Physical Chemistry

Transformation of Dielectric Polymer Composite into Electric Conducting Material at Temperature Treatment in the Range 800-1600 K

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(Presented by Academy Member Vladimer Tsitsishvili)

ABSTRACT. On the basis of the blends of phenolformaldehide and epoxy resin with silicon organic compound and fiber glass annealed at 800-1600 K in vacuum (10Pa) the new conductive monolithic materials were created and their both mechanical and electric conducting properties were investigated. Inclusion of fiber glass into compositions gives a possibility to obtain the monolith material thanks to formation of covalent bonds as a result of high temperature reactions between organosiloxanes and glass side groups disposed on the glass surface. It is established experimentally that the obtained products are characterized by semiconducting properties, the level of conductivity and conductive type of which are regulated by selection of technological methods. The properties of obtained materials are explained by intensification of processes promoting increase of the polyconjugation regions (infinitive clusters) and their drawing together, which result in continuous decrease of the potential barrier height, and conductivity approximates to the metal type. The density and mobility of carriers increase at increasing of annealing temperature up to definite levels. The temperature dependence of the electrical conductivity and charge mobility are described by Mott formulas. On the basis of obtained results it is proposed that formation of conducting clusters and the charge transport between them undergoes to the mechanism of charge jumping with alternative longevity of the jump. © *2017 Bull. Georg. Natl. Acad. Sci.*

Key words: phenolformaldehide and epoxy resins, fiber glass, pyrolysis, electric conductivity, charge mobility, paramagnetic properties

Interest to the processes proceeding at increased temperatures (up to 600 K) in polymer materials is stimulated by possibility of obtaining of systems with double conjugated bonds, which give the semiconductor properties to high-molecular compounds. Effectiveness of formation of the polyconjugation systems increases with temperature, if pyrolysis proceeds in vacuum or in inert atmosphere[1-3].

Deep transformations in the molecular system at high temperatures were studied well on the example of polyacrylonitrile [4]. Thermal transformation of polyacrylonitrile leads to formation of polymer, con-

sisting of condensed pyridine cycles with conjugation by C=C bonds, as well as by C=N ones. As a result of reactions proceeding at high temperatures in the vacuum or inert atmosphere the systems of double conjugated bonds are created, which are characterized with electric conductivity [5]. Physical and chemical transformations in polymers proceed at combination of temperature varying with introduction of various donor-acceptor inorganic or organic additives into reactor. Basing on the works [6-8] on obtaining organic semiconductors by pyrolysis of organic compounds one may conclude that the materials of this type, obtained until the present time, were generally applied in chemical reactions (for example, in catalysis and inhibition of various processes). At the same time, unique semiconducting properties, as a rule, were not used in practice. This is mainly explained by the powder-like state of the existing materials, and obtaining of construction materials on their basis requires various adhesives and plasticizers, which significantly reduce their electric conducting properties. Despite it there are several works, which contain methods of obtaining more or less monolithic conducting materials. For example, multistage pyrolysis of some phenoloformaldehyde resins at temperatures up to 3000 K gave, the so-called, glassy carbon, which name is devoted to the glassy-like structure of the material [8]. Glassy carbon is characterized by high electric conductivity, thermal resistance and resistance to aggressive media. However, very narrow range of specific resistance and increased friability of glassy carbon significantly decrease the suitability of this conducting material. But in this case, production of common articles from this material was also difficult due to high friability of pyropolymers.

The main aim of the presented work is obtaining of pyrolized monolithic materials with wide range of the electric conductivity.

Experimental

Epoxy resin (ER), novolac phenol-formaldehyde resin (PFR), polymethyl-silsesquioxane (PMS) and fiber glass (FG) were chosen as the initial substances. Pyrolysis of mixtures of the components mentioned, pressed in press-forms, was conducted at various temperature ranged within 800-1600 K in 10 Pa vacuum. Products obtained in this manner possess good mechanical and electric conducting properties, and are monolythic materials. The conductivity of the obtained materials was tested with the use of impedance method. The type and mobility of charge carriers were defined with the use of Hall effect technique.

