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PERCOLATION EFFECT IN HIGH-DENSITY POLYMER-BASED METAL-OXIDE COMPOSITES

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Abstract: Composite samples have been obtained by thermal pressing method using high-density polymer (HDPE) as a matrix, α-Fe_2O_3, TiO_2, α-Al_2O_3 as a filler and technical graphite. The electrical parameters (ρ_v, σ) of composite samples have been measured in direct and alternating current fields depending on the volume content (Φ%) of the fillers and Maxwell relaxation periods have been determined at high and low percolation rates of composite samples. On the other hand, it has also been determined that the absorption dose of γ-irradiation does not change the percolation threshold and in this case, only the conductivity (σ) increases.

Keywords: composite, resistance, conductivity, percolation, γ-radiation, cluster.

1. Introduction

Percolation (to filter, trickle through) refers to a phase transition. Percolation is observed while studying the electro physical, magnetic, transport, thermal, optical properties in composite system. Percolation theory is widely applied in other issues on random processes, as well as is a key in understanding the physical processes. The percolation theory covers a wide application area. Development of electroactive elements of different types of devices of modern electronics, including medical diagnostics on the base of percolation structures proves it [1].

It is known that many factors affect the properties of composite materials. Many studies confirm that [2] the type, concentration of the filler, size and shape of the particle, physical and chemical state features of surface structuring, type and physical condition of polymer, technological parameters and methods in processing and development of materials, as well as external factors – electromagnetic field frequency, temperature, pressure, electrical and magnetic fields affect the characteristics of the composite. Thus, when the volume content of the filler fully covers the matrix, the electrical conductivity of the matrix grows up to the electrical conductivity of the filler and this growth occurs non-monotonically. The main and most important parameter of the percolation theory is the percolation threshold ($\Phi*$). The percolation threshold is determined by the distribution of the filler in the matrix, form of filler particles and matrix type [3, 4].

When the volume content (Φ%) of the filler grows, the particles combine and create a cluster and it forms a web connected with each other. The appropriate concentration of the percolation threshold ($\Phi*$) which is connected with the size of clusters reaches the size of the system. Studies have shown that the percolation is accompanied by an abrupt change in physical properties of the system, this transition which is connected with the clusters formed by particles is characterized as a geometric phase transition [1, 5, 11].

2. Experimental part

In order to obtain composite samples, it has been used a high density polyethylene (ρ=0,93g⁄cm^3, ρ_v=1·10^{16}Om·cm) of 20806-024 brand as a matrix, α-Fe_2O_3 (ρ=5,3g⁄cm^3, ρ_v=1·10^{7}Om·cm), α-Al_2O_3 (ρ=3,99g⁄cm^3, ρ_v=1·10^{11}Om·cm), TiO_2 (ρ=4,4g⁄cm^3, ρ_v=1·10^{12}Om·cm) as a filler and technical graphite (ρ=2,25q⁄cm^3, ρ_v=1·10^{-3}Om·cm) as a conductor.

Obtain technology of composite samples is carried out by conducting the following operations:

– the materials which are used as a filler are sieved. – volume share of the fillers has been 1-50%.

– HDPE powdered matrix is mixed together with the filler in a porcelain bowl.

– composite samples with 130-200 microns thick and 20-40mm diameter are obtained from the homogeneous mixture being kept for 5 minutes in hydraulic press at 15 Mpa pressure at 423K temperature.

– samples have been provided with safe electric contacts consisting of thin aluminum foil in 7 microns size.

– the obtained samples are cooled instantly in water-ice mixture.

The electrical parameters of the samples have been measured by E6-13A teraohmmeter in direct current and by E7-20-type immitance meter in alternating current.

Composite samples have been exposed to γ-irradiation at room temperature (T=293K) by MPX-γ-25M-type device with radiation source ^{60}Co at 3,3·10^3 Gy/h absorption dose. The irradiation dose has been D=300 kGy.

