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THE POLYMERS FILLED WITH FERRITE PARTICLES: ELECTRIC PROPERTIES

Yerdos Amankulov[1], Ulzhagas B. Nazarbek[2]

[1]Eurasian Technological University, Almaty, Kazakhstan
[2]M. Auezov South Kazakhstan State University, Shymkent, Kazakhstan

Abstract

In work is investigated impact of ferromagnetic filler on dielectric properties of the polymeric composite materials (PCM) on the basis of the pitch modified epoxy- dean pitch. As fillers used barium hex ferrite powders with effective sizes of particles of 2 and 20 μm. Processes of structuration of PCM it was carried out in magnetic field at the increased temperatures. There are established temperature and frequency dependences of relative dielectric permeability and a tangent of angle of dielectric losses on degree of crystallinity of PCM, on concentration and dispersion of filler, technologies of the structural organization and conditions of influence of magnetic field.

Key words: *polymeric composite materials, magnetic field, the increased temperature, the structural organization, dielectric properties, temperature and frequency dependence.*

Introduction. Features of electric properties of polymeric dielectrics are studied rather in detail [1-4, etc.].

It is known that the dosed filling of a polymeric matrix particles of ferrodielectrics, metals and their alloys, graphite, soot, carbon particles, etc. of various form and the size allows to operate and give purposefully to a composite necessary electric, magnetic and physicomechanical properties. Recently in physics and chemistry of polymers become perspective development of the new polymeric composite materials (PCM) with creation of technological processes on their receiving, the allowing PCM to give controlled structure and beforehand the set properties. Intensively continuing regular researches of polymeric composites with various fillers are caused with variety of ways of production process of receiving PCM, existence of a wide class of the polymers entered by a kind of types, types and dimensions into a matrix of fillers synthesized so far and also variety of the studied properties.

Results of numerous experimental and theoretical works show, that electro physical properties of composites, such as conductivity, dielectric and magnetic permeability are most sensitive to changes of packing of particles in a composite, especially if in the course of receiving and structuration of PCM to influence, for example magnetic and temperature fields when the entered fillers have physical parameters necessary for this purpose [5-7 and references to articles]. However, aspects of regulation of electro physical properties of PCM are studied by impact on their structure by physical fields insufficiently, and data on influence of orientation factors of magnetic field on electro physical properties of the filled PCM remain beyond the scope so far of scientific publications.

Thus, studying of polymers with the disperse ferrimagnets' included in volume of a matrix is interesting from the point of view of researches of regularities of change of electric characteristics of PCM in interrelation with the structural organization of magnetic particles in a polymeric matrix and with the nature of their interaction.

In the present article is realized a basic opportunity to operate electro physical properties of the polymers filled with ferromagnetic particles with change of their chemical structure, dispersion, volume maintenance, orientation of ensemble of particles in volume of a polymeric matrix at impact on the three-phase environment of external magnetic field.

Technology of receiving PCM. ***Description of technological installation.*** For the purpose of management of distribution of ferrite filler in volume of polymer and also for an exception of sedimentation and agglomeration of particles of filler was used the electromagnetic installation creating in a gap between poles constant or variation magnetic field. The flowchart of technological installation with functional elements is provided on Fig. 1.

