Physical Studies of
Foamed Reinforced Rubber Composites
Part II-The Electrical Properties of Foamed EPDM
and NBR Rubber

A.M.Y El-Lawindy, W.E.Mahmoud, and H.H.Hassan[*]

*Department of Physics, Faculty of Science, Suez Canal University,
Ismailia, EGYPT*

**Department of Physics, Faculty of Science, Cairo University,
Giza, EGYPT*

Reinforced Ethylene Propyline Diene Terpolymer, EPDM, and Nitrile Butadiene Rubber, NBR, were mixed with different concentrations of asodicarbonamide, ADC/K, as a foaming agent to obtain EPDM and NBR rubber foams. The investigated foams were subjected to electrical, A.C. and D.C, measurements. Electrical conduction mechanisms were studied. Poole-Frenkel and Schottky conduction mechanisms were detected. The dielectric permittivity and loss were found sensitive to oscillating field. It was found that the increase of foaming agent content affects markedly all the electrical parameters.

1. Introduction:

In this series of experiments, different physical parameters of foamed EPDM and NBR vulcanizates were measured to illustrate the effect of foaming agent concentration on the mechanical, electrical, physico-mechanical and swelling parameters. The effects of static deformation on the mechanical parameters of foamed EPDM and NBR vulcanizates have been recently published [1]. In that study, the decrease in volume fraction of carbon black concentration, due to the addition of foaming agent, was considered responsible for the monotonic decrease of the measured mechanical parameters. In addition, the effect of temperature on the mechanical parameters was found to have a similar effect of foaming agent concentration.

In the present work, the effect of foaming agent concentration on the D.C. and A.C. electrical properties was studied. In addition, the type of conduction mechanism and the dielectric losses were discussed.

2. Experimental Technique:

The foamed EPDM and NBR rubber composites were compounded according to the recipe shown in Table 1, using a two-roll mill. The ingredients were added in the same order as listed.

The specifications of the used mill and the milling procedure are mentioned elsewhere [1]. The mixing time and vulcanization conditions were fixed for all samples. The samples are of a cylindrical shape of ~ 0.01 m both in diameter and height. Brass electrodes were attached to the parallel faces of samples during vulcanization.

In D.C. measurements a digital electrometer (616 Kiethly, USA) was used. The A.C. measurements were performed using an RCL bridge (3531 Z- Hitester, Hioki, Japan) in the frequency range of 42 Hz to 5 MHz. The bridge was calibrated to short and open circuit compensation. The testing speed was set to afford high accuracy. The data were automatically collected using a suitable interface and data acquisition PC code.

Table (1): Ingredients of the investigated foamed EPDM (WE's) and NBR (WN's) rubber composites. MBTS is dibenzthiazole disulphide, PBN is phenyl-β-naphthyl amine, and phr means part per hundred part of rubber by weight.

Sample name Ingredients(phr)	WE0	WE5	WE10	WE15	WN0	WN5	WN10	WN15	Mixing time(min)
EPDM	100	100	100	100					10
NBR					100	100	100	100	10
Stearic acid	2	2	2	2	2	2	2	2	3
Zinc Oxide	5	5	5	5	5	5	5	5	5-7
HAF-N330	50	50	50	50	50	50	50	50	3-5
Processing oil	15	15	15	15	15	15	15	15	5
MBTS	2	2	2	2	2	2	2	2	3
PBN	1	1	1	1	1	1	1	1	3
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	5
ADC/K	**0**	**5**	**10**	**15**	**0**	**5**	**10**	**15**	6-8

3. Results and Discussion:

Figures (1) and (2) represent the log (I)- log (V) characteristics of foamed EPDM and NBR vulcanizates at different temperatures, ~ 303 K, 323 K, 343 K, and 363 K respectively. The applied D.C voltage was increased up to 800 Volt, which is less than the least power required for Joule heating

($\simeq 10^5$ watt/m^3). Two distinct regions were obtained, in both types of foams. The Ohmic conduction prevails up to ~ 400 volt for both EPDM and NBR samples. The slope of the second region is greater than 1 in case of EPDM whereas, for NBR, it is less than 1.

