

The Order Addition Effect of Carbon Black/Graphite on the Electrical Properties of Rubber Composites

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ABSTRACT: Acrylonitrile-butadiene rubber (NBR) filled with two types of fillers [high abrasion furnace carbon black (C), and graphite (G)] is made to find out the effect of order addition of C and G on the electrical conductivity of the composites. The temperature and frequency dependence of the (dc and ac) conductivity and dielectric constants have been measured. The values of the thermal expansion and thermal conduction coefficient of NBR rubber lead to the difference in I - V characteristics between CB- and G-NBR rubber composites during the measurement. When graphite is first added to NBR, the electrical conductivity of (GC₂₀₋₂₀) matrix is larger than that of the (CG₂₀₋₂₀) matrix, whereas the carbon black is added first. At low temperature ($T < 90^\circ\text{C}$), the higher values of the dielectric constant (ϵ') for the sample GC₂₀₋₂₀ compared with that of the CG₂₀₋₂₀ sample is due to the conducting nature and structure of graphite, whereas the carbon

shows less crystallinity and conductivity than graphite. Opposite behavior is noticed at temperature higher than 90°C . The dc conductivity of all composites increases with increasing temperature exhibiting a positive temperature coefficient of conductivity (PTC σ). The conductivity at high temperatures region is controlled by the thermal excitation transport mechanism, whereas at low temperatures region is dominated by tunneling process. The increase in the value of dielectric constant (ϵ') with temperatures for the sample GC₂₀₋₂₀ compared with the sample CG₂₀₋₂₀ is due to the conducting nature and structure of graphite, and the carbon less crystalline than the graphite. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: dielectric properties; a.c conductivity; acrylonitrile-butadiene rubber; carbon black; graphite; processing sequences

INTRODUCTION

Polymers are used as insulators, but with suitable fillers their conductivity may be changed in a very wide range.¹ In some cases, the polymer matrix and the filler have a specific influence on composite conductivity.^{2,3} In recent years, composites with resistances close to those of metals have been produced by compounding with high conductive fillers (carbon black, graphite, and metal powder). Until now, polymer composites possessing semiconducting properties comparable with characteristic features of inorganic semiconductors have not been developed. The electrical conductivity has been generally shown to depend on the nature of the polymer, filler, and filler matrix interactions. The processing technique is the key factor in the determination of the physical

properties. Processing conditions, especially those involving considerable shear of the polymer-filler mixture, can have a greater effect on conductivity than major changes in the compounds.⁴ More attention has been focused on the relationship between the effects of structure of carbon black, graphite, and the conductivity of polymer composites. For rubber/carbon black composite, it is generally accepted that the bound rubber is divided into two components. The first is formed by the rubber/filler interactions around the filler (filler-gel),⁵ and the other is formed by crosslinking of rubber molecules during the mixing (rubber-gel).⁶ Nitrile butadiene rubber (NBR) has semiconducting properties, high resistance to environmental degradation, excellent resistance to acids and bases, good adhesion to metal, glass, and concrete, and good thermal stability.⁷ Carbon black (C) and graphite (G)-filled conductive polymeric composites have been used in aerospace industries, for flooring materials to dissipate static electricity charges, electromagnetic shielding material, in modern electrical components, and devices.^{8,9}

In this article, we report the preparation of NBR-filled C and G composites with the order of adding C and G filler is to improve the physical properties

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of polymers by a conventional roll-mill method. Where C has a high ability to form a continuous network in the polymer matrix and, hence, leads to higher conductivity. In addition, C exhibits no X-ray diffraction peaks and exhibits only an amorphous halo and quite dense. When compared, graphite gives strong X-ray diffraction peaks, indicating a high degree of "order" and a high level of X-ray diffraction determined crystallinity and exhibit considerable porosity.¹⁰ Another important property of carbon is a good thermal conductivity, which imparts to it a high level of resistance to thermal shock. Graphite has a huge specific area, high adsorptive capacity, and large occluded volume. It has strong appetite for nonpolar molecules.^{11,12} Understanding the chemical and physical nature of these factors, on the composite structure, helps greatly to evaluate and interpret the electrical conduction mechanism taking place in the composite bulk.¹³

Current-voltage (I - V) characteristics are very important electrical properties of CB-polymer composites.¹⁴ For most CB-polymer composites, the current does not vary linearly with applied voltage and temperature except at low field.^{15,16} There are many studies in the literature, which concern the dielectric and electric behavior of the polymer/CB or G composites above room temperature; the general result of these studies is that polymer/CB composites exhibit a positive temperature coefficient (PTC) of resistivity.¹⁷⁻¹⁹ All these studies concluded that polymer/CB composites behave electrically as semi-conducting materials above room temperature.^{20,21} This study deals with the effects of the order of insertion of two kinds of additives tested: synthetic graphite particles G and carbon black CB, into the NBR composite is very necessary for finding its suitable application. Dielectric constant, d.c., and, a.c., electrical conductivity have been determined with varying parameters the temperature and frequency and analyzed. The discussion which forms composites with both C/G and G/C suggests how the two structures, as present in polymer/filler systems, might be further analyzed to explain the phenomena.

