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SELF-ASSEMBLY PROCESSES OF THE MAGNETIC POLYMER NANOCOMPOSITES IN MAGNETIC FIELDS

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Abstract. Processes of self-assembly were studied in the magnetic polymer carbon nanocomposites doped with cobalt nanoclusters. These processes proceed due to the diffusion of magnetic nanoparticles stimulated by a combined effect of an outer steady magnetic fields and heating. The obtained polymer composites are promising for practical applications.

Keywords: magnetic carbon nanopowders, polymer nanocomposites, diffusion, self-organization, resistance.

1. Introduction

In the last decade the investigation of such new nanostructure forms of carbon as nanoparticles, nanotubes, nanowires has become very topical. This is associated with the fact that, due to their sizes and peculiarities of their atomic structure, nanostructural particles reveal such unique physico-mechanical properties that the range of their promising applications covers many areas of activity from microelectronics to medicine.

In recent years, the interest in technologies of carbon-based materials production oriented on the production of doped carbon nanoparticle modifications (nanotubes, nanoclusters, nanowires) was growing. This gives scientists and engineers the opportunity of aimed control of these materials unique properties, which are their natural properties [1].

As a matter of fact, the nanoobject control at the nanometer level using nanoparticles with the aim to arrange them in rows, signatures and grids is the clue to the production of new functional materials. Hence, in recent years, for obtaining the constructional units of different nanometric sizes, many methods of self-assembling and synthesis were developed. In this connection, the possibility to control perfectly the self-assembling and synthesis processes of nanoparticles is a serious challenge from the point of view of both fundamental and applied investigations.

Based on the fundamental principles, the process of self-assembling requires the existence of interaction between atoms and clusters, as well as thermodynamic and kinetic driving forces, so that the organization of atoms and clusters for creation of nanosize domain structures should be realized. From this point of view, magnetic nanoparticles deserve a particular interest due to their unique physico-chemical properties and applicability in the new functional material technologies.

Carbon shells provide both the protection of ferromagnetic impurities against aggressive environments and new unique properties for the hydride nanostructures. The self-assembling of magnetic clusters coated with carbon shells represents just such an example that could be used in the contemporary materials, for instance, in strong rare-earth free bonded magnets, analytical instruments (nuclear magnetic resonance tomographs) and nanosensors using magnetic one-dimensional nanowires.

Moreover, currently, due to their low toxicity, magnetic carbon nanoparticles are under testing for therapeutic and diagnostic applications.

In recent years the magnetic field was used for the creation of nanoscale materials, which resulted in significant achievements in fabrication of macro- and microstructure synthesized materials possessing unique properties.

In contrast with other existing self-assembling technologies, ordering induced by the magnetic field defines the formation of magnetic nanoparticles in ordered structures with unique properties. Therefore, the area of application of carbon magnetic nanoparticles is quite large. It is enough to name such applications as magnetic fluids, plastic scratch-resist glasses, information storage magnetic media, sensors, biomedicine, *etc*. It should be noted that, in spite of their broad prospects for multifunctional applications, the carbon nanoparticles doped with ferromagnetic clusters have not been well researched [2].

In work [3] the electric and magnetic properties measurements were carried out to study the gradiently

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anisotropic conducting and magnetic polymer composites synthesized due to self-assembly processes of nanoparticles under the influence of the elastic forces developed by the stretching of polymer film composites fabricated on the basis of polyvinyl alcohol doped with graphite powder and nickel nanoparticles.

In this work the study of self-assembling properties of carbon nanoparticles doped with cobalt nanoclasters in magnetic polymer nanocomposites under the combined influence of magnetic field and heating will be carried out using methods similar to ones developed in work [3].

2. Experimental

To achieve this goal, we planned experiments with magnetic nanopowders, preparation of filled and unfilled polymer films, and the study of self-organization processes in them. This process was facilitated by heating the films above the glass transition temperature. The particles in conventional composites are essentially immobile in contrast to polymer nanocomposites (PNC) particularly above the glass transition temperature T_a. The nanoparticles mobility can affect polymer dynamics resulting in changes in the viscosity modulus, kinetics of the particle-cluster formation, *etc*. [3].

The tensile measurements showed that, below T_a, the conventional composites and PNCs behave similarly with respect to mechanical properties. Though, above T_a, the toughness of PNC can increase by an order of magnitude with increasing temperature. It was assumed that the mechanism of toughness enhancement is the mobility of nanoparticles. The development of self-healing materials and coatings, where nanoparticles migrate towards various defect sites, requires better understanding of the process of nanoparticle diffusion. Heating of PNC above T_a enhances the mobility of polymer chains, which should facilitate the boundary diffusion between polymer interfaces, and this effect should be visualized using the magnetic nanoparticles introduced in the polymer. This process could be improved by applying additional stimuli, in particular a low-frequency (ac) magnetic field, a stationary magnetic field, pressure, heating separately or in combinations, *etc*. Such an impact stimulates self-assembling processes in the prepared films in the result of which one could produce the films "glued" to each other without using other type glues and polymer melting temperature. One of the objectives of this work was the development of a simple technology of production of carbon nanoparticles doped with ferromagnetic clusters and the study of their morphology and composition.

