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Effect of Chromium Chloride on the Mechanical and Dielectric Properties of EPDM Rubber

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Abstract: Measurements of Young's modulus, dielectric loss and a.c. conductivity have been carried out on EPDM rubber samples loaded with different concentrations of $CrCl_3$ (0,2,4 and 6 phr). The values of Young's modulus was found to be linearly dependent on the $CrCl_3$ content. Variation of the dielectric loss with temperature showed that $CrCl_3$ may act as plasticizer. However, at higher frequencies the dielectric loss was found to be independent of frequency and the rubber samples may behave as non-polar dielectric. Investigations of the a.c conductivity suggested that the conduction in these rubber samples can be described by small polaron tunneling. In addition, conductivity was found to increase with $CrCl_3$ content.

Keywords : EPDM rubber, Young's modulus, dielectric, a.c. conductivity.

Introduction

Ethylene-propylene-diene terpolymers (EPDM) rubber is an ideal material for outdoor applications because it exhibits high tensile strength and excellent resistance to puncture, UV radiation, weathering and microbial attack. It shows also excellent resistance to ozone and heat, good color stability and dielectric qualities. However, EPDM rubber is not recommended for applications involving petroleum derivatives because it is generally attacked by mineral oils, solvents and aromatic hydrocarbons.[1-3]

EPDM rubber is commonly used as a dielectric material used for electric insulation of high voltage cables[4,5] due to its good chemical, mechanical and electrical properties. The dielectric strength of this polymeric material is one of the most significant properties for the evaluation of its performance, which is a function of operation conditions and environment.[6]

Considerable research efforts have been directed towards the effect of reinforcing carbon black (C.B), as its type and concentration, on the electrical and mechanical properties of rubber vulcanizates.[7-9] The effect of white filler concentration and characteristics on the mechanical and dielectric properties of EPDM rubber has been also investigated in previous works.[10,11] Studies of electrical conductivity and creep characteristics of EPDM rubber loaded with carbon black indicated that the conduction in these materials is of metal-like type and that the increase of C.B content enhances the hardness of the samples.[12] However, such high conductivity is sometimes not required or even undesirable for some practical purposes.

Previous study on the effect of $CoCl_2$ on creep characteristics of EPDM rubber indicated that creep parameters are strongly dependent on $CoCl_2$ content and a decrease in viscosity of rubber samples was achieved.[13] However, study of literature showed that little attention has been directed to the effect of inorganic additives on mechanical and dielectric properties of EPDM rubber.

The aim of the present work is to investigate the effect of chromium chloride ($CrCl_3$) as an inorganic additive on the mechanical and dielectric properties of EPDM rubber. The function of $CrCl_3$ in modifying the physical properties of these materials to find uses in many static and dynamic applications is also aimed.

Experimental

The samples of EPDM rubber were commercially vulcanized at 150 °C for 20 min and under pressure of 100 kg/cm^2 by Heliupolis Company for Chemical Industries (Cairo, Egypt). The ingredients of the investigated rubber samples

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Table I. Ingredients of the Studied EPDM Rubber Samples

Ingredients	Quantity (phr)
Royalene 512	100
Zinc Oxide	5
Stearic Acid	1
ZA (antioxidant)	2
Sulfur	1.5
TMTD (accelerator)	1
MBT	1.5
Chromium Chloride ($CrCl_3$)	0,2,4 and 6

are given in Table I. The inorganic additive $CrCl_3$ was added to the rubber samples as a powder during their manufacturing.

Stress-strain graphs of the samples were gained by using Ametek force gage at ambient temperature, where stresses are recorded automatically. The a.c. conductivity as well as the dielectric measurements were carried out in the frequency range between 100 Hz and 100 kHz by the aid of a programmable automatic RCL meter (PM6304). The temperature of the tested samples was recorded with a chromel-p-constantan thermocouple.

Results and Discussion

Modulus of Elasticity. Figure 1 shows the stress-strain curves of the studied EPDM rubber samples, where Hook's law is obeyed. It can be seen that at certain value of stress, the strain increases with $CrCl_3$ concentration. The computed values of the Young's modulus were found to decrease linearly with $CrCl_3$ as illustrated in Figure 2. This behavior indicated that the addition of $CrCl_3$ to EPDM rubber may reduce the intermolecular forces and this in turn results in decreasing the cross-linking density of the material. In other words the addition of $CrCl_3$ to the rubber samples makes it more soft and increases the chain flexibility i.e $CrCl_3$ may act as plasticizer.

