Vol. 6, No. 3, 2012 Chemistry

Jimsher Aneli[1], Levan Nadareishvili[2], Grigor Mamniashvili[3], Anatoli Akhalkatsi[3] and Gennady Zaikov[4]

GRADIENTLY ANISOTROPIC CONDUCTING AND MAGNETIC POLYMER COMPOSITES

[1]Institute of Machine Mechanics, 10, Mindeli str., 0186 Tbilisi, Georgia; jimaneli@yahoo.com
[2]Institute of Cybernetics of Georgian Technical University, 5, S. Euli str., 0186 Tbilisi, Georgia
[3]Institute of Physics of Tbilisi State University, 6, Tamarashvili str., 0186 Tbilisi, Georgia
[4]N.Emanuel Institute of Biochemical Physics of Russian Academy of Sciences, 4, Kosygin str., 119334 Moscow, Russia

Received: December 01, 2011 / Revised: February 02, 2012 / Accepted: May 14, 2012

Abstract. The character of the local electric resistance variations of film polymer composites on the basis of polyvinyl alcohol with graphite powder on the one hand and the magnetic susceptibility of the same polymer with nickel nano-particles on the other hand has been studied. It has been established that the changes of these parameters essentially depends on both initial shape of the films and on the direction of their orientation. It is concluded that the films of gradiently anisotropic polymer composites may be used in electronics.

Keywords: polymer film, filler, stretching, anisotropy, local electrical resistance, magnetic susceptibility.

1. Introduction

It is well known that there are several methods for obtaining materials with anisotropic properties by chemical methods (copolymerization, polymer-analogous transformation, radiation-chemical modifications, *etc*.) [1, 2]. At present the orientation of polymer films in the definite direction and environment conditions is one of the best methods for obtaining such structures. It is also known that at stretching thermoplastic polymers above glass temperature the material in the orientation state is formed. Such polymers are characterized by mono-axis crystal symmetry. In this state the principal direction of macromolecules coincides with the direction of stretching. If the polymer is filled with different dispersive fillers, particularly with electric conductive and magnetic materials (graphite, carbon black, metal powders), the particles distribution of the latter ones interacting with macromolecules transforms from the chaotic state to the orientation one. The change of polymer microstructure significantly defines the material electric and magnetic properties [3, 4].

In the presented work the character of electric conductivity and magnetic susceptibility change of polymer composite films based on polyvinyl alcohol, graphite and nickel at their mechanical stretching has been investigated.

2. Experimental

The films were prepared using the following technology.

The water solution of fine grained graphite (average diameter of grains less than 10 μm) or nickel (average diameter of grains less than 20 nanometers) suspensions in polyvinyl-alcohol was prepared. The mixture was filtrated and the film was formed on the dryer table.

The specific volumetric electric resistance of the polymer films was changed in the interval 10–50 kOhm·cm. The selection of such an interval of the composite resistance was dictated by preliminary selection of conducting composites effectively reacted on the mechanical deformations [4]. The composites contained the magnetic filler are characterized simultaneously by both electrical and magnetic properties.

The experiments were carried out on the basis of polymer composite films with a rectangle and trapezoidal shape. The thickness of films was no more than 0.2 mm. The deviation of the resistance values for any local region of the film was no more than 10 %. These films were fixed in special clamps, placed to the heater and were stretched on 50–150 % at rate 50 cm/min and temperatures 273–293 K. Stretching was conducted for the rectangle form sample along a long side and for trapezoidal sample in parallel to bases direction (Fig. 1).

After stretching of the deformed films local ohmic resistances were measured. First of all, it was necessary to mark the film with square grid. In our case the length of square side was equal to 5 mm. The local resistances were measured by using twin needles after application them to the film surface. The measuring of elementary cages resistance was performed several times and then the average values of resistances were calculated.

Another series of investigations were proceeded on establishment of local magnetic characteristics of gradiently-anisotropic magnetic polymeric composites with magnetic powder fillers like a nickel powder.

The films from magnetic polymer composites were subjected to the similar stretching procedure as it was previously described.

