

# Dielectric Studies of Conductive Carbon Black Reinforced Microcellular Ethylene–Propylene–Diene Monomer Vulcanizates

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**ABSTRACT:** The alternating-current and electrical conductivity of conductive, carbon black reinforced, microcellular ethylene–propylene–diene monomer vulcanizates was measured in the frequency range of 100 Hz to 1 MHz. The effects of variations in the filler and blowing-agent loadings on the dielectric constant and percolation behavior were studied. The phenomenon of percolation was examined on the basis of measured changes in the electrical conductivity and morphology of composites with different concentrations of the filler. Scanning electron microphotographs showed the agglomeration of the filler above these concentrations and the formation of a continuous network structure. The experimental results were not in agreement with

the predictions of the statistical percolation theory; this deviation was explained in light of the formation of an interphase or mesostructure in the composites. The variation of the dielectric constant with the filler and blowing-agent loadings was explained on the basis of polarization of the filler in the polymer matrix. Additionally, the use of dielectric mixture laws in describing the dielectric constants of both solid and microcellular composites was investigated. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 192–204, 2007

**Key words:** blowing agents; dielectric properties; rubber; vulcanization

## INTRODUCTION

Conductive polymer composites are prepared by the incorporation of electrically conductive fillers into the polymer matrix. These composites have recently received considerable attention because of their technological importance in a wide variety of applications, such as electrostatic charge dissipation materials in pressure-sensitive sensors, transducers, electromagnetic interference shielding materials, and packaging materials in electronics, aircraft, and telecommunications. They are also used as antistatic materials in low-temperature heaters, in energy storage devices such as batteries, fuel cells, and supercapacitors, and in hybrid power sources. Among available fillers, excess conductive carbon black (Vulcan XC 72, Cabot Corp., Ltd.) has been used because of its ability to impart high electrical conductivity to insulating polymers at relatively low filler contents. The electrical and dielectric properties of polymer composites filled with conductive carbon black have been studied by many researchers.<sup>1</sup> The dielectric relaxation of carbon–silica dual-phase filler reinforced chlorobutyl vulcanizates has been studied

very recently.<sup>2</sup> Dielectric and alternating-current (ac) conductivity studies on ionically conducting, plasticized, polymer-composite poly(ethylene oxide) films have already been reported.<sup>3</sup> Ethylene–propylene–diene monomer (EPDM) rubber, filled with excess conductive carbon black, has good aging and weathering properties as well as good electrical properties.<sup>4</sup> The electrical properties of EPDM and blends of EPDM with polyethylene vinyl acetate have already been reported with the incorporation of conductive carbon black and short carbon fibers.<sup>5</sup> The dielectric properties of polymeric foams were studied by Stutov and Chaikin.<sup>6</sup> The dielectric properties of polystyrene foams and their blends in the X-band microwave region were studied by Chaki and co-workers.<sup>7–10</sup> Closed-cell, microcellular EPDM has immense scope for applications as microwave dielectric materials, for packaging materials in radio and electronic engineering, and for aviation and space applications. However, very few studies of the electrical and dielectric properties of closed-cell, cellular and microcellular, flexible materials can be found in the literature.<sup>11</sup> EPDM, especially a conjugated long-chain branching (CLCB) grade rubber, shows a reduced sensitivity to carbon black scorching in comparison with EPDM-based conventional technology. Keltan 7341A (DSM Elastomers, Singapore) shows better overall performance at higher compound loadings.<sup>12</sup>

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TABLE I  
Formulations of Unfilled and Vulcan XC 72 Filled EPDM Vulcanizates

	G <sub>0</sub>	G <sub>2</sub>	G <sub>4</sub>	G <sub>6</sub>	EB <sub>1</sub>	EB <sub>2</sub>	EB <sub>3</sub>	EB <sub>4</sub>	EB <sub>5</sub>	EB <sub>6</sub>	EB <sub>7</sub>	EB <sub>8</sub>	EB <sub>9</sub>	EB <sub>10</sub>	EB <sub>11</sub>	EB <sub>12</sub>
Keltan 7341A	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120	120
Vulcan XC72	0	0	0	0	20	20	20	20	40	40	40	40	60	60	60	60
Paraffin oil	0	0	0	0	2	2	2	2	4	4	4	4	6	6	6	6
ADC 21	0	2	4	6	0	2	4	6	0	2	4	6	0	2	4	6

Each mix contained 5 phr ZnO, 1.5 phr stearic acid, and 1 phr DCP (98% pure).

The morphology, physicomechanical properties,<sup>13</sup> compressive deformation, and energy-absorption characteristics<sup>14</sup> of closed-cell, microcellular EPDM (Keltan 7341 A) filled with excess conductive carbon black (Vulcan XC 72) have been reported recently; the effects of the filler and blowing agent on the aforementioned properties have been described. The dynamic mechanical properties of these composites have also been studied.<sup>15</sup>

The objective of this work was to study the dielectric and ac conductivity of a CLCB-grade, oil-extended EPDM (Keltan 7341 A) solid and closed-cell, microcellular rubber filled with excess conductive carbon black (Vulcan XC 72) vulcanizates. The effects of the blowing agent (density), temperature, and frequency on the dielectric constant and ac conductivity of the vulcanizates were studied. The dielectric loss of the vulcanizates was also studied with the variation of the temperature and blowing agent.

## EXPERIMENTAL

### Materials

An oil-extended EPDM rubber [Keltan 7341A (a new CLCB-grade rubber); 7.5 wt % ethylene-norbornene, 20 phr oil, and Mooney viscosity of 53 (at 150°C)] was used. Vulcan XC72 (excess conductive carbon black) was used as the filler. The curative was dicumyl peroxide (DCP) with a purity of 98% (manufactured by Aldrich Chemical Co., Milwaukee, WI). The blowing agent was azodicarbonamide (ADC-21, manufactured by High Polymer Lab, India), and the paraffin oil was Sunpar oil (supplied by Sun Oil Co., Pvt., Ltd., Kolkata, India).

