Electrical Conductivity and Electric Modulus of Stable Kevlar® Fiber Loaded HAF/NBR Rubber Composite

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ABSTRACT: DC, AC conductivities and dielectric properties of high abrasion furnace carbon black (HAF)/acrylonitrile butadiene rubber (NBR) composite have been studied with varying the aramide Stable Kevlar® fiber content, temperature, and frequency. Generally, the electrical conductivity was decreased with increasing Stable Kevlar® fiber content, which was confirmed by the positron annihilation lifetime spectroscopy. Negative temperature coefficient of conductivity (NTCC) behavior between 353 and 413 K was detected, except for the composite containing 10 phr Kevlar which showed positive temperature coefficient of conductivity (PTCC) behavior above 383 K. These NTCC and PTCC behaviors were further manifested by differential scanning calorimetry (DSC). For the composite with 10 phr Kevlar, the interfacial polarization between the fibers and the polymeric composite can be ascribed to Maxwell-Wagner-Sillars mechanism. The (MWS) relaxation disappeared for higher fibers content. The analysis of the electric modulus in the frequency range from 1 kHz to 1 MHz shows that the interfacial relaxation obeys Cole–Davison distribution of relaxation times. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 1359–1365, 2012

Key words: stable Kevlar®; fiber; rubber composites; ac conductivity; electric modulus

INTRODUCTION

Because of high specific stiffness and strength, Stable Kevlar® fiber is widely used in composite materials. Stable Kevlar® fiber reinforced composites have a wide range of industrial applications, for instance, in aircraft and space applications such as rocket motor casings and nozzles. Studies available in literature[1,2] have been done on the mechanical, microstructure properties, and adhesion force between Kevlar and polymers. In contrast, little attention has been given to the electrical and dielectric properties of Stable Kevlar® fiber–rubber composites.[3] The incorporation of conductive fillers such as carbon black[4–6] and carbon fibers[7] enhanced the electrical properties of the polymer composites. The electrical conduction process in conductive polymer composites is complicated and depends on a large number of parameters such as the filler (concentration, particle size, structure, filler–matrix interaction) and processing techniques.[8] The electrical conductivity of these conductive composites may increase with increasing temperature i.e., positive temperature coefficient of conductivity (PTCC) and/or decrease i.e., negative temperature coefficient of conductivity (NTCC).

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The remarkable (NTCC) effect was mainly observed for conductive filler-filled polymers and the (NTCC) effect is often followed by a (PTCC) effect with further increase of temperature.[9] The most common explanation for the (NTCC) effect is that as the melting temperature of the polymer is approached, conductive paths are broken due to a large thermal expansion of the polymer matrix. It is also well accepted that the (PTCC) phenomenon is due to the formation of the new conduction networks of carbon black particles when the viscosity of the polymer is sufficiently low at elevated temperatures.[10]

The presence of the (PTCC) effect and the poor reproducibility of conductivity over a long period of time have an adverse influence on the application of (NTCC) materials. Many researchers have proposed and developed methods to eliminate the (PTCC) effect and improve the stability of the conductivity, among these methods, either chemical or radiation crosslink could increase the viscosity of the polymer and produce a gel-like structure, thus leading to the stabilization of the CB distribution in the polymer melt.[11] There are several applications for the NTCC materials such as self controlled heaters, current limiters, over current protectors and sensors.[12] The PTCC materials can be used as electromagnetic and radio frequency interference shielding and electrostatic dissipation of charges.[13]

In polymeric composites, interfacial polarization is almost always present because of the different additives which make these systems heterogeneous. The interfacial polarization of the conductive polymeric

composites has been studied in terms of the electric modulus formalism.[14] An advantage of using the electric modulus formalism to interpret bulk relaxation properties is that variations in the large values of permittivity and conductivity at low frequencies are minimized. In this way, the difficulties caused by electrode nature and contact which appear to obscure relaxation in the permittivity presentation, can be resolved or ignored.