One may suggest a space-charge-limited conduction mechanism, SCLC, either of the Poole-Frenkel or of Schottky type. To confirm this assumption, plotting log J vs E$^{1/2}$ checked the following equation [2],

$$J = A \, exp((\beta_{exp}/2kT)E^{1/2}) \qquad (1)$$

where *J* is the current density, *E* is the applied electric field and k is Boltzman's constant and β_{exp} is a constant characterizing the type of conduction. The deduced values of β_{exp} were then compared to the calculated values of β at very high frequency of Pool-Frenkel and Schottky, respectively. Such comparison is shown in Table 2.

For EPDM, the comparison shows that the conduction, in the second region, is of the Schottky type, whereas in NBR it is of the Poole-Frenkel. One may attribute the small slope, (<1), in case of NBR foams, to the formation or previously existing ions near from the electrodes. These ions are scarcely neutralized before arriving at the electrodes. In this region then, the ion density increases, increasing the space charges and reducing the current.
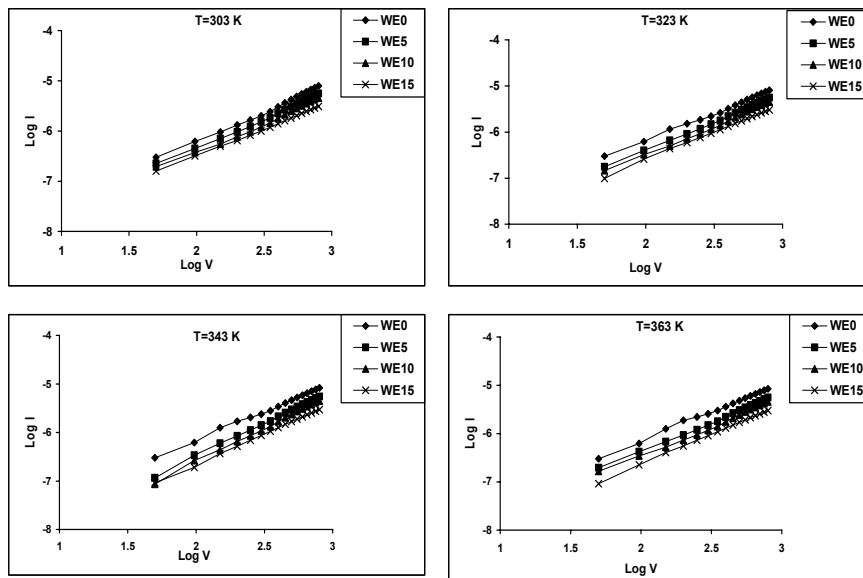
Fig.(1): The I-V characteristics for EPDM samples at different temperatures; 303, 324, 343 and 363 K.
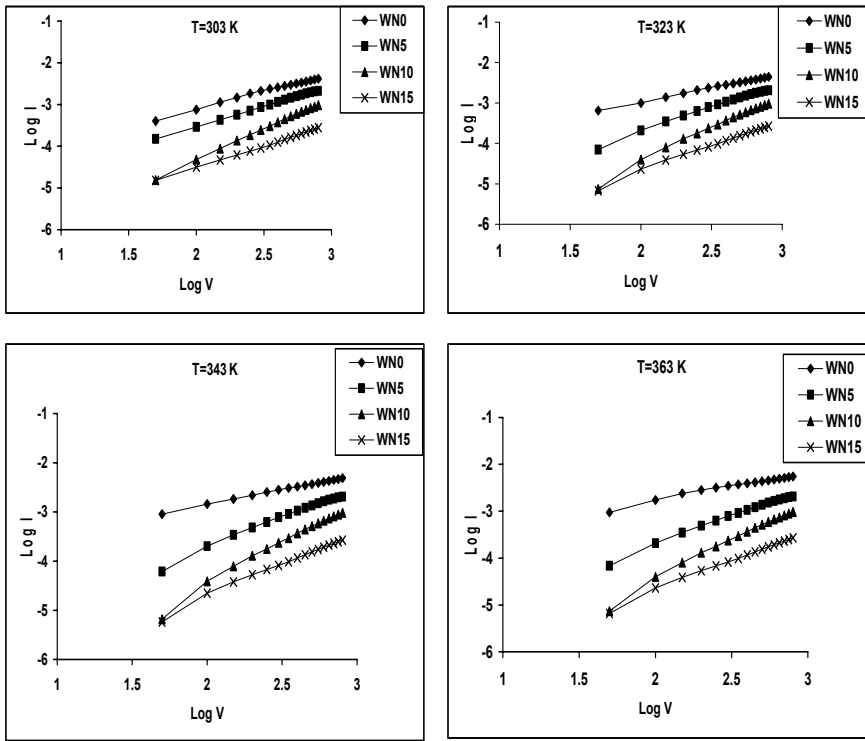
Fig.(2): The I-V characteristics for NBR samples at different temperatures; 303, 324, 343 and 363 K.