### Sample preparation

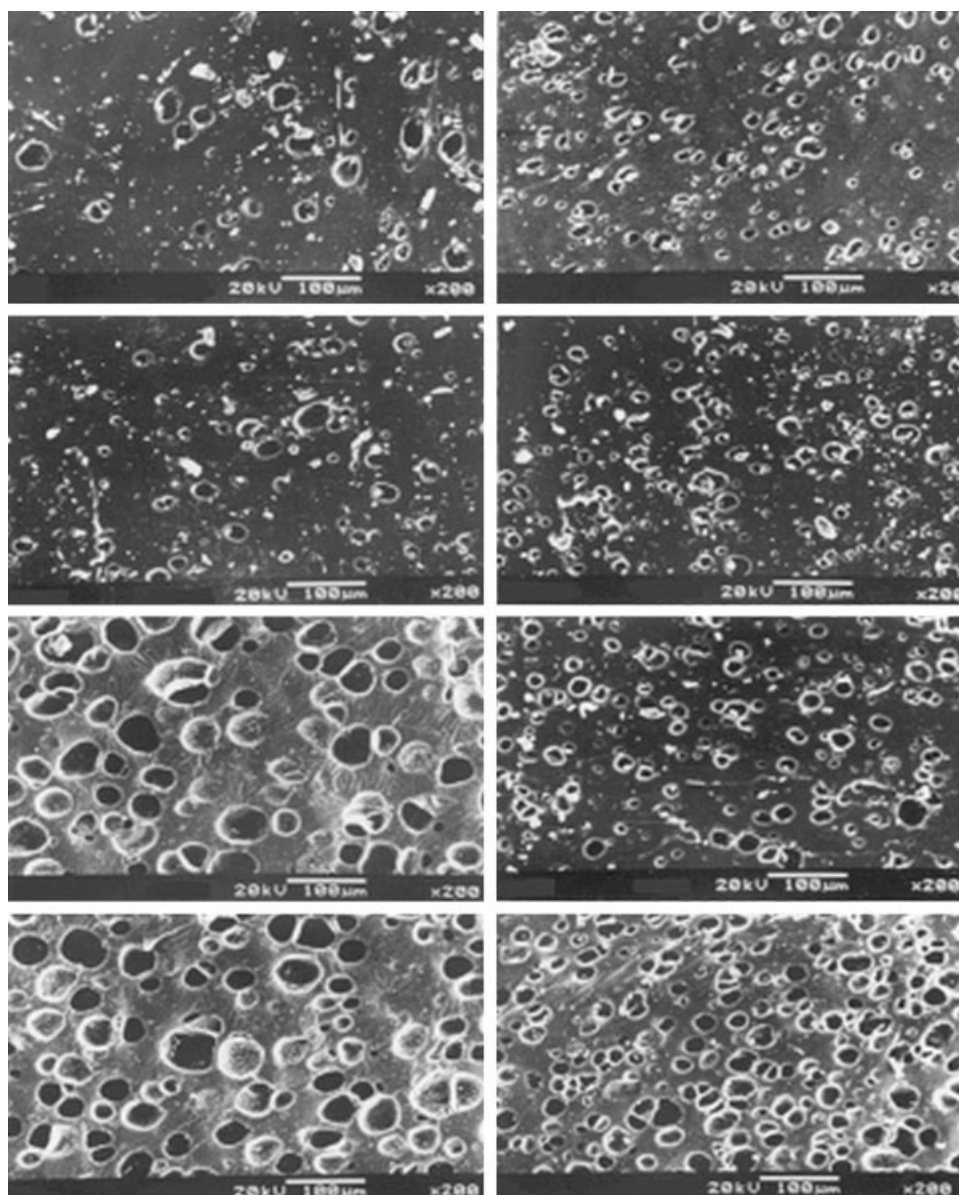
The rubber was compounded with the ingredients according to the formulations of the mixes given in Table I, and the blowing agent was added at the end. Compounding was performed in a laboratory-size, two-roll mixing mill at room temperature according to ASTM D 3182. The cure and blowing characteristics of the compounds were determined

with a Monsanto R-100 rheometer. The vulcanizates were press-molded at 160°C to 80% of their respective cure times to obtain a closed-cell, microcellular sheet. All sides of the mold were tampered to 30°C to facilitate the expansion of the molded compounds to closed-cell, nonintercommunicating, microcellular products with better mold release. As the press was closed, the compounds completely filled the mold, expelling the air and sealing the cavity. The typical compound flowed readily into the molds, coalesced, and eliminated trapped air blisters. As the stock temperature increased, the cure started, and the decomposition of the blowing agent began. Carbon dioxide was released, and the formation of the cell started. As the decomposition progressed, an exotherm developed, and pressure built up. These factors accelerated the curing rate. The press was opened before the cure was completed. A very small closed cell was obtained after the expansion. The precured sheet was then postcured at 100°C (for 1 h) to complete the curing. From the sheets, a fixed, circular sample of the sheet thickness was cut for dielectric measurements. Scanning electron microscopy (SEM) photomicrographs of the razor-cut surfaces of unfilled, 20 phr Vulcan XC 72 filled, 40 phr Vulcan XC 72 filled, and 60 phr Vulcan XC 72 filled, microcellular Keltan 7341A are shown in Figure 1 with blowing-agent loadings of 4 and 6 phr.

### Testing

An analysis of the dielectric properties of solid and microcellular, oil-extended EPDM rubber vulcanizates was carried out with impedance spectroscopy via the application of a small ac signal across the sample cell with a blocking electrode (aluminum foil). Measurements were performed with a Hioki (Japan) LCR Hi-Tester model 3532 computer-controlled impedance analyzer. The dielectric function [dielectric constant or relative permittivity ( $\epsilon'$ ) and dielectric loss tangent ( $\tan \delta$ )] was observed as a function of the frequency and temperature. The ac conductivity ( $\sigma_{ac}$ ) was evaluated from the dielectric data in accordance with the following relation:

$$\sigma_{ac} = \omega \epsilon_0 \epsilon' \tan \delta \quad (1)$$



**Figure 1** SEM photomicrographs of razor-cut surfaces of unfilled and Vulcan XC 72 reinforced, microcellular EPDM vulcanizates with increasing filler loading (from top to bottom: 0, 20, 40, and 60) and blowing-agent loading (from left to right: 4 and 6).

where  $\omega$  is equal to  $2\pi f$  ( $f$  is the frequency) and  $\epsilon_0$  is the permittivity of the vacuum.  $\epsilon'$  is determined as follows:

$$\epsilon' = C_p/C_0 \quad (2)$$

where  $C_p$  is the observed capacitance of the sample and  $C_0$  is the vacuum capacitance of the cell.  $C_0$  is calculated with the expression  $(\epsilon_0 A)/d$ , where  $A$  is the area of the sample and  $d$  is the thickness of the sample.

#### Bound rubber

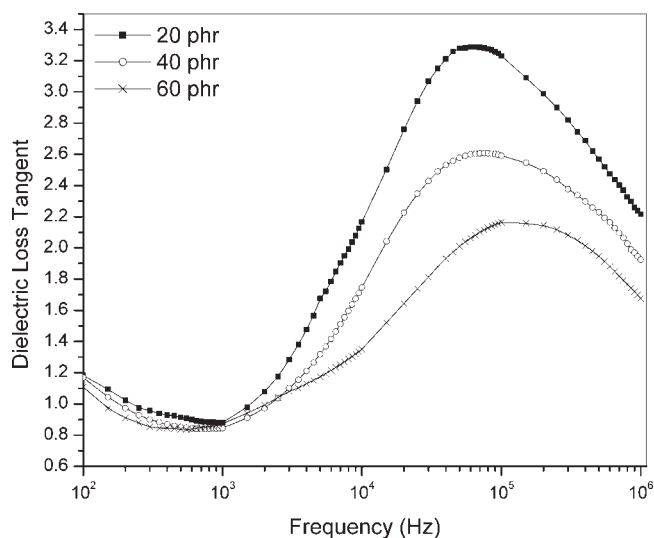
The amount of bound rubber in the compound was determined by the extraction of unbound materials such as ingredients and free rubber with a solvent

for 7 days, followed by drying for 2 days at room temperature. The weights of the samples before and after the extraction were measured, and the bound rubber content (BdR) was calculated with the following expression:

$$\text{BdR} = 100 \times \frac{W_{fg} - W_1 \left[ \frac{m_1}{m_1 + m_r} \right]}{W_1 \left[ \frac{m_1}{m_1 + m_r} \right]} \quad (3)$$

where  $W_{fg}$  is the weight of the filler and gel,  $W_1$  is the weight of the sample,  $m_1$  is the fraction of the filler in the compound, and  $m_r$  is the fraction of rubber in the compound.