Dielectric Loss. It is well known that the parameters which characterize the dielectric losses (ε'' and tan δ) depend on the features of the molecular motion in polymers. The magnitude of the dielectric loss (tan δ) is thus an important parameter which is determined by the chemical and physical structure of polymeric material.

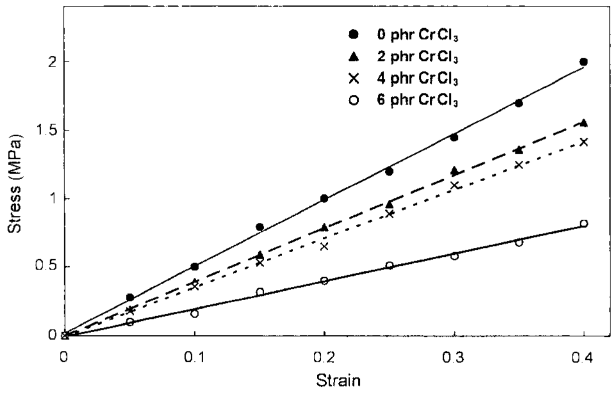

Figure 1. Stress-strain graphs of the studied samples at ambient temperature.

The temperature dependence of the dielectric loss (tan δ) at 500 Hz is shown in Figure 3 . The results show the presence of a maximum in tan δ which shifts toward lower temperature as $CrCl_3$ content increases.The value of this maximum increases also with increasing $CrCl_3$ content which is expected for polar additive. In this case addition of $CrCl_3$ may lower the viscosity of the rubber and hence the value of the relaxation time can be decreased. $CrCl_3$ can be implemented between rubber chains leading to the reduction of the cohesive forces between them which in turn increase the segmental mobility. The reduction in intermolecular forces is most likely due to a decrease in the cross-linking density of the rubber sample. The behavior of dielectric loss supports the idea that $CrCl_3$ may act as polar plasticizer and results also in increasing the value of dielectric loss of the sample.

The frequency dependence of the dielectric loss in the fre-

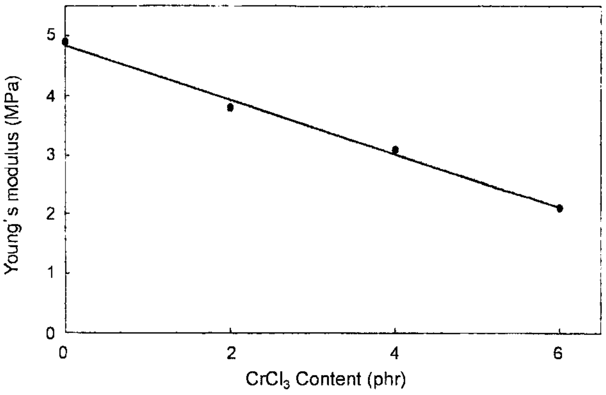

Figure 2. Dependence of Young's modulus on Cr Cl_3 content.

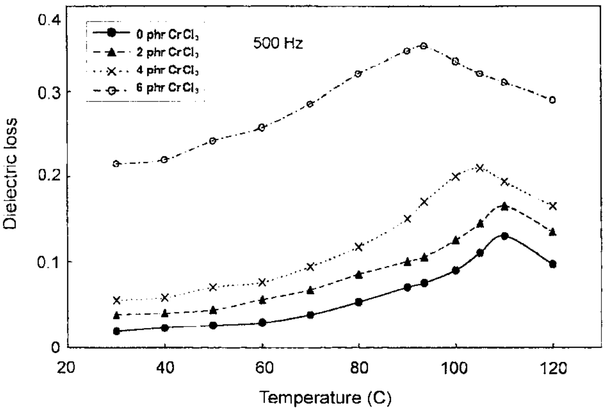

Figure 3. Dielectric loss of the samples as a function of temperature at 500 Hz.

quency range between 100 Hz and 100 kHz were measured at 40°C for all studied samples and represented in Figure 4. An anomalous behavior is observed for all samples with a dielectric loss peak at about 650 Hz. The value of this peak seems to be independent of $CrCl_3$ concentration. This type of behavior can be described with a well defined Maxwell-Wagner mechanism[14] and may be attributed to the presence of a.c. current which is in phase with the applied potential. The current itself results from the differences in the conductivity and permetivity of the different constituents of the rubber samples.

