RUBBER THIN FILMS MICROWAVE ABSORBERS OBTAINED BY MAGNETIC FIELD APPLICATION

N. Dishovsky, K. Ruskova, M. Marinov, V. Vassilev

University of Chemical Technology and Metallurgy,
8, Kliment Ohridski blvd, 1756 Sofia, Bulgaria
E-mail: dishov@uctm.edu

Abstract

The influence of external constant homogeneous magnetic field on the electrical and microwave properties of nitrile butadiene rubber based filled films, containing soft and hard magnetic fillers is investigated. The magnetic field was applied during the process of the films formation. It was found that magnetic modification increases both the electrical conductivity and electromagnetic waves absorption of the films. The effects observed may be connected to the conductive phase particles secondary fibrous structures formation due to the magnetic field orientating action.

1. INTRODUCTION

It is very well known that filler particles distribution in the polymer matrix is one of the most important factors for the determination of polymer composites properties[1]. This is why a number of attempts have been made to create and to maintain a specific type of orientation and organization in filler particles ordering in polymer matrix[2]. The external magnetic field (EMF) application is a promising technique for solving of such kind of problems and as a result a lot of polymer properties were successfully modified[3-5]. The preparation of electrically conductive filled composites for shielding application with high performance and reproducible microwave properties, requires a perfect control of the dispersion of the fillers in the matrix. Some parameters are especially important:

- morphology distribution of conductive fillers and formation of aggregates,
- electrical properties,
- microwave characteristics

In an effort to improve the electrical and microwave characteristics as well as the distribution of the fillers and formation of secondary aggregates in thin filled nitrile butadiene rubber based films we have assumed that a EMF may be used to create a specific filler particles organization when hard and/or soft magnetic substances are used as fillers. The results of these studies are applied to improve the exploitation properties of rubber thin films microwave absorbers for shielding applications.

2. EXPERIMENTAL

2.1. Samples preparation

Butadiene acrylnitrile rubber (NBR) Perbunan 3807 NS (product of Bayer) with acrylnitrile content 39±1 %, Mooney viscosity ML4(100°C) 45±5 and density 1,00 g/cm^3 was used as polymer matrix. Strontium hexaferrite $SrFe_{12}O_{19}$ with coercive force of 2800 Oe and natural magnetite (cubic structure, coercive force of 100 Oe), both with average particle size of 1-3μ (determined by electron microscopy) were used as fillers. The mixing process of the elastomer with the fillers has been carried out by Brabender Plasticorder at starting temperature of 50°C, shear rate - 60 min^{-1} and volume of the mixing chamber - 50 cm^3. The rubber-filler ratio was varied from 10 till 60 phr. The films (average thickness of 100μ) have been prepared from 5 mass% acetone solutions of the rubber-filler compositions, cast on three different types of substrates-high transparent microscope glasses (for optical microscope investigations), aluminum foils (for electrical measurements) and paper with special treated surface - for measuring of the microwave properties. A constant external homogeneous magnetic field with strength of 1800 Oe was applied during the process of film formation, as is shown in Figure 1, for the period of 24 hours.

2.2. Samples investigations

The volume and surface resistivity of the films has been measured by Teralin III (Germany) at room temperature. The measurements of the microwave attenuation in 8-12 GHz frequency range were carried out by Hewlett Packard waveguide line, containing spectroanalyzer, powermeter, coefficient of reflection meter and coefficient of attenuation meter. Optical microscope investigations were carried out by using of standard microscope MI-8 (produced in Russia). The standard single factor ANOVA (analysis of variances) test was used to indicate similarities or differences between the experimental data obtained when electrical and microscope properties have been measured. Briefly the test was used to determine with statistical significance level of 0.05, whether the differences in the experimental data are due actually to the magnetic field application.