MATERIALS AND METHODS

Composites preparation and properties

Acrylonitrile-butadiene rubber (NBR) (density 0.98 g/cm³ and acrylonitrile content 32%) was used as polymer matrix. High abrasion furnace (HAF) carbon black (29 nm particle size diameters, 45 m²/g surface area) and graphite (40 nm particle size diameter, density 2.1 g/cm³) were used as electrically conductive fillers. Other compounding ingredients like zinc oxide and stearic acid (activators), dibenz

TABLE I
The Ingredients of the Investigated NBR Rubber Composites

| Sample ingredients (phr) ^a | CG ₀₋₀ | CG ₂₀₋₂₀ | GC ₂₀₋₂₀ | CG ₄₀₋₀ |
|---------------------------------------|-------------------|---------------------|---------------------|--------------------|
| NBR | 100 | 100 | 100 | 100 |
| Stearic acid | 2 | 2 | 2 | 2 |
| Zinc oxide | 5 | 5 | 5 | 5 |
| HAF | 0 | 20 | 20 | 40 |
| Graphite | 0 | 20 | 20 | 0 |
| DOP | 10 | 10 | 10 | 10 |
| MBTS | 1.5 | 1.5 | 1.5 | 1.5 |
| TMTD | 0.5 | 0.5 | 0.5 | 0.5 |
| PBN | 1 | 1 | 1 | 1 |
| Sulfur | 2 | 2 | 2 | 2 |

^a Part per hundred parts of rubber.

thiazyl disulphide (MBTS) semi-ultra accelerator, phenyl-*b*-naphthyl-amine (PBN) antioxidant (melting point 105°C), dioctyl phthalate (DOP) as plasticizer, and sulfur (vulcanizing agent) were used and the vulcanization time 30 min at temperature 150°C. These materials were supplied by Bayer Company (Germany) and used as received. The formulations for the materials and order of mixing used in this work were compounded according to the recipe listed in Table I.

For the compounding, a home-made two-roll mixing mill (length 0.3 m, radius 0.15 m, speed of the slow roll is 18 rpm, and gear ratio 1.4) was used. The mixing occurred for 40 min at a temperature of 25°C. The compounded rubbers were compression molded into disks (diameter, 1 cm and thickness, 0.2 cm) using standard dies. The vulcanization was conducted under a heating press (KARL KOLB, Germany) at a pressure of $P = 0.40$ MPa. The optimum conditions of temperature and time were $T = 150^\circ\text{C}$ and $t = 30$ min. The vulcanized samples were shelf aged for 48 h before test. The mixing time and vulcanization conditions were fixed during compounding process for all samples. In this study, the composites are identified by an alphanumeric system. The first 2 letters represent the fillers used based in the rubber. The first number after the letters represents the first filler content; the second number indicates the second loadings of filler in the rubber. For example, CG₂₀₋₂₀ represents a 20/20 carbon black/graphite (20 phr) of conductive filler. All composite ratios described are related to percentage by weight.

DC electrical measurements

The current (I)-voltage (V) measurements were done at various temperatures from 303 to 423°K, using simple power supply (Pasco scientific model 1030A-USA) as voltage source, Keithley digital electrometer

model 616 (Keithley Inst.) for current measurements and Digi-sense temperature controller (R/S) Model 89,000-15 (Eutech Instruments) with On/Off or PID Control, and several modes in between, and temperature range from -99.9° to 999.9° (Resolution 0.1°). Before taking measurements, each sample was heated at 343 K for about 1 h to remove absorbed moisture. The specimens (diameter, 1 cm and thickness, 0.2 cm) with silver electrodes were sandwiched between two brass electrodes of a special home-made "sample holder" (multipurpose cell) for electrical measurements. The cell was calibrated in National Institute of Standards NIS-Egypt. This formed the metal-insulator (polymer)-metal (M-P-M) system, which was placed in the furnace. The electrical conductivity σ for the investigated samples was calculated using the equation.

$$\sigma = \frac{I d}{V A} \quad (\text{S/cm}) \quad (1)$$

where d is the thickness of the sample and A is its surface area (cm^2).