The resulting distribution of magnetic particles density in polymer composites was recorded by the method of LC-generator similar to the one used by us in work [5] for NMR detection in europium garnet at low temperatures.

It is also interesting to note that a similar method was used for the first precision determination of the magnetic field penetration length in superconductors [6].

A LC generator of sinusoidal oscillations was used for assessment of magnetic susceptibility distribution over the surface of gradient magnetic films [5].

The procedure of measurements the magnetization changes is realized through the sensitive detection of the inductance change of the LC generator oscillatory contour coil supplied with a tipped ferrite rod core at scanning by it over the investigated surface (Fig. 2). On the whole, the susceptibility measurement system consists of the following stages: LC generator, sinusoidal oscillation amplifier and frequency meter.

The frequency of LC generator oscillatory contour is defined by its fixed total capacitance and inductance. The oscillatory contour is an isolated system and tuned on a reference frequency providing its operation on the maximal sensitivity as a result of which the slightest contour inductance changes result in the significant changes of its frequency.

Let us note that the induction coil of oscillatory contour was brought away on 30–40 cm from the LC generator by a screened transmission line and the contour inductance with its spurious capacitance enters into contour effective parameters.

The frequency detuning is possible using a 2 mm thick and 15mm long tipped ferrite core put into the coil during its scanning over the film. Namely this principle is used for the definition of the contour quality factor change expressed in the frequency units. During the displacement of the coil having a tipped ferrite core near the surface of the gradiently magnetized film surface the change of the coil inductance takes place followed by the corresponding change of LC generator frequency in a quite significant range giving one possibility to evaluate the value change of the susceptibility real part related to frequency.

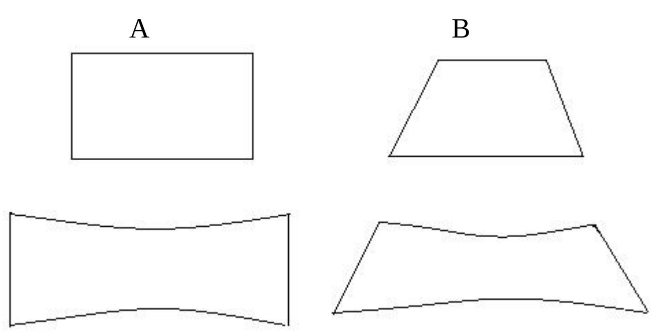


Fig. 1. Rectangle (A) and trapezoidal (B) shape films before (top) and after (bottom) stretching along long sides

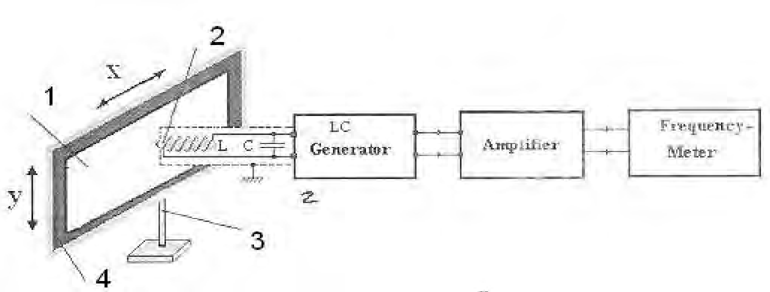


Fig. 2. Scheme of measuring magnetic characteristics of the polymer films:
1 – sample; 2 – ferrite tip, 3 – support, 4 – frame

The experimental set-up is presented in Fig. 2. In the inductive coil of the resonance contour of LC-generator cylindrical tipped ferrite rod is used as a probe. The investigated rectangular shape magnetic polymer composite film is displaced relatively the immovable ferrite tip. The scanning of the film surface is realized along the previously marked net contour (Fig. 3).

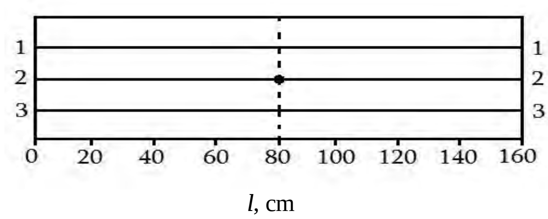


Fig. 3. Scheme of ferromagnetic film for investigation of the local magnetic susceptibility along directions 1-1, 2-2 and 3-3; dotted line – the middle of the film

Measurements of the dependences *F* – *l* were provided with using the ferromagnetic film, the scheme of which is presented in Fig. 3.