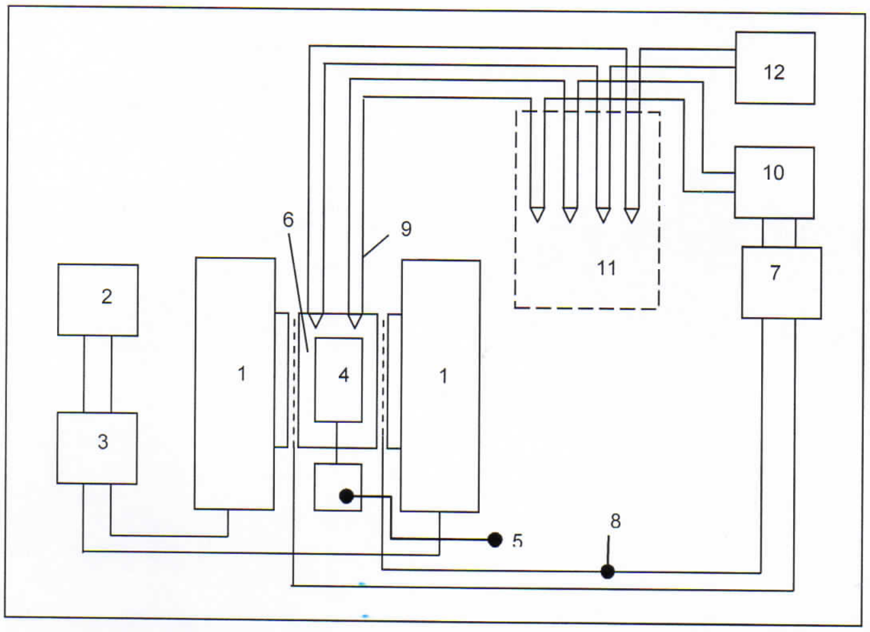

Fig. 1. Flowchart of technological installation: 1 – an electromagnet with coils, 2 – tension regulator for food of windings of an electromagnet, 3 – the rectifier, 4 – a container of a cylindrical form for filling and rejection of PCM, 5 – the mini-electric motor of a direct current, 6 – the thermostat for hardening of PCM at the increased temperature, 7 – the laboratory autotransformer for power supply of electric heating elements of the thermostat, 8 – resistance electric heaters from a nikhromovy wire, 9 – a chromfir-tree-kopelevye thermocouple, 10 – the high-precision regulator of temperature, 11 – zero thermostat, 12 – the digital voltmeter.

Technological installation allows to receive the filled PCM with chained, quasihomogeneous and another, the nature of distribution of magnetoactive particles of filler beforehand set in volume of a polymeric matrix. Samples of PCM received at influence of the rotating magnetic field, with simultaneous hardening of a polymeric matrix at the increased temperature. The rotating magnetic field was created by means of rotation of a container with the cured PCM in the field of influence of uniform power lines of constant magnetic field.

Prescription structure of PCM. As binding ED-20 pitch was applied epoxy диановая. An important technological stage was used modifying of ED-20 pitch, as the modifier DEG-1 diethylene glycol in the ratio of 100% of mass parts respectively. At this DEG-1 acts at the same time as thinner for decrease in viscosity of polymeric binding. Polymeric binding this compounding it is cured at a temperature of 438 K within 3 hours, with energy of activation of hardening E = 64 kJ/mol [8].

For giving to a polymeric matrix of the accelerated polymerization, the increased heat stability and the best dielectric properties it was used low-viscous (0,06 Pas·s) at T = 295 K hardener isomers methyltetrahydrophthalic anhydride izo-MTGFA. The mass amounts of the modified pitch and hardener defined from stoichiometric structure equaled: ED-20 + DEG-1 – 100 masses an hour, izo-MTGFA – 90 masses an hour. As a result of addition izo-MTGFA and also due to the continuous Brownian and orientation movements of magneto active particles of filler in the conditions of influence of the rotating magnetic field and magneto caloric effect process of sewing together of a polymeric phase was intensified and time of hardening was reduced from 3 to 1,5 hours.

By preliminary researches it was established that for polymeric binding on the basis of dianovo-epoxy resin with the set prescription structure time of jellification was about 30 minutes since the beginning of process of hardening of a polymeric phase. With increase in content of ferrite filler jellification time was also reduced at the maximum filling about 15 minutes.

As ferromagnetic filler was chosen two types of magneto solid powder of hex ferrite of barium with a structural formula $BaO_6Fe_2O_3$ and with effective sizes of particles of 2 and 20 μm. Magnetic and physical characteristics of $BaO_6Fe_2O_3$ are described in article [9-11].

For the qualitative analysis of processes of structuration in the environment of a polymeric phase in its low-viscous state made visual observations of behavior and dynamics of ensemble of particles of ferrite at influence of magnetic field, with use of a container with transparent walls. At the same time varied the size of induction of magnetic field, dispersion and concentration of filler, rotation frequency ditches with magnetorheological polymeric suspension in the field of power lines of magnetic field.