Results and Discussion

Inclusion of fiber glass into compositions was induced by the following idea. At high temperatures organosiloxanes react with side hydroxyl groups and dispose on the fiber glass surface. In this reaction they form covalent bonds with those side groups according to the following reaction scheme:
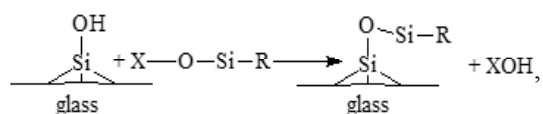
where X = H, Na, K; R is a hydrophobic organic residue.

Moreover, proceeding of the following reaction is possible:
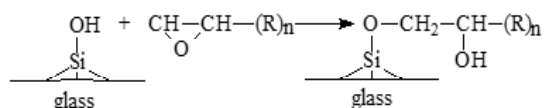
After high-temperature treatment silsesquioxanes obtain a structure, close to inorganic glass with spheres of regulation due to formation of three-dimension siloxane cubic structures and selective sorption of one of the composite elements is possible on the filler surface in the hardening composite.

Control tests on pyrolysis conducted in air showed that all tested composites displayed proceeding of ash formation and mechanical degradation with increase of pyrolysis temperature. These products will not be discussed below.

Fig. 1-5 reflect changes of some mechanical and electric conducting properties of polymer compos-
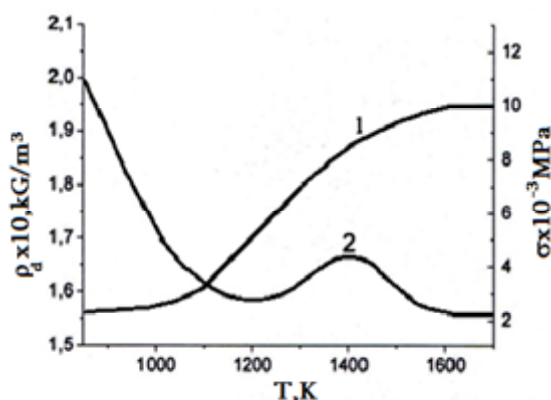
Fig. 1. Dependences of ρ_{den} (1) and resistance at elongation σ (2) on pyrolysis temperature for the composite ED-20 + PFR + KO-812 + FG.

Fig. 2. Dependences of electric conductivity γ (1) and mobility of charge carriers μ (2) on pyrolysis temperature for the composite ER + PFR + PMS + FG.

ites depending on temperature of pyrolysis in amorphous medium. These dependences are the result of proceeding of deep physicochemical transformations in materials, the heterogeneity of which increases with pyrolysis temperature. Combined analysis of the change of density of materials (Fig. 1) with the increase of pyrolysis temperature induces a conclusion that excretion of some volatile fractions of organic part of the material, carbonization of organic residue and caking of glassy fibers cause the increase of pyrolyzate density, based on the composite with polymethylsilsesquioxane. The limit of pyrolyzate density is reached at temperatures in the region of 1600 K (Fig.1, curve 1), followed by a decrease of the material density due to intensification of thermal degradation processes with pyrolysis.

Changes in resistant properties of composites at pyrolysis are more complex. For example, Fig. 1 shows that the material strengthening at elongation extremely depends on the pyrolysis temperature, possessing an intermediate maximum near 1400 K. Comparison of the microstructure schemes for pyrolyzed composites and the dependence of the electric conductivity on temperature of pyrolysates shows that burning out of organic part of the composite and, consequently, weakening of adhesion forces in the interphase lead to decrease of the material resistance with pyrolysis temperature increase up to a definite value. At further increase of pyrolysis temperature the resistance increases also and then decreases at higher
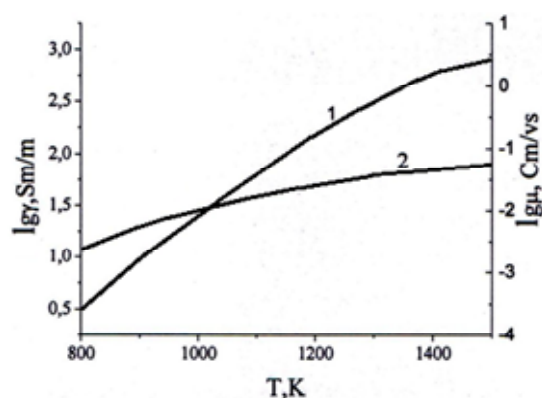
temperatures after passing a maximum. Moreover, formation of covalent chemical bonds is quite probable in this case. Such bonds were mentioned at the beginning of the present part, formed between organic and inorganic parts of the composite. This, evidently, promotes increasing of resistant properties of the material.

