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STRUCTURING AND ELECTRIC CONDUCTIVITY OF POLYMER COMPOSITES PYROLYSED AT HIGH TEMPERATURES

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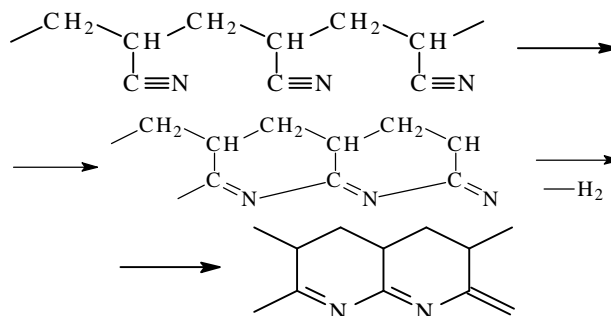*4, Kosygin str., 119334 Moscow, Russia*

Abstract. On the basis of mixes of phenolformaldehide and epoxy resins at the presence of some silicon organic compounds and fiber glasses annealed in vacuum and hydrogen media the new conductive monolithic materials have been created. Conductive, magnetic and some other properties of these materials were investigated. It was established experimentally that the obtained products are characterized by semiconductive properties, the level of conductivity and conductive type of which are regulated by selection of technological methods. 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 were described by Mott formulas. The magnetic properties of the annealed materials were investigated by ESR method. It was established that at annealing free radicals and other paramagnetic centers are formed. On the basis of the obtained results it was proposed that formation of conducting clusters and the charge transport between them is provided by mechanism of charge jumping with alternative longevity of the jump.

Keywords: conductivity, pyrolysis, high temperature, structuring, electric properties.

1. Introduction

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

Intramolecular transformations with further change of supermolecular system were studied well on the example of polyacrylonitrile [4]. Thermal transformation of polyacrylonitrile leads to formation of a polymer consisting of condensed pyridine cycles with conjugation by C=C bonds as well as by C=N ones. Reactions proceeding at heat treatment (usually called as pyrolysis) of polyacrylonitrile fall under the following scheme [5]:

In this case coupled electrons, which do not participate in chemical bonds, separate at nitrogen atoms entering compounds with conjugated bonds. In such separated state electrons enter intensive collective interaction. Concentration of paramagnetic particles increases with the temperature of pyrolysis. It is known that the ESR signal is one of the signs of polyconjugation appearance in polymer systems [6]. According to the point of view of many authors, electrons delocalized in the conjugation system are responsible for ESR signal, although some of the authors think that similar contribution into the ESR signal formation (a singlet line with *g*-factor close to 2.0) can be made by paramagnetic centers, localized in various traps (for example, near structural defects) [3]. Deep physical and chemical transformations in polymers proceed at combination of temperature varying with introduction of various donor-acceptor inorganic or organic additives into the reactor.

In summary, basing on the works 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, excluding very few of them, were not used in practice. This is mainly explained by the powder-like state of the existing materials and the fact that obtaining of construction materials on their basis requires various adhesives and plasticizers, which significantly reduce their electrically conducting properties. Despite the situation in this branch of study on electrically conducting materials several works can be named 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, the name of which is devoted to the glassy-like structure of the material [7]. Glassy carbon is characterized by high electric conductivity, thermoresistance, 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. Samples of the fiber type, obtained by pyrolysis of polyacrylonitrile fibers, were studied in [8]. 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 electric conductivity.
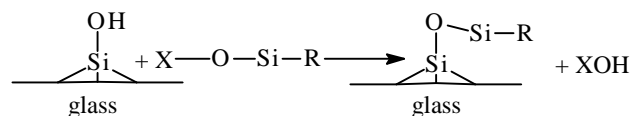
2. Experimental

Epoxy resin (ER), novolac phenoloformaldehyde 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 500–1500 K in 10 Pa vacuum. Products obtained in this manner possess good mechanical and electroconducting properties, and are monolythic materials. Pyrolized samples or pyrolyzates were tested by polarization microscopy technique in order to determine their microstructure. The paramagnetic properties of pyrolizates were investigated by using of ESR spectrometer of Brukker type. The type and mobility of charge carriers investigated were measured by the Hall effect technique.
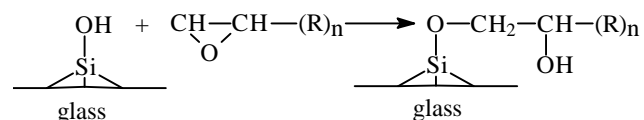
3. Results and Discussion

Inclusion of fiber glass into compositions was induced by the following idea. It is known [9] that at high temperatures organosiloxanes react with side hydroxyl groups, disposed on the fiber glass surface. In this reaction they form covalent bonds with those side groups according to the following reaction scheme:

$$\underset{\text{glass}}{\equiv Si-OH} + X-O-Si-R \longrightarrow \underset{\text{glass}}{\equiv Si-O-Si-R} + XOH$$

where X = H, Na, K;   R is a hydrophobic organic residue.