It is known that relaxation time is a function of temperature and consequently the dielectric properties are temperature dependent. Figure 5 illustrates the temperature dependence of the dielectric loss (tan δ) for the sample loaded with 4 phr $CrCl_3$ at different frequencies. The results show a maximum in (tan δ) at temperature of about 105°C which is shifted towards higher temperatures as the frequency increases. At certain temperature the magnitude of the dielectric loss increases by lowering the frequency. The frequency dependence of the dielectric constant for the same sample at different temperatures is shown in Figure 6. Generally, the dielectric constant was found to increase with temperature, whereas it decreases with frequency up to about 3.5 kHz. However, at higher frequencies the dielectric constant is frequency independent and the sample may behave as non-polar dielectric.

A.C. Conductivity. Figures 7 and 8 show the frequency

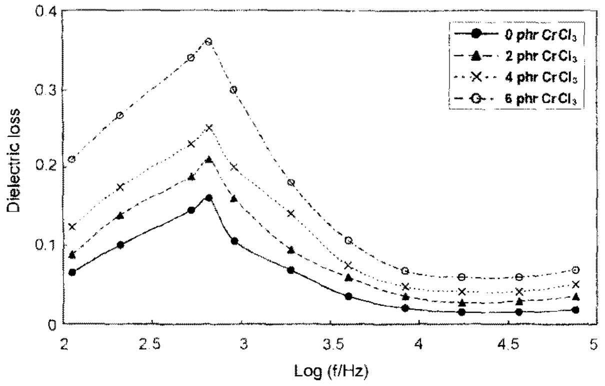

Figure 4. Dependence of dielectric loss on the frequency, *f*.

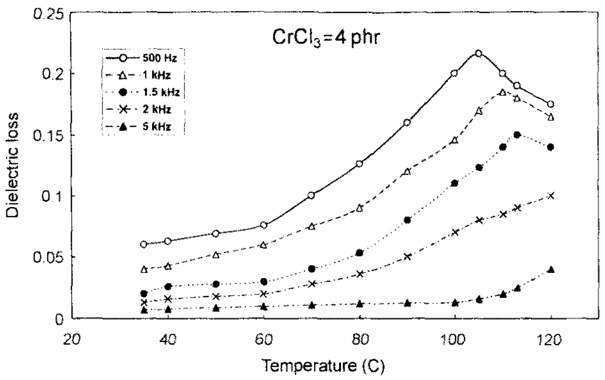

Figure 5. Dielectric loss as a function of temperature for the sample of 4 phr $CrCl_3$ at different frequencies.

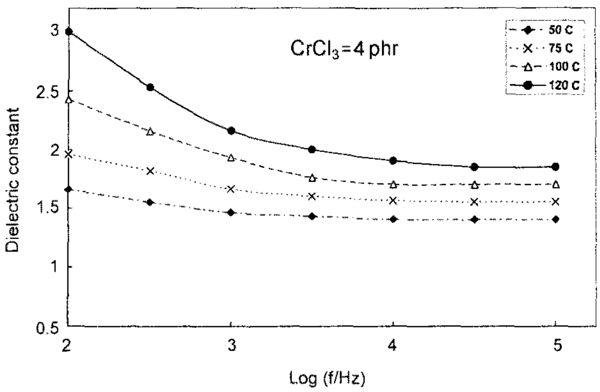

Figure 6. Dependence of dielectric constant on frequency for the sample of 4 phr $CrCl_3$ at different temperatures.

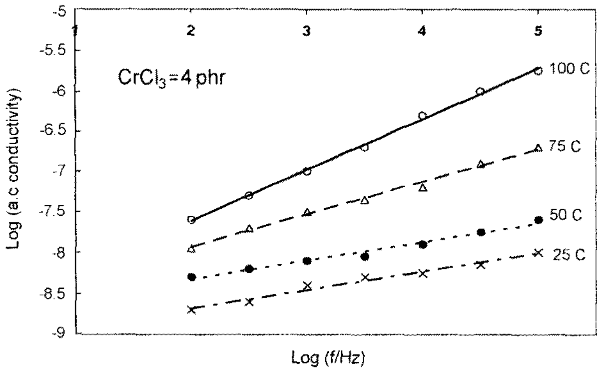

Figure 7. Graphs of Log(a.c. conductivity) versus Log(frequency) at different temperatures for the sample of 4 phr $CrCl_3$.