Dielectric and AC conductivity measurements

The permittivity (ϵ') of the investigated samples were measured using LCR-bridge (Hioki 3531z Hitester, Japan) with frequency range (50 kHz–1 MHz), which is fully computerized with guard electrodes; putted in furnace in the temperature range 25–150°C. Heating rate was kept constant at $1^{\circ}\text{C}/\text{min}$. The samples were in the form of disks of about 1 cm diameter and 0.2 cm thickness was cut from the molded plates. Relative permittivity was calculated by using the formula:

$$\epsilon_r = \frac{C d}{\epsilon_0 A} \quad (2)$$

where A (cm^2) is the area of the electrodes, d (cm) is the thickness of the sample, and C is the capacitance (pF). The A.C. conductivity ($\sigma_{a.c}$) was calculated using the relation:

$$\sigma_{a.c} = \omega \epsilon' \tan \delta \quad (3)$$

where $\epsilon' = \epsilon_0 \epsilon_r$, ϵ_0 is the permittivity of the free space ($8.85 \times 10^{-12} \text{ F m}^{-1}$), $\tan \delta$ is the dissipation factor, and ω is the angular frequency, which is equal to $2\pi f$.

RESULTS AND DISCUSSION

Current-voltage characteristics

The current-voltage (I - V) characteristics of pure NBR (0-0) C-G, (20-20) C-G of filled composites with

the order of insertion of two kinds of additives, and (40-0) C-G of filled composites have been investigated at temperatures between 303 K and 423 K and shown in Figure 1(a-d). These studies can provide useful information on the conduction mechanism.

The relationship between I and V for CB-polymer composites can be expressed as.²²

$$I = A V^B \quad (4)$$

where A and B are constants representing capability and property of the electrical conduction, respectively. In ohmic region, $B = 1$, and A is electrical conductance, which is usually expressed as A_0 . In nonohmic region, $B \neq 1$, and A has relevance to electrical conductance, which is usually expressed as A_N . Making a logarithmic operation into eq. (4) gives

$$\log I = \log A + B \log V \quad (5)$$

It can be found from eq. (5) that, in both ohmic and nonohmic regions, there is a linear relationship between $\log I$ and $\log V$ with slope equal to B .

Figure 1(a) illustrates the I - V curve of the individual NBR (CG₀₋₀) and shows a linear relationship for all temperatures, indicating an ohmic behavior. Log I versus log V plots of the CG₀₋₀ sample at different fixed temperatures have resulted in straight lines, which indicates the ohmic conduction ($B = 1$). For pure polymer, NBR is polar and has a high resistivity ($\sim 10^{10}$ ohm cm),²³ which lead to extremely low current. This tiny current results in insignificant self-heating in the whole measuring voltage and temperature ranges.

Figure 1(b-d) shows the I - V characteristics, at different fixed temperatures, of the investigated CG₂₀₋₂₀, GC₂₀₋₂₀, and CG₄₀₋₀ samples, respectively. At low temperatures ($\leq 70^{\circ}\text{C}$), it is found that the I - V of the C and G filled NBR vulcanizates show an ohmic behavior. However, at high temperatures ($> 90^{\circ}\text{C}$), a departure from linearity (Ohm's law) in the I - V curves is observed. The current values are below the straight line that stands for the extrapolated ohmic behavior. This observation can be explained. For conducting fillers loading less than or equal to the percolation threshold, little or very limited establishment of continuous conducting pathways through a test sample leads to the formation of some new conductive networks that were not previously contributing to the conduction of the system.

To determine the constant B of the conducting fillers, log I is plotted against log V in the nonohmic region, see Figure 2. It is found that B is smaller than 1 and decreases when graphite is first added to NBR, which are quite different from other kinds of CB-butylrubber¹⁵ or CB-polyethylene composites.²⁴ In nonohmic region, B is higher than 1 and tends toward 1 with the increase of CB loading.