Moreover, proceeding of the following reaction is possible:

$$\underset{\text{glass}}{\equiv Si-OH} + \underset{\diagdown O \diagup}{CH-CH}-(R)_n \longrightarrow \underset{\text{glass}}{\equiv Si-O-CH_2-CH-(R)_n} \;\; OH$$

It is known that 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 [9].

Control tests on pyrolysis conducted in air showed that all tested composites displayed proceeding of ash formation and mechanodegradation with increase of pyrolysis temperature. The products obtained by pyrolysis possess no clear physical properties. These products will not be discussed below.

Then pyrolyzed samples or pyrolyzates were tested by polarization microscopy technique in order to determine their microstructure. The photos obtained are schematically shown in Fig. 1. These images of microstructure of pyrolyzates level the morphological changes in sample morphology with increase of pyrolysis temperature. Structural changes in composites at pyrolysis significantly depend on the presence of polymethyl-sisquioxane in their composition. Thus, comparison of schemes 2 and 3 with 2' and 3' in Fig. 1, respectively, allows to conclude that carbonization of the composite containing polymethylsesquioxane (composite 1) induces formation of lower amount of caverns (cavities) than in analogous composite containing no organosiloxane of this type (composite 2). In this case, the difference increases with pyrolysis temperature. The attention should be paid to the fact that the structure of pyrolyzate, obtained from the composite 1, is highly monolythic: caked glassy fibers, cavities are remote from them. This, evidently, means good adhesion of carbonized substance to the glass surface. Pyrolyzate obtained from the composite 2 possesses no such advantages (from technical point of view): badly caked fibers and numerous cavities. Naked parts of glassy fibers and spheric forms of carbonized regions of the second pyrolyzate determine bad adhesion of carbonized substance to glass. Increase of the amount of cavities at pyrolysis of this composite may be explained

by intensification of thermal degradation of organic part of the composite with pyrolysis temperature. As a consequence, this causes formation of volatile products. Basing on qualitative comparison of the schemes shown in Fig. 1, one may conclude that at pyrolysis of the composites mentioned polymethylsesquioxane acts as the inhibitor of thermodegradation processes and increases adhesion of carbonized substance to glass.

Spheric cavities of various sizes occur near the sample surface at increased pyrolysis temperatures. This is caused by softening and melting of glassy fibers at simultaneous increase of concentration of connections between fibers. Mechanical tensions appearing in this case are the reason of occurrence of new caverns (cavities) and splits both in carbonized part of pyrolyzates and in glassy fibers.
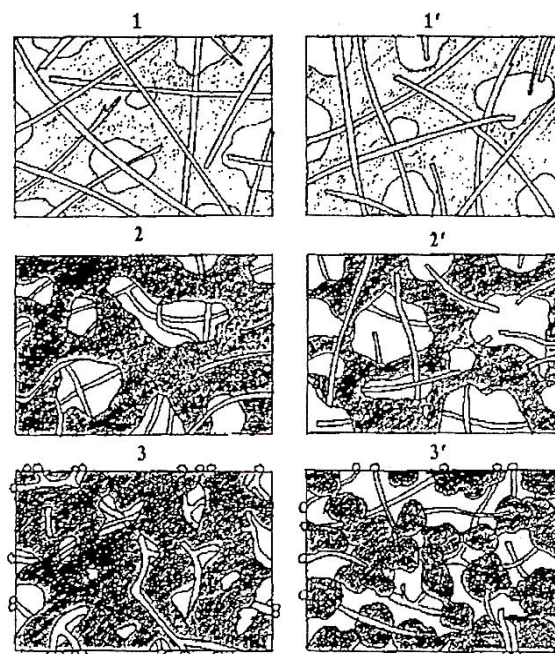
Thus, analysis of schematic images, depicted by microscope, allows to state that the composition and conditions of pyrolysis are the limiting factors for estimation of morphological changes in pyrolized organo-inorganic composites.

Figs. 2-7 reflect changes of some mechanical, electric and paramagnetic properties of polymer composites 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 microstructure (Fig. 1) and density of materials (Fig. 2) 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 poly-

methylsesquioxane. The limit of pyrolyzate density is reached at the temperatures near 1273 K (Fig. 2, *curve* 1), followed by a decrease of the material density due to intensification of thermal degradation processes with pyrolysis temperature increase above 1273 K. Similar behavior is displayed by pyrolyzates obtained on the basis of composites containing no polymethylsesquioxane (Fig. 2, *curve* 2), but at total decrease of density and shift of the maximum to the side of lower pyrolysis temperature.

