Electrical and Mechanical Properties of Manganese Dioxide (Magnetite) Filled NBR Rubber Blends

K.F. El-Nemr, M.R. Balboul*, M.A. Ali
National Center for Radiation Research and Technology, P.O.Box 29, Nasr City, Cairo, Egypt

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ABSTRACT

Different concentrations of fillers $\text{MnO}_2$ and $\text{Fe}_3\text{O}_4$ were incorporated into acrylonitrile butadiene rubber (NBR) interlinked composites. The prepared composites systems were irradiated by electron at constant dose of 50 kGy to induce radiation crosslinking under atmospheric conditions. The effect of different contents of fillers and temperature variation on dc electrical conductivity, $\sigma_{dc}$, in NBR/$\text{MnO}_2$ and NBR/$\text{Fe}_3\text{O}_4$ mixture system was investigated. The calculated activation energy, $\Delta E_{dc}$, from $\sigma_{dc}$ was found to be highly affected by both the type and concentration of the fillers. Whilst, the dielectric properties namely; dielectric constant, $\varepsilon'$, dielectric loss, $\varepsilon''$, and the ac electrical conductivity, $\sigma_{ac}$, were measured as functions of frequency, temperature and for different filler concentrations of $\text{MnO}_2$ and $\text{Fe}_3\text{O}_4$. The ac electrical conductivity was calculated from dielectric measurements and by employing a simple relationship. The analysis of the $\sigma_{ac}$ results shows that the conductivity increases up to a temperature of about 330 K. Further increase of temperature reduces the conductivity of $\text{Fe}_3\text{O}_4$ samples, while, the conductivity of $\text{MnO}_2$ samples tends to show almost constant values after this temperature. Mechanical properties, tensile strength (TS), tensile modulus at 100% elongation (M100), and hardness were established as a function of different concentrations of filler $\text{MnO}_2$ and $\text{Fe}_3\text{O}_4$. It was found that, filler incorporation into the NBR matrix is one of the major factors that enhance the tensile strength as well as hardness resistance. While, the elongation at break shows an adverse behavior by increasing content of $\text{MnO}_2$ and $\text{Fe}_3\text{O}_4$ filler.

Keywords: Acrylonitrile butadiene rubber; Cross Linking; Electrical Properties; Mechanical Properties.

INTRODUCTION

The incorporation of fillers into rubbery polymers imparts many interesting and useful properties to the particle filled composite materials [1-3]. Fillers are introduced into rubbery polymers for many varied reasons, more generally to help in tailoring the physical and/or chemical properties of the rubber for various applications where flexibility is an important parameter [4, 5]. The ability of fillers to interact physically and/or chemically with rubber compounds, under suitable conditions, is also an important aspect of reinforcement; primarily contributed by the crosslinked [6]. Whilst, the physical and chemical nature of the filler will determine its effectiveness in a functional role, the extent to which this occurs depends on many factors including the amount of filler present, possible interactive effects between the filler and rubbery polymer, or between the filler particles themselves.

Electrical properties of such composites are of particular importance, not only from the application point of view but also from the fundamental point of view, as these composites are essentially very good dielectrics [7]. Therefore, study of these materials, particularly in an ac field sheds light on the behaviour of charge carriers mobility and the mechanism of conduction. A filled
rubbery polymer differs substantially from the free one in a wide range of properties. The presence of filler affects both the electrical, as well as, mechanical properties. A survey of literature reveals that the conductivity studies on MnO₂ and Fe₃O₄ incorporated rubber composites are rather scarcely or seldom reported.

Various rubbers are being widely used for preparation of such conductive composites, e.g., NR, SBR, NBR, Q, IIR, EPR and EPDM [8-10]. In the present study, we used acrylonitrile butadiene rubber (NBR), which has good low temperature flexibility, heat, and aging resistance, swelling resistance, and especially remarkable oil resistance because of the polar nitrile groups [11]. Manganese dioxide (MnO₂) and Magnetite (Fe₃O₄) were prepared and used as the conductive filler because metals are unstable to oxidation. In addition, the relationship between NBR composites loaded with different concentrations of filler and dclac electrical conductivity, dielectric properties as well as mechanical properties were investigated.