Table (2): A comparison between deduced β_{exp} and that calculated from Poole-Frenkel, β_{pf}, and Shottky, β_{sh}, respectively. β's are measured in (J C m)1/2.

Temp.	Sample	WE0(10-5)	WE5(10-5)	WE10(10-5)	WE15(10-5)
303 K	β_{exp}	1.05	1.20	0.873	0.906
	β_{sh}	1.03	1.13	0.861	0.895
	β_{pf}	2.06	2.26	1.72	1.79
323 K	β_{exp}	1.00	1.76	0.798	0.502
	β_{sh}	0.991	1.70	0.897	0.683
	β_{pf}	1.98	3.41	1.79	1.37
343 K	β_{exp}	0.891	1.20	0.732	0.554
	β_{sh}	0.914	1.29	0.669	0.528
	β_{pf}	1.83	2.60	1.34	1.06

363 K	β_{exp}	0.863	1.32	0.885	7.23
	β_{sh}	0.882	1.51	0.798	6.08
	β_{pf}	1.77	3.03	1.60	1.22
303 K	β_{exp}	1.03	2.11	1.52	1.76
	β_{sh}	0.609	0.938	0.664	0.807
	β_{pf}	1.21	1.87	1.33	1.61
323 K	β_{exp}	1.11	1.41	0.920	1.62
	β_{sh}	0.627	0.829	0.406	0.744
	β_{pf}	1.25	1.65	8.11	1.48
343 K	β_{exp}	1.18	1.53	1.92	1.05
	β_{sh}	0.602	0.788	0.944	0.522
	β_{pf}	1.20	1.57	1.88	1.04
363 K	β_{exp}	1.23	1.65	7.12	1.54
	β_{sh}	0.594	0.766	0.446	0.733
	β_{pf}	1.18	1.53	0.691	1.46

The temperature dependence of D.C conductivity is shown in Fig. (3) for foamed EPDM and NBR vulcanizates. In general, the conductivity is decreasing, as the foaming agent concentration is increasing.

