

Electrical response of microcellular EPDM rubber composites: complex dielectric modulus formalism and current–voltage characteristics

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Abstract Electrical response of conductive carbon black (Vulcan XC 72)-reinforced microcellular EPDM rubber composites has been studied as a function of variation in blowing agent and filler loading in the frequency range of 10–10⁵ Hz. The data was analyzed by dielectric modulus formalism. The examined system exhibit a strong dependence of dielectric modulus on the applied frequency. A gradual increase of real part of dielectric modulus with frequency is observed for all fillers and blowing agent loadings. The imaginary part of the dielectric modulus exhibited one relaxation peak with frequency at each filler and blowing agent loading. With increase in filler loading the peak shifts toward higher frequency whereas, with blowing agent loading the relaxation peak shifts toward lower frequency. The relationship between real and imaginary part of dielectric modulus shows a semicircular trend followed by a linear increase for all filler and blowing agent loadings. Hence, the presence of non-Debye type of relaxations has been confirmed. The effect of variations in filler and blowing agent loading on current–voltage characteristics has also been investigated. It is observed that with increase in filler and blowing agent loading, the nonlinearity of the curves increases and the point from which this nonlinearity starts decreases to lower voltage values. It is also observed that the electrical current is free from time when the measuring voltage is low. But as the applied voltage increase to 30 and 40 V, the electrical current changes with time.

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Introduction

Many materials being used in our daily life are composites, which often are made up of at least two constituents or phases. The outstanding the mechanical properties of many composites, and especially the unique combination of low density with high strength and stiffness, have led not only to extensive research but also to highly developed technologies [1, 2]. In comparison, relatively little attention was given to their other physical properties, which in parallel affected their use in electrical applications. The main advantage of composites is the ability to tailor materials for special purposes. Their applications are being evolved day by day through developments that lead to better precision in their manufacturing. The addition of fillers into polymeric materials imparts many advantages like improved mechanical, dynamic mechanical, and dielectric properties. Electrically, a reinforced composite is extremely heterogeneous, consisting of a dispersion of particles of a degenerate semiconductor in an insulating matrix.

The pace of research on thermal and dielectric properties of heterogeneous materials has accelerated in recent years. This is because electronics packaging has continuously provided the impetus pushing the development of new materials in a fascinating and rich variety of applications [1]. Carbon black and conductive carbon black-reinforced polymer materials have been extensively used as packaging substrates [2, 3]. Thermal properties and dielectric properties of the material used in plastic packaging play an important role in device performance. Materials for electronic packaging should have high thermal conductivity for dissipating heat generated in devices and match the coefficients of thermal expansion to that of silicon chips to reduce thermal failure. Both the dielectric constant ϵ' and the dielectric loss ϵ'' influence the signal carrying capacity and propagation speed of the device. In general, composites with low dielectric constant and low dielectric loss provide better device performance.

The effect of addition of conductive carbon black, Vulcan XC 72, and blowing agent on dynamic mechanical and dielectric relaxation characteristics of microcellular EPDM composites [4] has been reported. The effect of variation in Vulcan XC 72 loading and blowing agent loading (density) on dielectric characteristics like impedance, dielectric constant, and conductivity has also been studied [5]. Recently, dielectric properties of multi walled carbon nanotubes (MWCNTs)-reinforced butyl elastomer composites [6] have been studied. It has been demonstrated that the percolation thresholds for MWCNTs were lower than for carbon black and, more important, more than two orders of magnitude lower than theoretical values predicted by statistical percolation theory [7]. In this study, the dielectric data obtained was analyzed by electric modulus formalism. The study reports dielectric relaxation behavior microcellular EPDM rubber composites in the frequency range of $10\text{--}10^5$ Hz as function of Vulcan XC 72 loading and blowing agent loading. The effects of variation in filler and blowing agent loading on complex dielectric

modulus (both real and imaginary parts) have been studied. The relationship between real and imaginary part of complex dielectric modulus (Argand diagram) has also been studied for both solid and microcellular composites. In addition, the current–voltage relationship has been studied.