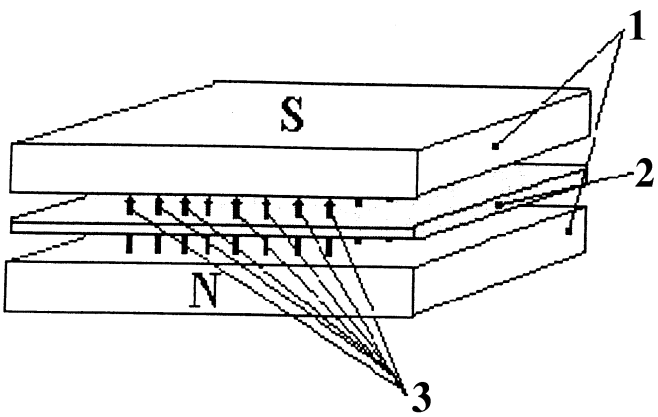


Figure 1. Diagram of external constant homogeneous magnetic field application:
1- magnets poles; 2-sample;3-magnetic field lines of force

2.3. Results and discussion

The volume resistivity of the films, obtained in the presence and absence of EMF is compared in Figure 2 (magnetite) and Figure 3 (hexaferrite). It is obvious from the figures that EMF decreases film volume resistivity.This effect is better expressed when magnetite has been used as a filler, which is due to its lower own resistivity ($10^{-2}\Omega$.cm) in comparison with the resistivity of strontium hexaferrite (10^{6} Ω.cm). One can see, for example, that the conductivity of the sample, containing 30 phr magnetite at H>0 is almost equal to the conductivity of the sample, containing 60 phr of filler when H=0. This effect is very important from a technological point of view. It may be seen also (Figure 2) that at H=0 a very well expressed percolation threshold exists at 10 phr. After the threshold the resistivity decreases rapidly. At H>0 the percolation threshold can not be observed in the investigated region of filler concentrations (probably it is situated at lower concentrations) The differences between the ρ_v values in the presence and absence of EMF are more considerable at lower filler concentrations. The higher the filler concentrations, the lower the difference between the ρ_v values. This effect may be explained with the possibilities for physical contacts among the conductive