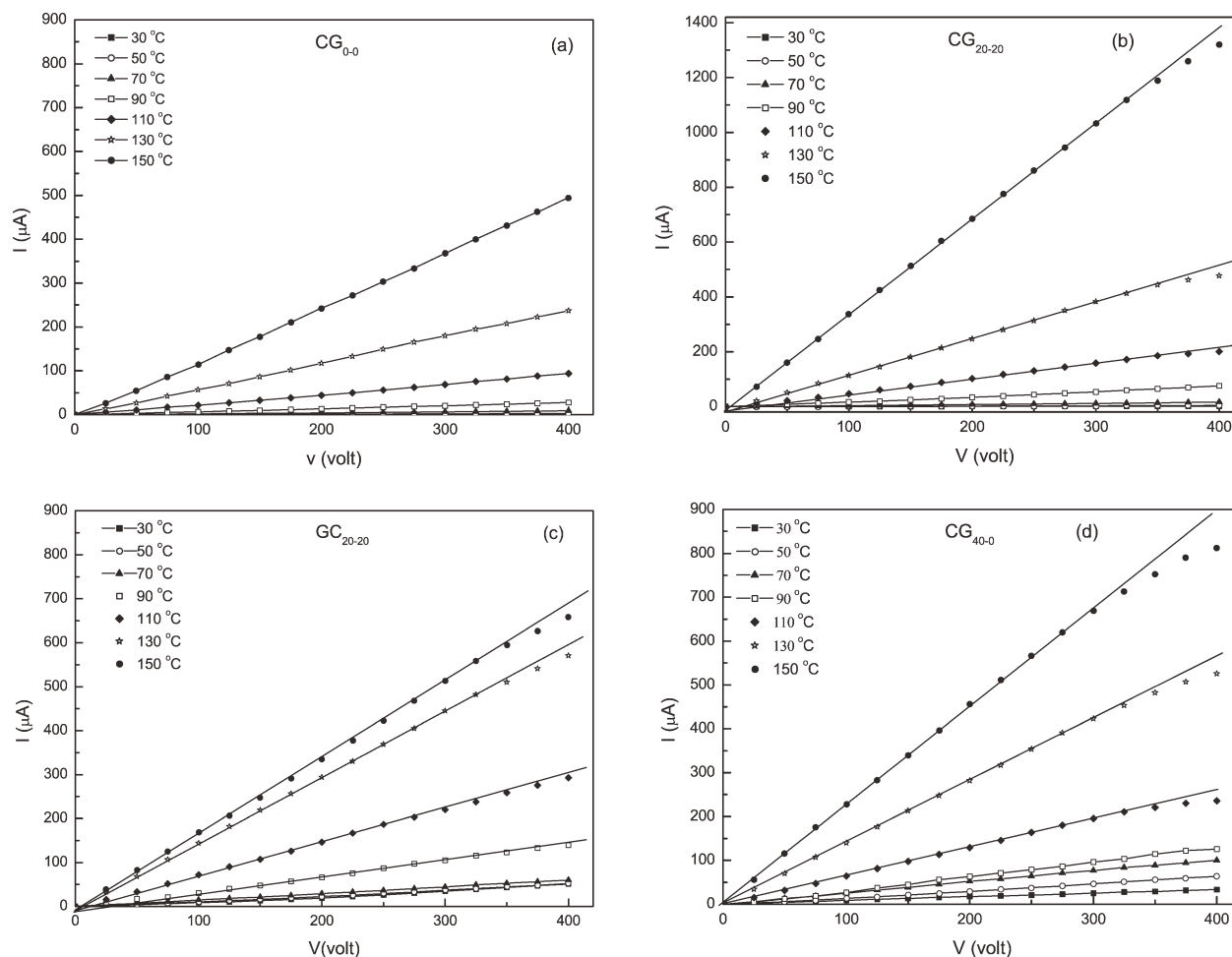


Figure 1 I - V characteristics for graphite/carbon-black filled (NBR) rubber samples: (a) CG_{0-0} , (b) CG_{20-20} , (c) GC_{20-20} , (d) CG_{40-0} .

The current flowing through the investigated CG_{20-20} , CG_{40-0} , and GC_{20-20} samples increases with increasing the applied voltage and temperature as shown in Figure 1. At relatively high voltage and temperature, the CG_{20-20} current is the highest value while GC_{20-20} shows a minimum value. The apparent thermal expansion coefficient of NBR, C and G can be responsible for creating different conducting path of CB or G aggregates in the composites, which lead to the above current variations. Then, the dominant conduction mechanism tunnels through the gap of CB aggregates, assisted by thermal fluctuations.^{25,26} Sheng et al.²⁷ showed that a special type of tunneling activated by thermal fluctuations of the electrical potential is suitable to CB-polymer composites. The conduction of these samples becomes nonohmic [$B < 1$] at certain high voltage where the resistance increases with increasing voltage and temperature. Therefore, it can be concluded that the unbalance between the heat generated and the heat lost is the main reason for nonohmic conduction of conductive NBR rubber.

The values of the thermal expansion and thermal conduction coefficient of NBR rubber lead to the difference in I - V characteristics between CB- and G-NBR rubber composites. This is also the reason for low current in the GC_{20-20} sample in compare with that of sample (CG_{20-20}), as shown in Figure 2, though the resistance of the second sample at room temperature is higher than that of the first one.