The change of magnetic particle concentration causes the inductance change *dL* of the resonance contour of LC-generator resulting in the frequency displacement of LC-generator *df* related with *dL* by relation $df/f = 1/2dL/L$. This frequency displacement could be precisely measured that stipulates the high sensitivity of the method.

At the natural frequency of used LC-generator near ~ 2 MHz the observed range of the frequency change *df* was about ~ 1000 Hz at the precision of the frequency measurement ~ 1 Hz.

3. Results and Discussion

3. 1. Gradiently-Anisotropic Electric Conducting Polymeric Composites

As a result of local resistances measurements of oriented along the parallel to a long side of the rectangle shape samples it was established that maximum change of this parameter was noticed along symmetry axes of the rectangle along orientation direction. This change has an extreme character (the maximum is at the central part of the film) and its full shape has Gaussian form. Fig. 4 shows that the maximum heights of the local resistances depend on the value of stretching. This result is in good agreement with the known conception on the mechanism of conductive polymer composites conductivity [3]. Investigation of obtained films using the metallographic microscope shows that the average optical density of penetrated light through the film nearly exponentially depends on the ordinates of the elementary squares. Therefore it may be proposed that the dependence of the conducting particles concentration in the local regions of the film has the same character. However the basis of such distribution of the filler particles in the uniaxially stretched polymer composites is not yet clear.

By analogical shape of the same dependence the one of local resistances in rectangle to stretching directions is characterized, although these dependences are somewhat weaker.

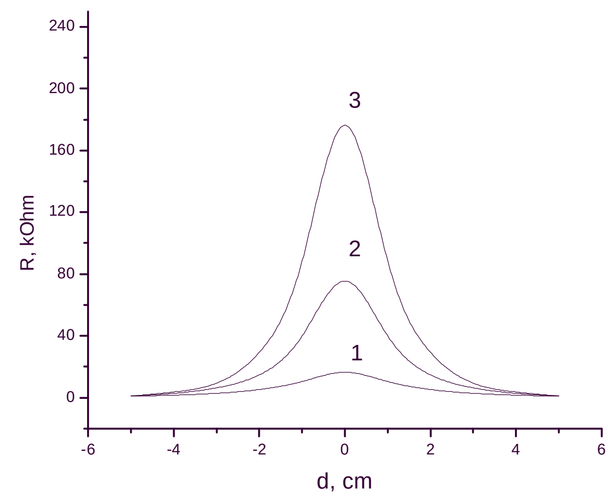


Fig. 4. Dependence of polymer film local resistances on the value of stretching parallel to a long side of the rectangle on 50 (1), 100 (2) and 150 % (3). The curves maximums are located on the central line with abscissa coordinate "0"

It was interesting to establish the character of considered above functional dependences of the local resistances on the concentration of the electric conducting particles. Fig. 4 shows that the increase of filler concentration leads to reduction of the resistance change intensity at stretching. This phenomenon may be described by the following processes. It is known that the filler particles at stretching of polymer composites commit the mutual transition in the polymer matrix initiated by interacting macromolecules segments with them, in a result of which the average distances between these particles and consequently the charge transition change accordingly [7]. Here the inverse processes – approach and removing of the particles and consequently the probability of creation the conducting chains changes respectively. However in case of composites with high concentrations of the conducting particles the probability of arising new contacts between them is higher than in opposite case, since the frequency of these elementary processes is higher than in case of composites with relatively low concentrations of these particles. Here the described process is analogical to reserving of the switching con-