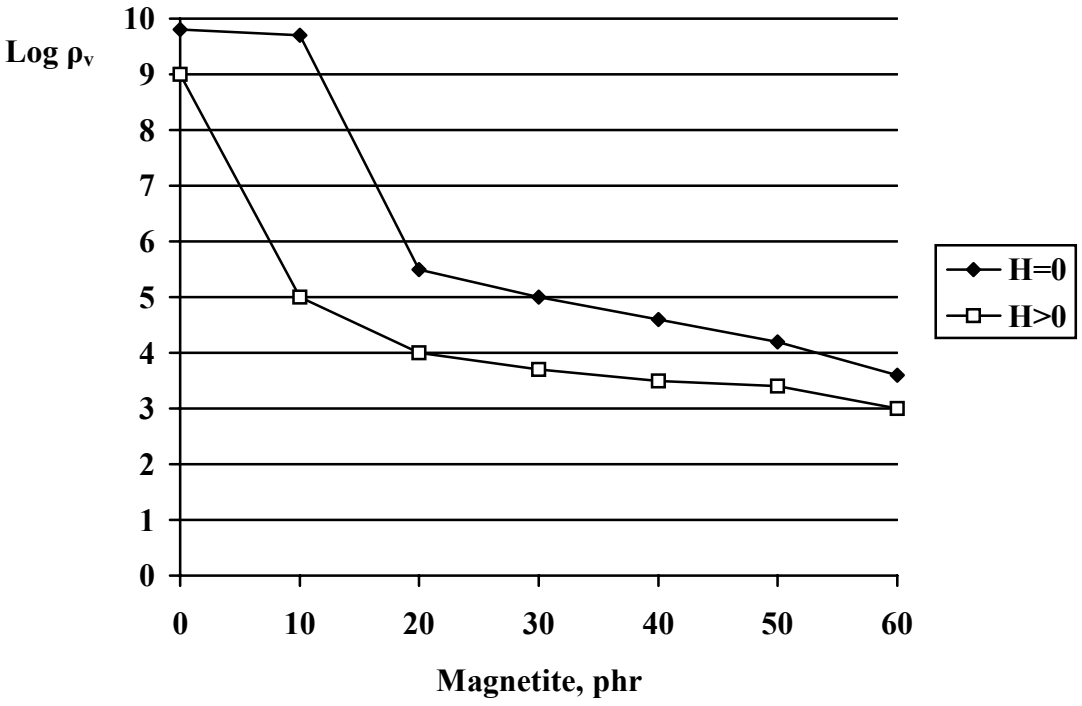


Figure 2. Volume resistivity ρ_v of NBR based films, containing different amounts of magnetite (H=0 - corresponds to EMF off; H>0 - corresponds to EMF on)

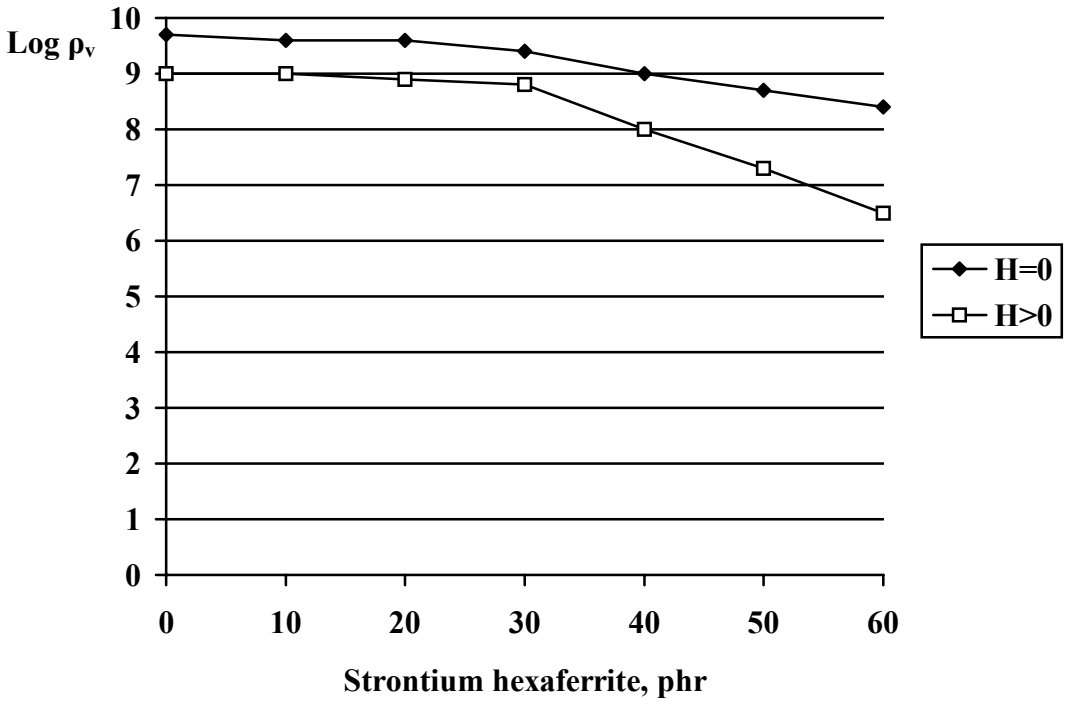


Figure 3. Volume resistivity ρ_v of NBR based films, containing different amounts of strontium hexaferrite (H=0 - corresponds to EMF off; H>0 - corresponds to EMF on)

phase particles, independent on EMF presence or absence. Due to lower own resistivity the percolation threshold has not been observed in the investigated region of concentrations, when $SrFe_{12}O_{19}$ is used, but it is evident that at H>0 the ρ_v decreases also. The EMF influence on the surface resistivity is absolutely insignificant (Figure 4)