As a result of these researches it was established that uniform rotary motion of a container in magnetic field leads to gradual destruction of agglomerates of particles of ferrite, to their aspiration to be reconstructed and guided periodically along power lines of magnetic field, to intensive interaction of particles with polymeric binding, with walls ditches and to inelastic collisions among themselves. In the course of it particles were enveloped polymeric binding and with growth of viscosity of a polymeric matrix effect of hobby of chains of ferrite particles for the environment began to prevail over their orientation effects in magnetic field. At the same time was reached chained structures broke up to separate particles, there was a gradual stabilization and localization of particles of ferrite to their adjustable orientation and, the main thing, uniform (matrix) distribution of filler on all volume of a binding phase.

Production of samples of PCM of the set form. For receiving the studied PCM samples in previously prepared vessel filled in modified binding the chosen compounding on the basis of ED-20. This mix heated to 333 K and at its continuous mechanical hashing added disperse hex ferrite of barium (samples prepared the content of filler in the number of 20, 40 and 60% of masses in hour from the mass of polymeric binding). Duration of mixing was 20-30 minutes. The prepared suspension filled in in a container from the ftoroplast of a cylindrical form. Before filling of polymeric mix the cover, internal walls, laying of a container were processed by anti-adhesive. Laying from the ftoroplast is inserted on a bottom of a container and serves for extraction of a ready sample of PCM as its pushing out through an opening at the bottom of a container. After filling of a container easy-flowing PCM, densely closes a cover and the container with a compound with the known concentration of filler is established on the drive of the rotation mounted in the device of the thermostat and is ready for carrying out processes of hardening and structuration. For receiving several identical samples with the set concentration and dispersion of particles of hex ferrite of barium prepared one batch.

After installation of the container in the thermostat installed in interplay space by means of tension regulator in a gap between poles of an electromagnet was created constant magnetic field from magnetic induction B = 65,0 mTl. Joined the furnace of the thermostat and on reaching temperature of polymerization of T = 438 K a container with a composite was given to rotation with frequency f =1 Hz. After time t = 30 min. (jellification time) from the moment of process of hardening of a compound, rotation of a container stopped and further hardening of a polymeric phase proceeded in lack of magnetic field. After the expiration of time of hardening of PCM the thermostat was switched-off and made cooling of the polymerized PCM. After that monolithic PCM of a cylindrical form with height of 30 mm and with a diameter of 15 mm was taken out from a container, and by means of its cutting received samples with thickness of 1,5 - 2,0 mm. For carrying out further researches samples were exposed to grinding and polishing, with observance of all requirements of methods of carrying out such operations. Etching with use of solutions of H_2SO_4, H_3PO_4 acids was made for cleaning of surfaces of samples. Before etching samples were degreased in acetone or alcohol. Polishing of surfaces of samples was carried out on cloth or with use of thin powder of oxide of chrome. After polishing they were degreased and washed out by the distilled water. The drained PCM samples depending on concentration and dispersion of filler were sorted by groups for carrying out experiments.

Experiment and discussion of results. There are investigated temperature and frequency dependences of relative dielectric permeability of ε and tangent of angle of dielectric losses of tgδ PCM on the basis of an epoxy dean of ED-20 pitch modified by DEG-1 diethylene glycol and isomers methyltetrahydrophthalic anhydride izo-MTGFA and filled with disperse hex ferrite of $BaO_6Fe_2O_3$ barium. The average sizes of particles $BaO_6Fe_2O_3$ were 2 and 20 μm. When receiving samples concentration of ferrite filler in the number of 20, 40 and 60% varied. All concentration specified in work are shown in mass parts.

Value ε and tgδ determined by two-electrode system in the range of frequencies from 1 to 50 kHz, at a temperature from 295 to 463 K with application of the special screened and grounded warmed measuring cell like "sandwich" having the system of measuring and potential electrodes with a diameter of 15 mm. Samples were located in a measuring cell with clamping electrodes from stainless steel.

Device to carrying out measurements of capacity with and tgδ of samples with a fine precision used the P5016. Then on the basis of the measured values of the specified parameters and the geometrical sizes of samples the sizes were defined by standard methods ε and tgδ.