**Figure 2** Dielectric loss tangent ( $\tan \delta$ ) as a function of the filler loading in Vulcan XC 72 filled, solid rubber vulcanizates as a function of the frequency at 30°C.

## RESULTS AND DISCUSSION

One of the most valuable tools for characterizing the relaxation behavior of polymer systems is dielectric relaxation spectroscopy (DRS). Dielectric spectroscopy is a useful complement to the more customary mechanical methods of probing the viscoelastic properties of polymers. Dielectric spectroscopy offers advantages for the study of the high-frequency dynamics of polymers. Dielectric spectra reflect the same chain motions as the mechanical modulus; however, they have reduced interference because of symmetry from shorter process times, and this makes them more accurate than traditional dynamic mechanical analysis.<sup>16</sup> The frequencies of testing in DRS correspond to the extraordinarily broad range of relaxation times associated with polymer chains.<sup>17,18</sup>

### Effects of the filler and foam contents on the dielectric loss tangent

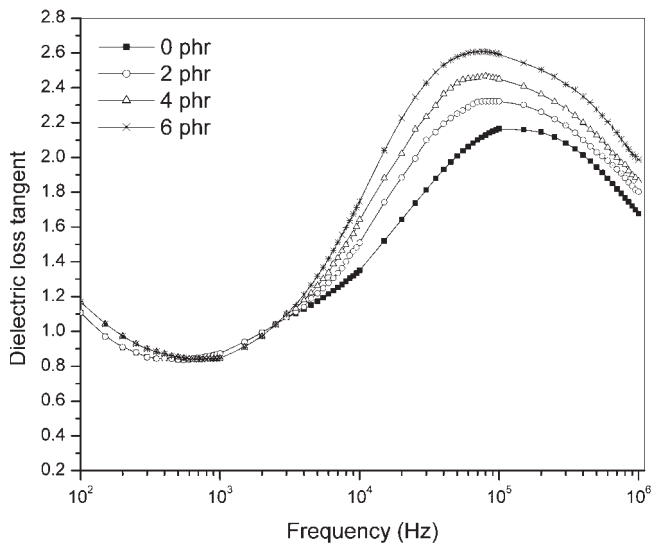
Figure 2 shows the variation of the dielectric loss tangent with the frequency in Vulcan XC 72 reinforced EPDM vulcanizates as a function of the filler loading. At lower frequencies (up to  $10^3$  Hz), the effect of the frequency is marginal, with all the composites showing almost equal loss tangent values. However, at higher frequencies ( $\sim 10^3$ – $10^5$  Hz), there is a tremendous increase in the loss tangent values of the composites, with higher filler loadings showing lower peak values. This can be explained on the basis of the mechanical and viscoelastic properties of crosslinked and reinforced multiphase polymeric materials. The arrangement of the filler particles has a significant effect on the samples' dielectric behav-

ior. The addition of functional fillers such as carbon black and silica not only results in hydrodynamic interactions but also leads to complex physicochemical interactions between the polymer matrix and the filler surface.<sup>19,20</sup> These elastomer–filler interactions are often characterized by the content of the apparent bound rubber, which is determined as the amount of insoluble rubber adhering to the dispersed carbon black aggregates before vulcanization. Because the amount of bound rubber is related to the filler loading, it can be regarded as a measure of the interactions between the filler and matrix.<sup>21,22</sup> An increased filler loading leads to increased polymer–filler interactions, thereby making a considerable portion of the polymer matrix attached to the filler surface. This was confirmed by bound-rubber measurements, shown in Table II, which show an increase in the bound rubber with an increase in the filler loading. Above  $10^5$  Hz, there is a steep decrease in the loss tangent values with higher filler loading samples, showing a transition at slightly lower frequencies.

The effect of the foaming-agent loading on the dielectric loss tangent in 40 phr Vulcan XC reinforced EPDM is shown in Figure 3. Initially, there is no effect of the frequency on the loss tangent, with all the composites showing equal values. However, from  $10^3$  Hz onward, there is a tremendous increase until  $10^5$  Hz, after which there is a steep fall. This steep fall is dependent on the foaming-agent loading, with the higher foaming agent loading samples showing a drop in the loss tangent value at lower frequencies. Moreover, with an increase in the foam content in the composites, the loss tangent value increases, and this indicates more loss behavior of the vulcanizates. A similar observation for the loss tangent values was also observed in dynamic me-

**TABLE II**  
Bound Rubber (Extracted in Acetone)  
in EPDM Compounds

Mix	Bound rubber
G <sub>0</sub>	35
G <sub>2</sub>	33
G <sub>4</sub>	31
G <sub>6</sub>	28
EB <sub>1</sub>	49
EB <sub>2</sub>	45
EB <sub>3</sub>	39
EB <sub>4</sub>	37
EB <sub>5</sub>	53
EB <sub>6</sub>	52
EB <sub>7</sub>	50
EB <sub>8</sub>	50
EB <sub>9</sub>	59
EB <sub>10</sub>	56
EB <sub>11</sub>	53
EB <sub>12</sub>	51

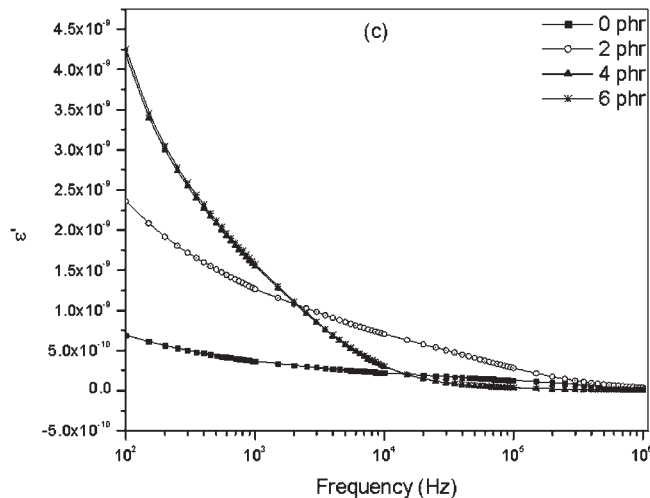
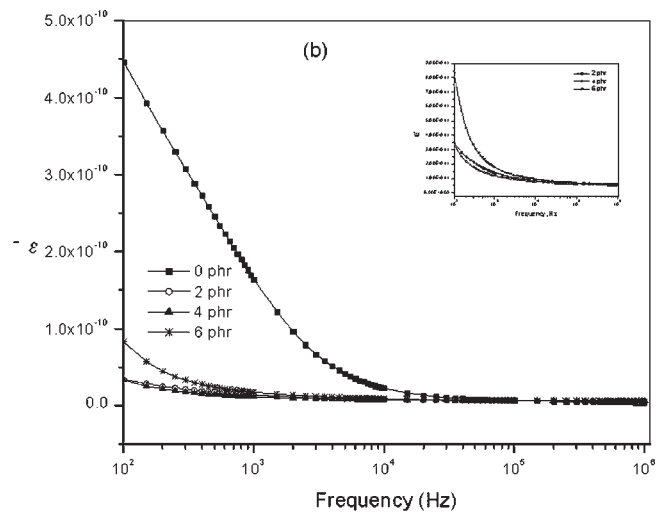
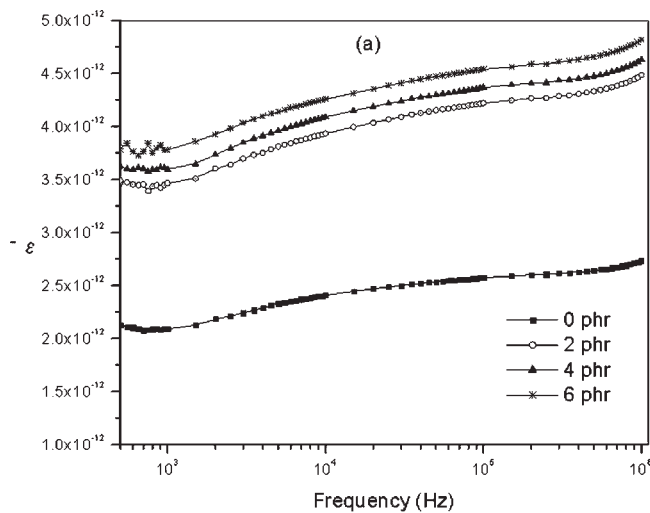