The positron annihilation lifetime spectroscopy (PAL) technique has been applied to microstructure determination in polymers, which gives direct information about the free volume size and concentration.[15,16] Doppler broadening profiles of the annihilation radiation (DPAR) give the electron momentum distribution at the site of annihilation characterized by the line shape parameter, *S*, and the wing parameter, *W*, corresponding to annihilation with valence and core electrons, respectively.[15] The aim of this work is to investigate the effect of short stable Kevlar® fiber on the electrical and dielectric properties of high abrasion furnace carbon black (HAF)/ acrylonitrile butadiene rubber (NBR) composite.

EXPERIMENTAL

Materials

The elastomer used in the present study was acrylonitrile butadiene rubber (NBR): acrylonitrile content 33%, specific gravity 1.17, supplied by JSR Corp. Tsukiji Chuo-ku, Tokyo, Japan. The product stable Kevlar® fiber (Kevlar 49 aramide fibers) supplied by the E.I. DU Pont de Nemours were used as filler which had the following properties: mean length of fibers 2 mm, diameter $\cong$ 14 μm and specific gravity 1.44.[17] To promote fibers/rubber adhesion, resorcinol with specific gravity 2.36; supplied by E. Merc, Mumbai, India has been used. High abrasion furnace carbon black, *N*-330 (HAF): Black granulated powder has a particle size of 40 nm and specific gravity 1.78–1.82.was used as conductive filler.

The composition of all samples in this work is expressed in part per hundred parts of rubber by weight (phr). The blend formulation contains NBR (100 phr), HAF (30 phr), ZnO (5 phr), stearic acid (1 phr), processing oil (10 phr), *N*-cyclohexyl-2-benzthiozyle sulfonamide (1.5 phr), resorcinol (10 phr) and different contents of Stable Kevlar® fiber up to 20 phr. The vulcanizing system used for these samples contains: elemental sulfur (1.5 phr); tetramethylthiuram disulfide TMTD (1 phr) and dibenzothiazyl disulphide MBTS (1.5 phr). The composites were prepared on a two-roll mill 170 mm in diameter with working distance 300 mm, speed of slow roll 24 rev min^{-1} and gear ratio 1.25. The rubber samples were left for at least 48 h before being vulcanized. The vulcanization process was conducted at 153°C ± 2°C under a pressure of 4 MPa for 20 min.

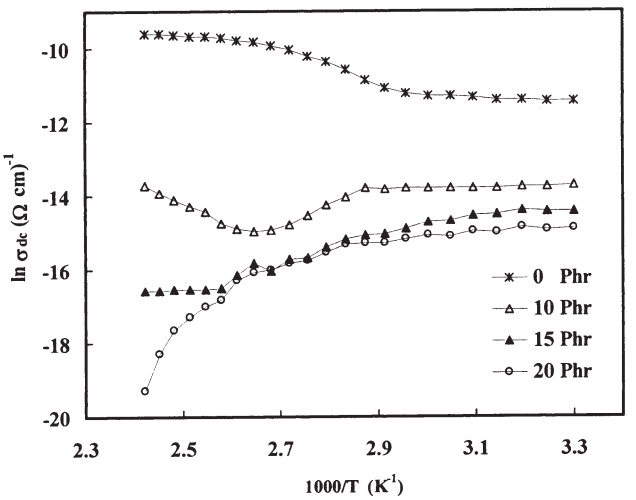

Figure 1 The temperature dependence of dc electrical conductivity for HAF/NBR composites loaded with different concentrations of Kevlar fiber.