**EXPERIMENTAL**

**Materials:**

NBR with acrylonitrile content 34%, was manufactured by EniChem company Inc, Italy, Europrene N3345. The antioxidant used is 1, 2-dihydro 2, 2, 4-trimethyl quinoline (TMQ) was obtained from Birla Tyres Limited, India. Activators: zinc oxide and stearic acid, dioctyl phthalate are of commercial grade, China. The acrylate polyfunctional monomer, Trimethylol propane trimethacrylate (TMPTMA) was obtained from Aldrich Chemical Company Inc., Germany. Magnetite (Fe₃O₄), Fe = 88% and manganese dioxide (MnO₂), Mn = 92% were supplied by El Nasr chemicals company, Egypt.

**Mixing and compounding:**

The rubber composites were prepared on two-roll opened laboratory mixer under identical condition of mixing time, temperature, and gap between the rolls. NBR rubber was masticated firstly for 2 minutes followed by addition of ingredients, antioxidant (TMQ), stearic acid, ZnO, then the curing agent TMPTMA, finally the fillers Fe₃O₄, and MnO₂ were added. The nip-gap, mill roll speed ratio and the number of passes were kept constant for all mixtures. Compounds finally sheeted again in the rolling direction into slabs of about 1 mm thickness, the sheets pressed in clean molds of an electric press. The molds were brought to 160°C and held at this temperature for 5 minutes at a pressure of 160 kg/cm². The different formulation of mixes and the sample code are tabulated in Table (1).

**Irradiation of samples:**

The samples were irradiated at constant dose of 50 kGy by an electron beam accelerator in the presence of air at the National Center for Radiation Research and Technology, Cairo, Egypt. The irradiation was done at beam current of 5 mA, accelerator energy of 1.5 MeV and conveyor speed 3.2 m/min.

**Table (1): Formulation of the mixes**

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Electrical measurements:

Electrical conductivity measurements were carried out in a cell with brass electrodes in the temperature range of 293–383 K, using an electric heater in isolated chamber and a thermo couple placed very close to the sample. For the dc conductivity measurements, a Keithly-617 electrometer was used for measuring resistance of the samples at different temperatures within the range. For the dc conductivity measurements, a Keithly-617 electrometer was used for measuring resistance of the samples at different temperatures within the range. The frequency-dependent measurements of impedance, $Z$, capacitance, $C$, dissipation factor, $\tan\delta$, and the phase angle, $\theta$, between the applied ac voltage and the resulting current through the sample, were obtained using a computer controlled LRC bridge model HIOKI 3535 at different frequencies range from 50 Hz to 5 MHz and a temperature from 293 to 383 K.

Mechanical measurements:

Five individual dumbbell shaped specimens were cut out from the sheets using a steel die of standard width (4 mm). The minimum thickness of the test specimens was determined by gauge graduated to one-hundredth of the millimeter. A benchmark of 1.5 cm was made on working part of each test specimen. Tensile strength was carried out according to (ASTM D412-66T, 1967) at a crosshead speed 500 mm/min on a rubber tensile testing machine HOUNS FILD, England, Modulus at 100% elongation estimated from stress-strain curve, and expressed by MPa. Hardness was carried out by using durometer type A (Model 306L), from pacific Trasducer Corp., Los Angeles USA, according to (ASTM d 2240, 2000).