The conductivity of foaming agent-free rubber samples is monotonically thermally activated. Moreover, there are two distinct regions of different slopes, in case of foamed samples. One may explain the decrease in conductivity, at low temperature up to ~ 350 K, to be due to a competition between thermal activation and either hopping or tunneling effects. At higher temperatures, thermal expansion equilibrium may be acquired and the void volume is then unchanged. Consequently, an increase of conductivity is expected, as far as the retraction forces which hold the rubber chains are in equilibrium with gas pressure experienced by a unit cross-sectional area of the rubber matrix. At higher temperature region, it is noticed that the activation energies are independent of the foaming agent concentration.
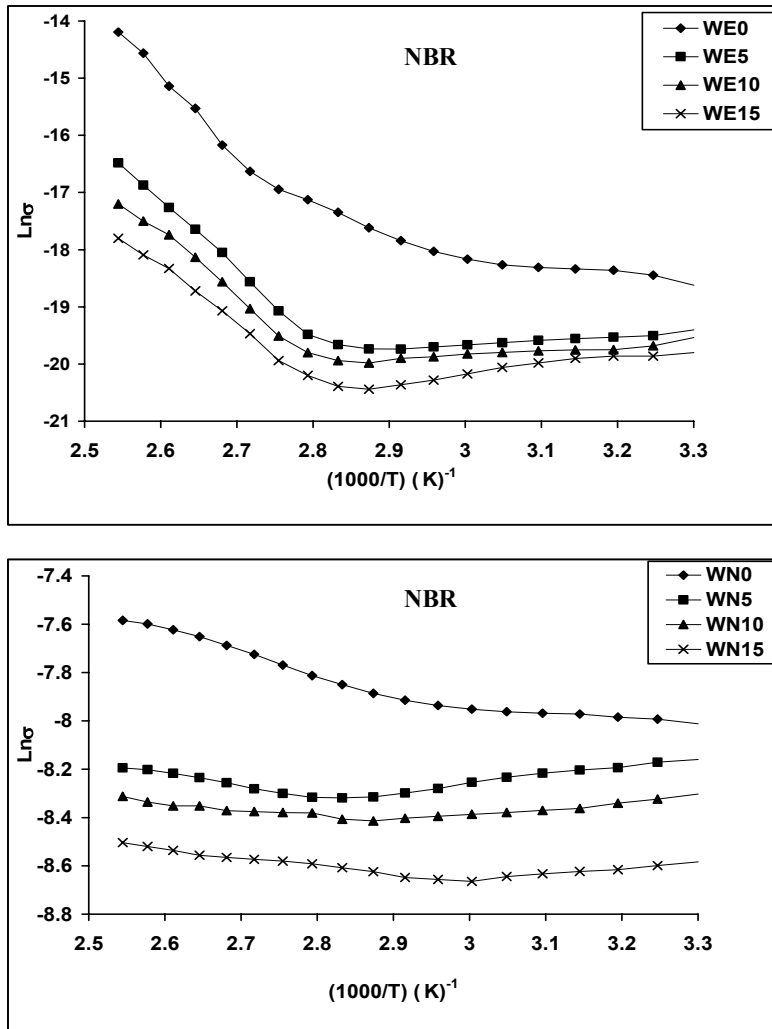
Fig.(3): The D.C. conductivity as a function of temperature, for EPDM and NBR. Following Mott and Gurney [2], the following equation

$$J=J_o \sinh (eaE/2kT) \qquad (2)$$

can be used to calculate the hopping distance, *a*, which may be considered as the inter-particle distance between carbon black aggregates at different working temperatures for all EPDM and NBR rubber composites. *e* is the electronic charge. The parameters *a* and J_o were calculated using an iterative method and are listed in Table (3).

**Table (3):** The calculated fitting parameters for EPDM and NBR samples at different temperatures.

T (K)	303		323		343		363	
Sample	a (nm)	j_o (A/m²)	a (nm)	j_o (A/m²)	a (nm)	j_o (A/m²)	a (nm)	j_o (A/m²)
WE0	481±11	0.37±0.06	483±13	0.39±0.02	486±11	0.38±0.02	481±12	0.38±0.01
WE5	513±13	0.29±0.02	542±12	0.16±0.02	561±11	0.06±0.01	552±11	0.05±0.02
WE10	596±12	0.16±0.03	602±12	0.05±0.01	632±12	0.04±0.01	623±13	0.03±0.02
WE15	12±11	0.05±0.01	643±12	0.03±0.01	675±12	0.03±0.01	652±13	0.02±0.01