Measurements

DC conductivity measurements were previously described.[18] AC conductivity and the dielectric properties were measured from room temperature up to about 420 K at different frequencies ranging from (1 kHz up to 1 MHz) using LCR meter (Hioki model 3532 "Japan"). The samples were in the form of disks 2-mm thick and 5 mm in radius. The DSC measurements were carried out from room temperature up to 430 K by using Shimadzu (50) differential scanning analyzer with a scanning speed of 5°C min^{-1}. in the microanalysis unit at the University of Cairo. The spectroscopic arrangements used for (PAL) and (DPAR) measurements were described previously elsewhere.[19,20]

RESULTS AND DISCUSSION

DC electrical conductivity

Figure 1 depicts the temperature dependence of the DC electrical conductivity of HAF/NBR rubber composites loaded with different concentrations of Kevlar fibber. It was found that at relatively low temperatures from 303 to 353 K, the conductivity is slightly dependent on temperature. This may be ascribed to the direct contact of carbon black aggregates, which resist breakage as the rubber is thermally expanded. On the increase of temperature above 353 K, the conductivity was decreased i.e., a negative temperature coefficient of conductivity has been noticed, which may be attributed to breakdown of the conducting network. This breakdown could be due to the relatively high differential thermal expansion of rubber matrix compared to the filler.[21] This breakage

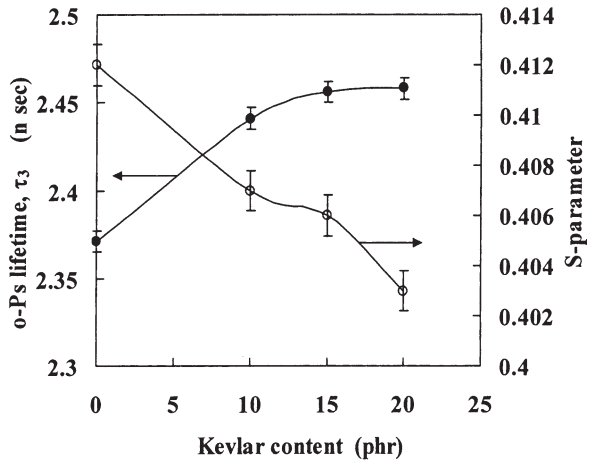

Figure 2 The o-Ps lifetime, τ_3 and the *S*-parameter as a function of the Kevlar fiber concentration.

of carbon aggregates results in an increase in gaps between the carbon particles or aggregates. So, the probability of carrier transfer is reduced. Furthermore, the conductive particles of HAF black may redistribute among the insulating Kevlar particles as the polymer expands. Both of the carbon structures breakage and the possibility of its redistribution decrease the number of conductive paths which was behind the reduction in the electrical conductivity. Besides, the conductivity decreases with increasing the concentration of stable Kevlar® fiber, which causes wider gaps between the conductive particles. Hence a barrier is created against the flow of charge carriers through the composite.

Figure 2 shows the *o*-Ps lifetime, τ_3 and the *S*-parameter as a function of the Kevlar concentration. The increase in τ_3 may be due to agglomeration of the fibers particles to form a lump that acts like a foreign body within the matrix. These lumps in-turn increase the number and the size of the free volume hole. As the size of the free volume hole increases, the positron has a lower chance of annihilation within the free volume, which is responsible for the increase in τ_3. Besides, the decrease in *S*-parameter with increasing stable Kevlar® fiber content might be attributed to the decrease of the valence (free) electron density by adding the insulator Kevlar inclusions. This decrease in the free electron density decreases the probability of trapping the free positrons in the polymer.[22]

AC electrical conductivity

Figure 3 shows the relation between ln(σ)ac and the reciprocal of absolute temperature (1000/*T*) at a frequency of 3 kHz. From this figure it is clear that, the dc and ac conductivity measurements for the composites loaded with 15 and 20 phr of stable Kevlar® fiber have nearly the same trend i.e., from 303 to 353 K, the conductivity is slightly dependent on temperature or constant and begins to decrease on increasing temperature above 353 K. On the other hand, at lower Stable Kevlar® fiber content (10 phr), a peculiar behavior was found above 383 K where the conductivity begins to increase with increasing temperature (PTCC). This PTCC behavior can be explained in the frame of some phenomena which may operate in the system. Flocculation of HAF-black particles leads to the formation of additional networks during heating. Electron emission between two black aggregates at high temperature is also another factor for the improvement of electrical conductivity. Air oxidation of the composite at high temperature also leads to the generation of some polar groups, which decrease the resistivity of the composites.[23] All these phenomena increase the conductivity with increasing temperature. The PTCC disappeared for the composites containing higher fibers content (15 and 20 phr). The relatively larger gaps between the conductive paths, arises from the distribution of Stable Kevlar® fiber in between them, thus suppressing most of the above phenomena responsible for PTCC effect.