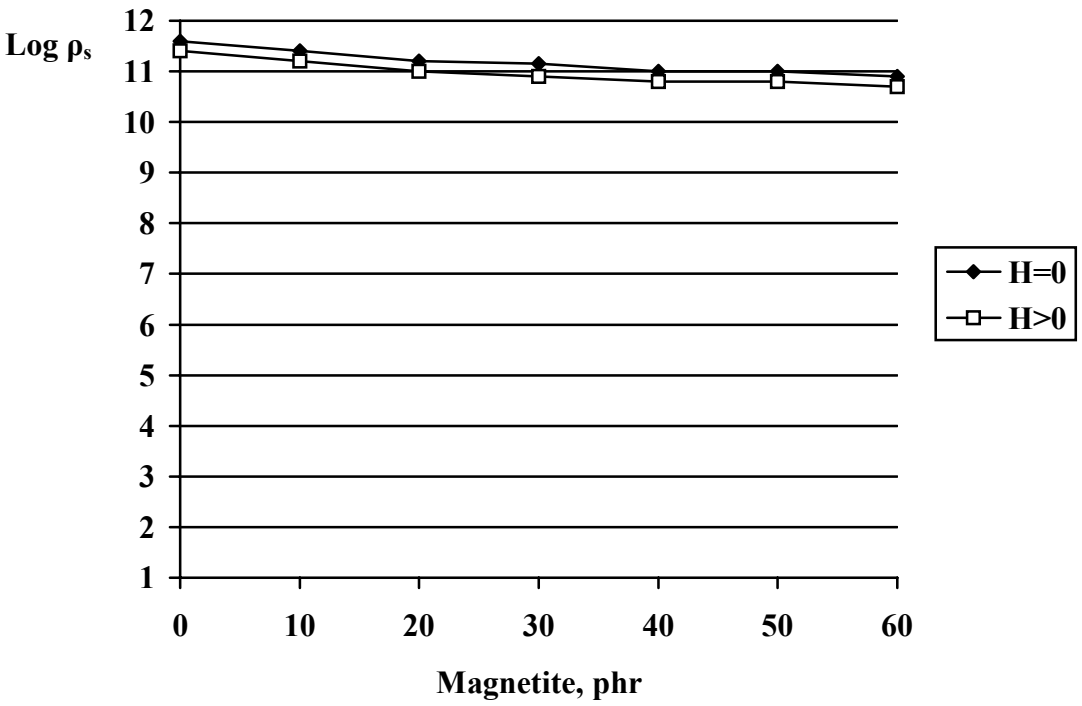