RESULTS AND DISCUSSION

Dc conductivity:

The dc electrical conductivity of NBR rubber composites with different filler concentrations of MnO$_2$ and Fe$_3$O$_4$ and irradiated at 50 kGy is computed at different temperatures. The electrical conductivity is calculated according to the following equation

$$\sigma_{dc} = \frac{t}{R \times A},$$

where $t$ is the thickness of the test piece, $A$ is the cross-sectional area and $R$ is its resistance. The dependence of the electrical conductivity on temperature can be described according to the Arrhenius equation:

$$\sigma_{dc} = \sigma_0 \exp\left(\frac{-\Delta E_{dc}}{kT}\right),$$

where, $\sigma_0$ is the pre-exponential factor and $\Delta E_{dc}$ is the activation energy. The conductivity mechanism in this temperature range is expected to be due to the thermally activated conduction of electrons over the potential barrier [12, 13]. Figure 1 shows the variation of the activation energy of NBR rubber composites with respect to the concentration of filler MnO$_2$ and Fe$_3$O$_4$. The calculated activation energy is found to be highly affected by both the type and concentration of the filler. The response of $\Delta E_{dc}$ to MnO$_2$ concentration remains near a constant activation energy level up to 50 phr, but then it suddenly increases when the fraction of MnO$_2$ in the mixture exceeds this amount. This concentration is known as the critical concentration. On the other hand, the activation energy increases almost linearly with increase of Fe$_3$O$_4$ concentration. These behaviors of $\Delta E_{dc}$ with both types of filler concentrations (MnO$_2$ and Fe$_3$O$_4$) are evident that the fillers are dispersed in the NBR matrix uniformly to forming an interconnected conducting network.
Dielectric studies:

The frequency dependence of dielectric constant ($\varepsilon'$), dielectric loss ($\varepsilon''$) and dielectric loss tangent ($\tan\delta$) are studied for all composites under investigation at different frequencies, varying from 50 Hz to 5 MHz, within the temperature range 293–383 K. The values of the dielectric properties are calculated from the frequency–capacitance measurement and the complex dielectric constant is described by

$$
\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)
$$

(3)

where $i = (-1)^{1/2}$, $\omega = 2\pi f$, and $f$ is the frequency of the applied electric field. The real part of the permittivity, $\varepsilon'(\omega)$, is a measure of the energy stored from the applied electric field in the material and identifies the strength of alignment of dipoles in the dielectric. The imaginary part, $\varepsilon''(\omega)$, or loss factor, is the energy dissipated in the dielectric associated with the frictional dampening that prevents displacements of the bound charge from remaining in phase with the field changes [14].

The values of the real part of the dielectric constant ($\varepsilon'$) at various frequencies are calculated using the measured capacitance values ($C$) according to the relation [15]

$$
\varepsilon' = \frac{Ct}{\varepsilon_o A},
$$

(4)

where $A$ is the area of the sample and $\varepsilon_o$ is the permittivity of free space charge ($8.854\times10^{-12}$ F/m). The imaginary part, or loss factor ($\varepsilon''$) is expressed as

$$
\varepsilon'' = \varepsilon' \tan\delta.
$$

(5)

The dissipation factor ($\tan\delta$) is recorded directly from the equipment.

Figures 2 and 3 represent the experimentally obtained comparison plots of the temperature dependence of $\varepsilon'$ and $\varepsilon''$, respectively, at frequency of 1MHz as an example, for the composites under investigation. It is obvious from these figures that the values of $\varepsilon'$ and $\varepsilon''$ show a strong dependence on temperature as well as filler concentration (MnO$_2$ and Fe$_3$O$_4$). The change in dielectric constant (samples F1, F2, F3 and M2) exhibits a pronounced peak at about 333 K. While, for the other samples (control, M1, M3) the dielectric constant is observed to increase with increasing temperature up to about 333 K and then remains almost constant at higher temperature. On the other hand, Fig. 3 shows
well defined peak formed for the dielectric loss at about 303 K with a maximum value and then tends to decrease rapidly at further higher temperatures.

![Graph](image_url_1)

**Fig. (2):** Temperature dependence of the dielectric constant, $\varepsilon'$, measured at fixed frequency (1MHz) of NBR composites loaded with different filler concentrations of (a) MnO$_2$ and (b) Fe$_3$O$_4$ and irradiated at 50 kGy.