Figure 4 represents the temperature dependence of the ac conductivity of some selected curves in the frequency range (1–500 kHz) for the sample containing 10 phr of stable Kevlar® fiber as representative example. It is clear from this figure that, as the frequency increases, ln (σ) increases. This may be explained as follows: the ac conductivity sums the dissipative effects including an actual ohmic conduction and the dielectric losses as a result an increase in the conductivity.[24] The data collected from the ac conductivity measurements were in harmony with

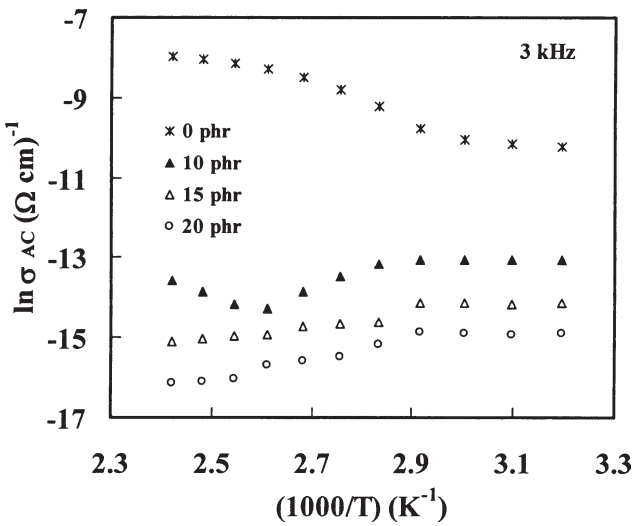

Figure 3 The temperature dependence of ac electrical conductivity for HAF/NBR composites loaded with different concentrations of Kevlar fiber at frequency of 3 kHz.

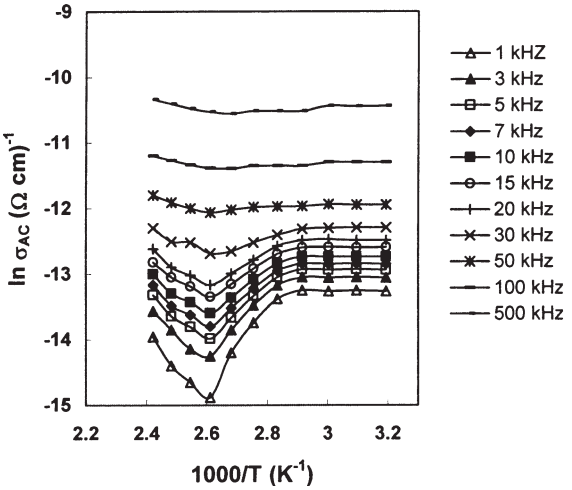

Figure 4 The temperature dependence of ac electrical conductivity for HAF/NBR composite loaded with 10 phr of Kevlar fiber at different frequencies.

the results of DSC technique. Figure 5 depicts differential scanning calorimetry thermograph of HAF/NBR composite loaded with 10 and 20 phr of stable Kevlar® fiber. It is clear that the heat flow variations with temperature show the same behavior as the ac conductivity. The thermal expansion for amorphous polymers and the redistribution of stable Kevlar® fiber substantially increase with rising temperature which increases the free volume.[25] This leads to an increase in the mean distance between neighboring chains, and hence, to an increase in the elastic constants related to the intermolecular interaction. As a result, both thermal conductivity and specific heat capacity decrease. However, the heat capacity increases with rising temperature above 390 K in the sample containing 10 phr of stable Kevlar® fiber