Experimental

Materials

An oil extended EPDM rubber [ENB (ethylene–norbornene) wt%—7.5, oil 20 phr, Mooney viscosity 53 (at 150 °C) manufactured by DSM Elastomers, Singapore] was used. The conductive filler used in this study was Vulcan XC 72 supplied by Cabot Corporation Ltd., USA. The curative used was the dicumyl peroxide (DCP) with a purity of 98%, manufactured by Aldrich Chemical Company, USA. The blowing agent used was azo di carbonamide (ADC-21), manufactured by High Polymer Lab, India and Paraffinic oil used was Sunpar oil, supplied by Sun Oil Company Pvt. Ltd., Kolkata.

Sample preparation

The rubber was compounded with the ingredients according to the formulations of the mixes given in Table 1 and blowing agent was added at the end. Compounding was done in a laboratory size two-roll mixing mill at room temperature according to ASTM D3182. Cure and blowing characteristics of the compounds were determined in a Monsanto Rheometer, R-100. The composites were press molded at 160 °C to 80% of their respective cure times to obtain a closed cell microcellular sheet. The pre-cured sheet was then post-cured at 100 °C (for 1 h) to complete the curing. From the sheets, a fixed circular size sample of sheet thickness was cut for dielectric measurements.

Testing

Dielectric relaxation spectra

Dielectric relaxation spectra of the composites were obtained by a Hioki HiTester LCR meter in the frequency range of 10–10⁵ Hz using aluminum foil as blocking

Table 1 Formulations of unfilled and Vulcan XC 72-filled EPDM composites

Mix no.	EPDM	Vulcan XC 72	Paraffinic oil	ADC 21
G ₀	120	0	0	0
EB ₁	120	20	2	0
EB ₂	120	40	4	0
EB ₃	120	40	4	2
EB ₄	120	40	4	4
EB ₅	120	40	4	6
EB ₆	120	60	6	0

Note Each mix contains ZnO—5 phr; stearic acid—1.5 phr, and DCP—1 phr, 120 phr of rubber includes 20 phr of oil

electrodes. The complex dielectric modulus (M^*) have been calculated from the dielectric parameters like dielectric permittivity (ϵ') and dielectric loss (ϵ'') using the following relations [8]:

$$M^* = \frac{1}{\epsilon^*} = \frac{1}{\epsilon' - i\epsilon''} = \frac{\epsilon'}{(\epsilon')^2 + (\epsilon'')^2} + i \frac{\epsilon''}{(\epsilon')^2 + (\epsilon'')^2} = M' + iM'', \quad (1)$$

where M' is real part and M'' imaginary part of complex electric modulus and $i = \sqrt{-1}$. Based on the above equation the dielectric data can be represented as $M'(\omega)$ and $M''(\omega)$ instead of $\epsilon'(\omega)$ and $\epsilon''(\omega)$, respectively. ω denotes an angular frequency, i.e., $2\pi f$ and f is measured frequency in Hz.

Note that in Eq. 1, $\epsilon' = C_p/C_0$, C_p is the measured capacitance of the sample and C_0 is the vacuum capacitance of the cell and is calculated using a relationship $\epsilon_0 A/d$ (where A is the area of the sample and d is the thickness of the sample). The dielectric loss in Eq. 1 is given in a form, $\epsilon'' = \epsilon' * \tan\delta$, where $\tan\delta$ is the dielectric loss tangent.

Scanning electron microscopy (SEM)

Morphology of the compounds has been studied using JEOL JSM 5800 Scanning Electron Microscope, after auto sputter coating of the sample surface with gold. The SEM photomicrographs of razor cut surface of 40 phr Vulcan XC 72-reinforced microcellular EPDM composites are shown in Fig. 1. From the figure, it can be observed that with blowing agent loading average cell size decreases and cell density increases.