![Graph](image_url_2)

**Fig. (3):** Temperature dependence of the dielectric loss, $\varepsilon''$, measured at fixed frequency (1MHz) of NBR composites loaded with different filler concentrations of (a) MnO$_2$ and (b) Fe$_3$O$_4$ and irradiated at 50 kGy.

The observed behavior of increasing $\varepsilon'$ and $\varepsilon''$ with temperature may be due to a decrease in bond energies and to the consequent increase in diffusion or oscillation process through the NBR rubber matrix. In other words, as the temperature increases two effects on the dipolar polarization may occur: (i) the NBR rubber network relaxes which weakens the intermolecular forces and hence the ions displacement i.e., orientation polarization becomes easier (ii) it increases the thermal agitation and hence strongly disturbs the orientation vibrations [16, 17]. While, the observed behavior above 333 K and 303 K for $\varepsilon'$ and $\varepsilon''$, respectively, can be explained as follows: when the temperature is increased more, the dipoles will no longer be able to rotate sufficiently rapidly so that their oscillations begin to lag behind temperature. From Figs. 2 and 3 it is notable that $\varepsilon'$ and $\varepsilon''$ increase by increasing MnO$_2$.
and Fe₃O₄ content in the NBR rubber. This increase is attributed to the presence of permanent electrical dipoles in the matrix that arise from charge pairs formed by the Fe and Mn ions (cations) and non-bridging oxygen (anions). As the MnO₂ and Fe₃O₄ concentration increases, more of these permanent dipoles will be present, contributing to the dipolar polarization.

Figures 4 and 5 show the frequency dependence of $\varepsilon'$ and $\varepsilon''$, respectively, for the composites under investigation, at temperature of 383 K as an example. These figures clearly display that $\varepsilon'$ and $\varepsilon''$ decrease abruptly with increase in the applied frequency. These increases of dielectric properties, $\varepsilon'$ and $\varepsilon''$, towards lower frequency regions may be attributed to the presence of polarization process, which could be effective at low frequency [18, 19]. On the other hand, beyond 1000 Hz, the change in dielectric properties, of $\varepsilon'$ and $\varepsilon''$, continues slightly to decrease and also remains almost constant at higher frequencies (10–5000 KHz), with increasing frequency. This behavior in dielectric properties, $\varepsilon'$ and $\varepsilon''$, at low frequencies may be due to that the ions in the composites matrix are able to oscillate and respond to the applied field and thus contribute fully to the polarization. At higher frequency, where the ions cannot oscillate as quickly as the applied field, dispersion takes place and $\varepsilon'$ and $\varepsilon''$ decrease to a constant value. Which means that, the carrier lifetime of the charges is much larger than $1/\omega$ at very high frequency, that is, the charges cannot follow the ac signal [20-22]. It is also notable that $\varepsilon'$ almost increases by increasing MnO₂ and Fe₃O₄ content in the NBR rubber as compared with the blank one, especially MnO₂ content, as can be seen in Fig. 4. This may be attributed to the increase in electronic contribution to the polarizability.
Ac conductivity:

The frequency dependent of the ac electrical conductivity, \( \sigma_{ac}(\omega) \), is obtained by subtracting the dc conductivity \( \sigma_{dc} \) from the measured total conductivity \( \sigma_{tot} \) according to the formula

\[
\sigma_{ac} = \sigma_{tot} - \sigma_{dc}.
\]  

(6)

The ac electrical conductivity, for NBR composites loaded with different concentrations of filler Fe\(_3\)O\(_4\) and MnO\(_2\) and irradiated at 50 kGy, is computed for different frequencies and also at different temperatures. Figure 6 represent the frequency dependence of ac electrical conductivity for all composites under investigation at temperature of 398 K, as an example. As can be seen from this figure, the electrical conductivity generally shows a sharp increase with increasing frequency. In addition, as it is expected, conductivity also increases with increasing filler Fe\(_3\)O\(_4\) and MnO\(_2\) concentration in the NBR rubber. This indicates that a continuous conductive network forms in the rubber permitting a higher percentage of electrons to flow through the samples. Similar behaviors are observed in the literature [19, 23]. The increase in the electrical conductivity leads to an increase in the eddy current, which in turn increases the energy loss tan\( \delta \). This behavior can be attributed to a gradual decrease in series resistance with increasing frequency [24].