Changes in resistant properties of composites at pyrolysis are more complex. For example, Fig. 2 shows that the material strengthening at elongation extremely depends on the pyrolysis temperature, possessing an intermediate maximum near 1273 K. Comparison of the microstructure schemes for pyrolized 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. This maximum of resistance dislocates near 1273 K. Sintering of glassy fibers increases at this temperature (Fig. 1, scheme 3). 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. The second maximum in the $s–T_{pyr}$ curve is, probably, explained by an increase of material friability due to degradation of the bonds mentioned between phases and occurrence of cavities in pyrolyzate.

Fig. 1. The microstructure scheme of the composites based on epoxy and phenol-formal-dehyde resins, and fiber glass, containing (schemes 1-3) and not containing (1'-3') polymethylsilsesquioxane polyorganosiloxane before (1, 1') and after (2, 2', 3, 3') pyrolysis. Shaded areas on schemes 1 and 1' correspond to the initial organic matrix, and on other schemes – to carbonized mass of composites. Light areas cycled by contours mark cavities (caverns), light bands – fiber glass, light cycles at the borders of schemes 3 and 3' – glass cavities
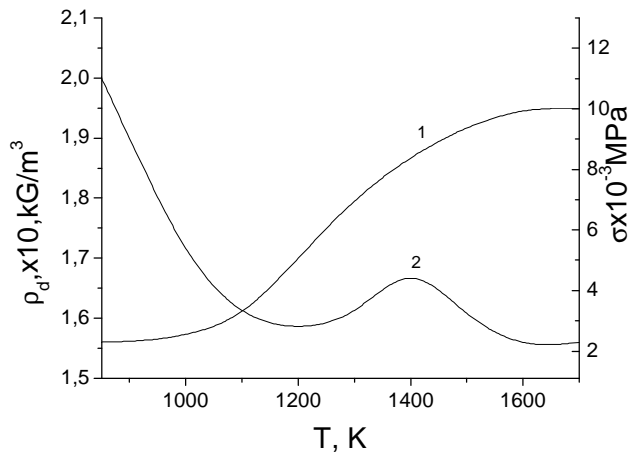
Fig. 2. Dependences of r_{den} (1) and resistance at elongation s (2)
on pyrolysis temperature
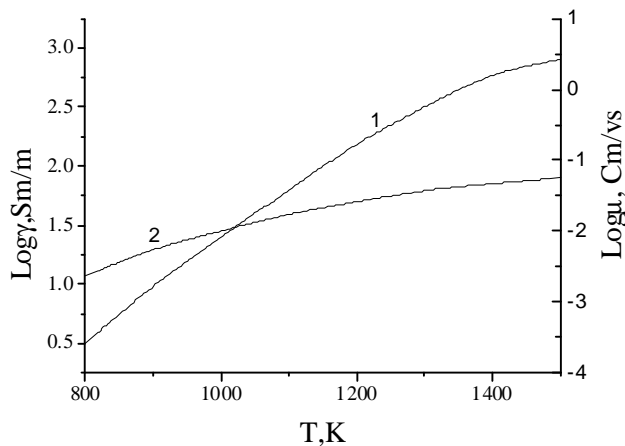for the composite ED-20 + PFR + KO-812 + FG

Fig. 3. Dependences of electric conductivity g (1)
and mobility of charge carriers m (2) on pyrolysis temperature
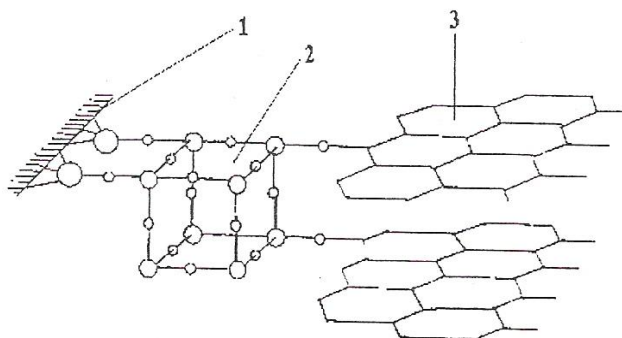for the composite ER + PFR + PMS + FG

Fig. 4. Schematic image of disposition of glassy structures (1),
pyrolyzed polymethylsilsesquioxane (2) and polyconjugation
systems (3) in pyrolzedcompositeepoxy resin +
phenoloformaldehide resin + polymethyl-silsesquioxane +
glassy fiber. Big circles mark atoms of silicon, small circles –
oxygen atoms

The g–T_{pyr} dependence for pyrolyzate 2 differs from that for pyrolyzate 1 both quantitatively and qualitatively (low values of g, absence of a maximum of g–T_{pyr} curve). This, evidently, correlates with the above mentioned conclusion about deterministic role of polymethylsesquioxane in the structure of the composite 1 in improving adhesion of carbonized part of the pyrolyzate to the glass surface.