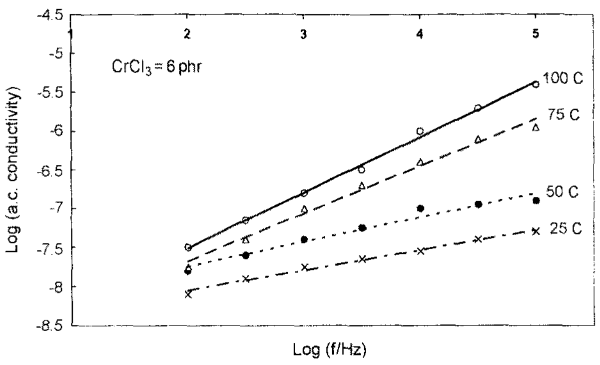

Figure 8. Graphs of Log(a.c. conductivity) versus Log(frequency) at different temperatures for the sample of 6 phr $CrCl_3$.

dependence of the a.c. conductivity for two samples containing 4 and 6 phr $CrCl_3$ at different temperatures. From these graphs it can be assumed that the a.c. conductivity (σ_{ac}) of the samples depends on the frequency (ω) according to the power law[15]

$$\sigma_{ac} = A\omega^n \tag{1}$$

where A is constant and n is the frequency exponent ($n \leq 1$). The ω^n power law is very frequently observed in a wide range of materials among which are the polymers.

On comparing the results of Figures 7 and 8 it can be noted that the a.c. conductivity increases with increasing $CrCl_3$ content in the sample. $CrCl_3$ may act to facilitate segmental motion and dipole orientation and hence enhances a.c. conduction. This behavior of a.c. conductivity revealed that $CrCl_3$ may act as plasticizer.

The temperature dependence of the frequency exponent (n) is illustrated in Figure 9, which indicates that n increases linearly with temperature for both studied samples. Such behavior can be explained in terms of small polaron tunneling or hopping mechanism. Small polarons are generally assumed to be localized that their distortion clouds do not overlap. In this case the activation energy for polaron transfer (W_H; $W_H = W_p/2$, where W_p is the polaron energy ; is independent of the interstice separation. The tunneling distance (R) at a frequency (ω) is given by[16]

$$R = \frac{1}{2\alpha}\left[ln\frac{1}{\omega\tau} - \frac{W_H}{kT}\right] \tag{2}$$

Equation (2) implies that the distance (R) depends on the temperature (T), which consequently means that the exponent (n) will be also temperature dependent[16]

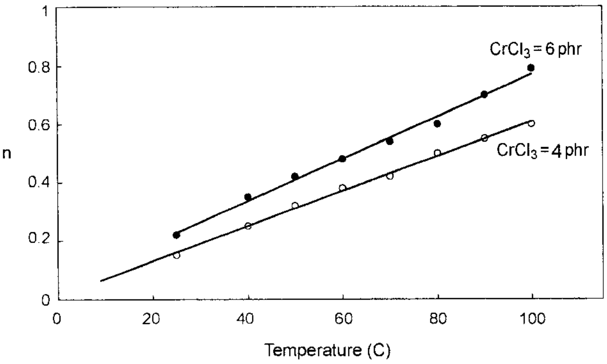

Figure 9. Dependence of the exponent (n) on temperature for the samples containing 4 and 6 phr $CrCl_3$.

$$n = 1 - \frac{4}{ln\frac{1}{\omega\tau} - \frac{W_H}{kT}} \tag{3}$$

According to Equation (3) the exponent (n) increases with temperature, which agrees with the experimental results and thus supporting the suggestion that the conduction mechanism in these rubber samples is by small polaron tunneling.

Conclusions

Based on the results of Young's modulus, dielectric loss and a.c. conductivity of EPDM rubber samples loaded with $CrCl_3$, it may be concluded that :

(1) addition of $CrCl_3$ in appropriate concentration can improve the elasticity as well as monitoring the dielectric properties i.e. $CrCl_3$ may act as plasticizer.

(2) a dielectric loss peak at nearly 650 Hz was observed and found to be independent of $CrCl_3$ content.

(3) at frequencies higher than 3.5 kHz the dielectric constant is frequency independent and the samples may behave as non-polar dielectric.

(4) the a.c. conductivity increases with $CrCl_3$ content and the conduction mechanism may be due to small polaron tunneling.

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