T (K)	303		323		343		363	
Sample	a (nm)	j_o (A/m²)	a (nm)	j_o (A/m²)	a (nm)	j_o (A/m²)	a (nm)	j_o (A/m²)
WE0	365±12	50±1	365±12	50±1	362±12	376±11	57±1	0.38±0.01
WE5	443±13	33±2	443±13	33±2	482±11	494±11	23±2	0.05±0.02
WE10	469±13	25±1	469±13	25±1	502±11	517±11	15±1	0.03±0.02
WE15	491±11	16±2	491±11	16±2	552±13	578±12	7±1	0.02±0.01

One can observe, in general, that the inter-spacing distance, *a*, is increased with the increase of foaming agent concentration which reflects the influence of decreasing the cross-linking density on pushing up the carbon aggregates to be apart from each other. In addition, *a* is found nearly constant for unfoamed samples. This may be reflected in a constant conductivity unless a thermal activation occurs. This confirms the results obtained in conductivity measurements, as seen in Fig. (3). On the other hand *a*, for foams, are increasing by increasing temperature up to ~ 343 K after which *a* is no longer increasing. This may denote that thermal expansion equilibrium may be acquired and the void volume is then unchanged. This confirms that the increase of conductivity, previously obtained, above 350 K is mainly due to thermal activation.

Figure (4) shows a decrease in dielectric permittivity with both increasing frequency and foaming agent concentration. In such composites, it is difficult to expect a typical type of polarization such as dipolar or orientation polarization especially at high frequency and the existence of voids. One may

expect an interfacial polarization to dominate in the low frequency region and gradually diminishes to zero at high frequencies [3-4].
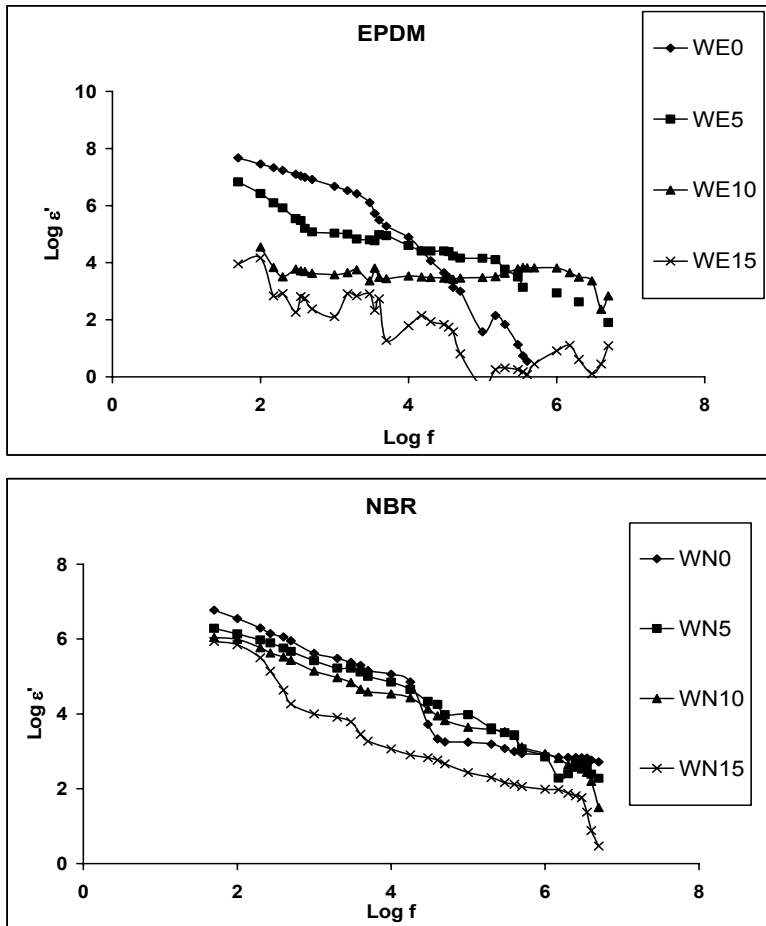
Fig.(4): The relation between permittivity, $\varepsilon^{'}$, and frequency, *f,* at 303 K for EPDM and NBR samples .

