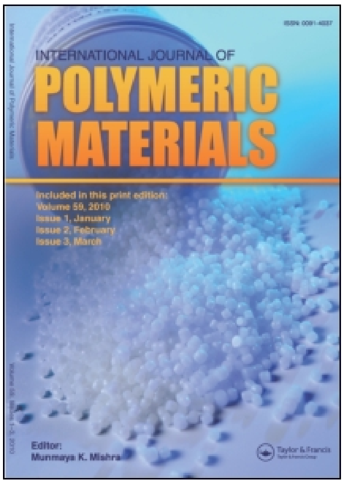

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Electrical Properties of Graphytized and Degraphytized Carbon-Blacks Filled Rubbers

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The ac-electrical properties of graphytized and degraphytized carbon-blacks filled rubbers were investigated at room temperature in the frequency range 100 Hz–10 kHz. The volume fraction of the fillers varies from 15% to 60%. The observed conductivity for graphytized filled samples was found to be much higher than degraphytized filled samples. This behavior was interpreted in terms of the defective zones which were dramatically reduced by the graphytization process. The Voet model was applied for both categories of filled rubbers which exhibit two distinct mechanisms of electrical conduction depending on the filler concentration.

KEY WORDS Filled rubbers, carbon-black, graphytic, electrical properties.

INTRODUCTION

The electrical conductive polymer composites are becoming an increasingly important class of materials for variety of applications in industry and technology. The applications of such composites include wire and cable sheathing, shielding against electromagnetic interference and antistatic materials.[4] The technological importance of such materials is due to its mechanical and electrical properties which can be improved by changing the content and type of fillers.[5–8] For electronic applications the main question concerning the composite is how the electrical conductivity changes with the content of the conductive filler. However, one of the most important class of the composites is a mixture of rubbers with graphite and carbon blacks powder or fibers which have the subject of extensive research.[9–18]

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The work included in this paper is concerned with studying the ac-electrical properties of filled rubbers with different volume graphite concentration varies from 15% to 60%. Two types of specimens were used. The filler in the first type of specimens is in the form of graphytized and the second is degraphytized carbon-blacks fillers.

The ac-impedance of both categories was measured at room temperature in the appropriate frequency range (100 Hz–10 kHz) of the used apparatus. The ac-electrical conductivity and dielectric constant were determined from the ac-impedance and phase angle results.

EXPERIMENTAL

Samples of graphytized (Corax N660) and degraphytized (Corax N600) carbon-blacks filled rubbers were commercially manufactured in the form of sheets by Degussa A. G (Germany) as 1 mm thickness sheets. Discs specimens of 2 cm diameter were cut from the composite sheets. The ac-electrical measurements were carried out using an electrical bridge described in details elsewhere.[19-20] The ac-impedance and the phase angle were measured using a gain-phase meter. The applied frequency was varied from 100 Hz to 10 kHz. The magnitude of the applied field was less than 200 V/m. This was necessary to avoid any perturbation in the sample bulk.

RESULTS AND DISCUSSION

The measured values of the phase angle (ϕ) of graphytized and degraphytized carbon-blacks filled rubbers is negative as shown in Figure 1 for both graphytized and degraphytized samples at 100 Hz and 1 kHz, respectively. Therefore, the composite material can be considered to consist of capacitive and resistive networks, it can be represented by a bulk resistance and a capacitor in parallel. In this case the ac-impedance (Z) as well as the dielectric constant (ε) can be represented by complex quantities such as,

$$Z^* = Z - jZ_c \tag{1}$$

$$\varepsilon^* = \varepsilon' - j\varepsilon'' \tag{2}$$

where $Zr = Z\cos\phi$ is the real component, $Zc = Z\sin\phi$ is the imaginary component of the complex ac-impedance (Z^*), and ε' and ε'' are the real and loss dielectric constants respectively. The ε' and ε'' are related to the components of impedance and frequency (f) by the relations,