Results and discussion

Complex dielectric modulus

Electrical response of the samples can be analyzed in terms of complex dielectric modulus formalism, which provides an alternative approach based on polarization

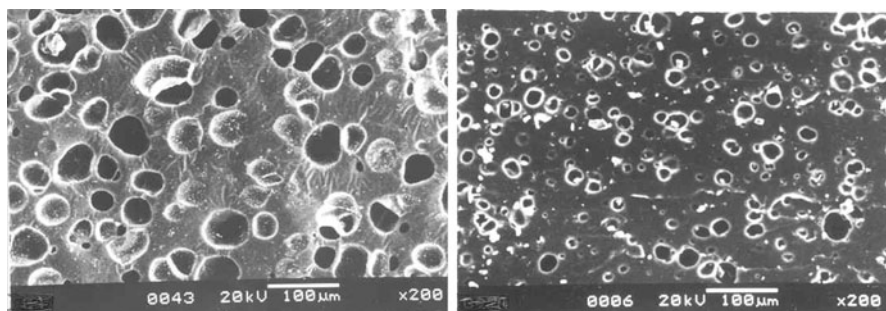


Fig. 1 SEM photomicrographs of razor cut surfaces of 40 phr Vulcan XC 72 reinforced, 4 and 6 phr blowing agent (left to right)-loaded microcellular EPDM composites

analysis. Complex impedance spectrum gives more emphasis to elements with the largest resistance, whereas, complex dielectric modulus plots highlight with smallest capacitance. Using the complex dielectric formalism the inhomogeneous nature can be probed into bulk and grain boundary effects, which may not be detected from complex impedance plots. The other advantage of the dielectric modulus formalism is that the electrode effect can be suppressed.

Real part of complex dielectric modulus

Figure 2 shows the variation of real part of complex dielectric modulus (M') as a function of frequency. A gradual increase of real part of complex dielectric modulus with frequency is observed for all Vulcan XC 72 loadings. It is characterized by a very low value M' in the low-frequency region. A continuous dispersion with increase in frequency has a tendency to saturate at a maximum asymptotic value in the high-frequency region for all filler loadings. Such observations may possibly be related to a lack of restoring force governing the mobility of charge carriers under the action of an induced electric field. This behavior supports the long-range mobility of charge carriers. Further, a sigmoidal increase in the value of M' with increasing frequency approaching ultimately maximum value may be attributed to the conduction phenomenon due to the short range mobility of charge carriers. With filler loading electric modulus increases and attains saturation at higher loading, which indicates (i) electrode polarization makes a negligible contribution to M' and (ii) dispersion is mainly due to conductivity relaxation.

Figure 3 shows the variation of M' as a function of frequency at various blowing agent loading. At low blowing agent loading the frequency independent and dependent region are observed but with increase in blowing agent loading M' value continuously increases with frequency may be due to increase in ac conductivity,

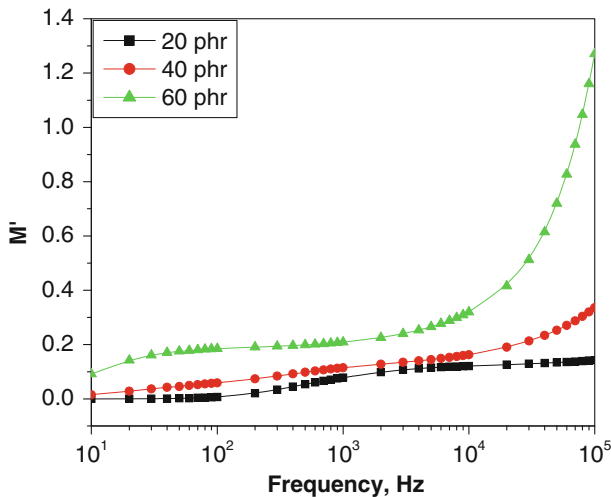


Fig. 2 Variation of real part of complex dielectric modulus (M') with frequency in Vulcan XC 72-reinforced EPDM rubber composites