In particular, for production of carbon-based nanopowders and nano-coatings, the method of chemical vapor deposition (CVD) is used mainly along with application of the process of hydrogen reduction of volatile chlorides.The carbon nanoparticles doped with cobalt magnetic nanoclusters with mean sizes in the range of 50–100 nm were synthesized by technology using the combination of ethanol (and other hydrocarbons) pyrolysis, vapour pyrolysis and the CVD process in the mode of a closed recirculation cycle with monitored technology parameters.

The developed technological process was realized in the installation, the reactor design and basic units of which provided the possibility of parameters monitoring such as the vapor content in reactor zones, catalytic capacity of substrates, partial oxygen pressure (over the range of 10^{-20}–10^{-25} atm). This allows carrying out the investigations with the aim to establish the optimal technological parameters for production of finely dispersed carbon nanopowders doped with magnetic nanoclusters. Detailed description of this technology is given in work [4].

For preparation of polymer films, polyvinylbutyral (PVB) polymer with low T_g (~318–328 K) was chosen. Polymer PVB is a resin mostly used wherever strong binding, optical clarity, adhesion to many surfaces, toughness and flexibility are required. As a filler we used the carbon nanopowder doped with magnetic (Co or Fe) nanoclusters (C/Co) of our production. For a comparative study, we used commercial Co nanopowder with average diameter of 28 nm (Sun Co., USA). The concentration of used Co-doped carbon nanopowders in the polymeric composite was in the range of 10–50 wt %, while for the Co nanopowder filled polymer composite concentration was equal to 20 wt %.

At first 10 % alcohol solution was prepared, then this solution was poured into Teflon press molds and, after their drying for 48 h, the films of 1 mm thick were obtained. The filled composites were prepared as follows: magnetic nanopowders were taken in the appropriate proportion (in terms of dry weight) and PVB was mixed with alcohol in a usual way, then the ultrasonic treatment was applied for 10–15 min for the destruction of magnetic nanopowder agglomerates. After thorough mixing for 7–10 min, magnetic polymer composite films similar to unfilled ones were obtained in Teflon press molds. From these films, the circular shape disk samples were cut.

To study the self-assembly processes in these polymer nanocomposites at different concentrations of carbon magnetic nanopowder, we used a simple method from work [5]. In this case, circular samples of the polymer composite (diameter – 28 mm, thickness – 1 mm) were exposed to the magnetic field provided by two attached permanent neodymium magnets and temperature of 358 K for 2 h (Fig.1).

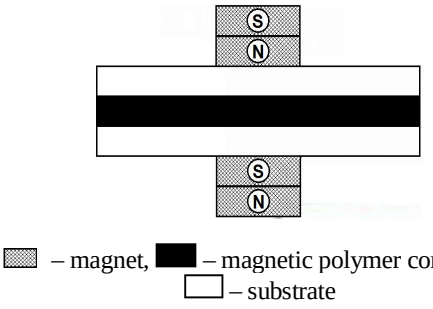

Fig. 1. Geometry of the samples

3. Results and Discussion

Resulting self-assembly of C/Co nanopowders caused changes in their concentration and modulation of local resistance along the radius of the sample, which was measured by a two-contact method as in our previous work [6] (Figs. 2-7). The resistance was measured between the points spaced 2 mm apart along the radius in all following cases except for Fig. 3 where the resistance was measured between the sample centre and the points of 2 mm.

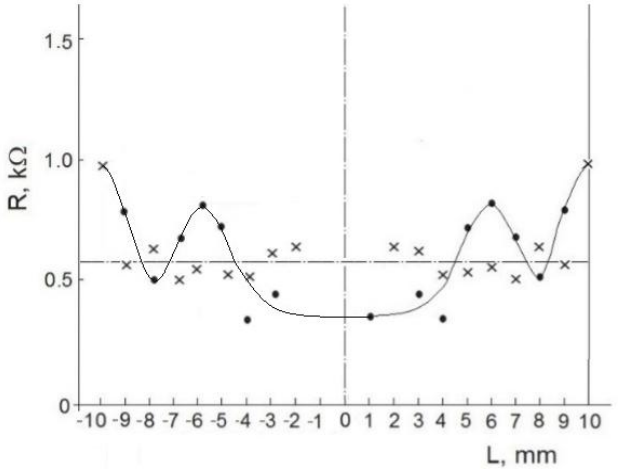

Fig. 2. Polymer composite C/Co, 30 wt %
Samples prepared without magnetic field treatment (´)
and samples prepared under combined magnetic field and heat treatment (•)