$$\varepsilon' = Zc/21\pi f Z^2 C_0 \tag{3}$$

$$\varepsilon'' = Zr/2\pi f Z^2 C_0 \tag{4}$$

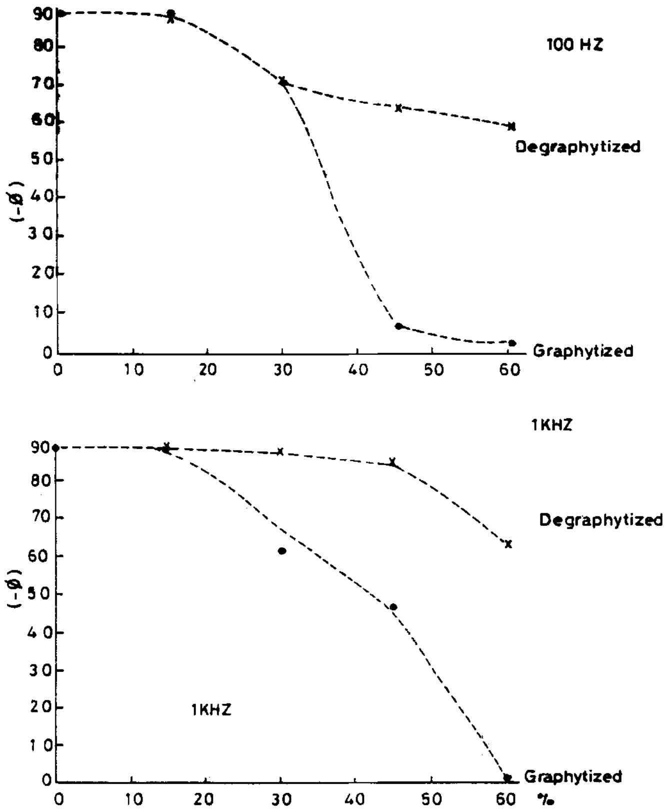

FIGURE 1 Phase angle (ϕ) at 100 Hz and 1 kHz vs. fillers content for graphytized and degraphytized carbon-blacks filled rubbers.

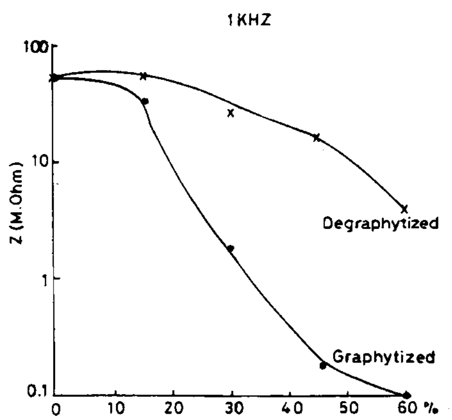

FIGURE 2 ac-impedance (Z) vs. fillers content at 1 kHz for graphytized and degraphytized carbon-blacks filled rubbers.

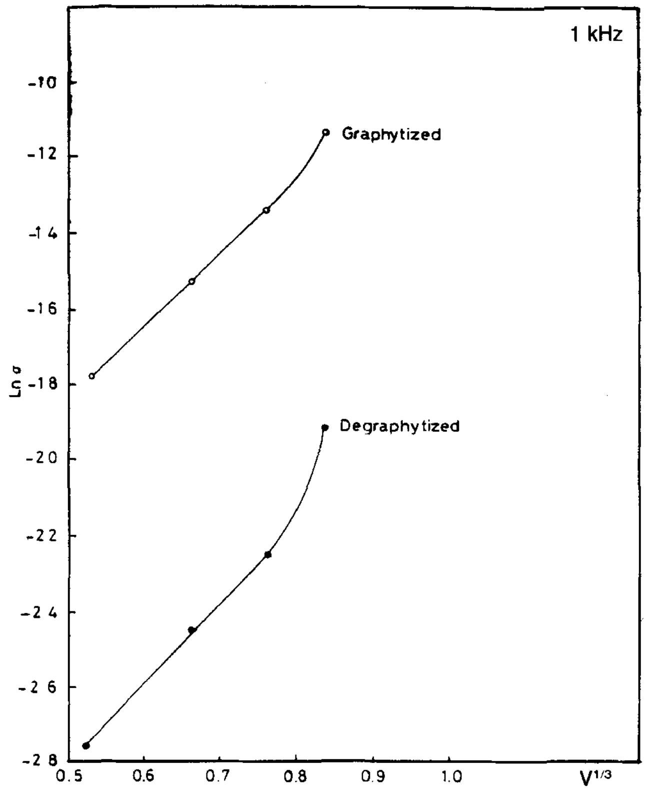

FIGURE 3 In conductivity vs. $V^{1/3}$ (volume fraction) for graphytized and degraphytized vs. filler content for graphytized and degraphytized carbon-blacks filled rubbers.