The experimental data over the considered frequency range was analyzed using the power law $\varepsilon' = a\,f^{-b}$, where a and *b* are two carbon black concentration dependent parameters [5]. Figs. (5 & 6) show the dependence of the fitting parameters a and b on carbon black volume fraction, ϕ, for both EPDM and NBR samples respectively.
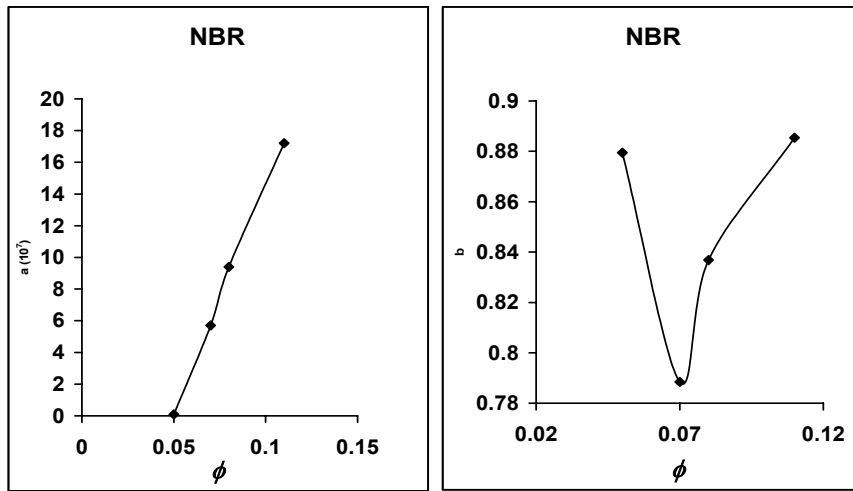
Fig.(5): The relation between fitting parameters a and b with the volume fraction ϕ of carbon black for EPDM samples.
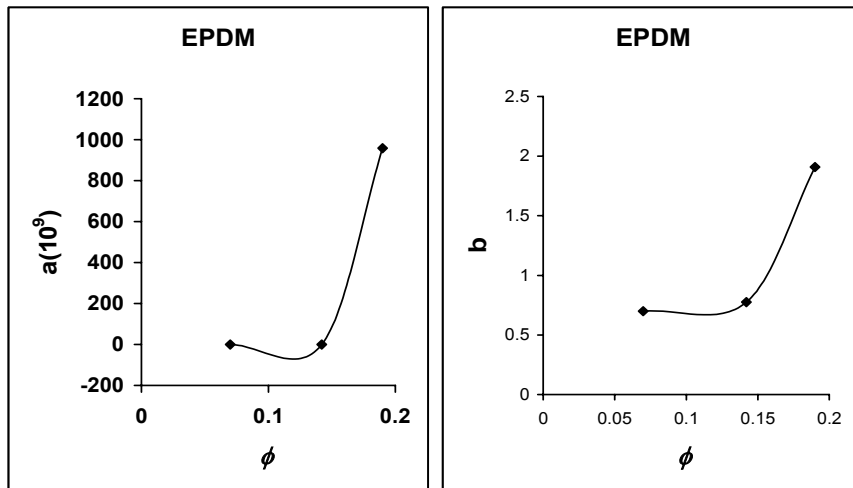

Fig.(6): The relation between fitting parameters a and b with the volume fraction ϕ_c of carbon black for NBR samples.

It is noticed that both *a* and *b* are increasing by increasing the carbon black volume fraction or alternatively decreasing the foaming agent concentration up to a certain concentration, after which saturation was acquired. The low value of the exponent *b,* less than 1*,* may indicate tunneling conduction mechanism, [6].