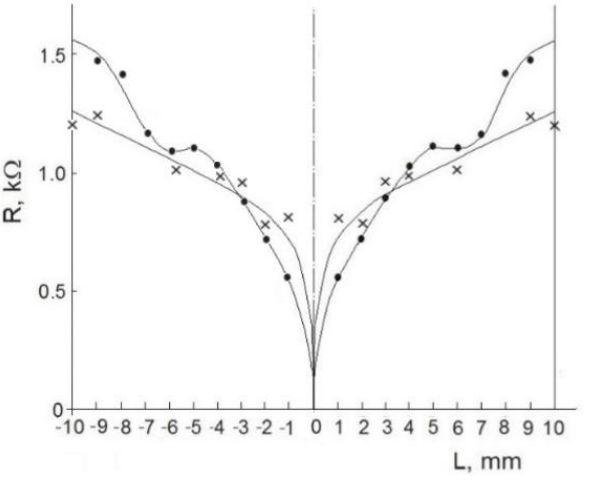

Fig. 3. Polymer composite C/Co, 30 wt %
Samples prepared without magnetic field treatment (´)
and samples prepared under combined magnetic field and heat treatment (•)

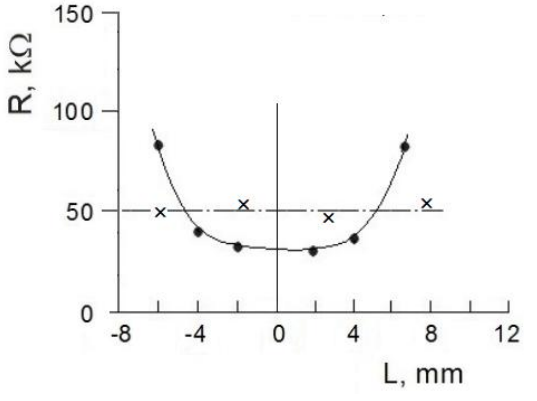

Fig. 4. Polymer composite C/Co, 50 wt %
Samples prepared without magnetic field treatment (´)
and samples prepared under combined magnetic field
and heat treatment (•)

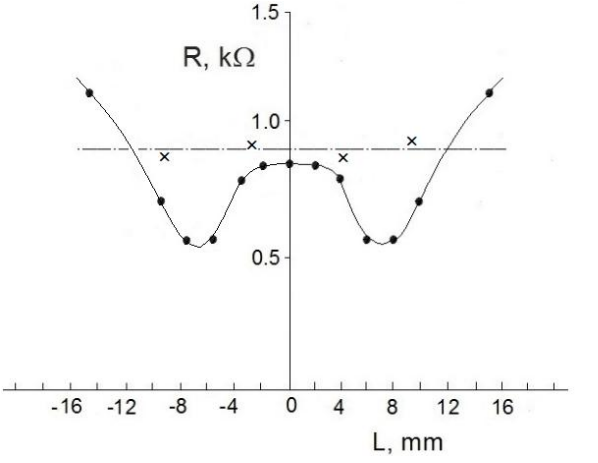

Fig. 5. Polymer composite C/Co, 20 wt %
Samples prepared without magnetic field treatment (´) and
samples prepared under combined magnetic field
and heat treatment (•)

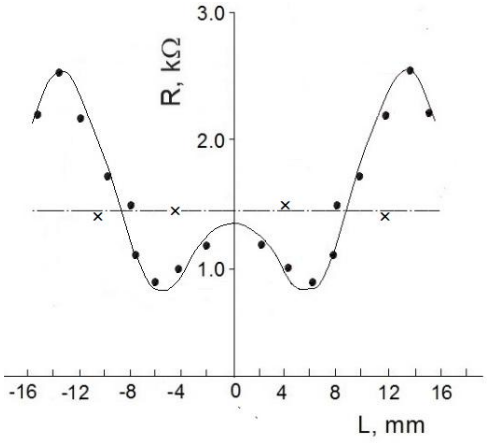

Fig. 6. Polymer composite C/Co, 15 wt %
Samples prepared without magnetic field treatment (´) and samples prepared under combined magnetic field and heat treatment (•)

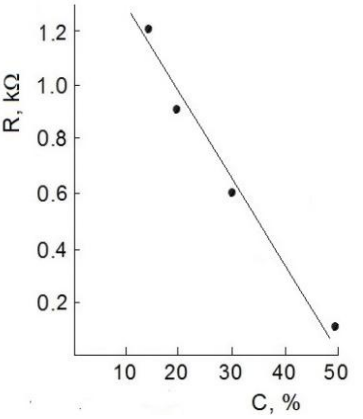

Fig. 7. Dependence of resistance of initial untreated samples on the nanopowder concentration