where Z is the measured ac-impedance, and C_0 is the capacitance of the electrodes. The ac-conductivity (σ) can be determined from the relation,

$$\sigma = 2\pi f \varepsilon_0 \varepsilon'' \qquad (5)$$

where ε_0 is the permittivity constant.

Figure 2 shows the variation of the ac-impedance with filler content. A dramatic decrease in (Z) with filler content was observed. The decrease in (Z) is more pronounced in carbon-blacks filled graphytized samples with much lower values compared to degraphytized samples. This observed difference in (Z) for graphytized and degraphytized samples can be related to defective zones and to preferred orientation of the graphytized fiber crystallites.[21,22] W. G. Peng[23] showed that graphytization process reduces dramatically the number of defects and the concept of graphite-layer stacks with distinct stacking height becomes valid.

In order to study the variation of ac-conductivity with filler content a plot of ln σ versus $V^{1/3}$, where V is the volume fraction of the fillers, was constructed according to Voet model.[24] This model was originally proposed for low concen-

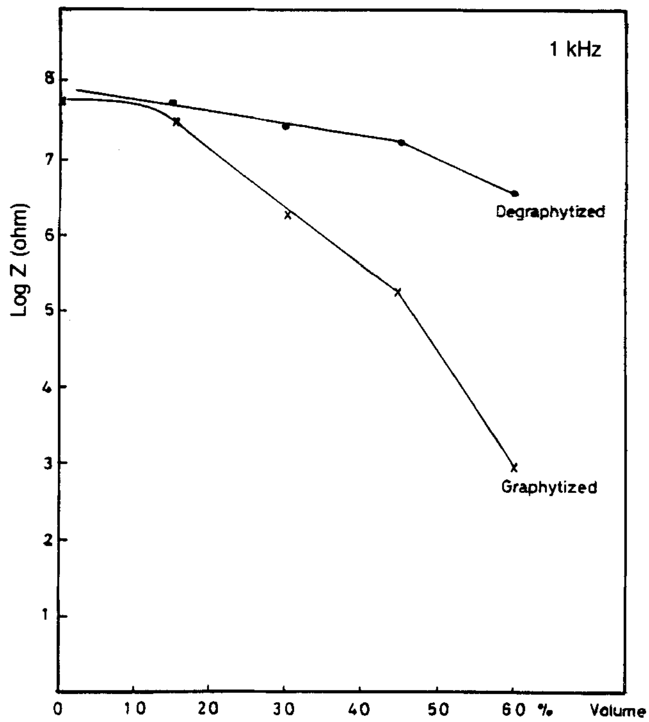

FIGURE 4 log(Z) impedance vs. filler content for graphytized and degraphytized carbon-blacks filled rubbers.

tration content of the filler. It relates the conductivity with the volume fraction of the filler by the relation,

$$\ln \sigma = KV^{1/3} \tag{6}$$

As shown in Figure 3 a straight line up to the volume fraction of the filler 45% can be constructed for both graphytized and degraphytized samples. The slope (K) of the lines is nearly the same. The figure shows two distinct regions which are more obvious in degraphytized carbon-blacks filled samples. These two regions can be observed clearly in the plot of Log Z with filler volume fraction as shown in Figure 4. This may indicate that there are two different mobilities of the charge carriers during the electrical conduction process. In the first region the filler distributed-homogeneously in the volume of the insulating host. Therefore, it can be suggested that the conduction process in this region in both categories of the samples is nonohmic which is mainly due to electronic movement or to the electronic emission effect. The difference in ac-conductivity in the first region for graphytized and degraphytized samples is mainly due to the structural differences as a result of degraphytization process of the fillers, nâmely, packing density, layer diameter, stacking height, defective zones and lubricostratic disorder.[1] At high concentration the fillers particles begin to form agglomerates, (in contact with each other), which