The main results of researches of temperature and frequency and temperature dependences of ε and tgδ of samples of a polymeric matrix on the basis of the modified ED-20 and the filled $BaO_6Fe_2O_3$ PCM on its basis are presented in Fig. 2-4.

Apparently from Fig. 2 and 3, for all filled PCM samples with increase in concentration of hexaferrite of barium is observed the noticeable growth of tgδ and ε. This effect can be explained with growth of crystal areas in a polymeric matrix due to crystal structure of particles of hexaferrite of barium with high in comparison with epoxy binding values of the studied dielectric parameters.

However, on temperature dependences the nature of growth of tgδ for the considered sizes of particles of ferrite is shown on a miscellaneous: at dispersion of particles of d = 2 microns' growth of tgδ is observed to T = 413 K and curves pass through maxima, and further at temperature increase (within T = 433 – 443 K) there is a falling of tgδ values to a minimum, to a tendency of its increase at the increased temperatures (Fig. 2, a). In this case losses are caused by polarization, and with a growth of temperature of tgδ passes through a maximum. This results from the fact that at low temperatures the viscosity is high and there are no losses, and at high temperatures the viscosity is small and dipoles are displaced, without experiencing friction.

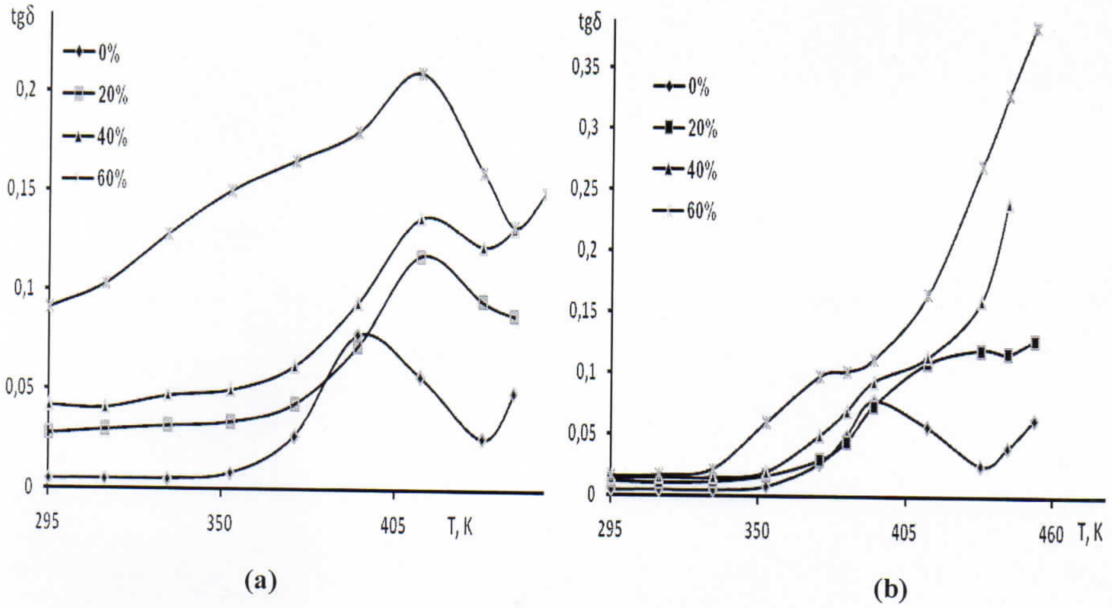

Fig. 2. Temperature dependences of a tangent of angle of dielectric losses of tgδ PCM at frequency F = 5 kHz, concentration of $BaO_6Fe_2O_3$ in masses. hour, d = 2 μm, (b) d = 20 μm.

At dispersion of particles of d = 20 μm on temperature dependences growth of tgδ is observed is more expressed, the weak maximum is shown in the field of T temperatures = 373 - 413 K, is observed further at temperature increase the essential growth of tgδ (Fig. 2, b).