Temperature dependence of DC electrical conductivity

The effect of temperature on the conductivity of a conductive composite is rather complex. Various factors influence the variation of conductivity against temperature. To understand the dominant transport mechanism, the temperature dependence of conductivity was measured in the temperature range of 303–423 K. The obtained results for all the examined samples are plotted in Figure 3. It is seen that, at relatively low temperature range (303–343 K), the conductivity is slightly dependent on temperature. This

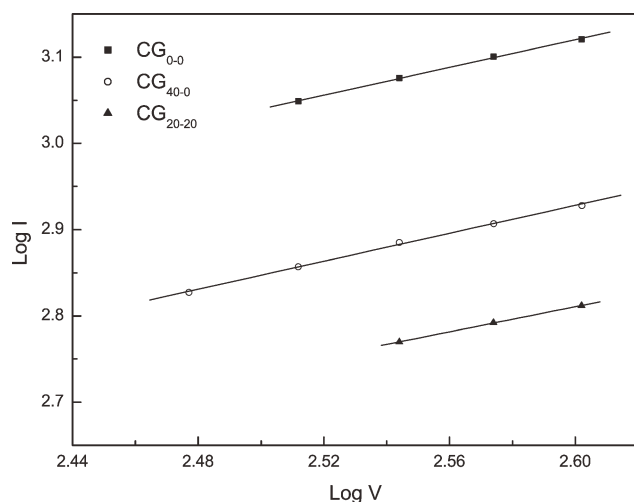


Figure 2 Log I versus log V for graphite/carbon-black filled (NBR) rubber samples: CG_{20-20} , GC_{20-20} , and CG_{40-0} in nonohmic region.

may be attributed to the direct contact of conductive aggregates, which resists the breakage as the rubber is thermally expanded. The conductivity begins to increase with rising temperature up to the highest measurement temperature of 423 K with positive temperature coefficient of conductivity (PTC) is attributed to the polymer chains and/or segments have sufficient mobility carriers. Therefore, the PTC phenomena can be related to the formation of conductive phases resulting from relaxation of the blend structure and the agglomeration of conductive particles. Generally, the conductivity increases with increasing temperature for all batches. The probable reason for this phenomenon could be explained in the following way. With increasing temperature, the rubber matrix expands which in turn decreases the gap width between CB or G particles. At high temperatures, the low viscosity of NBR (ML_{1+4} @ 100°C

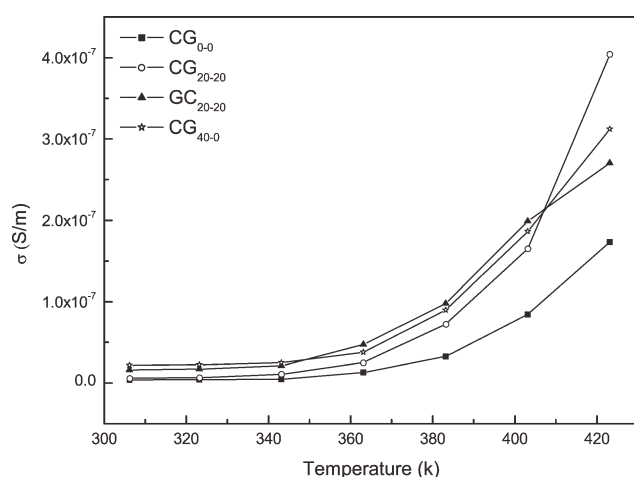


Figure 3 DC conductivity versus temperature for graphite, carbon-black filled (NBR) rubber.

= 51)²³ matrix was leading to increase diffusion of the charge carrier mobility within the NBR matrix. Therefore, the decrease in gap width and the increase of the charge carrier's mobility with temperature are responsible for increasing conductivity. It is interesting to note that the concentration of conductive filler depends on the base polymer matrix, mainly on its viscosity.²⁸ If the polymer matrix has higher viscosity the percolation limit for conductive filler to form a continuous conductive network is also higher, compared with a polymer with lower viscosity.