3. Results and discussion

In figure 1 it is given the dependence of specific volume resistance of HDPE+graphite, HDPE+α-Fe_2O_3, YSPE+α-$Al_2O_3$and YSPE+TiO_2 composite samples formed by fillers of which specific resistance differ from each other, on volume share of the filler ($\lg\rho_v=f(\Phi\%)$). Here (fig.1), we can distinguish three areas in the curves 2-4. The first area is high ohmic in Φ=1, 3, 5,% volume share of the filler, in the second one the specific resistance sharply decreases within the range of 7÷30% and in the third one the resistance gets the minimum value Φ>30%.

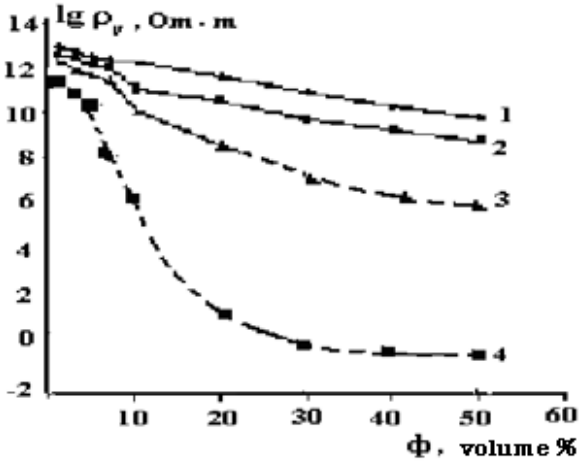

Fig. 1. Dependence $\lg\rho_v=f(\Phi\%)$ of special resistance on volume share of filler in direct current field: 1-YSPE+TiO_2; 2-YSPE+α-Al_2O_3; 3-YSPE+α-Fe_2O_3; 4-YSPE+qrafit 4-YSPE+graphite

Intersection of tangents of the second and third area curves is observed in Φ≈14-17%, and it can be considered Φ≈15% percolation threshold (upper percolation threshold) for HDPE+graphite composite system. It should be mentioned that in the shown samples each area has its own transition phase and it is characteristic for temperature dependence of electric conductivity and also volume shares of the filler. In the work [12] the percolation threshold in $lg\sigma=f(T)$ dependence of HDPE+α-Fe_2O_3composite system has been shown to be 7-9% (transition from the first area to the second, that is lower percolation threshold).

21-23% can be considered upper percolation threshold for HDPE+α-Fe_2O_3composite system. It should be noted that an increase in electrical resistance in the pre-percolation threshold area during thermal processing of the composites and a decrease in electrical resistance for the composites located in the post-percolation threshold area is characteristic for percolation systems [13, 14, 15]. It should also be mentioned that while increasing the concentration of filler particles in polymer matrix, the size of the clusters formed in the sample grows and as a result, generates infinite conductive clusters in channels, so it leads to an increase in electrical conductivity of the composite system in big concentrations of filler particles.

It should be noted that depending on the volume share of the filler, there is lower and upper percolation threshold in composite samples and this threshold is directly proportional to electrical conductivity. Maxwell relaxation time for HDPE+α-Fe_2O_3composite system at lower and upper percolation thresholds can be calculated with the formula $\tau_M=\varepsilon'\varepsilon_0/\sigma$, here at lower percolation threshold $\tau_M=1{,}47\cdot10^{-2}$sec, while upper $\tau_M=3{,}36\cdot10^{-3}$sec. The calculated values of Maxwell relaxation time indicate that at lower percolation threshold the relaxation period is ~4,4 times greater than the upper one, so it is due to an increase in conductivity at upper percolation threshold depending on volume share of the filler.

In the range of 5÷20% of the filler in HDPE+graphite composite system there has been observed a sharp decline in resistance, that is a sharp increase in conductivity, here the lower percolation threshold has been $5\% < \Phi^* \leq 7\%$.A complex net of conductive and insulation (polymer matrix) phases are formed in electrical conductivity of composite systems and it is determined by two mechanisms: 1) percolation in continuous network of conductive particles; and 2) tunnel effect between insulation phase of conductive particles. Existence of localized levels (C-H in amorphous matrix) leads to a sharp growth in fence transparency. It should be noted that magnetic, optical and other physical properties are closely connected with percolation threshold of heterogeneous system. Thus, the majority of the anomalies observed in physical properties of the composite system occur close to the percolation threshold of conductive phase concentration that is in the structure which conductive clusters are formed in dielectric matrix [16, 17].