These differences in behavior of tgδ are connected in the first case, perhaps, with high deficiency of initial structure of particles of hex ferrite of barium with sizes d = 2 μm. In the second case of a particle with d = 20 μm have more densely packed crystal structure and with growth of temperature the intensity of shift or movement of charges and loss increases are caused mainly by conductivity, and it leads to growth of tgδ.

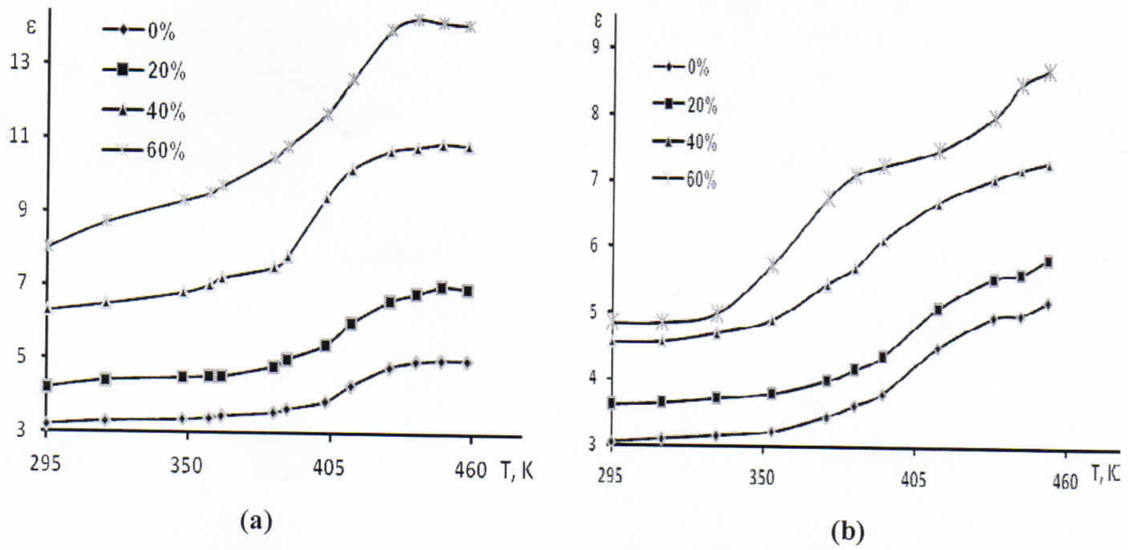

Fig. 3. Temperature dependences of dielectric permeability of ε PCM at a frequency of 5 kHz. (a) d = 2 microns, (b) d = 20 microns., concentration of $BaO_6Fe_2O_3$ in masses of hour.

It is known that ferrite have rather big dielectric permeability depending on frequency and composition of ferrite. With increase in frequency the dielectric permeability of ferrite falls and in ferrite is observed the magnetostriction phenomenon.