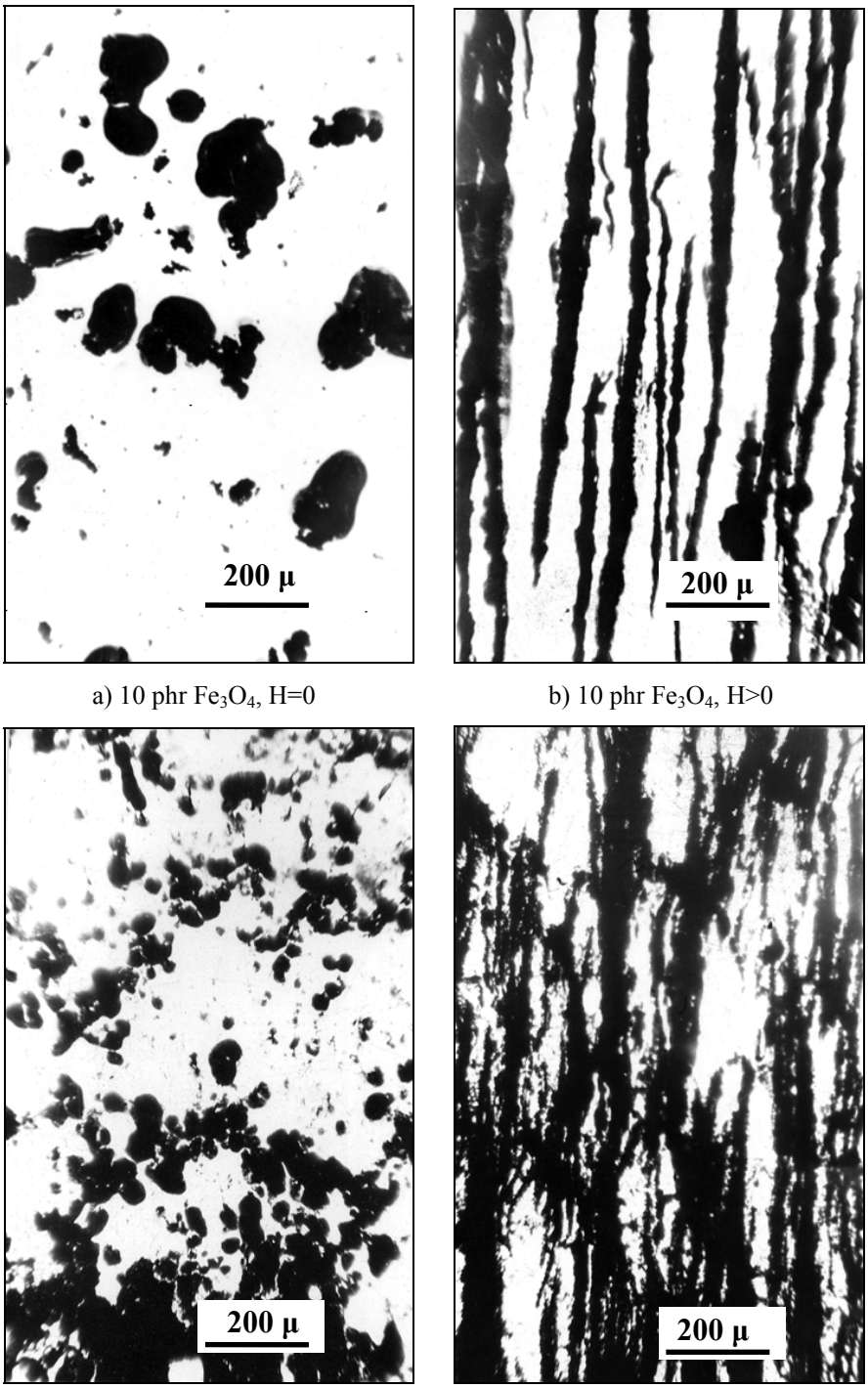