**Figure 3** Dielectric loss tangent ( $\tan \delta$ ) as a function of the blowing-agent loading in 40 phr Vulcan XC 72 filled, microcellular EPDM vulcanizates as a function of the frequency at 30°C.

chanical analysis.<sup>15</sup> The higher loss tangent values at higher blowing-agent loadings may be due to induced strain by decomposed gas pressure, which causes free intermolecular movement and hence a shift toward a lower frequency. Similar observations were made at other filler loadings (20 and 60 phr) and are not shown here for the sake of brevity.

#### Effect of the foam content on the dielectric constant

Figure 4(a–c) shows the variation in the real impedance versus the logarithm of the frequency as a function of the foam content in Vulcan XC reinforced EPDM vulcanizates at 20, 40, and 60 phr loadings. The nature of the dielectric constant/frequency curve of closed-cell, microcellular rubber is similar to that of solid rubber. The dielectric constant decreases with frequency as well as the blowing-agent loading. The incorporation of the blowing agent causes the



**Figure 4** Effect of the blowing-agent loading on the dielectric constant ( $\epsilon'$ ) in (a) 20, (b) 40, and (c) 60 phr Vulcan XC 72 reinforced, microcellular EPDM vulcanizates at 30°C.

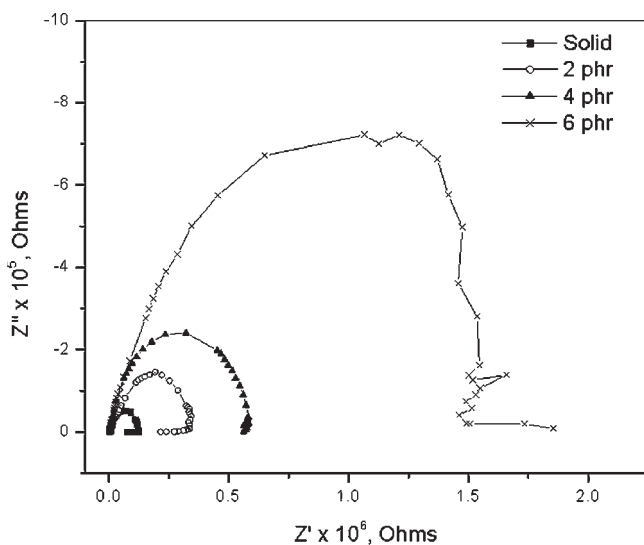
formation of gas inside the polymer matrix, which inhibits conduction in the filler–filler network. Regardless of the filler loading, with an increase in the frequency, there is a gradual reduction of the real impedance in all the vulcanizates at all foam compositions. However, an increased amount of foam in the composites shows a decrease in the impedance at lower frequencies, whereas at higher frequencies ( $\sim 10^4$ – $10^6$  Hz), all the samples tend to show almost constant values. This can be explained on the basis of a frequency-dependent phenomenon of cross-linked vulcanizates. Relaxations in crosslinked and reinforced polymers depend on the chemical and physical interactions between the viscoelastic polymeric and solid filler phases.<sup>23,24</sup> These interactions usually lead to the formation of an interphase, the thickness of which is inversely proportional to the interfacial tension between the two phases. This interphase is commonly quantified as bound rubber in elastomer technology. The interphase that forms between the filler and the polymer matrix has distinct properties that differ from those of the bulk. A polymer layer having a higher stiffness than that of the bulk polymer in the vicinity of the dispersed phase surface is created because of the interactions between the filler and polymer phases,<sup>25,26</sup> leading to different mechanical and dynamic relaxation properties resulting from the residual thermal stresses and density fluctuations.<sup>27</sup>

At all foam loadings in all composites, with an increase in the frequency, there is a rapid decrease in the dielectric constants that is more pronounced in the region of  $10^5$  Hz. However, as the foaming-agent loading increases, there is a gradual shift of this rapid decrease to slightly higher frequencies. This frequency range is related to the mean relaxation time of the process and characterizes the molecular mobility (at the temperature of the investigation).<sup>28</sup> An increase in the foam in the composite leads to lower interactions with the polymer matrix, thereby slightly increasing the frequency of occurrence of the drop in the dielectric constant. The width and asymmetry of the relaxation function in polymer composites usually deviate from the values of the Debye function. It is widely believed that the main obstacle to the electron flow in conductor–polymer systems is located at the interface between the primary particles of the different filler aggregates.<sup>29</sup> Another explanation for the aforementioned phenomenon is the formation of electrets in the composites. Recent studies have shown that an electrical charge arises during and after the deformation of rubbers, and the same mechanism was studied and explained later by Sessler.<sup>30</sup> Because the sample preparation of rubber involves operations such as compression, cutting, and friction, this causes electrical polarization, which leads to the formation of so-

called mechanoelectrets.<sup>31</sup> The lifetime of the polarization charge depends on the polymer nature and the conditions of electret storage and usage (temperature, dielectric characteristics of the polymer, fillers, etc.). This electret state of rubbers was studied in detail (especially the arising of the electret state during processing) by Pinchuk et al.,<sup>32</sup> and they proposed that nonconductive rubber, when subjected to high shear stresses, could lead to electret formation. It is known that long-living microradicals are present in processed polymeric materials, including rubbers. These radicals could participate in polarization according to several mechanisms: dipolar (directed orientation of molecules), ionic (orientation of quasi-dipoles created by weakly bonded ions), and bulk (radical displacement to a macrodistance). Therefore, when a rubber sample is subjected to external stress and thermal fields during compounding, processing, and curing, electrets are created that affect the polarization of the fillers in the polymer matrix. Negative excess charge on the filler particles have also been reported and attributed to the chemical interactions between the surface groups on the filler particles and the basic polymer matrix.<sup>31</sup> The ionic nature of the polymer matrix has also been shown to influence the charge density on the filler particles. The direct-current electrical field inside the sample is shielded by electrical double layers formed by mobile ions at the electrodes. However, this shielding does not occur in an ac field of sufficient frequency, and this results in the observed network formation. However, the small excess charges on the filler particles cannot prevent cluster formation in the bulk matrix; they are overcome by the strong van der Waals attractive forces.