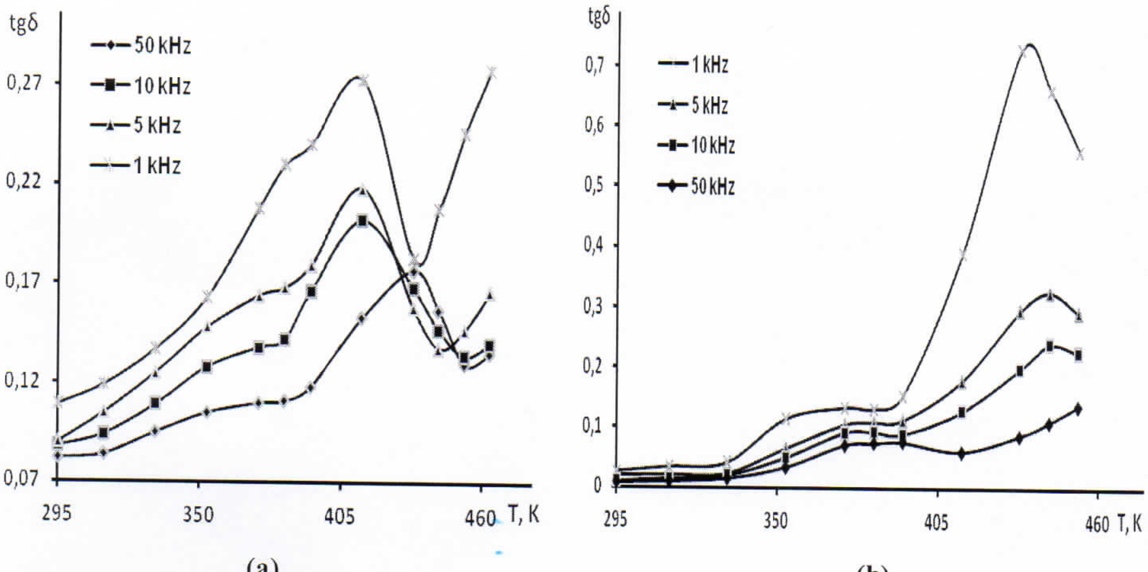

Fig. 4. Temperature dependences of a tangent of angle of dielectric losses of tgδ PCM from frequency, concentration of $BaO_6Fe_2O_3$ – 60% (in masses. h), d = 2 microns, (b) d = 20 microns.

Apparently from Fig. 3, at equal concentration of $BaO_6Fe_2O_3$ the greatest ε values are observed at PCM filled with particles with d = 2 μm that can be explained with rather high deficiency of crystal structure of these particles. The shown weak areas of a maximum are connected by processes of a disorientation of electronic, ionic, ion-relaxation and migration polarization at a temperature T = 438 K. At the same time the size of a contribution of everyone to total polarization eventually depends on energy of a crystal lattice of ferrite and a power condition of their specific surface. The behavior of ε in Fig. 3 (a) and (b) is confirmed by the above-stated explanations in behavior of tgδ depending on temperature: at d = 2 μm of particles of hex ferrite temperature increase causes growth of ε, since when heating dielectric the intensity of shift or movement of rather free charges increases, and at high temperatures the viscosity is small and dipoles are displaced, without experiencing friction.

To hex ferrite particles with d = 20 μm higher pack and crystallinity of structure unlike hex ferrite particles with d = 2 μm therefore the weak growth of ε can be connected with manifestation of migration polarization and also existence of a vitreous interphase layer on a surface of these particles are characteristic.

In Fig. 4 tgδ maximum shift towards the increased temperatures and falling of its values with increase in frequency of electric field is observed. With growth of frequency ions or dipoles do not manage to be displaced after the frequency of electric field thereof polarization begins to be shown poorly and tg considerably falls.

The minima observed in Fig. 4 (a) at T = 433 – 453 K and the further growth of tgδ can be connected with increase of migration polarization due to accumulation and approach of saturation of charging states at these temperatures that also 2 μm have a talk initial deficiency of structure of particles of hex ferrite with d = 2 μm.

Conclusions. The technology of receiving the filled PCM consisting of electromagnetic installation is developed of the thermostat, the device of rotation of a container and elements on management of technological parameters.

On the developed technology are created experimental samples of polymeric composite materials on the basis of epoxy resin, with the set concentration of filler - barium hex ferrite with a structural formula $BaO_6Fe_2O_3$ and with effective sizes of particles of 2 and 20 μm.

Uniform distribution of particles of hex ferrite of barium in a polymeric matrix was reached due to the rotation cured at the increased temperature of the filled compound in constant magnetic field.

Researches of dielectric are conducted properties of the created PCM samples in low-frequency area (1 kHz – 50 kHz) in the range of temperatures of T = 295 – 463 K.

Temperature and frequency dependences of relative dielectric permeability of ε and tangent of angle of dielectric losses of tgδ are received, discussion of results is carried out, the explanation and scientific justification for observed changes are offered dielectric properties of the PCM .

Effects of influence of high-disperse particles of $BaO_6Fe_2O_3$ with average sizes 2 and 20 of micron at a size of relative dielectric permeability ε and tangent of angle of dielectric losses of tgδ PCM are established that is caused by a condition of crystal structure of ferromagnetic fillers. The effect is more expressed with a diameter of particles of d = 20 μm and at concentration of micro particles of hex ferrite of barium up to 60 mass percent, and dielectric properties polymeric binding can be changed in 7 and more times.

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