According to Fig. 2, the dependence of electric conductivity on pyrolysis temperature for composites grows monotonously. This dependence points out a constant accumulation of polyconjugation systems due to complex thermochemical reactions, analogous to those discussed above on the example of polyacrylonitrile pyrolysis. As to our point of view, formation of polyconjugated systems is rather probable at pyrolysis of a compound containing phenoloformaldehyde or epoxy resin with inclusion of polymethylsilsesquioxane at the glass surface. These conjugated systems are covalently linked to Si-O groups on the glass surface by the skeleton of pyrolized polymethylsilsesquioxane (Fig. 3). Chemical bonds which link organic and inorganic parts of the composite reliably increase stability of polyconjugated structures, responsible for electrically conducting properties of materials. The electrically conducting system of the materials can be considered as a heterogeneous composite material, consisted of highly conducting spheres of polyconjugation and barrier interlayers between them [2, 9,10]. Volumetric part of the polyconjugation
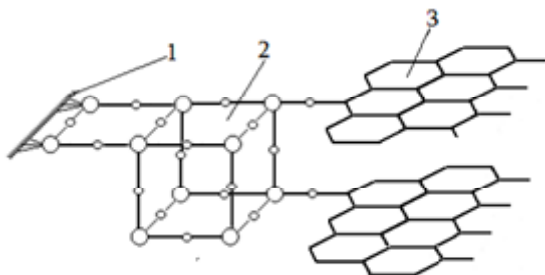
Fig. 3. Schematic image of disposition of glassy structures (1), pyrolyzed polymethylsilsesquioxane (2) and polyconjugation systems (3) in pyrolyzed composite: epoxy resin + phenoloformaldehide resin + polymethyl-silsesquioxane + glassy fiber. Big circles mark atoms of silicon, small circles – oxygen atoms.

spheres is determined by the pyrolysate production technique. It increases gradually with temperature of pyrolysis. Figure 2 shows that the number of charge carriers and their mobility increases with the volume of polyconjugation spheres (these parameters were measured by the technique of Hall effect).

The most apparently true model of electric conductivity in materials with the system of double conjugated bonds seems to be the change transfer in the ranges of polyconjugation possessing metal conductivity and jump conductivity between polyconjugation spheres.

An important information on the nature of conductivity of pyrolized polymer materials is given by investigation of the γ dependence on temperature (Fig. 4).

For semiconductive pyropolymers this dependence was studied in many works [6-8]. Excluding some small deviations, most of experimental data fit linear dependence of $\lg\gamma$ on $1/T$. The nature of such change of the conductivity was explained in the frames of electronic properties of irregular materials [9].

Comparison of the experimental data on dependence of γ - T with the use of known for organic semiconductors formula ($\gamma = \gamma_0 \exp(-dE/kT$, where γ_0 is γ at very high temperatures, E -activation energy, k - Boltzmann constant) [4] and the one proposed by N. Mott shows that the dependence obtained by us experimentally satisfies better to Mott law [10]:

$$\gamma = \gamma_0 \exp\left[-\left(\frac{T_0}{T}\right)^{1/4}\right], \qquad (1)$$

where T_0 and γ_0 are parameters of the presented model:

$$T_0 = \frac{\beta}{kg(\mu)a^3}, \quad \gamma_0 = \frac{3e^2\nu\Phi_0}{2}\cdot\left(\frac{g(\mu)a}{2\pi kT}\right)^{1/2},$$

where **a** is the radius of localized states, close to the Fermi level; **g(μ)** is the density of states at the Fermi level; **e** is the electron charge; **n** is the phonon frequency; $F_0 = 1$ is the constant; $\beta = 21.2 \pm 1.2$ is the coefficient, determined from the percolation theory [10].