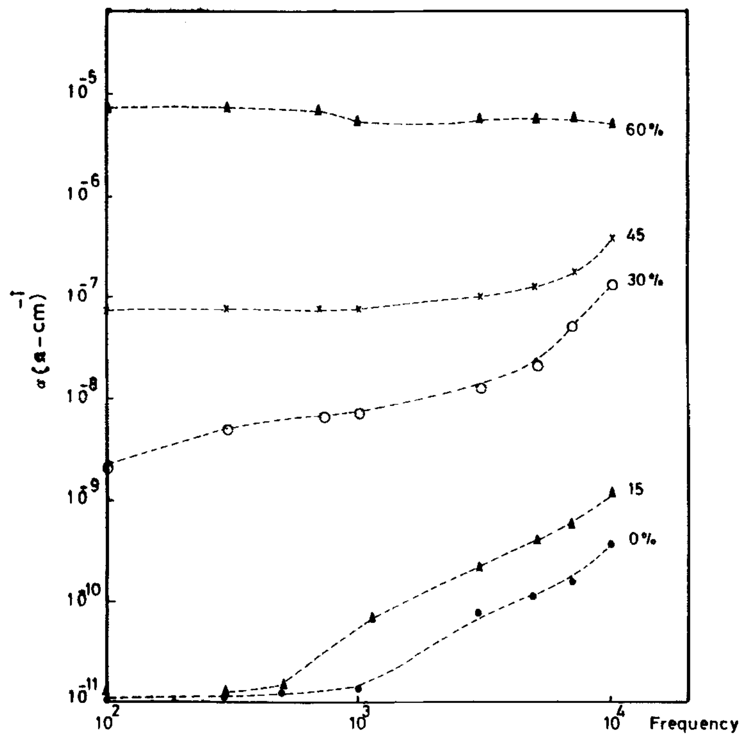

FIGURE 5 The ac-conductivity vs. frequency for different contents of graphytized carbon-blacks filled rubbers.

make the electrical conduction process to be ohmic in nature. The phase angle approaches zero at high concentration, as shown in Figure 1, and the ac-conductivity becomes nearly independent of frequency as shown in Figures 5 and 6 for different contents of graphytized and degraphytized carbon-blacks filled rubbers, respectively. The difference in the ac-conductivity between the two categories of specimens is mainly attributed to the defective zones which are highly reduced by the graphytization process.

Figures 7 and 8 show the variation of the real component of dielectric constant (ε′) with frequency for different fillers concentration. For degraphytized filler samples, ε′ is nearly independent of frequency up to filler concentration 45%. However, for graphytized filler samples ε′ is independent of frequency only for 15% filler concentration. This constancy in ε′ with frequency may be due to interfacial polarization (the Maxwell-Wagner process) of the unidirectional fibers which enhances ε′ and compensates for the decrease in ε′ caused by orientation polarization. This phenomenon occurs in heterogenous systems when one component has a higher electrical conductivity than the other.[25] In general, ε′ for graphytized filler samples is higher than degraphytized filler samples and this difference increases by increasing the filler content as shown in Figure 9.

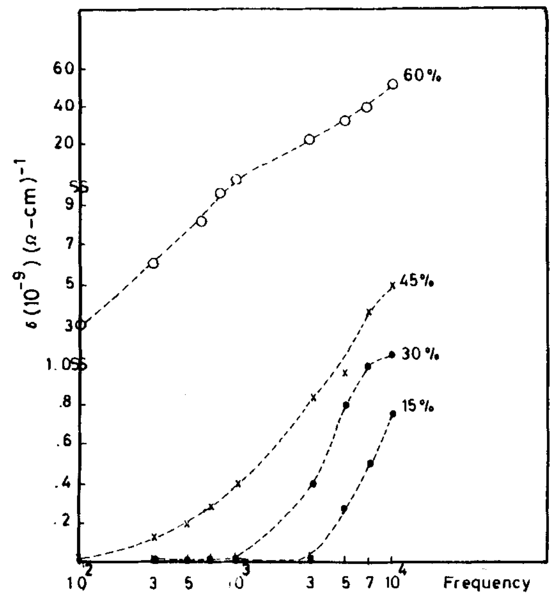

FIGURE 6 The ac-conductivity vs. frequency for different contents of degraphytized carbon-blacks filled rubbers.