### Cole–Cole plots

Figure 5 shows Cole–Cole plots, that is, the relationship between the complex and real parts of the impedance ( $Z'$  vs  $Z''$ ), of EPDM vulcanizates as a function of increasing blowing-agent variation in 60 phr Vulcan XC 72 at 30°C. At all frequencies, there is a tremendous effect on the dielectric properties with an increasing amount of the blowing agent in the composites, leading to more loss response, as observed by increasing area under the curve. This is a significant observation and can be attributed to the charge behavior of the filler in the polymer matrix. Studies have shown that carbon particles dispersed in a polymer matrix have a negative charge. These filler particles are electrically charged by fixed or adsorbed ions or polar molecules and are surrounded by small countercharges (of the polymer matrix), forming an electrical double layer. The resulting medium-frequency relaxation is caused primarily by interfacial polarization due to the buildup of charges



**Figure 5** Effect of the blowing-agent variation on a Cole-Cole plot of 60 phr Vulcan XC 72 reinforced, microcellular EPDM vulcanizates.

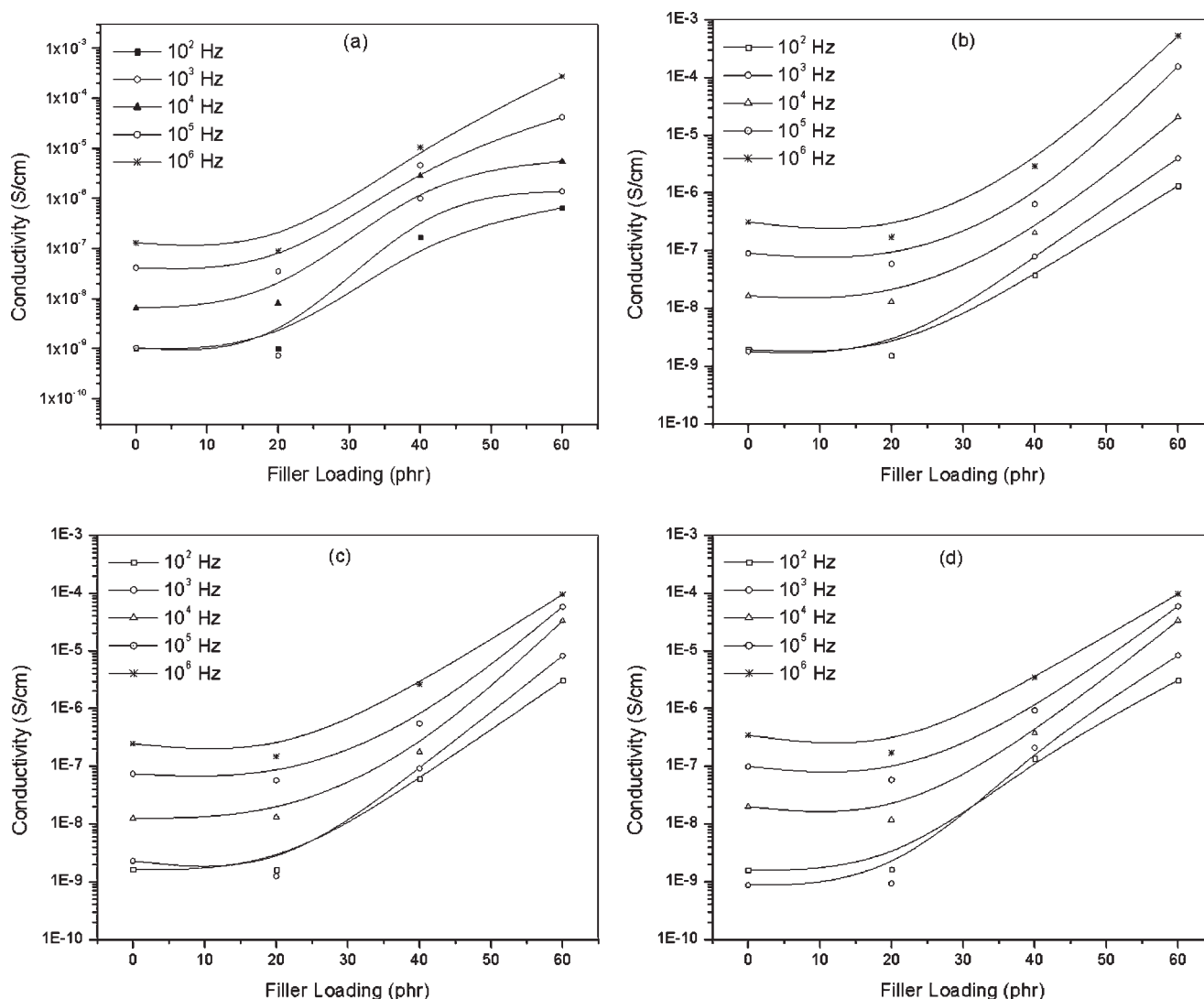
on boundaries and interfaces between materials with different electrical properties.<sup>33</sup> The imposition of an external ac field causes polarization of large colloidal particles and creates perturbation in a miniature double layer on each particle, which then behaves like a macroion.<sup>34</sup> Under the influence of an external electrical field, the counterions become redistributed along the surface of a filler particle, and the double layer becomes deformed and polarized, leading to interfacial polarization and the resulting relaxation or dispersion. However, the magnitude of relaxation of these counterions in the medium-frequency region is much larger than the relaxation due to the orientation of dipoles.<sup>35</sup> An increased blowing-agent loading in the composite seems to cause an increase in the negative charge of the carbon black particles, thereby resulting in the orientation of dipoles and thus making the filler particles more conductive.

### Percolation

Although there have been many studies on the percolation phenomenon in carbon black reinforced polymers, the same has been seldom investigated in microcellular composites. The variation of the electrical conductivity with increasing filler loadings in solid and 2, 4, and 6 phr blowing agent loaded, microcellular EPDM vulcanizates is shown in Figure 6(a–d). The electrical conductivity of a composite is generally characterized by its dependence on the filler volume fraction. Figure 6(a) presents the effect of the filler loading on the conductivity [calculated with eq. (1)] in solid (unfoamed) samples. At all frequencies ( $10^2$ ,  $10^3$ ,  $10^4$ ,  $10^5$ , and  $10^6$  Hz) above

a 40 phr loading, there is an abrupt increase in the conductivity, implying the occurrence of a percolation limit. As the filler amount in the composite is increased, the filler particles begin to touch one another, and a continuous path is formed through the volume of the sample for the electrons to travel. The formation of this conductive network is based on the principles of percolation theory. Experimental results for composites consisting of an insulating matrix and conductive filler particles are often analyzed with the help of statistical percolation theory, the formulation of which is attributed to Broadbent and Hammersley.<sup>36</sup> Medalia,<sup>37</sup> in his review on electrical conduction in carbon black reinforced composites, explained that percolation is due to the tunneling of electrons and that the conductivity is controlled by the gaps between the carbon black aggregates. Carbon blacks are supposed to exist as agglomerates, which compromise aggregates fused together in chains or clusters by spherical particles. The electrical conductance in carbon black/polymer composites depends on the distance between the aggregates, so composites can be regarded as a system composed of random arrays of closely spaced conductors dispersed in an insulating polymer matrix. Beyond a critical concentration of the filler, known as the percolation threshold, an increase in the composite conductivity of several orders of magnitude can be observed.