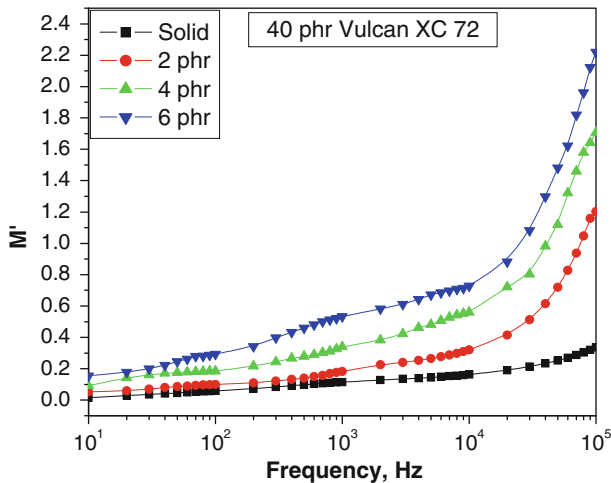


Fig. 3 Variation of real part of complex dielectric modulus (M') with frequency in 40 phr Vulcan XC 72-reinforced microcellular EPDM rubber composites

which can be attributed toward increase in filler–filler contact due to enclosed gas pressure.

Imaginary part of complex dielectric modulus

Figure 4 shows the variation of the imaginary part of the complex dielectric modulus (M'') with frequency at different Vulcan XC 72 loadings. In the accessible frequency range, the spectrum exhibits one relaxation peak for each filler loading. It is observed that the value of $\tan\delta$ decreases with an increase in filler loading. Decrease in the $\tan\delta$ is due to the reduction of chain mobility in the amorphous phase. The peaks shift systematically toward higher frequencies with increase in Vulcan XC 72 loading. For 20, 40, and 60 phr loading, the peak is observed at 10, 70, and 500 Hz, respectively. The broadening of the peak indicates the spread of relaxation time with different (mean) time constants, and hence a non-Debye type of relaxation in the materials is observed.

Figure 5 illustrates that, in case of microcellular composites, at 40 phr Vulcan XC 72-reinforced microcellular composites, the peak shifts toward lower frequency and shows higher value of $\tan\delta$ with blowing agent loading. The higher loss tangent value at higher blowing agent loading can be attributed toward induced strain by decomposed gas pressure on the cell membrane [9], which causes free intermolecular movement. Hence shifts toward lower frequency. The nature of this process is further explored using the Argand diagram (complex plane representation) for dielectric modulus.

Argand diagram

The relationship between the real part (M') and imaginary part (M'') of dielectric modulus so-called Argand diagram for all Vulcan XC 72 and blowing agent

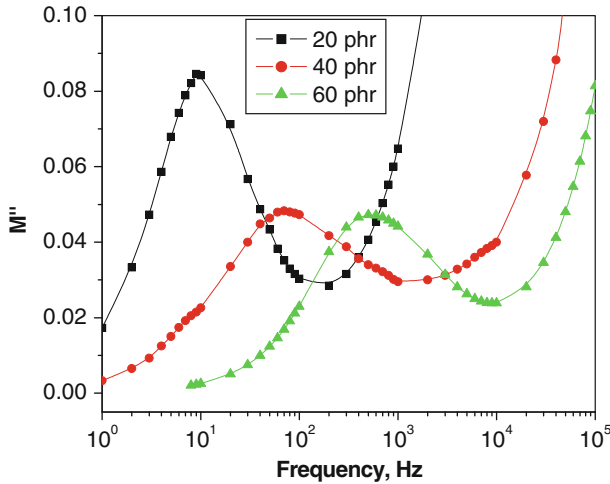


Fig. 4 Variation of imaginary part of complex dielectric modulus (M'') with frequency in Vulcan XC 72-reinforced EPDM rubber composites

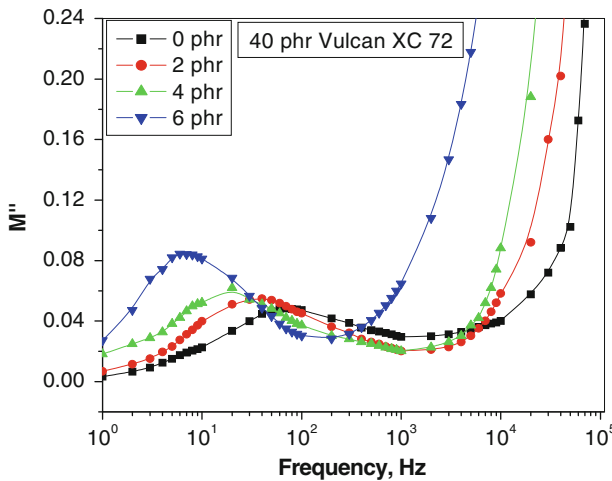


Fig. 5 Variation of imaginary part of complex dielectric modulus (M'') with frequency in 40 phr Vulcan XC 72-reinforced microcellular EPDM rubber composites