Figure 4. Surface resistivity ρ_s of NBR based films, containing different amounts of magnetite (H=0 - corresponds to EMF off; H>0 - corresponds to EMF on)

The above mentioned results may be explained with the formation of conductive filler phase secondary structures as a result of EMF application (Figure 5). One can see that EMF orientates the conductive phase particles depending on their magnetic characteristics in the direction of the magnetic field lines of force. As a result secondary electroconductive fibrous type structures have been formed in the rubber matrix, better expressed when magnetite is used (Figure 5b,f). It may be seen also that when hexaferrite is used as a filler, a trend for secondary structure formation may be observed even in the absence of EMF at higher filler concentrations(Figure 5g,h). This is the reason for the better expressed effects when EMF is applied to magnetite containing samples.The existence of secondary structures at H=0 is due to the hard

magnetic strontium hexaferrite high field of internal magnetic anisotropy. When isotropic soft magnetic magnetite is used, trends for secondary structure formation at H=0 can not be observed. It is evident that magnetic field can be used as a factor influencing the formation of the filled film microstructure. Figure 5 illustrates also the dependence of the secondary fibers, arranged with their major axes along the lines of force of the magnetic field, on filler concentration.

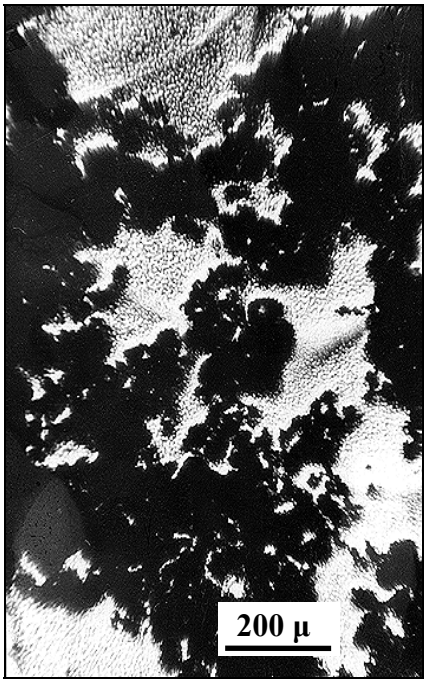


a) 10 phr Fe_3O_4, H=0

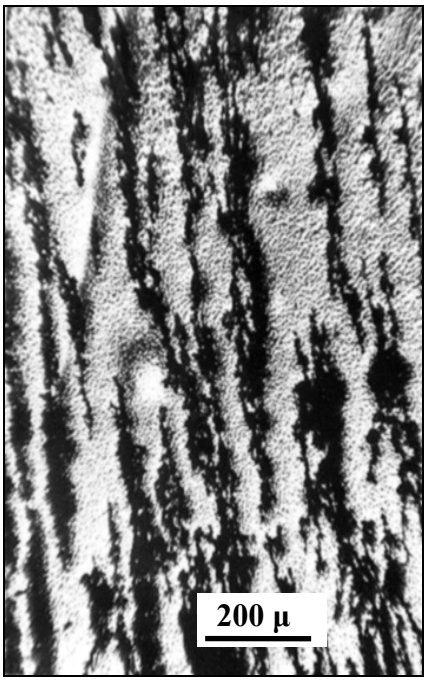
b) 10 phr Fe_3O_4, H>0

c) 50 phr Fe_3O_4, H=0

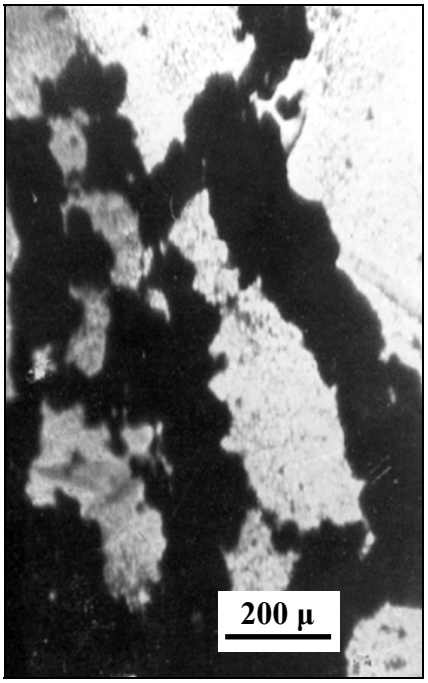
d) 50 phr Fe_3O_4, H>0



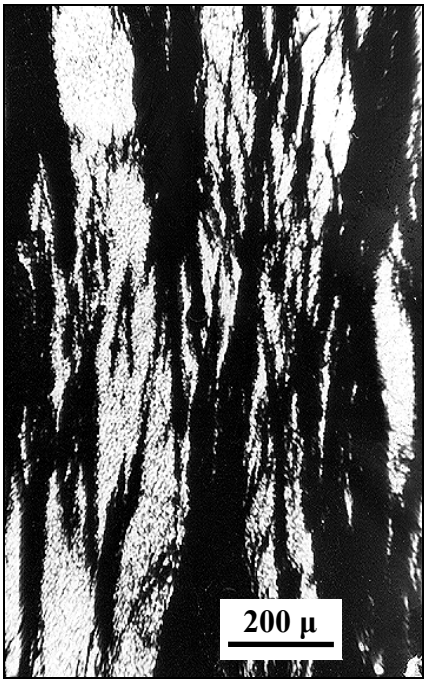
e) 10 phr $SrFe_{12}O_{19}$, H=0



f) 10 phr $SrFe_{12}O_{19}$, H>0



g) 50 phr $SrFe_{12}O_{19}$, H=0



h) 50 phr $SrFe_{12}O_{19}$, H>0

Figure 5. Optical microscope pictures (x 70) of NBR films

The influence of EMF application on the films microwave characteristics is shown in Figure 6. EMF leads to improving of microwave attenuation. The effect observed

depends also on the sample situation with respect to EMF lines of force - parallel or