Continuous clusters consisting of conductive particles are formed in HDPE+graphite composite system depending on the volume share (Φ%) of the filler. However, full conductivity (σ) is determined by sizes of conductive clusters consisting of metallic particles of which lower percolation threshold is isolated in granular structure and overall, by tunnel conductivity between clusters [6, 13, 18, 19, 20].

It should be mentioned that formation level of the conductive clusters in the areas observed in curves is different: 1) infinite clusters in high ohmic part of the curve have not been completed yet and the resistance is not dependent on the concentration of dispersed phase and is determined by the resistance of the matrix (HDPE); 2) the composite resistance in the area where the specific resistance sharply decreases is also determined by the capacity of the condenser generated by the dielectric matrix layer between them and dispersed filler particles; 3) infinite clusters have already been formed in the area where the resistance is minimum and it consists of the particles which are in contact with each other by touching (a filler without a polymer layer).

In this case, the composite resistance is determined by the filler resistance [7, 8].

If to pay attention to curves 1 and 2 in figure 2, we'll see that, the changing view of specific resistance in HDPE+TiO_2 and HDPE+α-Al_2O_3 composites depending on volume share of the filler is practically the same after Φ=10%, in HDPE+α-Al_2O_3sample there is observed approximately one order decrease after Φ=7%(for α-$Al_2O_3$$\rho_v=1\cdot10^{11}$om·cm, for $TiO_2$$\rho_v=1\cdot10^{12}$om·cm). While studying the percolation effects, many researchers [9, 10] have selected conductor and semiconductor as a filler and they note that: 1) fillers should have various resistance; 2)a part of fillers should be homogeneous, should not have oxide layer; 3) another part of fillers, on contrary, should have a complex structure and an oxide layer with different resistance on their surface.

Unlike that, it has been studied $\rho_v=f(\Phi\%)$ dependences of composites in alternating current field, consisting of α-Al_2O_3 and TiO_2 metal oxides, of which special resistances (ρ_v) slightly differ from each other. As it is seen from figure, (fig. 2) $0\leq\Phi\leq10$ and $0\leq\Phi\leq7$ intervals are high ohmic parts for YSPE+TiO_2 and YSPE+α-Al_2O_3, accordingly and here, the resistance practically does not depend on the concentration of conductive phase and it is determined by resistance of matrix. As it is seen from $\lg\rho_v=f(\Phi\%)$ dependence, percolation threshold for these composites is in the interval of $22\leq\Phi^*\leq25$.

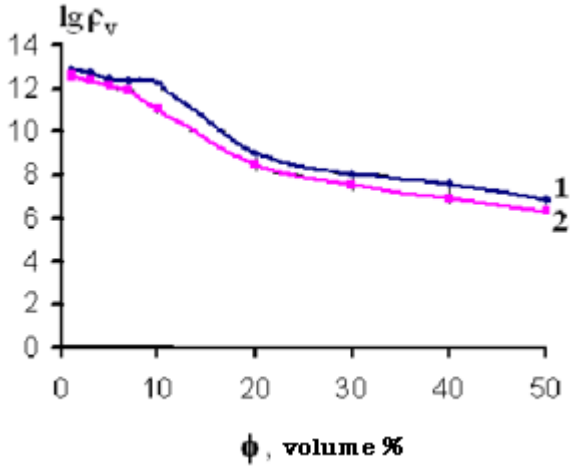

Fig. 2. Dependence $\lg\rho_v=f(\Phi\%)$ of special resistance on volume share of filler for YSPE+TiO_2 (1) and YSPE+α-Al_2O_3 (2) composite samples.

