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On the Correlation Between Electromagnetic Waves Absorption and Electrical Conductivity of Iron Powder Filled Nitrile Butadiene Rubber

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SUMMARY: In the present paper the correlation between the coefficient of attenuation of electromagnetic microwaves and resistivity in iron powder filled (0 - 500 phr) nitrile butadiene rubber based compositions has been investigated and evaluated by the coefficient of correlation. As a whole coefficient of correlation values between the electrical and microwave characteristics investigated are in the region (-0,99 ÷ -0,92), i.e. a reverse functional dependence, too close to the linear, is available, but a lightly expressed tendency to decreasing of correlation coefficients values when filler amount increases, has been observed. As a result above concentration of 300 phr the correlation is predominately stochastic.

Introduction

Electrically active composites containing conductive fillers have some important technical uses. In electromagnetic interference applications the shielding capability of such materials is used to exclude electromagnetic radiation from electronic devices (housings, etc.). In this case, a fair degree of conductivity is normally sufficient to achieve proper function. In a lot of recent publications ferromagnetic fillers have been considered as a promising possibility for obtaining elastomeric systems with excellent microwave characteristics[1-3]. In the same time the mechanism of absorption of ultra high frequency (UHF) electromagnetic radiations in these type of vulcanizates, containing metal or ferrite powder as fillers (if we assume that the loss in the rubber matrix may be ignored) depends strongly on the mechanism of absorption in the metal conductive phase, more specially on its electrical conductivity. On the other hand the conductivity of rubber composites is determined by a number of factors, all related to the degree of connectivity of the conductive particles in the insulating matrix. For instance, when the matrix consists of a crystalline polymer the degree of crystallinity determines to a large extent the particle concentration required in order to reach the percolation threshold, that is to say the concentration where the particles begin to form a connected network throughout the

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bulk of the material. The lower the crystallinity the higher the particle concentration needed to reach the percolation. In a previous investigations[4] it has been shown that the filler tendency to form continuous physical network is a determining factor for the correlation between the electrical and microwave properties. In the present paper the correlation between the coefficients of attenuation of UHF electromagnetic waves (α) and volume and surface resistivity (ρ_v and ρ_s) in iron powder (IP) filled nitrile butadiene rubber (NBR) has been investigated. Iron powder is a filler with very low expressed tendency to form secondary structures consisting of starting particles aggregates in the rubber matrix.

Experimental

Basic components in the samples investigated are nitrile butadiene rubber CKH-40M (produced in Russia, 39±1% of acrylonitrile content, Mooney viscosity ML (1+4)373K - 65±7, density - 1.0 g/cm^3) and iron powder NC 100.24 (produced by Höganäs, Sweden) with average particles size below 10 μm. The starting NBR blends (in phr: zinc oxide 5, stearic acid 2, zinc-N-diethyldithiocarbamate (Vulkacit LDA, product of Bayer) 1,2-mercaptobenzothiazole (Vulkacit Mercapto, product of Bayer) 0.5; sulphur 2, iron powder 0-500) were rolled for 10 min; with subsequent press vulcanisation into plaques (6x9x2 mm) for 10 min at 160°C under 15MPa. ρ_v and ρ_s have been measured by Teralin III (Germany) at room temperature under constant current. Microwave properties have been determined by Hewlett-Packard waveguide line, containing spectroanalyser, powermeter, coefficient of reflection meter and coefficient of attenuation meter. The measurements have been carried out at 8-12 GHz frequency range. The coefficient of correlation (r) has been determined by the equation:

$$r = \frac{\frac{1}{N}\sum_{u=1}^{N}(\alpha_{iu} - \overline{\alpha}_i)(\rho_{vju} - \overline{\rho}_{vj})}{S\alpha_i . S\rho_{vj}}$$

where:

i = 1,2,............., n; j= 1, 2, ..., m; u= 1,2,.............., N (N -number of the experiments, n and m stand for no matter which, at random chosen permissible value of i and j, res.);

$\overline{\alpha}_i$, $\overline{\rho}_{vj}$ - estimates of the mathematical expectations of the variables α_i and ρ_{vj}, for example:

$$\overline{\alpha}_i = \frac{1}{N}\sum_{u=1}^{N}\alpha_{iu} \quad .$$

$S\alpha_i, S\rho_{vj}$ - estimates of the meansquare (standard) deviation of the variables α_i and ρ_{vj}, for example:

$$S\alpha_i = \sqrt{\frac{1}{N-1}\sum_{u=1}^{N}(\alpha_{iu} - \overline{\alpha}_i)^2}.$$

Results and Discussion

First of all the dependencies of the above mentioned parameters on the filler concentrations have been studied (Fig.1-2).