Figure 4 shows that for four pyrolized composites dependences of electric conductivity on temperature in $\lg\gamma$ - T and $\lg\gamma$ - $T^{-1/4}$ coordinates display results better in the frames of the Mott dependence. However, as it follows from the same Figure the difference in temperature dependences of conductivity, composed in both coordinates, become so smooth with temperature increase that they are nearly drawn together for the sample with pyrolysis temperature higher than 1573 K. On the other hand, the same dependences show that the activation energies (according to the curve slope) decrease with pyrolysis temperature increase. It is explained by intensifica-
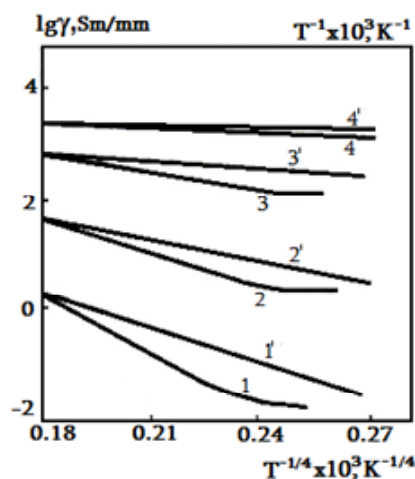

Fig. 4. Temperature dependence of γ for composite materials based on ED-20 + PFS + KO-812 + FG, pyrolized at 873 (1, 1'), 1173 (2, 2'), 1373 (3, 3') and 1573 K (4, 4') in the $\lg\gamma$ - T^{-1} (1-3) and $\lg\gamma$ - $T^{-1/4}$ (1'-3') coordinates, respectively.
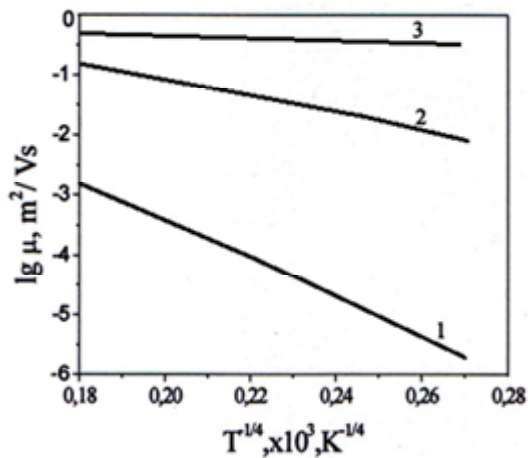
Fig. 5. Temperature dependence of charge carriers mobility μ for the composites ED-20 + PFS + KO-812 + FG, pyrolized at 873 (1), 1173 (2) and 1373 K (3), respectively.

tion of processes promoting increase of the polyconjugation regions (infinitive clusters) and their drawing together, which result in continuous decrease of the potential barrier height, and conductivity approximates to the metal type. Evidently, at very high temperatures electric conductivity dependences on temperature cannot be described by equations noted above. Fig. 4 shows also that temperature dependence of conductivity in narrow temperature ranges fits a straight line in the $\lg \gamma$ - T^{-1} coordinates. At the same time, the E value, corresponded to these temperature ranges, decreases monotonously with temperature.

In Fig. 5 the dependence of the carrier mobility on the temperature is presented.

According to [11] the increase of conductivity of semiconducting materials with temperature belongs to the growth of carrier mobility μ due to the expression:

$$\mu = \mu_0 \exp\left[-\left(\frac{T_0}{T}\right)^{1/4}\right]. \tag{2}$$

The character of dependence (2) is analogical to Mott formula for dependence of electric conductivity on the temperature, which is quite logical.

Conclusions

1. High-temperature treatment (pyrolysis) of polymer composites in the inert atmosphere or in the hydrogen medium stimulates processes of the polyconjugation systems, in the frames of which electric conductivity proceeds with a very low activation energy (it has semimetal character).

2. Charge transfer between poly-conjugation systems is ruled by the jump conductivity mechanism with variable jump length. In this case, its temperature dependence is described by the Mott formulas.