loadings are shown in Figs. 6, and 7, respectively. A semicircular trend (a requirement for non-Debye model) followed by a linear increase (in the low-frequency region) is observed for all loadings. The presence of single depressed arcs in the spectra indicates the existence of single relaxation time in such materials. As $M^*(\varepsilon) = 1/\varepsilon^*$, the semicircular arc in the complex electric modulus plot corresponds to the highest capacitance. It is observed that with increase in Vulcan XC 72 loading the size of the semicircular loop increases which confirms better conduction. One can see that the highest capacitance occurs at 60 phr Vulcan XC 72 loading, which

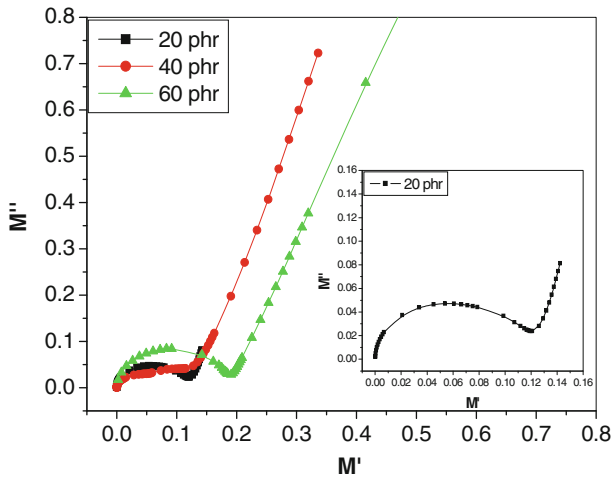


Fig. 6 Argand diagram (M' vs. M'') of complex dielectric modulus in Vulcan XC 72-reinforced EPDM rubber composites

implies that a dielectric anomaly may appear at higher loadings. In case of microcellular composites, as shown in Fig. 6, with blowing agent loading higher capacitance is observed. This can be attributed toward increase in filler–filler contact due to enclosed gas pressure. At higher blowing agent loading the decomposed gas pressure increases inside the cell. In this manner, it causes the filler particles to move closer to each other. This shortened gap between the filler particles reduces the “mean free path” for the electron transport thereby increasing the capacitance [10]. However, the semicircular trend of the plot in both solid and microcellular composites indicates the nonlinear nature of the polymer composites. Hence, the presence of a non-Debye type of relaxations has been confirmed by complex dielectric modulus analysis.

Current–voltage (I – V) characteristics

Effect of filler loading on I – V characteristics

Though many reports have been reported on the nonlinear properties in solid carbon black filled systems, no studies have been conducted in microcellular composites. In this study, the I – V characteristic of EPDM composites has been studied as a function of variation in filler and blowing agent loading. Figure 8 shows the relationship between the current and voltage characteristic of solid EPDM composites at increasing filler loadings. It can be observed that with increase in filler loading, the nonlinearity of the curves increases. For the samples loaded with the filler below the percolation threshold (40 phr), the current density flowing through them is extremely low, and the composites behave as insulators. But, as the filler loading is increased to 60 phr, the nonlinearity in the I – V characteristics changes to lower applied voltage. This phenomenon can be explained by the