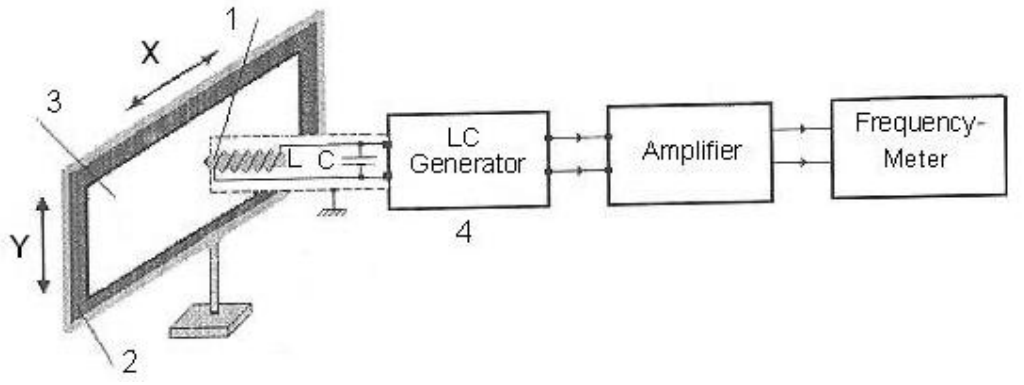

Fig. 8. Scheme of the measuring the magnetic characteristics of the polymer films: ferrite probe (1); frame (2); magnetic polymer nanocomposite film (3) and LC generator (4)

Since polymeric composites are magnetic carbon nanocomposites, we were able to study the processes of self-assembling of nanoparticles using radiofrequency resonance magnetic susceptibility measuring devices [5].

The experimental set-up is presented in Fig. 8. In the inductive coil of the resonance contour of LC-generator a 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 disk radius.

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 $df/f = \frac{1}{2} dL/L$. 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 δf was about ~1000 Hz at the precision of the frequency measurement ~1 Hz.

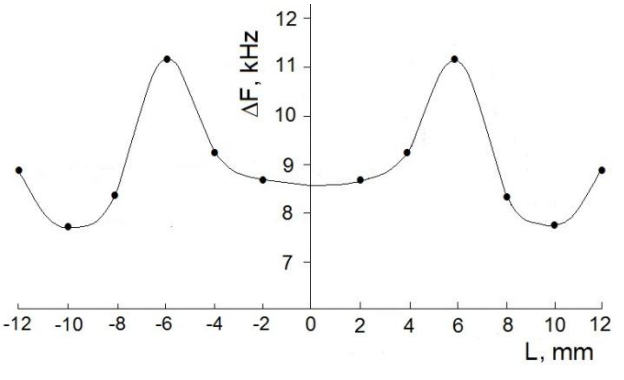

Fig. 9. Magnetic susceptibility measurements of Co/C 50% polymer nanocomposite along the polymer composite film circular disk diameter

For example, we represent the result of self-assembly measurements of Co/C magnetic nanocomposite film in the magnetic field of neodymium magnet (Fig. 9) one similar to the results obtained during electrical resistance measurements:

When we move along the diameter of the disk, the frequency measurements indicate a frequency change (frequency interval change of several kHz) associated with the change in the concentration of magnetic nanoparticles in the polymer composite.

Based on the obtained experimental results, it is possible to investigate the self-assembling processes in magnetic nanocomposite polymer films synthesized by the elaborated technology using the carbon magnetic nanopowders fabricated by a technology described in [4] under combined influence of magnetic field and heating.

4. Conclusions

The self-assembling processes were studied for the magnetic polymer nanocomposites on the basis of carbon nanoparticles doped with cobalt nanoclusters. Nanocomposites were synthesized by an unique CVD technology developed by the authors, under combined effect of magnetic field and heating. These processes took place with the diffusion of magnetic nanoparticles stimulated by the combined effect of outer steady magnetic field and heating. The obtained magnetic polymer nanocomposites have good electrical and adhesive properties and are promising for potential practical applications in magnetoelectronics.

Akcnowledgments

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ПРОЦЕСИ САМООРГАНІЗАЦІЇ МАГНІТНИХ ПОЛІМЕРНИХ НАНОКОМПОЗИТІВ В МАГНІТНИХ ПОЛЯХ

Анотація. *Вивчено процеси самоорганізації магнітних полімерних карбонових нанокомпозитів, що містять нанокластери кобальту. Встановлено, що ці процеси відбуваються завдяки дифузії магнітних наночасток, які стимулюються комбінованим ефектом зовнішніх постійних магнітних полів і нагрівання. Показано, що синтезовані полімерні композити перспективні для практичного застосування.*

Ключові слова: *магнітні карбонові нанопорошки, полімерні нанокомпозити, дифузія, самоорганізація, опір.*