However, the percolation limit observed in this study varies considerably from the theoretical value of the percolation threshold for randomly dispersed, hard, spherical particles, which has been determined to be about 16 vol %.<sup>38</sup> Moreover, in epoxy composites, percolation thresholds of less than 1 vol % for the spherical particles of carbon black have been reported.<sup>39,40</sup> A similar deviation in the percolation threshold from statistical percolation theory for carbon-based fillers such as carbon black and a carbon-silicon dual-phase filler in chlorobutyl vulcanizates has been observed by our group.<sup>41</sup> These studies indicate that the nature of the percolating network of fillers within the polymer matrix has to be considered. Carbon blacks are widely used as reinforcements in elastomers, primarily because of their high surface-to-mass ratio, molecular-scale forces, and their interactions with the polymer matrix. Because of van der Waal forces, carbon blacks usually flocculate in the polymer matrix, forming so-called secondary structures, whereas electrostatic charges or steric effects lead to a stabilization of the dispersion. Schuler et al.<sup>40</sup> used these concepts to explain their observation of process-induced changes in the percolation threshold for carbon black in an epoxy. They reported that both the addition of electrolytes and the application of suitable shear forces could lower the repulsive barrier between dispersed carbon black



**Figure 6** Effect of the blowing-agent loading on the conductivity in (a) solid EPDM vulcanizates, (b) 2 phr blowing agent loaded, microcellular EPDM vulcanizates, (c) 4 phr blowing agent loaded, microcellular EPDM vulcanizates, and (d) 6 phr blowing agent loaded, microcellular EPDM vulcanizates reinforced with Vulcan XC 72 at different frequencies at 30°C.

particles and lead to the formation of a conductive network at low filler contents. The percolation problem is effectively one of path or cluster formation through random processes on either a sample lattice or space; in the former case, it is called lattice percolation, whereas in the latter case, it is called continuum percolation. In general, this involves two processes: randomly adding or removing particles from a sample lattice or space until an infinite cluster is formed. A cluster is considered to be a group of particles that are connected to one another, and particles are considered connected if they occupy adjacent lattice sites or if they are within a certain encounter radius of each other. Figure 6(b–d) shows the variation in the conductivity with the filler loadings in 2, 4, and 6 phr foamed vulcanizates. At all the frequencies investigated, regardless of the

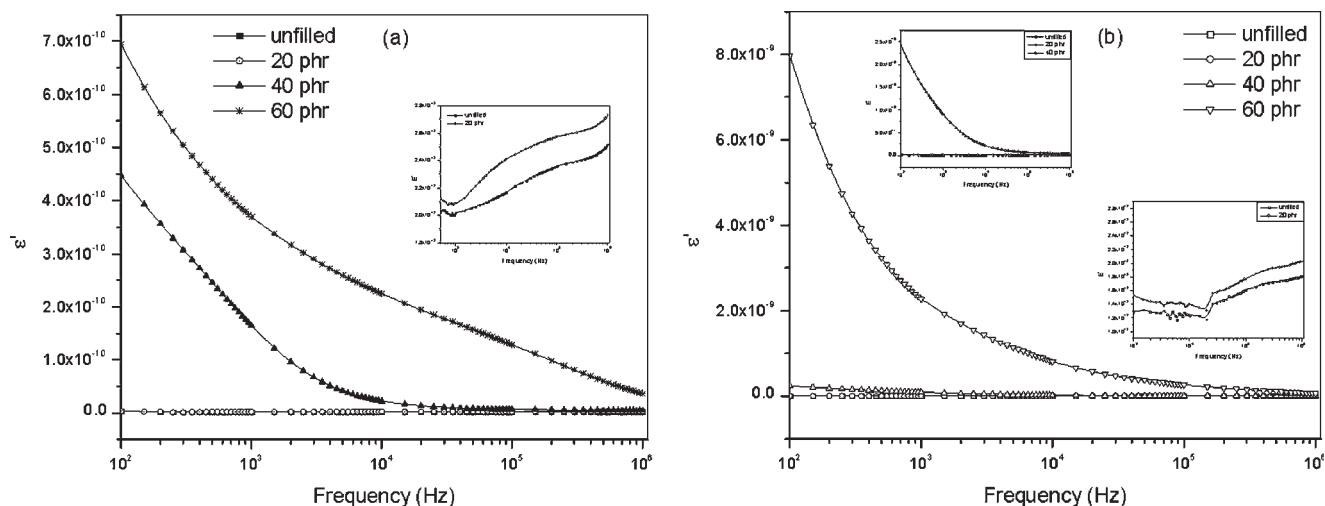
blowing-agent loading, a similar observation of an abrupt increase in the conductivity at 40 phr was made.

### Effect of the temperature on the dielectric constant

#### Effects of the filler and foam loading

Figure 7(a,b) shows the variation of the dielectric constant with the frequency of unfoamed EPDM rubber vulcanizates with different filler (Vulcan XC 72) loadings at room temperature (30°C) and at 100°C, respectively. The dielectric constant decreases with the frequency at all loadings and increases with the filler loading because of the filler–filler network inside the polymer matrix, which increases with the filler loading. At a higher frequency, that is, around





**Figure 7** Variation of the dielectric constant ( $\epsilon'$ ) with the frequency of solid, oil-extended EPDM rubber vulcanizates with different loadings of Vulcan XC 72 at (a) 30 and (b) 100°C.

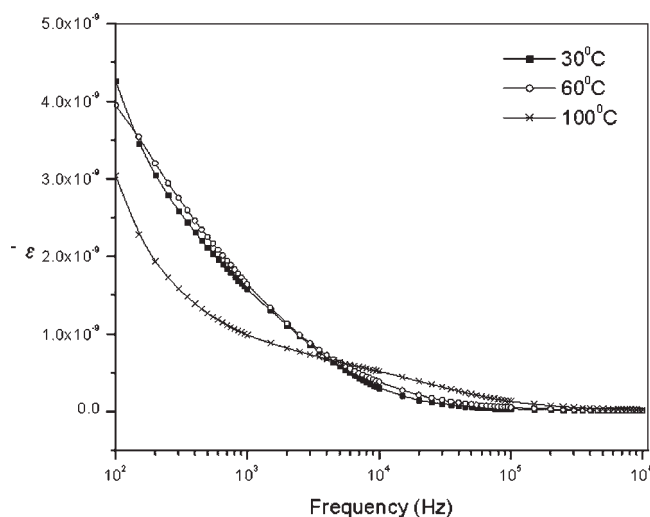
$10^6$  Hz, all solid composites show equal dielectric constants at both temperatures.