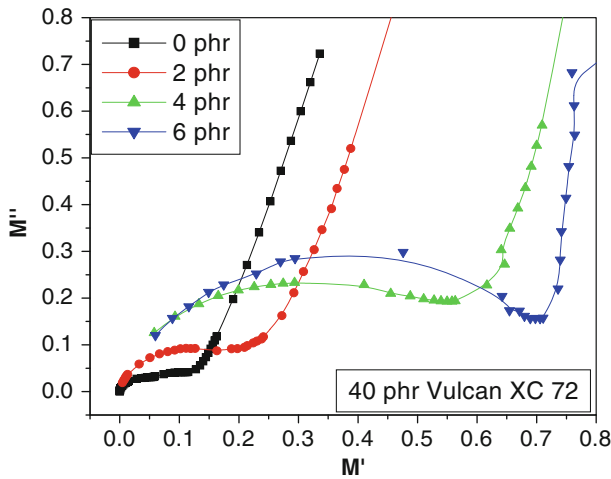


Fig. 7 Argand diagram (M' vs. M'') of complex dielectric modulus in Vulcan XC 72-reinforced microcellular EPDM rubber composites

“tunneling-hopping” mechanism of electrical conductivity. Increasing filler loading of the filler leads to formation of a continuous network which favors the electron transport through the polymer layers by tunneling [11]. This is because it magnifies the electrical fluctuations. These fluctuations lower the potential barrier established by the polymer between filler aggregates. This phenomenon promotes the decrease of the composite resistivity, because the electrons also can be transported through some zones of the matrix and not through the percolative mass only [12].

The relationship between current (I) and voltage (V) for filler–polymer composites can be expressed as:

$$I = AV^B \tag{2}$$

where A and B are constants representing capability and property of electrical conduction, respectively. In ohmic region, $B = 1$, and A is electrical conductance, which is usually expressed as A_0 . In the non-ohmic region, $B \neq 1$, and A has relevance to electrical conductance, usually expressed as A^N . Taking a logarithmic operation in Eq. 2 yields,

$$\text{Log}(I) = \text{log}(A) + B \text{log}(V). \tag{3}$$

Equation 3 denotes that, in both ohmic and non-ohmic regions, there is a linear relationship between $\text{log } I$ and $\text{log } V$. However, the nonlinearity was observed due to strong function of filler loading.

Effect of blowing agent loading on I–V characteristics

Figure 9 shows the I – V characteristics of microcellular EPDM composites reinforced with 40 phr Vulcan XC 72 at increasing blowing agent loadings. With decrease in density (increasing blowing agent), the nonlinearity in the I – V curves

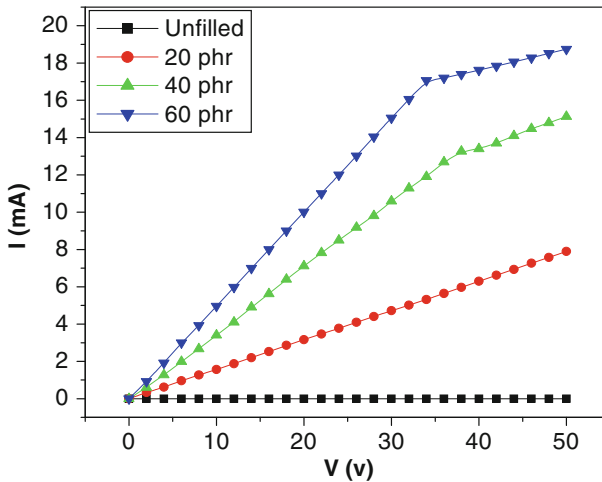


Fig. 8 Current–voltage (I – V) characteristics of Vulcan XC 72-reinforced EPDM rubber composites at increasing filler loadings

increase and the point from which this nonlinearity starts also decreases to lower voltage values. This is a significant observation and can be explained on the basis of increasing packing density of the filler with increasing blowing agent loadings. Generally, two kinds of I – V nonlinearity can be distinguished: irreversible electrical failures occurring due to application of high voltage (V , the so-called dielectric breakdown) or current (I) and reversible nonohmic (nonlinear) electrical conduction when the applied bias voltage is not very high [13]. Carbon black filled composites are known to exhibit both these types of behavior. When the applied voltage increases above a critical point termed as “breakdown voltage” the composite becomes typically nonlinear. The occurrence of this nonlinearity is dependent on a wide range of properties which includes (i) filler characteristics like filler size, the extent of loading of filler in the matrix, nature, and extent of chemical sites on the filler surface and (ii) the polymer characteristics like type of polymer, the level of interactions between the filler and the polymer matrix etc. [14].