The dielectric loss as a function of frequency at room temperature is shown in Fig. (7) for EPDM and NBR foamed rubbers. Dielectric losses are high in the low frequency range. This may be attributed to the interfacial polarization. Interfacial polarization induces a Debye type dielectric relaxation, [7-8] and the relaxation peaks shift to lower frequencies as the concentration of the carbon black increases, or the foaming agent concentration decreases. [3]
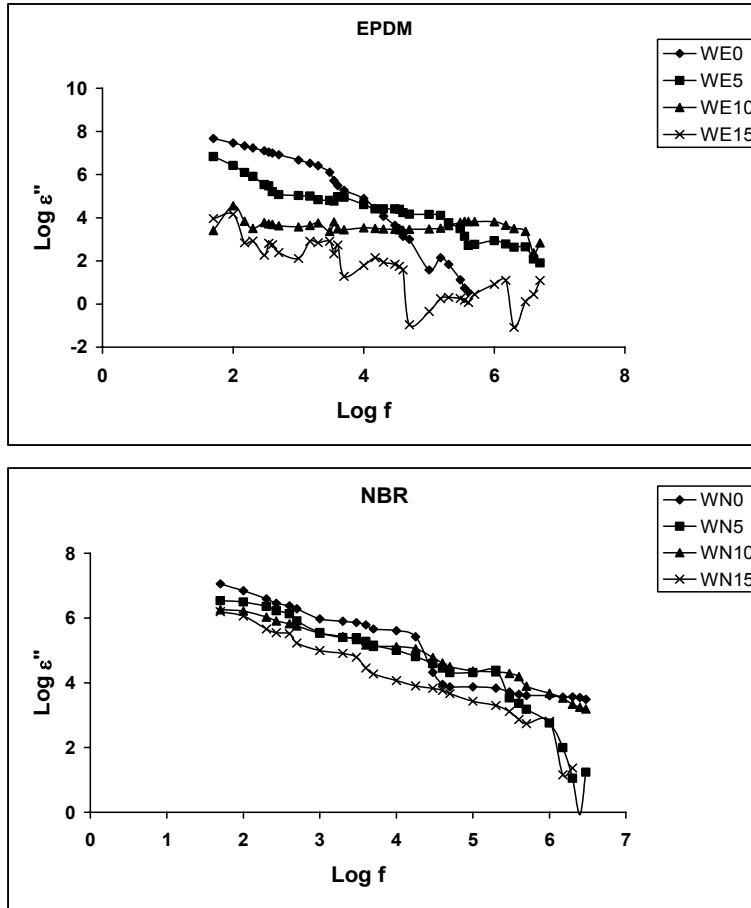
Fig.(7): The relation between dielectric loss, ε'', and frequency, *f,* 303 K for EPDM and NBR samples.

Dielectric losses diminish rapidly with increasing frequency, because interfacial polarization related to large dipole across interfaces is no longer active as the electric field changes direction with increasing rapidity.

4. Conclusion:

The I-V characteristics show two distinct regions, in both types of foams. The slope of the first region is about equal to 1, in both types of foams, indicating Ohmic conduction up to 400 volt. The slope of the second region is greater than 1 in case of EPDM whereas, for NBR, it is less than 1. One may suggest a space charge limited conduction mechanism, SCLC. SCLC was found of Schottky type for EPDM and of Poole-Frenkel for NBR.

From D.C. conductivity measurements, it was found that the conductivity, in general, decreases with increasing foaming agent concentration. Also it was found that there was a competition between two conduction mechanisms; tunneling and thermal activation.

The separation distances were found increasing up to a certain temperature, after which was found slightly changing.

The permittivity as well as dielectric loss was measured as functions of frequency, in the range 42 Hz to 5 MHz. They were found decreasing rapidly by increasing the frequency. This behavior may be attributed to interfacial polarization.

The power law fitting parameters a and b were found dependent on the carbon black volume fraction. The obtained small value of *b (<1)* confirmed the type of conduction mechanism obtained from D.C. measurements.

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