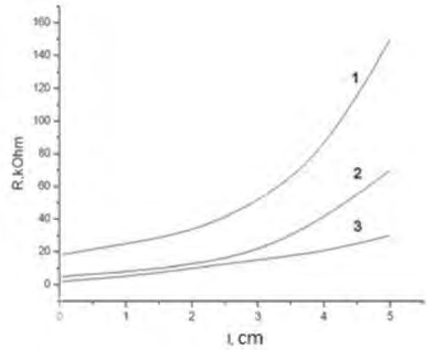
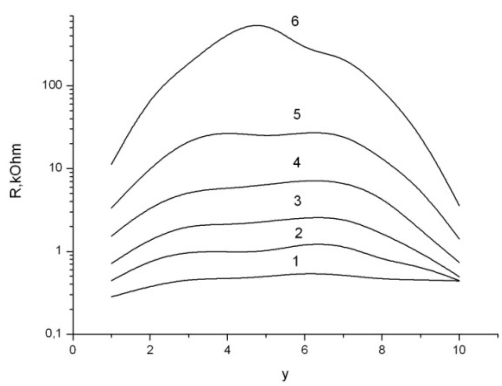
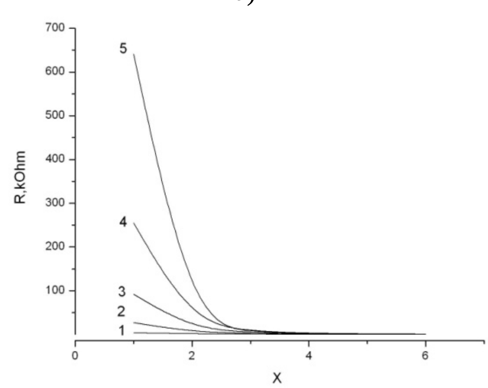


Fig. 5. Dependence of films local resistances on the stretching degree for composites based on PVA containing 30 (1), 40 (2) and 50 (3) mas % of graphite powder (curves correspond to left half side of a central strip of the film)



a)



b)

Fig. 6. Dependences of local resistances on the film (PVA with 25 mas % graphite) coordinates in the strips stretched on 150 % parallel to bases of trapezoidal shape films in perpendicular to stretching direction from the big base to the small one (a) and parallel to stretching direction from the small base to the big one (b). The numbers on the curves indicate the numbers of stripes in perpendicular (a) and parallel (b) to the stretching direction. The curve number 5 in Fig. 6b corresponds to the central strip of trapezoidal film and others (4-3-2-1) – to side ones. The asymmetry of the curves in Fig. 6a is due to certain inhomogeneous distribution of the filler particles in the polymer matrix

ducting chains in the complex electrical engineering schemes. The obtained results show that the process of displacement of the conducing particles and consequently the change of conductivity take place more intensively in the middle part of the stretched polymer film than in other ones, namely, this change has a gradient character with increasing from grips till middle of the film. The amount of this gradient is higher the lower is filler concentration (Fig. 5).

The following series was fulfilled on the trapezium shape conducting films. Here was created the mechanical stretch gradient in perpendicular to base direction, along which the stretching was realized. This gradient was increased from big base and was ended at more stressed small base with maximum.

The experimental data on the definition of character of the distribution dependence of the local resistances on both rectangle and trapezoidal form films on their coordinates show that the shape of these dependences essentially is defined mainly by two factors: i) the content of electrical conducting fillers in the selected part of the stretched film and ii) distribution of conducting particles in the polymer matrix after stretching along selected direction (Fig. 6). Nonlinearity of the dependence of local electrical conductivity both along and perpendicular direction of stretching is explained mainly by the nature of the conductivity of the polymers filled with conducting particles. Namely it is well known that the charge transfer in such systems obey to tunnel mechanism –nonlinear dependence of the conductivity on the distance between neighbor particles.

3.2. Gradiently-Anisotropic Magnetic Polymeric Composites

In Fig. 7 the results of generator frequency change measurements along contour lines 1-1, 2-2 and 3-3 are presented. Similar results are obtained at measuring the magnetic susceptibility of the film along rectangular to 1-1, 2-2 and 3-3 directions.

The presented results show that for magnetic polymer composite films with a rectangle shape the dependences $F - l$ have a similar form, as was obtained for conducting polymer composites (R - l) with the same shape. Such resemblance is based on the similar character of distribution of the filler particles – conducting ones – in rectangle electrical conducting polymer composites and magnetic particles in the magnetic analogues after their uniaxial stretching, because the maximum of dependences of the local resistance on film coordinates corresponds to rarefied regions of these films and the maximum of the curves $F - l$ corresponds to those regions (frequency increases), when magnetic particle concentration decreases and, consequently, local susceptibility and inductance decrease.