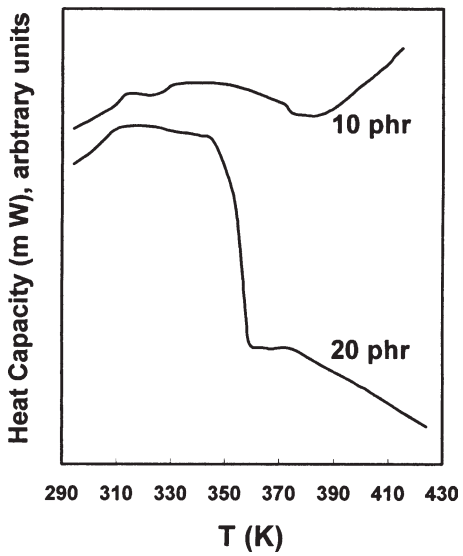

Figure 5 Differential scanning calorimetry thermograph of HAF/NBR composite loaded with 10 and 20 phr of Kevlar fiber.

TABLE I
Derived Values of the Activation Energy for Conduction E_c as a Function of Frequency

f (kHz)	E_c (eV)
1	0.42
5	0.29
10	0.26
20	0.24
50	0.12
500	0.09

because at high temperature the polymer undergoes degradation, resulting in main-chain scission, cross-linking, cyclization, and loss of volatile fragments.[26] Therefore, the DSC data support the results obtained from the conductivity measurements.

In the case of PTCC region, the temperature dependence of ac conductivity at constant frequency can be expressed as[27]:

$$\sigma_{ac} = B \exp(-E_c/k_B T) \quad (1)$$

where B is constant, E_c the activation energy for conduction and k_B is the Boltzmann constant. The calculated E_c values for the composite loaded with 10 of stable Kevlar® fiber in the temperature range from 383 to 413 K and different selected values of frequencies are listed in Table I.

The values of E_c decrease with increasing the applied frequency. This indicates that the applied field assists the redistribution and regrouping of the conductive particles which results in the lower activation energies for the conduction process. The slight temperature dependence and/or the decreasing conductivity with increasing temperature for composites with 15 and 20 phr of fibers mean that

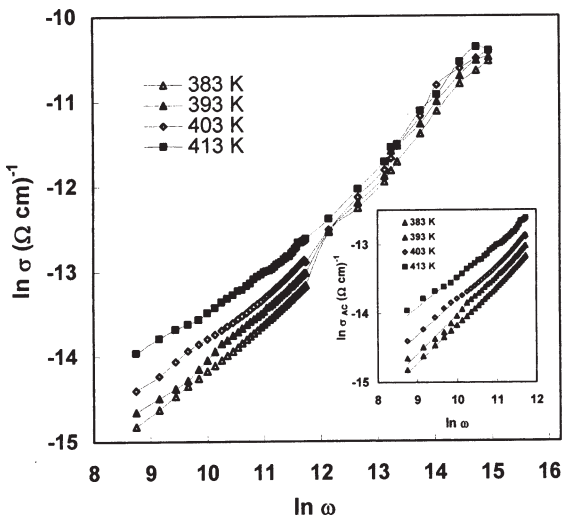

Figure 6 Variation of lnσ with lnω for the composite loaded with 10 phr of Kevlar fiber in the temperature range from 383 to 413 K. The inset is the magnification of the plots in the frequency range from 1 to 20 kHz.

TABLE II
The Calculated Values of the *s*-Exponent as a Function of Temperature

T (K)	*s*-exponent
383	0.57
393	0.55
403	0.52
413	0.45

the composites behave as metal and the conduction is therefore mainly due to direct contact between carbon black aggregates. On the other hand, for the composite containing 10 phr of Kevlar which shows (PTCC) above 383 K, the conduction mechanism is therefore suggested to be mainly due to thermal activation.