Time dependence of current at constant voltage

The time dependence of electrical current flowing in a 40 phr Vulcan XC 72 reinforced solid and 4 phr blowing agent added EPDM vulcanizates is shown in Fig. 10. The electrical current is free from time (t) when the measured voltages are low (10 and 20 V) for both solid and microcellular composites. But as the applied voltage increases to from 30 and 40 V, the electrical current changes with time. At the instant of loading ($t = 0$), the current reaches the maximum value, which is named I_0 . Then, the current flowing through the sample decreases consequently until it reaches a steady value of I_e . It can be observed that the value of I_0 and I_e increases with the applied voltage in both solid and microcellular composites.

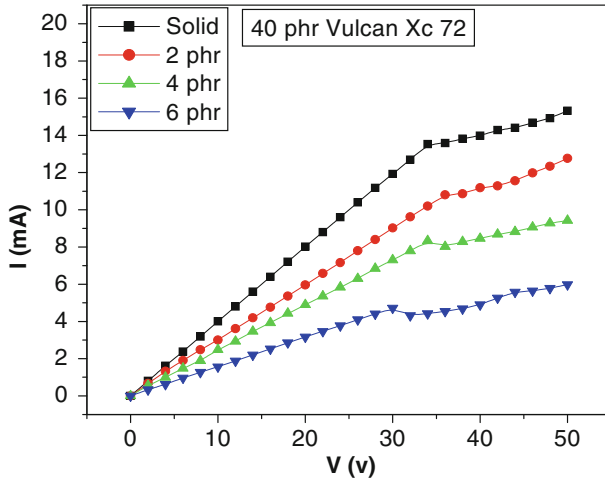


Fig. 9 Current–voltage (I – V) characteristics of 40 phr Vulcan XC 72-reinforced microcellular EPDM rubber composites at increasing blowing agent loadings

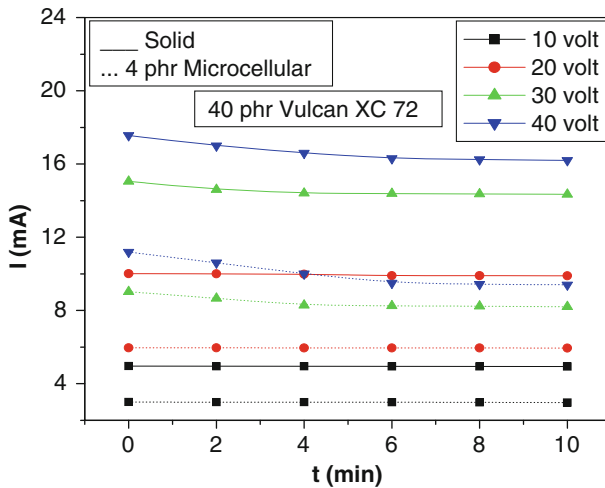


Fig. 10 Variation of current (I) with time (t) in 40 phr Vulcan XC 72-reinforced EPDM solid and 4 phr blowing agent-loaded microcellular composites

Conclusions

The dielectric relaxation behavior of Vulcan XC 72-reinforced solid and microcellular EPDM composites has been studied as a function of variation in blowing agent loading and filler loading. A sigmoidal increase in real part of dielectric modulus with increasing frequency approaches ultimately a maximum value. Imaginary part exhibits separate relaxation peak for all filler and blowing agent

loadings. The broadening of the peak indicates the spread of relaxation time with different (mean) time constants. The Argand diagram (complex plane representation) for dielectric modulus shows semicircular trend in both solid and microcellular composites, indicating the nonlinear nature of the polymer composites. Hence, the presence of a non-Debye type of relaxations has been confirmed by complex dielectric modulus formalism. The current–voltage characteristics also show nonlinear relationship due to strong function of filler and blowing agent loading. Time dependence on electrical current shows that at low voltage, current is free from time, however, as the applied voltage increases, current changes with time.

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