Figure 8 shows the effect of the temperature on the dielectric constant of 60 phr Vulcan XC 72 filled and 6 phr blowing agent loaded, microcellular vulcanizates. The dielectric constant increases with increasing temperature, and above  $10^5$  Hz, the dielectric constant is independent of the temperature, like solid vulcanizates. This can be explained on the basis of the positive temperature coefficient (PTC) of carbon black/polymer composites. The PTC phenomenon in polymer/carbon black composites has been explained with many models,<sup>42</sup> such as the conductive chain and thermal expansion model, the electron tunneling conductance model, the change in the polymer aggregative structure and carbon black migration model, and the Ohm conductance and phase change model. Ohe and Natio<sup>43</sup> proposed that the dielectric constant of a sample is composed of a large three-dimensional network constructed of a large number of low-resistance elements of filler grains, high-resistance elements of intergrain gaps, and much higher resistance elements of the polymer matrix and air bubbles. The resistance of the last elements are, however, so high that they do not contribute to the temperature variation of the dielectric constant of the sample. Another explanation was given by Kohler,<sup>44</sup> who proposed that the conductive filler is initially spread through the polymer in a network of conductive chains and that, as the material is heated, the conductive particles are separated further, thus increasing the resistance. Another model based on crystallinity was proposed by Klason and Kubat,<sup>45</sup> who suggested that at a low temperature, the carbon black structure is determined by the crystalline phase of the polymer and that carbon black particles distribute in an amorphous phase and form

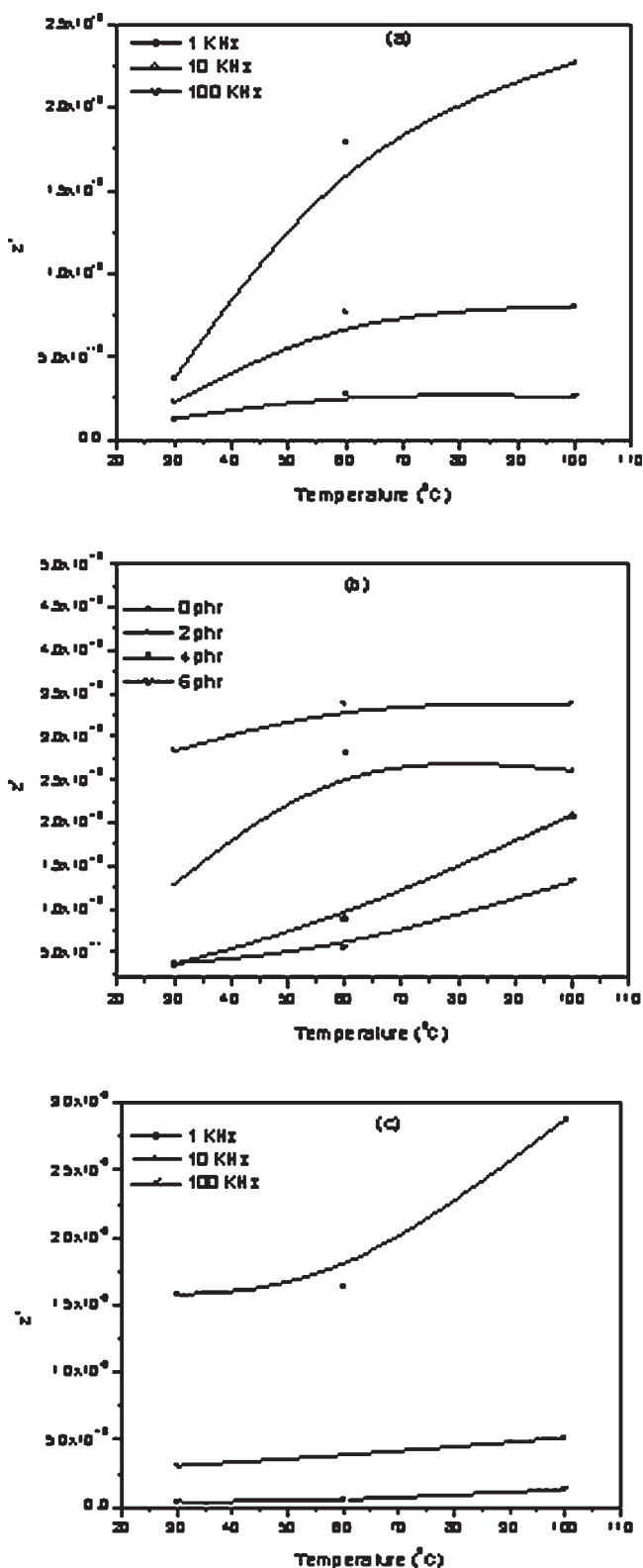
a conductive chain. At higher temperatures, the structure breaks up, and this causes a more homogeneous particle distribution and a sharp increase in the dielectric constant.

#### Effect of the frequency

Figure 9(a–c) shows the effect of the temperature on the dielectric constant in solid and foamed, microcellular EPDM vulcanizates. Figure 9(a) shows the effect of the frequency on the dielectric constant of 60 phr Vulcan XC 72 filled, solid rubber vulcanizates with the variation of the temperature. At a lower frequency, the dielectric constant increases with the temperature linearly, whereas with an increasing frequency, the rate of increase decreases and finally



**Figure 8** Effect of the temperature on the dielectric constant ( $\epsilon'$ ) of 60 phr Vulcan XC 72 filled and 6 phr blowing agent loaded, microcellular EPDM vulcanizates at 30°C.



**Figure 9** (a) Variation of the dielectric constant ( $\epsilon'$ ) in 60 phr Vulcan XC 72 as a function of frequency, (b) effect of the blowing-agent loading in 60 phr Vulcan XC 72 filled at 1 kHz, and (c) effect of the frequency in 60 phr Vulcan XC 72 and 6 phr blowing agent at 30°C.

shows a constant value at a higher frequency. Figures 9(b) show the effect of the blowing agent on the dielectric constant of 60 phr Vulcan XC 72 filled, solid and microcellular rubber vulcanizates with the variation of the temperature at 1 kHz. The dielectric constant of microcellular rubber vulcanizates increases with the temperature and decreases with the blowing agent at all frequencies, but the rate of increase decreases with the incorporation of the blowing-agent loading. Figure 9(c) shows the effect of the frequency on the dielectric constant of 60 phr Vulcan XC 72 filled and 6 phr blowing agent loaded, microcellular vulcanizates. With increasing frequency, the change in the dielectric constant of the microcellular rubber follows a trend similar to that of solid vulcanizates.

### Dielectric mixture laws

The calculation of the permittivity of dielectric mixtures and a wide array of proposed formulas were reviewed by Reynolds and Hough,<sup>46</sup> Van Beck,<sup>47</sup> Boettcher and Bordewijk,<sup>48</sup> Grosse and Graffe,<sup>49</sup> and Kraszewski.<sup>50</sup> However, power-law relationships are quite often used in the dielectric modeling of composite systems. Generally, for a composite composed of  $n$  number of components, the power-law mixture model can be written as follows:

$$\epsilon_c^\beta = \sum_{i=1}^n \phi_i \epsilon_i^\beta \quad (4)$$

where  $\epsilon_c$  and  $\epsilon_i$  are the complex dielectric permittivities of the composite system and constituent component of the composite, respectively;  $\phi_i$  is the volume fraction of the constituent component; and  $\beta$  is a dimensionless parameter representing the shape and orientation of the filler particles within the polymer bulk. The value of  $\beta$  ranges from 1 (linear mixture model) to 0.5 (Birchak model)<sup>51</sup> to 0.33, as given by the Landau–Lifshitz–Looyenga formula.<sup>52</sup> The general two-component power-law model for complex permittivity has been used extensively for a wide range of material systems with varied success, including air–particulate composites,<sup>53,54</sup> ceramic–ceramic composites,<sup>55</sup> and polymer–ceramic composites.<sup>56</sup>

These relationships model the effective permittivity of two-component systems with the volume fraction of each component according to the following expression:

$$\epsilon_c^\beta = \phi_1 \epsilon_1^\beta + \phi_2 \epsilon_2^\beta + (1 - (\phi_1 + \phi_2)) \epsilon_3^\beta \quad (5)$$

where  $\epsilon_1$ ,  $\epsilon_2$ , and  $\epsilon_3$  are the complex dielectric permittivities of the filler, polymer matrix, and entrapped carbon dioxide, respectively.  $\phi_1$  and  $\phi_2$  are the volume fraction of the foam and filler, respectively.