Practically coincide of percolation threshold of composites can be explained by the closeness of the resistances of fillers. On the other side, if we pay attention to the figures 1 and 2, we observe enough growth of conductivity in alternating current field. It is seen from 1st and 2nd curves of figure 4 that, ρ_v sharply decreases in 7÷20% interval in composite of YSPE+α-Al_2O_3 but, in YSPE+TiO_2, it decreases in 10÷20% interval. This decrease varies along a straight line in direct current (DC) field, but the change of ρ_v is nonlinear from 7% and 10% in alternating current field.

It should also be noted that, the value of electrical conductivity in alternating current field is more than the value in DC field. As the value of electrical conductivity in alternating current field is expressed by $\sigma_{ac}=\sigma_{dc}+\sigma_{rel}$, the value of electrical conductivity in alternating current field increases [21].

The dependence $\rho_v=f(\Phi\%)$ of special volume resistance on the volume share (Φ%) of filler has been given for YSPE+α-Fe_2O_3 composite sample in figure 3. As it is seen from unirradiated (original) state (1st curve) of samples, as volume share of filler increases there has

been observed the increase in conductivity and the decrease in special resistance. It should be noted that, in high volume share of filler, the volume of conductive cluster increases along the polymer matrix. It should also be noted that, border layers with special properties, formed around the filler, which is structural active than polymer matrix significantly, influence on properties of polymer composite materials [22,23]

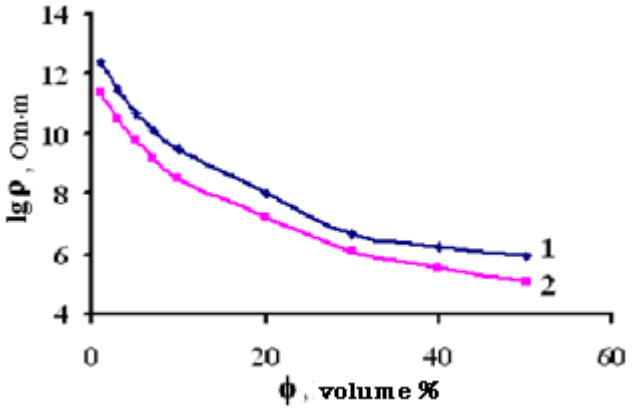

Fig. 3. Dependence $\rho_v = f(\Phi\%)$ of special volume resistance on volume share of filler ($\Phi\%$) for YSPE+α-Fe_2O_3 in direct current: 1- original (unirradiated); 2-irradiated (D=300 kGy).

Dependence $\rho_v = f(\Phi\%)$ in D=300 kQr γ-irradiation dose has been given in 2nd curve of the figure. As it is seen from the curve, percolation threshold ($\Phi*$) does not change as a result of irradiation. The increase in the conductivity is observed and it can be explained by the formation of electron-ion pair and other products of radiolysis.

It should also be noted that, beside the influence of fillers, that added to polymer matrix, on electrical conductivity of polymer composite materials, there is observed the influence of temperature. As heat play main role in strong electrical field in electron-heat process [24], it is related with electron-heat events that lead to temperature dependence of electrical conductivity of polymer in high flexibility by considering change effect in polymers, as well as flexibility properties of these materials.

It has been shown in figure 4, temperature dependences of electrical conductivity of composite samples with the fillers (Φ=10%), of which special resistances are different from each other.

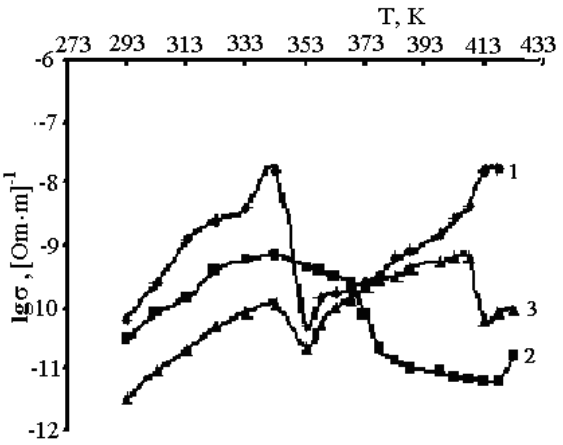

Fig. 4. Temperature dependences $lg\sigma = f(T)$ of electrical conductivity: 1-YSPE+10% α-Fe_2O_3 , 2-YSPE+10% α-Al_2O_3 3-YSPE+10% TiO_2

