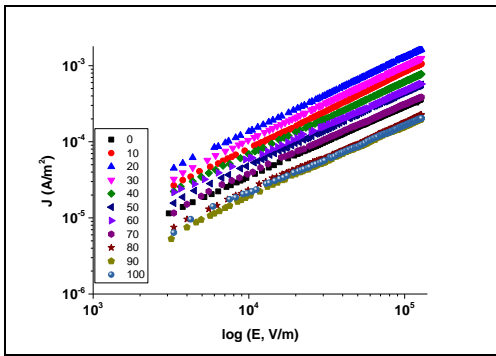

Figure (4): Current density dependence on the electric field intensity plotted on a log-log scale for LF loaded NBR composites at 300K.

The dependence of the DC conductivity (σ, $\Omega^{-1}m^{-1}$) for LF loaded NBR composites on electric field (E, V/m) is shown in figure (5). The non- linear trend for most of the samples especially at low electric field values confirms that the behavior of these samples is non-Ohmic. This gives a possibility for a space charge limited conduction (SCLC).
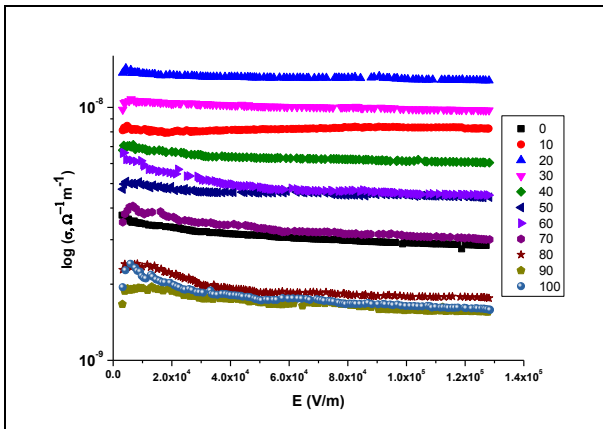

Figure (5): Dependence of log σ on the electric field intensity (E) for LF loaded NBR composites at 300K.

Both Richardson-Schottky and Poole-Frankel type conductions are associated with the injection of charge carriers [9]. The Richardson-Schottky (RS) mechanism involves the field assisted thermionic emission of charges from electrodes into samples. On the other hand, in the Poole-Frankel mechanism, the current is considered to be due to electric field assisted thermal excitation of electrons from traps into conduction band. Thus the main difference between RS and PF models is that former is electrode limited whereas in the later, the conductivity is a bulk limited process [9]. The current density for RS is expressed as:

$$J = AT^2 \exp\left[-\frac{\emptyset}{kT} + \beta_{SR}E^{1/2}\right] \qquad (1)$$

And for PF as:

$$J = J_o \exp\left(\frac{\beta_{PF}E^{1/2}}{2kT}\right) \qquad (2)$$

Where A, B, J_o and are constants, E is applied electric field, $\emptyset$ is the work functions, β_{SR} and β_{PF} are the Richardson-Schottky and Poole-Frankel coefficients.

Figure (6) represents the variation of log J with $E^{1/2}$ according to the above mentioned equations for LF loaded NBR composites. It is observed that all samples exhibit linear behavior in the high field region. This indicates that the conduction mechanism may be of either Richardson-Schottky or Poole- Frenkel type.
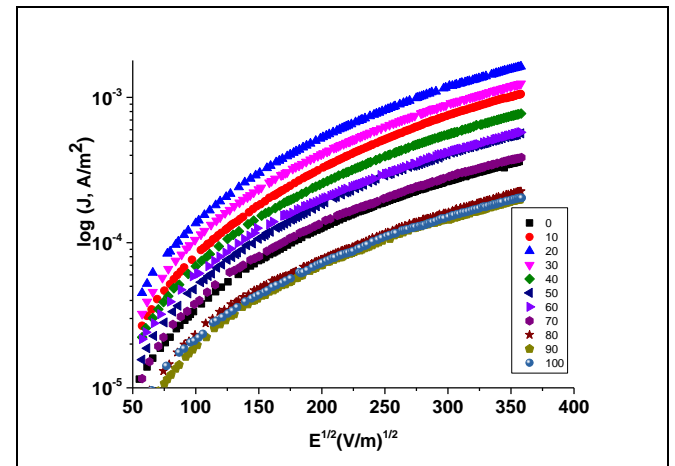

Figure (6): log J- $E^{1/2}$ relation for LF loaded NBR composites at 300K.

In order to check out the type of conduction mechanism in these samples, variation of logσ with square of the applied field plot has been made in accordance with the following Poole- Frenkel relation:

$$\sigma = \sigma_o \exp\left(\frac{\beta_{PF}E^{1/2}-\emptyset}{kT}\right) \qquad (3)$$

Thus for a PF conduction mechanism, the plot of (log σ) versus ($E^{1/2}$) should yield a straight line with positive slope at a constant temperature.
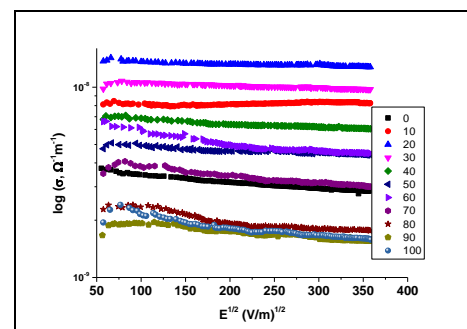

Figure (7): log J vs $E^{1/2}$ relation for LF loaded NBR composites at 300K.

Figure (7) shows that all samples show a nearly constant or negative slope relation which excludes

any possibility of Poole–Frenkel mechanism. This fact leads us to the conclusion that LF loaded NBR composites follow the Richardson-Schottcky conduction mechanism.

IV.Conclusion

From the forgoing results and discussion, one may conclude the following:

The measurement of the electrical conductivity of LF loaded NBR composites indicated that the addition of LF initially increased the DC conductivity up to the 20phr conc. then the conductivity decreased afterwards. This behavior was explained in light of the charge trapping effect of polymer chains close to the LF nanoparticles. All samples resulted in non-Ohmic current voltage relationship. The dc conduction mechanism for theses samples could be ascribed to the thermionic emission (Richardson-Schottcky) conduction mechanism. The prepared samples are mainly designed to be used as elastic microwave elements and in microwave shielding purposes. Besides, the insulating nature of these samples suggest their possible application in radio frequency (rf) magnetic cores due to low eddy current losses as expected from their low DC electric conductivity values.

V. References

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