In general, the conductivity is thermally activated and varies exponentially with temperature. The activation energy (E_A) of the composite could be estimated with an Arrhenius relationship²⁹:

$$\sigma_{dc}(T) = \sigma_0 \exp\left[-\frac{E_A}{K_B T}\right] \quad (6)$$

where σ_0 is the pre-exponential factor, E_A is the activation energy, and K_B is Boltzmann's constant. The plot of $\ln \sigma$ against $1/T$ (K^{-1}) for all the examined samples is linear with a break at a certain temperature; that is, it has two linear portions as shown in Figure 4. The apparent values of activation energy (E_A) in various compositions have been calculated for two different ranges of temperature (calculated from the two slopes) and listed in Table II. The existence of two linear regions in Figure 4 is attributed to different mobilities of the charge carriers during the electrical conduction as it was previously reported.^{10,30} From their analytical standpoint, graphite gives strong X-ray diffraction peaks, indicating a high degree of crystallinity and exhibit considerable porosity. However, carbon does not exhibit diffraction peaks and shows only amorphous halo

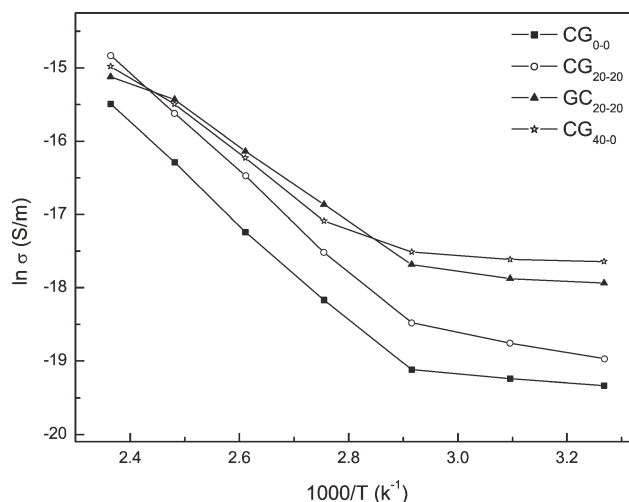


Figure 4 ln dc conductivity versus $(1000/T)$ for graphite/carbon-black filled (NBR) rubber.

TABLE II
The Calculated Values of Thermal Activation Energy for Samples

| Sample name | Low temperature region (I) E_a (eV) | High temperature region (II) E_a (eV) |
|---------------------|---------------------------------------|---|
| CG ₀₀₋₀₀ | 0.07 | 0.79 |
| CG ₂₀₋₂₀ | 0.14 | 0.62 |
| GC ₂₀₋₂₀ | 0.05 | 0.46 |
| CG ₄₀₋₀ | 0.03 | 0.55 |

and quite dense. Another important property of carbon, it has a better thermal conductivity than that of graphite. The values of activation energy are decreasing as the conductive filler added, which reflects the microstructure of the composites being a function of the mean radius of C or G particle "islands" and the mean interparticle separation.³¹ It is also found that, at high temperatures region, the activation energy value is comparatively higher than that at lower temperatures region. High E_A values, which are greater than kT , indicate that the conduction is due to thermal excitation of the charged carriers in the high temperatures region. In low temperatures region, the conductivity activation energy decreases to 0.037 eV, indicating that the transport mechanism could not be governed by the thermal excitation transport mechanism. Other possible transport mechanisms have been tested in the temperatures region and the conductivity data follow the relation

$$\sigma(T) = \sigma_o \exp \left[- \left(\frac{T_c}{T} \right)^Y \right] \quad (7)$$

where σ_o , T_c are constants and Y is a parameter which is related to the dimensionality by $Y = 1/(d_s + 1)$. The conductivity data fit a straight line only when $\ln \sigma$ values are plotted against $T^{-1/4}$. This result supports that the mechanism of conductivity is three-dimensional tunneling of electrons inside rubber matrix.³² To confirm the above fact, the hopping energy is calculated using the following equation:

$$\sigma T^{1/2} = \sigma_o \exp \left(\frac{E_h}{KT} \right) \quad (8)$$

The values of E_A and E_h are not the same for the studied composites, which indicates that the conductivity is controlled by tunneling process.

AC conductivity measurements

It has been reported that the processing sequence is one of the important factors that influence the electrical properties of C-filled polymer blends.^{33,34}

When C is initially blended to matrix, followed by the addition of the other filler (G), the electrical properties would vary with variation of the order of insertion of filler in the processing sequence factor. When graphite is initially mixed with monomers, the trends of results arise as a consequence of the following three factors: (i) increasing restriction in the mobility of NBR polymer chains due to enhanced degrees of filler-polymer interfacial interactions,³⁵ (ii) limited degree of possible chemical anchorage³⁶ of the segments of polymer on the active sites (such as $-\text{OH}$, $>\text{C}=\text{O}$, $-\text{COOH}$, etc.) of the filler particles, and (iii) more occlusion³⁷ of rubber chain segments into the void space of the porous conducting graphite particles. When followed by the addition of the carbon black, the interaction could not greatly change in the matrix.³⁸ Therefore, the primary particle which was added first to matrix was the basic conductive unit in the composites, and its conductivity was the upper limit value of the conducting composites. Indeed, some researchers^{8,39} have pointed out that the thickness of the adsorbed layer on the surface of a graphite particle varies with the structure of carbon black in polymerization. High structure graphite particles have thick adsorbed polymer layers, and the thin polymer layers are available for low structure carbon black particles.