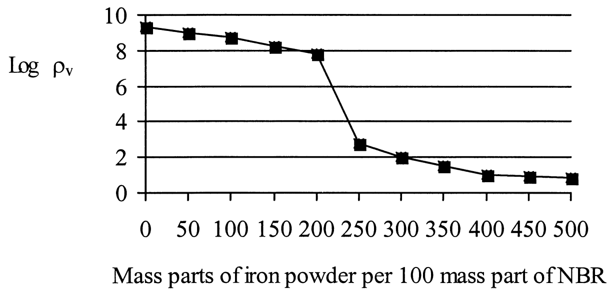

Fig.1: Volume resistivity dependence on iron powder concentration in NBR based compositions (ρ_v in Ω.m).

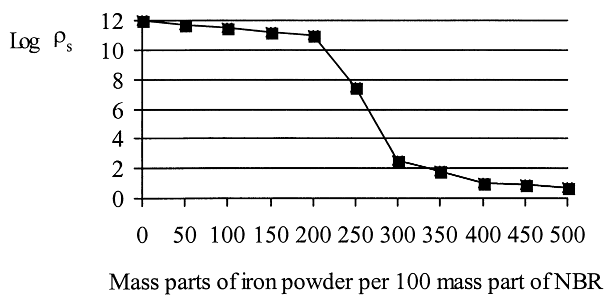

Fig.2: Surface resistivity dependence on iron powder concentration in NBR based compositions (ρ_s in Ω).

An existence of critical concentration at a 200 phr iron powder content leading to rapid volume and surface resistivities decreasing has been found. The rapid change of the electrical properties observed in the above mentioned critical region is due to the formation of a connected network (consisting of filler particles) throughout the bulk of the rubber matrix. When the filler content is raised beyond this threshold a stable conducting network is already obtained.

Some of the results, obtained on the microwave properties of the NBR IP filled compositions are summarized in Fig. 3-4. It is evident that up to 300 phr IP content the coefficient of attenuation increases in close to linear dependence. Above this critical value it increases more rapidly and a well expressed maximum at 400 phr may be observed. On the basis of a microstructural analysis it has been shown that the effective microwave energy absorption may be provided only by achievement of an optimum microstructural characteristic, which obviously occurs at a 400 phr IP content.Above this concentration the rubber insulating layers, covering all iron particles become thinner, begin to break down and possibilities for direct physical contacts between the particles appear, which are the main reason for the observed coefficient of attenuation decrease. It is obvious also that the coefficient of attenuation decreases with the increase of the frequency, especially at higher values of IP content in the compositions. Probably the high electrical conductivity of IP is responsible for this decrease.

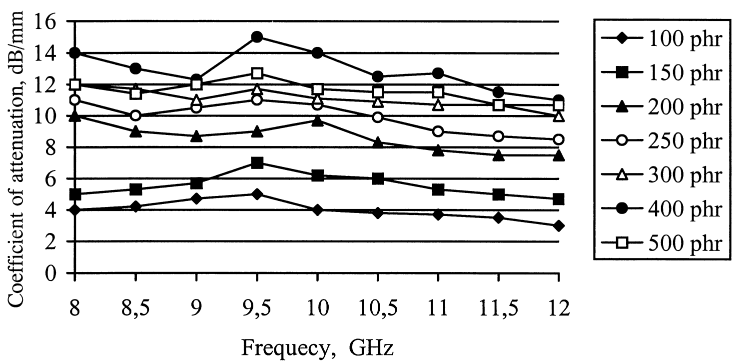

Fig.3: Frequency dependence of coefficient of attenuation in the region 8-12 GHz at different iron powder content.

As a whole the coefficients of correlation values between the electrical and microwave characteristics investigated in the IP concentration between 0-500 phr are in the region from -0.91 till -0.92, i.e. a reverse functional dependence, too close to the linear, is available (Table 1, rows 1, 5). A well expressed tendency to decreasing of correlation coefficients values when filler amount increases has also been observed.