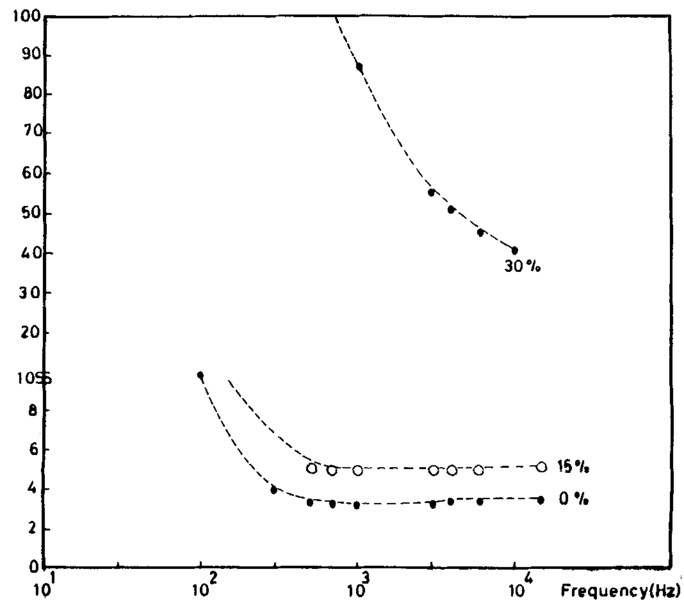

FIGURE 7 Dielectric constant (ε′) vs. frequency for different contents of graphytized carbon-blacks filled rubbers.

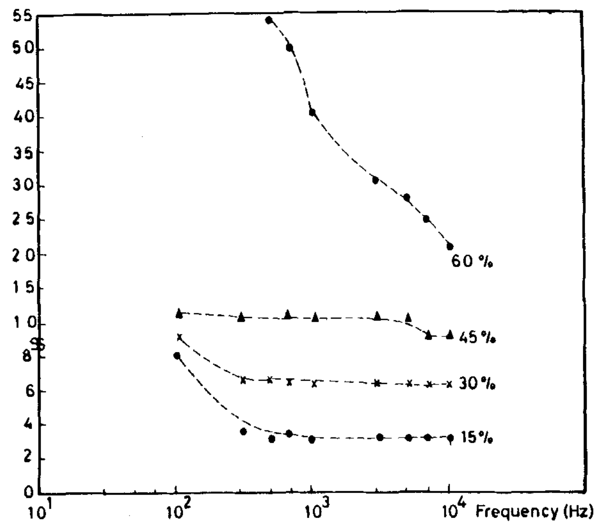

FIGURE 8 Dielectric constant (ε') vs. frequency for different contents of degraphytized carbon-blacks filled rubbers.

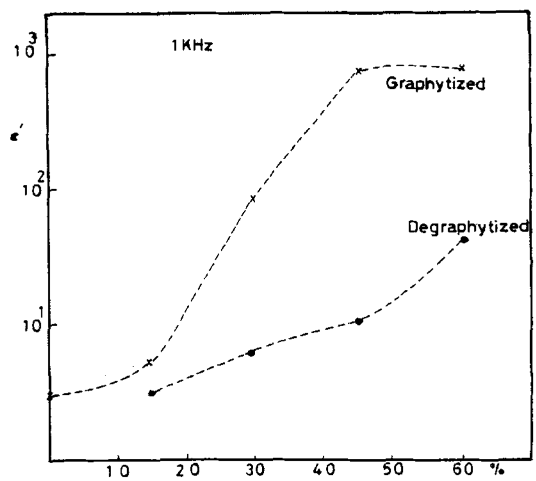

FIGURE 9 Dielectric constant (ε') vs. fillers content for degraphytized and graphytized carbon-blacks filled rubbers.