The effect of temperature on dielectric constant (ϵ') of the investigated CG₀₋₀, CG₂₀₋₂₀, CG₄₀₋₀, and GC₂₀₋₂₀ samples has been determined in the temperature range, 30–150°C at constant frequency (100 kHz) as shown in Figure 5. It is observed that ϵ' for the unfilled sample remains constant with respect to temperature variation. This may indicate that the temperature does not affect the polarization anymore, or the direct contact of conductive aggregates, being completely separated by insulating matrix.

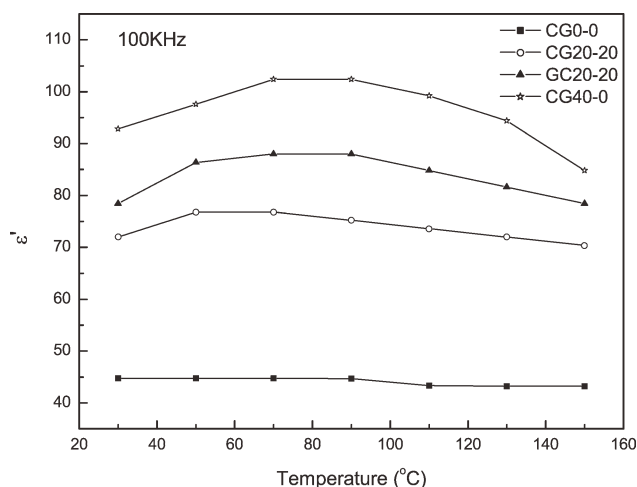


Figure 5 Variation of ϵ' with temperature for different composites at constant frequency (100 kHz).

The difference in the values of dielectric constant of the investigated CG_{20-20} , CG_{40-0} , and GC_{20-20} samples has increased as compared with pure sample CG_{0-0} , as well as the CG_{40-0} dielectric constant is the highest value, whereas CG_{20-20} shows a minimum value. At low temperatures ($\leq 70^\circ\text{C}$), it is found that the dielectric constant increases slowly of the C and G filled NBR with temperature. This suggests that when the temperature rises, the orientation of dipoles is facilitated. Psarras et al.⁴⁰ reported that the increase in temperature increased the dielectric constant due to increased segmental mobility of the molecules, which leads to an increase in dielectric constant. This can be explained in terms of a large number of dipoles (blocked at low temperature) relaxed at a certain temperature, which enhances the dielectric constant.⁴¹ This is similar to what is normally observed in polar polymer, such as NBR, where the specific volume of the polymer is temperature dependent, i.e., it increases with increasing temperature. As the temperature grows, the chaotic thermal oscillations of molecules are intensified and the order degree of their orientation is diminished, so the dielectric constant decreases, in other words this can be explained that at relatively high temperature the number of dipole segment per unit volume is lower due to the dilution of polymer matrix.⁴² Another interesting observation in dielectric constant (ϵ') versus temperature behavior of the sample CG_{20-20} and GC_{20-20} is that increase in the value of ϵ' for the sample GC_{20-20} than the sample CG_{20-20} . Nevertheless, the increase in ϵ' on adding graphite is due to the conducting nature of graphite as compared with C is less crystalline and thus less conductive.

The frequency dependent of the dielectric constant of the present samples has been also investigated.

The dielectric constant was less affected by the change in frequency for the pure sample. For other samples, the dielectric constant decreases as the frequency increases below 10^5 Hz, whereas above this frequency value, ϵ' remains nearly constant. It is found that the increase in ϵ' value is more pronounced, especially at lower frequencies, and may be due to the increase of the total polarization in polar dielectrics (dipolar, interfacial, and ionic polarization).⁴³ When the frequency is raised, the dipoles will no longer be able to rotate so rapidly that their oscillation will begin to lag behind those of the field. Therefore, the polarization will be decreased.