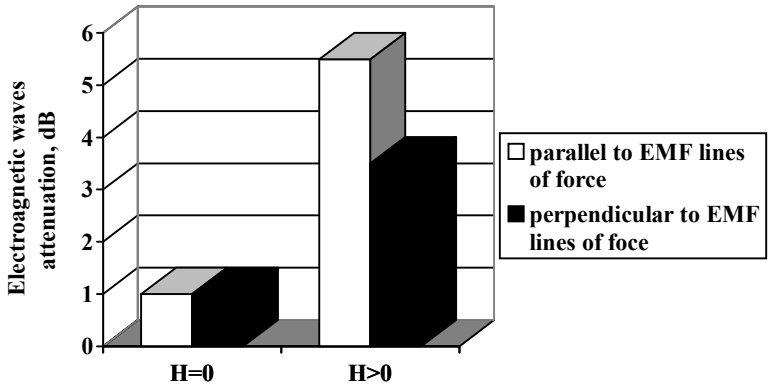


Figure 6. Effect of EMF application on NBR based magnetite filled films electromagnetic waves attenuation at 9,4 GHz (H=0 - corresponds to EMF off; H>0 - corresponds to EMF on).

perpendicular- and may be explained with the existence of an organization in the filler particles ordering, which increases the probability the propagating wave to meet on its way a filler particle instead a polymer matrix material. This probability in the absence of EMF, when the structure has the usual disordered nature and the filler particles are situated chaotic, is considerably less. The effect of the influence of the changed ratio between the electromagnetic waves length and filler secondary formations size is also possible, but it needs additional investigations. When the hexaferrite type of fillers are used, the effects are not so well expressed due to the existence of some extent of organization in the filler particles ordering even in the absence of EMF. The EMF application leads to improvement in films structure homogeneity which benefits the electromagnetic waves attenuation.

Further work is planned to continue first of all with the investigation of the possibilities for practical application of the effects observed. The final purpose is to obtain a rubber-textile coating with improved microwave attenuation for shielding application. Secondly, we plan to continue our investigations on the correlation between the electrical and microwave properties of the polymer filled composites. Some results in this field has been already published [6].

4. CONCLUSIONS

1. External constant homogeneous magnetic field application during the rubber filled film formation induces changes both in the electrical and microwave films response.

2. The reason for the changes observed as a result of the magnetic modification is the appearance of secondary formed structures of the filler particles in the polymer matrix.

3. The improved structure homogeneity after the EMF application leads to improving of the level of interaction between the films and electromagnetic waves and as a result the part of the absorbed waves increases.

REFERENCES

[1] R. H. Krock and L.J. Broutman, in: L.J. Broutman, R. H. Krock (Eds), Modern Composite Materials, Addison-Wesley Publishing Company, Reading, Massachusetts, 1967, pp.11-40.

[2] V. M. Volker, in: H. S. Katz, V. Milewski (Eds), Handbook of Fillers and Reinforcements for Plastics, Van Nostrand Reinhold Company, New York, 1981, pp.213-226.

[3] A. Alexeev, A. Kornev, Magnetic Elastomers, Khimia, Moscow, 1987 (in Russian).

[4] Yu. Rodin, Mehanika Kompositnih Materialov, 2(1992)255-261 (in Russian)

[5] J.Takimoto and K. Kayama, Proceedings XIIth Intern. Congr. On Rheology, August 18-21, Quebec city, Canada (1996)454-456

[6] N. Dishovsky, M. Grigorova, Mater. Res. Bull 35(3)(2000)