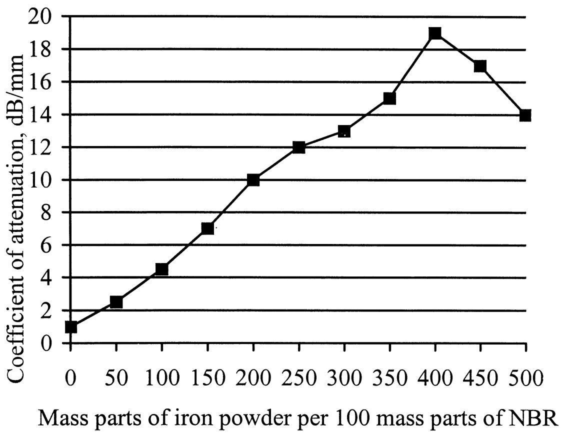

Fig.4: Coefficients of attenuation dependence on iron powder concentration in NBR based compositions at 9.4 GHz.

On the base of the detailed analysis of the experimental results and the calculated r-values it has been shown that:

- at IP concentrations < 200 phr (below percolation threshold) the volume and surface resistivities keep their high values. In the same concentration interval the increase of the attenuation coefficients is close to linear and the correlation coefficients values are close to 1, i.e. there is a close to linear functional dependence between investigated microwave and electric properties (Table 1, rows 2,6).

- the rapid decreasing of ρ_v and ρ_s at IP concentrations around and above the percolation threshold (200 phr) has been characterized with nonlinear changing of coefficients of attenuation and well observed maximum at 400 phr. In the concentration region of 200 - 300 phr a decreasing of the coefficients of correlations values has been observed, but they yet keep comparatively high values (Table 1, rows 3,7).

- the increasing in IP concentration up to 500 phr does not change the electrical conductivity but considerably influences composites coefficients of attenuation. The decreasing of the coefficients of attenuation in the region 400-500 phr is probably due to the possibilities for the physical contacts between the particles. It is evident that in the region 300-500 phr in practice there is a stochastic dependence only between microwave and electric properties investigated (Table 1, rows 4,8).

- with the increasing of the frequency the correlation between electrical properties and microwave absorption improves, judging by the increased values of the coefficients of correlation at 12 GHz in comparison with the ones at 9.4 GHz.

It is obvious from these data that the most important factors for the correlation between microwave and electric properties of IP filled NBR is the filler concentration, strongly influencing both the conductivity and the attenuation. The properties of conductive composites are often discussed in terms of common percolation concepts. However on closer examination of the data it may be found that such interpretations are not free from substantial element of ambiguity. Not only may it be difficult to distinguish between bond and site percolation, but also the shape and dimensions of the conductive entities are factors of decisive importance in this context.

Table 1. Coefficients of correlation (r) between volume resistivity (ρ_v), surface resistivity (ρ_s) and coefficient of attenuation (α) at 9.4 GHz and 12 GHz depending on IP concentration.

N	Functions	IP concentration, phr	Coefficient of correlation at 9.4 GHz	Coefficient of correlation at 12 GHz
1	ρ_v - α	0 - 500	- 0.913	-0.920
2	ρ_v - α	0 - 200	- 0.950	-0.954
3	ρ_v - α	200 - 500	- 0.770	-0.850
4	ρ_v -α	300 - 500	- 0.590	-0.601
5	ρ_s - α	0 - 500	- 0.915	-0.897
6	ρ_s - α	0 - 200	- 0.980	-0.980
7	ρ_s - α	200 - 500	- 0.880	-0.932
8	ρ_s - α	300 - 500	- 0.730	-0.752

Conclusions

The results obtained give us grounds to emphasize on the fact that IP concentration as well as composition microstructure characteristics are factors determing both the microwave absorption and electrical properties of the systems investigated. The microwave properties of the systems studied remain strongly dependent on IP concentration even in the ranges where electroconductivity is high and relatively constant.The lack of a tendency for a formation of a physical IP particles network turns to be an additional dominant component.

As seen from the results the good and close to linear agreement between investigated microwave and electric properties exists only till IP concentrations of 300 phr, above this concentration the correlation between the investigated properties is predominately stochastic.

The influence of the electromagnetic waves frequency on the correlation between electrical and microwave properties has been found also, but in the range 8-12 GHz it is not too considerable.

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