The effect of temperature on the dielectric loss (ϵ'') and conductivity ($\sigma_{ac} = \epsilon''\epsilon_0\omega$) of the investigated CG_{0-0} , CG_{20-20} , CG_{40-0} , and GC_{20-20} samples has been determined in the temperature range, 30–150°C at constant frequency (100 kHz) as shown in Figure 6(a,b). Because the conductivity was directly related to the dielectric loss, it will show the same behavior as that of dielectric loss. It is also obvious, from the

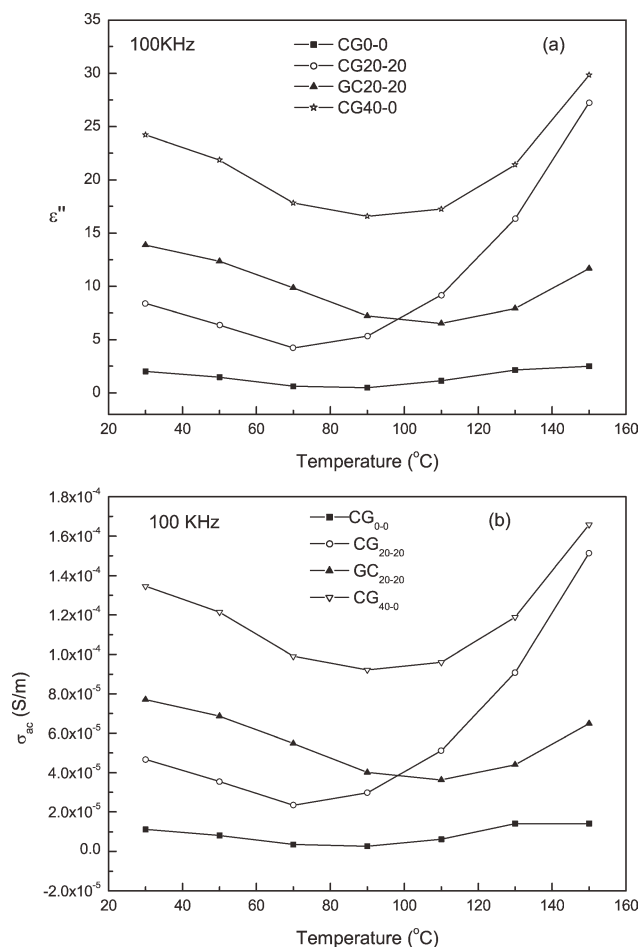


Figure 6 (a) Variation of ϵ'' versus temperature for different composites at constant frequency (100 kHz). (b) The AC conductivity (σ_{ac}) as a function of temperature for different composites at 50°C.

above figures, that the dielectric loss and conductivity of the CG_{40-0} sample are higher than the corresponding values of other samples. The ϵ'' is a measure of both the friction associated with changing polarization and the drift of conduction charges. The carbon black or graphite are a semiconductive material and does not work as dielectrics by itself. If it is covered with insulation materials, however, it shows a dielectric property by generating the space charge polarization at the interfaces. This can also be explained by Maxwell-Wagner-Sillars theory, which is to account for the dielectric loss due to the interfacial polarization of heterogeneous materials having the volume fraction of conductive filler lower than the percolation threshold.⁴⁴ The interfacial polarization can be more easily occurred at the lower frequency and/or with the number of interfaces between the C or G and matrix and, consequently, contribute to the improvement of dielectric properties of composite filled with Carbon black. As the frequency is increased, the time required for the interfacial charges to be polarized or for the dipoles

to be arranged is delayed.⁴⁵ The temperature dependence of ac conductivity at constant frequency 100 kHz for all samples, was studied from 30°C up to 150°C, and shown in Figure 6(b). From the figure, it is noticed that the conductivity values are shifted upward with increasing C or G and gradually decrease with increasing temperature up to 70°C, otherwise at high temperature region the conductivity would begin to increase.

CONCLUSIONS

The electrical conductivity of the G/C- and C/G-based rubber composites is dependent on the order of addition of the two tested additives: synthetic graphite particles G and carbon black C. It is concluded that when graphite (GC₂₀₋₂₀) is first added to an NBR matrix, the electrical conductivity increases more than when carbon black (CG₂₀₋₂₀) is first added. The high values of the dielectric constant (ϵ') for the sample CG₂₀₋₂₀ in compare with those obtained for the GC₂₀₋₂₀ sample are due to the conducting nature and crystallinity of graphite. The dc conductivity of all composites increases with increasing temperature (PTC σ) is mainly due to the difference in thermal expansion of rubber and filler. When graphite is first added to NBR, the electrical conductivity of (GC₂₀₋₂₀) matrix is larger than that of the (CG₂₀₋₂₀) matrix, whereas the carbon black is added first. The conductivity at high temperatures region is controlled by the thermal excitation transport mechanism, whereas at low temperatures region is dominated by tunneling process.

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