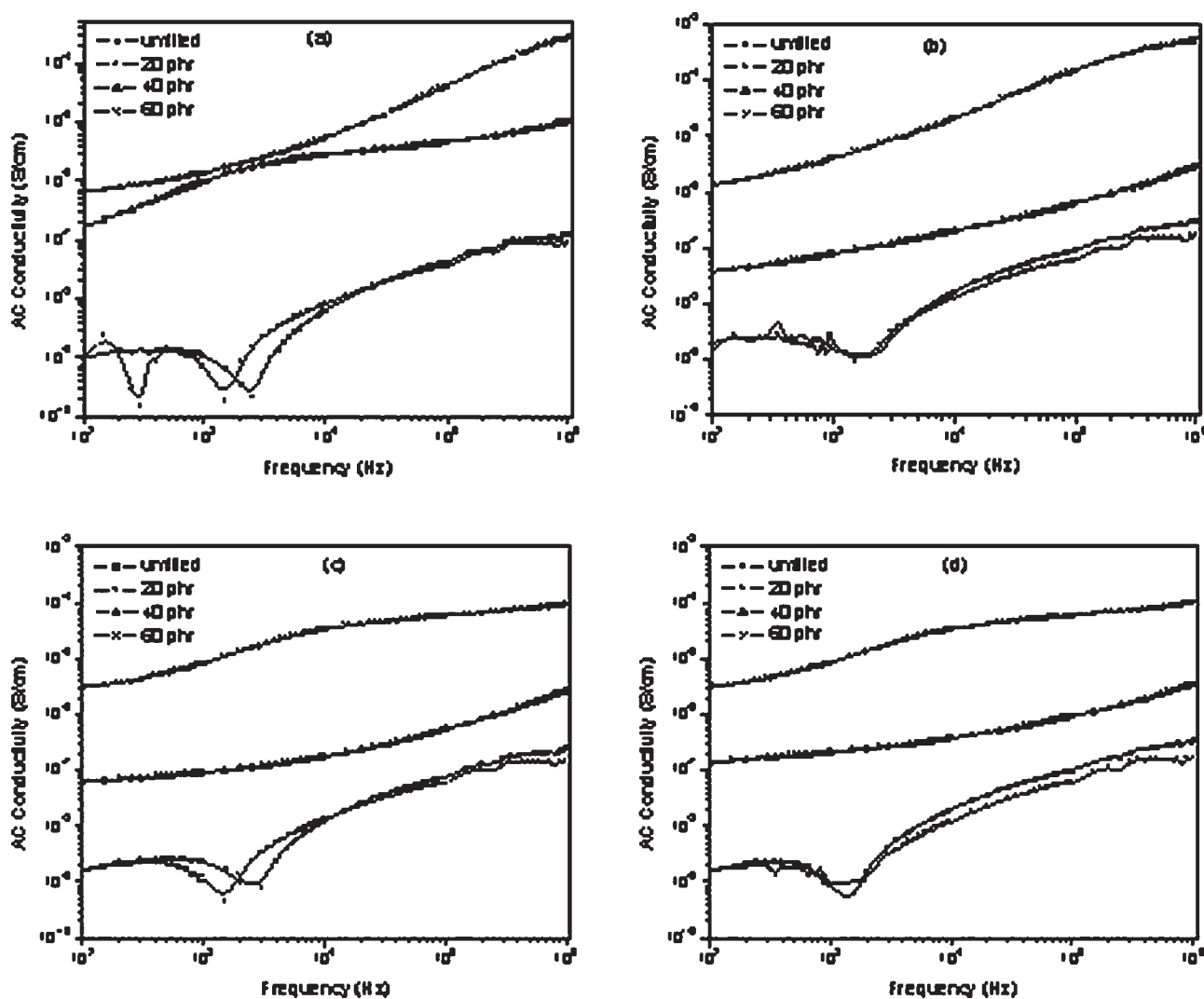


Figure 10 Variation in the ac conductivity with the frequency at various loadings of Vulcan XC 72 reinforced and solid, microcellular EPDM vulcanizates as a function of the blowing agent: (a) solid, (b) 2 phr, (c) 4 phr, and (d) 6 phr.

In this work, a linear, three-component model was used. The dielectric constant as a function of the filler and foam loading was modeled with the aforementioned expression, and  $\beta$  in the solid and 2, 4, and 6 phr, microcellular vulcanizates was found to be 1.23, 1.17, 0.94, and 0.88, respectively. The observed values of  $\beta$  show considerable deviation from the values of both Birchak ( $\beta = 0.5$ ) and linear mixture models ( $\beta = 1$ ). This deviation can be attributed to the nonlinear nature of the composites. Though quite successfully used to model a wide range of composite systems, the power-law mixture model does not account for interactions between the components of the composite, as reported in many publications.<sup>53–56</sup>

#### AC conductivity

Figure 10(a–d) shows the effect of the variation of the blowing-agent loading on the ac conductivity of

unfilled and Vulcan XC 72 reinforced EPDM vulcanizates. With an increase in the frequency, all the composites show an increase in the electrical conductivity. Regardless of the blowing-agent loading, the unfilled and 20 phr carbon black reinforced composites show almost similar conductivity values. At low filler loadings, the conductivity of the composite is slightly higher than that of the base polymer because the filler particles are isolated from one another by the insulating polymer matrix, and this reduces the likelihood of electron hopping.<sup>37</sup> As the filler loading is gradually increased, contact between the filler aggregates is established, and at particular filler loadings, there is a sharp increase in the conductivity. Moreover, the ac conductivity increases up to  $10^5$  Hz and then is almost constant at all filler and blowing-agent loadings.

Reinforced, microcellular vulcanizates are three-phase systems consisting of a polymer matrix, a filler,

and air bubbles entrapped in the composite. Many questions about the actual mechanism for electrical transport through such heterogeneous materials are still prevalent. It is largely admitted that their electrical properties primarily depend on the way in which the filler particles are dispersed in the polymer matrix. There are several models that are supposed to describe this dispersion, usually called the mesostructure.<sup>57,58</sup> However, even though it accounts for the existence of a conductivity threshold at some critical value of the filler concentration and for the power-law dependence of the electrical properties, it fails to predict the location of the threshold. It has long been recognized that the conductivity depends not only on the geometry of the filling particles but also on the actual processing of the materials.<sup>59</sup> As far as the discrepancy between the actual and lattice exponents is concerned, it may be considered proof of the inadequacy of the lattice percolation theory to account fully for conduction through such media. However, the relationship between such models and the actual mesostructure of the materials still remains unclear.

### CONCLUSIONS

The ac conductivity and dielectric impedance spectroscopy of conductive, carbon black reinforced, microcellular EPDM vulcanizates was studied in the frequency range of 100 Hz to 1 MHz. Increased filler content in the composites made the polymer more nonlinear in nature, as shown by higher dielectric loss tangents. This was explained on the basis of bound rubber. In both solid and foamed composites, at low frequencies, the effect of the filler loading on the dielectric constant was almost negligible, whereas at higher frequencies, it was clearly visible. The percolation of the filler in the composite was studied by direct-current conductivity. The percolation limit was found to be in the vicinity of 40 phr in all the composites. The applicability of a power law to model the dielectric constant of the composites gave a value of the critical exponent,  $\beta$ , in the range of 1.23–0.88.

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