CONCLUSIONS

The present study of the ac-electric properties of the graphytized and degraphytized carbon-blacks filled rubbers reveals the following results.

1. The ac-impedance of graphytized carbon-blacks filled rubbers decreases dramatically with fillers content and has much lower ac-impedance compared with the degraphytized samples.

2. The composite materials exhibit two distinct conductivity mechanisms namely, ohmic and non-ohmic type depending on the filler content.

3. Voet-model is applicable for this type of fillers up to filler concentration 45%.

4. The dependence of ac-conductivity on frequency is highly pronounced in degraphytized samples where it is nearly independent of frequency for graphytized samples with filler concentration more than 30%.

5. The dielectric constant ε' is independent of frequency up to 45% filler content for degraphytized samples, while for the graphytized sample ε' is frequency up to 15% filler content.

References

1. A. R. Bunsell, "Fiber Reinforcements for Composite Material," Elsevier, ch. 3, pp. 73–148, 1980.
2. R. H. Norman, "Conductive Rubbers and Plastics," Elsevier, 1970.
3. M. Markis, A. Ram and F. Flashner, *Polym. Eng. Sci.*, **18**, 649 (1978).
4. P. B. Jana, A. K. Mallick and S. K. De, *Polym. Composite*, **22**, 1 (1991).
5. A. I. Medalia, *Rubber Chem. Technol.*, **60**, 45 (1987).
6. S. Radhakrishnan, *Polymer. Commun.*, **26**, 153 (1985).
7. R. J. Cembrola, *Polym. Eng. Sci.*, **22**, 601 (1982).
8. W. M. Hess and J. Wiedenbaefer, *Rubber World*, **86**, 5 (1982).
9. J. Meyer, *Polym. Eng. Sci.*, **13**, 462 (1973).
10. D. M. Bigy, *Polym. Eng. Sci.*, **19**, 1188 (1979).
11. Y. S. Wang, M. A. Gvrkis and J. T. Lindt, *Polym. Compos.*, **7**, 349 (1986).
12. J. Martinsson and J. L. White, *Polym. Compos.*, **7**, 302 (1987).
13. J. Kost, M. Markis and A. Fouz, *Polym. Eng. Sci.*, **23**, 567 (1983).
14. G. Obliego and U. Herman, *Kunststoffe*, **74**, 97 (1984).
15. F. J. Balta-Calleja, J. A. Ezquerra, D. R. Rueda and J. Alonso-Lopez, *J. Mater. Sci. Lett.*, **3**, 165 (1984).
16. S. Miyavcht, Y. Sortmachi, M. Mitsui, H. Akihide and K. Ohkita, *J. App. Polym. Sci.*, **29**, 251 (1984).
17. M. Sitting, "Carbon and Graphite Fibers, Manufacture and Applications," Noyes Data, NJ, 1980.
18. M. Markis, A. Ram and Z. Stein, *Polym. Eng. Sci.*, **21**, 1049 (1981).
19. A. M. Ziblif, *J. Electronal Chem. Interface Electrochem.*, **143**, 121 (1983).
20. T. Tanaka, M. Tsukioka, E. Bannai, M. Shimazu and S. Ehara, *J. Mater. Sci., Lett. 1*, 133 (1982).
21. S. G. Bennet, D. J. Johonson and W. Johnson, *J. Mater. Sci.*, **18**, 3337 (1983).
22. M. J. Yasin, I. E. EL. Rihail, M. S. Ahmad and A. M. Zihlif., *Mater. Chem. and Phys.*, **15**, 353 (1989).
23. W. G. Peng, M. Strauss, T. Pieper and H. G. Kilian, *Molecular Phys.*, **80**, 419 (1993).
24. A. Voet, W. N. Whitten and F. R. Cook, *Kolloid Zeitschrift*, **39**, 201 (1965).
25. R. J. Meakins, *Progress in Dielectrics*, **7**, 69 (1967).