Figure 6 shows the variation of ln (σ_{ac}) with ln (ω) from 1 kHz up to 500 kHz for HAF/NBR composite loaded with 10 of Stable Kevlar® fiber in the temperature range from 383 to 413 K. It is clear from this figure that, as the frequency increases, ln (σ_{ac}) increases linearly and becomes slightly dependent on temperature. This behavior follows the universal power law:

$$\sigma_{ac} = A(T)\omega^{s(T)} \quad (2)$$

where the prefactor A(T) and s(T) are function of temperature. The slopes of the lines of ln (σ_{ac}) versus ln (ω) at different values of temperature represent the exponent term [$s(T)$; $0 \leq s \leq 1$] related to the conduction mechanisms. The calculated s values in the frequency range from 1 to 20 kHz are listed in Table II. It is clear that, the values of s decreased with increasing temperature. From this it can predicted that, the conduction mechanism is due to the classical hopping of electrons.[28]

Dielectric properties

Figure 7 shows the frequency dependence of the real, M', and imaginary, M'', parts of the electric modulus for the composite containing 10 phr of fiber at different temperature. It can be clearly seen that, the values of M' and M'' increase with frequency. At relatively low temperature in the range from room temperature up to 383 K, both M' and M'' values increased with increasing temperature. Meanwhile, an opposite trend was recorded above 383 K. Besides, above 383 K peaks in the values of M'' are