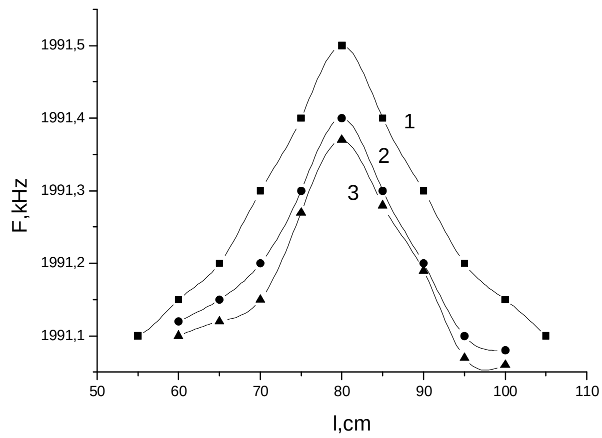


Fig. 7. Dependences of the oscillation frequency of the ferrite sensor on the coordinates of the film made from polymer composite along directions 2-2 (1), 1-1 (2), 3-3 (3)

Results of detailed measurements will be published further.

4. Conclusions

1. Gradiently anisotropic structures are the form after orientation (stretching) under spatial conditions of thin polymer composites based on polyvinyl alcohol, graphite and nickel powders with electrical conducting and magnetic properties. Structure anisotropy leads to anisotropy both electrical conductivity and magnetic properties of these films.

2. The distribution of the value of local resistance in the rectangular shape electric conducting film oriented along direction parallel to any side of this film obeys to Gaussian law.

3. Gradient distribution of the local resistances in the stretched films along and rectangle to stretching direction is due to gradient of local deformations in the same directions.

4. Gradient distribution of magnetic particles in the stretched direction leads to equivalent change of magnetic properties of these films.

5. The experiments described above open the perspectives in the field of creation of the films with desirable anisotropy of electric conductive and magnetic properties. The perspective is in application of these materials for creation of the so called printed schemes. In electronics these films will be useful for preparing multifunctional micro-schemes.

Acknowledgements

We acknowledge the Ministry of Defence of Georgia for funding and support.

References

[1] Lekishvili N., Nadareishvili L. *et al.*: Polymers and Polymeric Materials for the Fibre and Gradient Optics. VSP, Utrecht-Boston-Koln-Tokyo 2002.
[2] Nadareishvili L. *et al.*: J. Appl. Pol. Sci., 2004, **91**, 489.
[3] Aneli J., Khananashvili L. and Zaikov G.: Structuring and Conductivity of Polymer Composites. Nova Sci. Publ., NY 1998.
[4] Aneli J., Khananashvili L. and Zaikov G.: J. Appl. Pol. Sci., 1999, **74**, 601.
[5] Pavlov G., Chekmarev V., Mamniashvili G. and Gavrilko S.: Pat. USSR 279893, 1988.
[6] Schawlow A. and Devlin G.: Phys. Rev., 1959, **113**, 120.
[7] Aneli J., Zaikov G. and Mukbaniani O.: Chem. & Chem. Techn., 2011, **5**, 75.

ГРАДІЄНТНО АНІЗОТРОПНІ ПРОВІДНІ ТА МАГНІТНІ ПОЛІМЕРНІ КОМПОЗИТИ

Анотація. *Вивчено характер зміни локального електричного опору плівки полімерних композиційних матеріалів на основі полівінілового спирту з графітовим порошком, з одного боку, та магнітної сприйнятливості того ж полімеру з нікелевими нано-частинками з іншого. Встановлено, що зміна цих параметрів істотно залежить і від первинної форми плівок, і від напрямку їх орієнтації. Показано, що плівки градієнтно анізотропних полімерних композиційних матеріалів можуть бути використані в електроніці.*

Ключові слова: *полімерна плівка, наповнювач, розтягнення, анізотропія, локальний електричний опір, магнітна сприйнятливість.*