Fig. (6): Frequency dependence of the ac conductivity measured at 398 K of NBR composites loaded with different filler concentrations of (a) MnO\(_2\) and (b) Fe\(_3\)O\(_4\) and irradiated at 50 kGy.
The variations of conductivity with temperature for different compositions are shown in Fig. 7. This figure shows that the conductivity increases up to a temperature of about 330 K. Further increase of temperature reduces the conductivity of ferrite samples. While, the conductivity values of the manganese dioxide samples tend to be almost constant after this temperature. The influence of temperature on conductivity can be explained by considering the mobility of charge carriers responsible for hopping. As temperature increases, the mobility of hopping ions also increases thereby increasing conductivity [25]. The electrons, which are involved in hopping, are responsible for electronic polarization in these ferrite's and manganese's. The decrease in conductivity at higher temperature can be due to the thermal expansion of NBR rubber. At higher temperatures, the NBR rubber density is reduced by thermal expansion and this reduces the conductivity [25].

**Mechanical properties:**

Figure 8 shows the mechanical properties of NBR composites loaded with different concentrations of ferrite and irradiated at 50 kGy, from this figure it can be seen that the values of tensile strength as well as hardness increase by increasing filler content. On the other hand, the values of elongation at break decrease by increasing the content of ferrite filler. This data indicate that the ferrite filler is considered as a reinforced filler for NBR rubber, and some type of adhesion occurs between ferrite filler and rubber matrix.
Figure 9 illustrates the effect of concentration of MnO$_2$ on the mechanical properties like; tensile strength, elongation at break and hardness of NBR composites irradiated at 50 kGy. The data obtained from this figure showed that the values of tensile strength increases with increasing filler content up to 100 phr, then it tends to decrease at higher content namely, 150 phr. In addition, the values of hardness increase sharply up to 150 phr of filler. Meanwhile, the values of elongation at break decrease by increasing the filler content. The data obtained for tensile strength may be explained also by the fact that the MnO$_2$ acts as a reinforcing filler in NBR matrix up to 100 phr, some type of chemical adhesion occurs between filler and rubber matrix during milling and pressing under heating and also by electron irradiation, results in increased cross-link density as shown in Fig. 10. On the other hand, the decrease in values of tensile strength at higher loading 150 phr may be due to agglomerates of filler, which act as nods and separate macromolecules from attaching with each other, leading to a decrease in the values of tensile strength at higher concentration of MnO$_2$ filler. Generally, the hardness increases by increasing the cross-link density, while the elongation decreases by increasing the latter.
**Fig. (9):** Tensile strength, elongation at break and hardness of NBR composites loaded with different concentrations of manganese dioxide and irradiated at 50 kGy.

**Fig. (10):** Modulus at 100% elongation of NBR composites loaded with different concentrations of filler MnO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub> and irradiated at 50 kGy.

**CONCLUSION**

The dc conductivity results indicate that the increase in filler (MnO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>) concentrations yielded a significant increase in the conductivity and lowering of the activation energy of the NBR rubber matrix. The ac electrical conductivity is directly proportional to the frequency.
shows an increase in conductivity with increasing frequency for both types of filler MnO$_2$ and Fe$_3$O$_4$. In addition, it has been observed that both dielectric constant and dielectric loss decrease exponentially with increasing frequency for all composites under investigation. This is ascribed to the decrease in electronic contribution and increase in dipolar contribution to the total polarizability. The dc/ac electrical conductivity proved that both types of filler are dispersed in the NBR matrix uniformly to form an interconnected conducting network. The mechanical properties of composites show that the tensile strength as well as hardness increase by increasing filler content MnO$_2$ and Fe$_3$O$_4$. This increase is attributed to the improvement of interfacial bonding between filler and NBR matrix.

REFERENCES

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