1. Presence of a glassy fiber and polymethylsilsesqwioxane in composites promote formation of covalent bonds between organic and inorganic parts of the composite at pyrolysis. This leads to improving of mechanical properties of materials together with the electric ones.

ფიზიკური ქიმია

დიელექტრიკული პოლიმერული კომპოზიტის გარდაქმნა ელექტროგამტარ მასალად თერმოდამუშავებისას 800-1600 K ტემპერატურულ შუალედში

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** ივანე ჯავახიშვილის სახელობის თბილისის სახელმწიფო უნივერსიტეტი, რ. აგლაძის არაორგანული ქიმიის და ელექტროქიმიის ინსტიტუტი, თბილისი, საქართველო

        შემუშავებულია ახალი ელექტროგამტარი მონოლითური მასალები ფენოლფორმალდეჰიდისა და ეპოქსიდური რეზინის ბაზისური ნარევის გამოწვით სილიციუმორგანულ ნაერთსა და ბოჯკოვან მინასთან ერთად ვაკუუმსა და წყალბადის გარემოში 800-1600 K ტემპერატურულ შუალედში. გამოკვლეულია ამ მასალების ზოგიერთი მექანიკური, ელექტროგამტარული და სხვა თვისებები. ექსპერიმენტულად დადგენილია, რომ მიღებული პროდუქტები ხასიათდება ნახევარგამტარული თვისებებით და მათი გამტარობის დონე რეგულირდება ტექნოლოგიური მეთოდის შერჩევით. მუხტის მატარებელთა სიმკვრივე და ძვრადობა იზრდება გამოწვის ტემპერატურის განსაზღვრულ დონემდე ზრდისას. მათი ელექტროგამტარობის ტემპერატურული დამოკიდებულება და მუხტის ძვრადობა აღიწერება მოტის ფორმულებით. მიღებული შედეგების საფუძველზე გამოთქმულია გარაუდი, რომ გამტარი კლასტერების ფორმირებასა და მუხტის ტრანსპორტირებას მათ შორის უზრუნველყოფს მუხტის გადატანის მექანიზმი ნახტომის ცვლადი სიგრძით.

REFERENCES

1. Jampolskii Y.P. (1981) Issledovanie elementarnykh reaktsii v processe piroliza. Doct. Thesis Institute of Chem.Phys. M. (in Russian).
2. Enzel P., Bein T. (1992) Semiconducting materials based on some pyrolyzed polymers. *Chem.Materials*, 4: 819-824.
3. Aneli J.N., Khananashvili L.M., Zaikov G.E. (1998) Structuring and Conductivity of Polymer Composites, Nova Sci. Publ. N-Y. 326 p.
4. Aviles M.A., Gines J.M., Del Rio J.C., Pascual J., Perez J.L., Sanchez-Soto P.J. (2002) Thermal analysis of acrylonitrile polymerization in the presence of N,N-Dimethylformamide. *J.Thermal Analysis and Calorimetry,* **67:** 177- 188.
5. Osugi J., Hara K. (1966) Application of electroactive polymers. *Rev.Phys.Chem.Jap.* **36**: 81-86.
6. Todd MK., Wu-Wong Hsi, Broadbelt L.I. (2003) Mechanistic modeling of polymer pyrolysis: polypropylene.
7. Blum Y.D., Shwartz K.B., Laine R.M. (1989) Preceramic polymer pyrolysis. *Journal of Mater.Sci.,* **24,** 5:1707-1718.
8. Fialkov A.S. (1979) Uglerod-graphitnye soedinenia. M. (in Russian).
9. Shklovskii B.I., Efros A.L. (1979) Electronnye svoistva legirovannykh poluprovodnikov. M. (in Russian).
10. Shklovskii B.I., Efros A.L. (1975) Teoriia perkoliatsii i provodimost visoko-geterogennykh tverdykh tel. *Uspekhi fizicheskikh nauk,* **117,** 3: 36-46 (in Russian).
11. Mott N.F., Davis E. (1979) Electron Processes in noncrystalline materials, 2nd Ed., oxford, Clarendon Press.