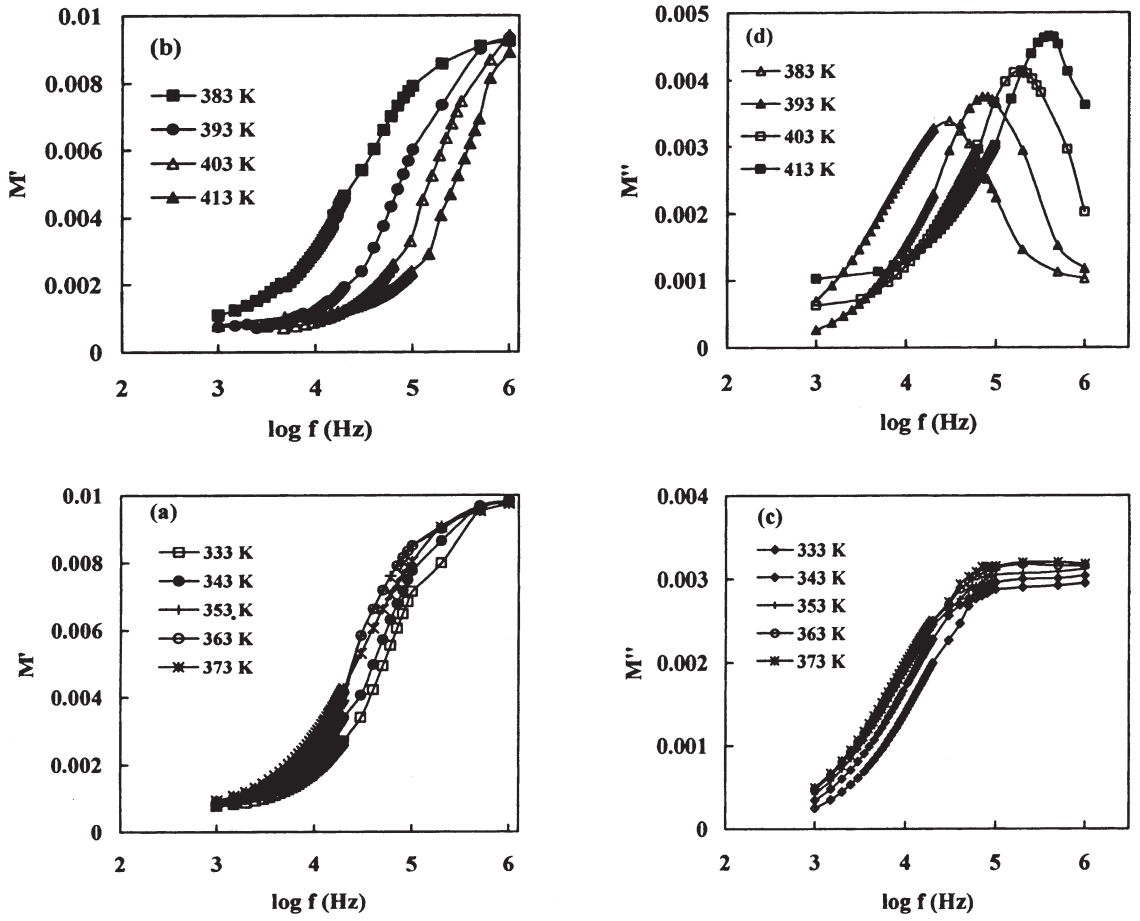

Figure 7 The real part of the electrical modulus M' versus log f (a and b) and the imaginary part of the electrical modulus M'' versus log f (c and d) for the composite containing 10 phr of fiber at different temperatures.

developed and shifted to higher frequencies on increasing temperature indicating a relaxation process which was attributed to MWS effects. Furthermore, the composites loaded with higher fiber content (15, 20 phr) exhibit no loss peak over all the temperature range.

Figure 8 represents the normalized plots of (M''/M''_{max}) versus log (f/f_{max}) for the composite containing10 phr of fibers over the temperature range from 383 to 413 K. It is clear that, the distribution of relaxation times is nearly the same over all the temperature range and has an asymmetric shape showing a certain deviation from the pure Debye behavior. This is significant evidence for the involvement of a single asymmetric distribution of relaxation times in this system.

The Cole–Davidson approach,[29] which anticipates an asymmetric distribution of relaxation times, was expressed in the electric modulus mode of the form.[3]

$$M' = \frac{M_\infty M_s[M_s + (M_\infty - M_s)(\cos\varphi)^\gamma \cos\gamma\varphi]}{M_s^2 + (M_\infty - M_s)(\cos\varphi)^\gamma[2M_s\cos\gamma\varphi + (M_\infty - M_s)(\cos\varphi)^\gamma]} \quad (3a)$$

$$M'' = \frac{M_\infty M_s(M_\infty - M_s)(\cos\varphi)^\gamma \sin\gamma\varphi]}{M_s^2 + (M_\infty - M_s)(\cos\varphi)^\gamma[2M_s\cos\gamma\varphi + (M_\infty - M_s)(\cos\varphi)^\gamma]} \quad (3b)$$

where M_s and M_∞ are the values of M' when ($\omega \to 0$) and ($\omega \to \infty$), respectively, ($0 \le \gamma \le 1$),$tg\varphi = \omega\tau$, $\omega_{max.}\tau = tg\left(\frac{1}{\gamma+1}\frac{\pi}{2}\right)$.

Figure 9 depicts the complex plane diagrams of the electric modulus for the experimental results (points) obtained and the solid lines show the theoretical data obtained by applying the Cole–Davidson function represented by [eq. (3)]. There is an agreement between the values obtained from the theoretical model and the experimental data. The fitting parameters are listed in Table III. It is clear that, the value of γ increases from 0.81 to 0.9 with increasing temperature indicating more homogeneity of the system. It is well known that, $\gamma = 1$ for the single relaxation time process i.e., showing optimum homogeneity, for pure Debye type of relaxation. The activation energy of the relaxation processes (E_m) can be estimated according to

$$\tau_m = \tau_o \exp(E_m/kT) \quad (4)$$

From the variations of τ_m with the reciprocal of absolute temperature ($1000/T$) reported in the inset of Figure 9, activation energy of 1.19 eV is obtained for this MWS relaxation process.