As it is seen from figure, the characteristics of conductivity at 293÷343K are similar in all three composite samples, the conductivity gets maximum values at T=343K in all three samples and it first sharply decreases and passes through a minimum at 353K before increasing again. But, in YSPE+10%α-Al_2O_3 sample, the decrease is less in conductivity and conductivity decreases at 368÷418K. The conductivity reaches to a maximum at T=343K in YSPE+10% TiO_2 sample, then it sharply decreases, passes through a minimum at T=353K and increases again. This increase is not big.

It should also be mentioned that, α-Fe_2O_3 and TiO_2 oxide fillers are micro, but α-Al_2O_3 is nano size (30, 50 mkm and 50 nm). We consider that, the difference in $\lg\sigma=f(T)$ dependences of investigated composites is that, α-Al_2O_3 filler is nano size.

4. Results

1. High and low percolation threshold exists in composite samples depending on volume share of filler and this threshold is directly proportional to electrical conductivity. In high and low percolation thresholds for YSPE+α-Fe_2O_3 composite system, Maxwell relaxation time is $\tau_M=1{,}47\cdot10^{-2}$sec. in low percolation threshold, $\tau_M=3{,}36\cdot10^{-3}$sec. in high percolation threshold. It is seen from these values of Maxwell relaxation time that, relaxation time in low percolation threshold is ~4,4 higher than high percolation time and it is related to the increase in conductivity in high percolation threshold depending on volume share of filler.
2. The result of conducted research showed that, absorption dose of irradiation does not change percolation threshold and percolation threshold depends on volume share of filler. The influence of irradiation dose leads to the increase in conductivity.

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ЭФФЕКТ ПЕРКОЛЯЦИИ В ВЫСОКОМОЛЕКУЛЯРНЫХ МЕТАЛЛООКСИДНЫХ КОМПОЗИТАХ

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Резюме: Композиционные образцы были получены методом термического прессования с использованием полимера высокой плотности (HDPE) в качестве матрицы, α-Fe_2O_3, TiO_2, α-Al_2O_3 в качестве наполнителя и технического графита. Электрические параметры (Ф%) композитных образцов измерялись в полях прямого и переменного тока в зависимости от объема наполнителей (ρ_v, σ), а периоды релаксации Максвелла были определены при высоких и низких скоростях

перколяции композитных образцов. С другой стороны, также было установлено, что поглощающая доза γ-облучения не меняет порог перколяции, и в этом случае увеличивается только проводимость (σ).

Ключевые слова: композит, сопротивление, проводимость, перколяция, γ-излучение, кластер.

YÜKSƏK SIXLIQLI POLİMER ƏSASLI METAL – OKSİD KOMPOZİTLƏRDƏ PERKOLYASİYA EFFEKTİ

N.Ş. Əliyev, A.M. Məhərrəmov, M.M. Quliyev, R.S. İsmayılova, M.N. Bayramov, İ.İ. Abbasov

Xülasə: Matrisa kimi yüksək sıxlıqlı polimer(YSPE), doldurucu kimi isə α-Fe_2O_3, TiO_2, α-Al_2O_3 və texniki qrafitdən istifadə edilməklə termik presləmə üsulu ilə kompozit nümunələr alınmışdır. Doldurucuların həcmi payından(Φ%) asılı olaraq kompozit nümunələrin elektrik parametrləri (ρ_v, σ) sabit və dəyişən cərəyan sahələrində ölçülmüşdür və kompozit nümunələrin aşağı və yuxarı perkolyasiya hədlərində Maksvell relaksasiya müddətləri müyyən edilmişdir.Digər tərəfdən o da müyyən edilmişdir ki, γ-şüalanmanın udulma dozası perkolyasiya həddini dəyişmir və bu halda ancaq keçiriciliyin(σ) qiyməti böyüyür.

Açar sözlər: Kompozit, müqavimət, keçiricilik, perkolyasiya, γ-şüalanma, klaster.