CONCLUSIONS

The effect of addition of Stable Kevlar® fiber on the electrical conductivity and dielectric properties of

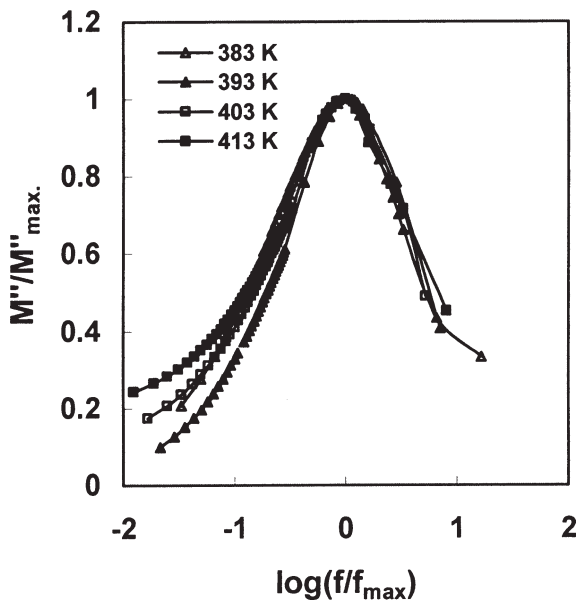

Figure 8 The normalized plots of (M''/M''_{max}) versus log (f/f_{max}) for the composite containing 10 phr of fiber over the temperature range from 383 to 413 K.

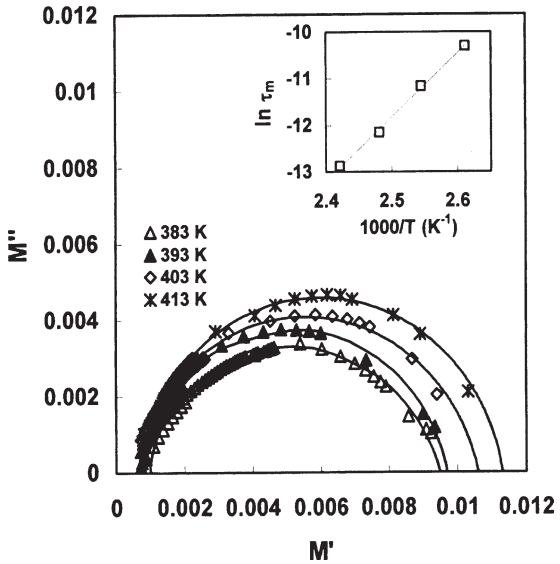

Figure 9 The complex plane diagrams of the electric modulus, points represent the experimental data and the solid lines represent the Cole–Davidson function [eq. (3)]. The inset is the variations of with the reciprocal of absolute temperature ($1000/T$).

TABLE III
The Fitting Parameters Used/Evaluated for the Cole–Davidson Function

Temperature (K)	M_S	M_∞	γ	τ_m (S)
383	1×10^{-3}	9.50×10^{-3}	0.81	3.34×10^{-5}
393	8×10^{-4}	9.71×10^{-3}	0.86	1.43×10^{-5}
403	8×10^{-4}	1.06×10^{-2}	0.87	5.27×10^{-6}
413	8×10^{-4}	1.13×10^{-2}	0.90	2.55×10^{-6}

HAF/NBR composite has been investigated at temperature and frequency ranges (303–413 K) and (1 kHz–1 MHz), respectively. The incorporation of stable Kevlar® fiber decreases the electrical conductivity which has been confirmed by the positron annihilation lifetime spectroscopy. The temperature dependence of conductivity showed an NTCC behavior which was attributed to the relatively high thermal expansion of rubber matrix compared to the filler and the possibility of redistribution of HAF-black particles among the insulating Kevlar inclusions. However, PTCC behavior has been observed for the composite containing lower fibers content (10 phr) above 383 K. These NTCC and PTCC effects were further manifested by differential scanning calorimetry. The dielectric behavior of the composites loaded with (10 phr) of stable Kevlar® fiber, above 383 K exhibits peaks in the values of M'' shifted to higher frequencies on increasing temperature indicating a relaxation process which was attributed to MWS effects. The composites loaded with Kevlar content above 10 phr exhibit no loss peak over all the temperature range. Furthermore, remarkable consistency has been noticed between Cole–Davidson function for the asymmetric distribution of relaxation times in the electric modulus mode and the obtained experimental data.

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