According to Fig. 3, 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 ('a cube'), schematically shown in Fig. 4. 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 consisting of highly conducting spheres of poly-conjugation and barrier interlayers between them [2, 10]. Volumetric part of the polyconjugation spheres is determined by the pyrolysate production technique. It increases gradually with temperature of pyrolysis. Fig. 3 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 [7].

Important information on the nature of conductivity of pyrolized polymer materials is given by investigation of the g dependence on temperature. For semiconductive pyropolymers this dependence was studied in many works [6-9]. Excluding some small deviations, most of experimental data fit linear dependence of lg$g$ on $1/T$. In some cases, graphics of the dependence possess bendings. The nature of such change of the conductivity was explained in the frames of electronic properties of irregular materials [10, 11].

Comparison of the experimental data on the dependence of g–T with the known ones for organic semiconductors [4]:

$$g = g_0 \exp(-dE/kT) \qquad (1)$$

and one proposed by N. Mott shows that the dependence obtained by us experimentally satisfies to Mott law [12]:

$$g = g_0 \exp\left[-\left(\frac{T_0}{T}\right)^{1/4}\right] \qquad (2)$$

where T_0 and g_0 are parameters of the present model:

$$T_0 = \frac{b}{kg(m)a^3} \qquad g_0 = \frac{3e^2 n\Phi_0}{2} \cdot \left(\frac{g(m)a}{2pkT}\right)^{1/2}$$

where a is the radius of localized states, close to the Fermi level; $g(m)$ is the density of states at the Fermi level; e is the electron charge; n is the phonon frequency; $\Phi_0 = 1$ is the constant; $b = 21.2 \pm 1.2$ is the coefficient determined from the percolation theory [10, 11].

Fig. 5 shows that for four pyrolized composites dependences of electric conductivity on temperature in $\lg g$–T and $\lg g$–$T^{1/4}$ coordinates display results better in the frames of the Mott dependence. However, as it follows from the same Fig. 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 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 intensification of processes promoting increase of the polyconjugation regions (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 the equations noted above.

Fig. 5 shows also that temperature dependence of conductivity in narrow temperature ranges fits a straight line in the $\lg g$–T^{-1} coordinates. At the same time, the E value, corresponding to these temperature ranges, decreases monotonously with temperature (Table 1).
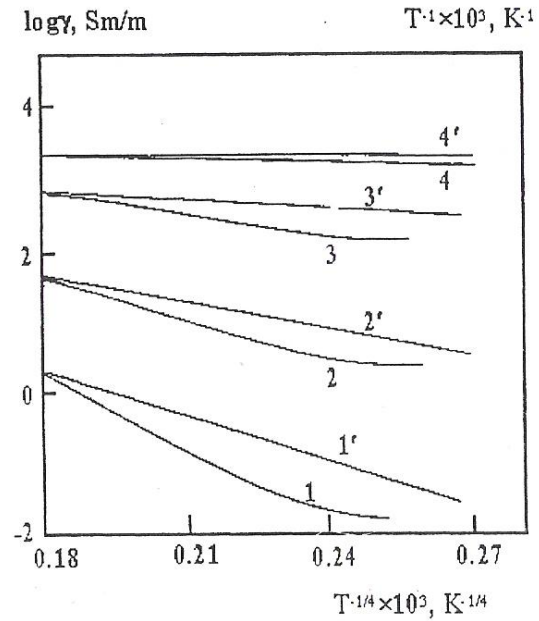

Fig. 5. Temperature dependence of g for composite materials based on ED-20 + PFS + KO-812 + FG, pyrolized at 873 (1, 1'), 1173 (2, 2'), 1373 (3, 3') and 1573 K (4, 4') in the $\lg g$–T^{-1} (1-3) and $\lg g$–$T^{1/4}$ (1'-3') coordinates, respectively.

According to [12] the increase of conductivity of semiconducting materials with temperature belongs to the growth of carriers mobility μ due to the expression:

$$m = m_0 \exp\left[-\left(\frac{T_0}{T}\right)^{1/4}\right].$$

Temperature dependences of m in the $\lg m$–$T^{1/4}$ coordinates measured for pyrolized composites fit straight lines (Fig. 6). Following from this, one can make a conclusion that semiconducting pyrolysates represent heterogeneous systems, the conductivity of which in the wide temperature range is that with variable jump length $\overline{r}$. Temperature dependence of this parameter is described by the following expression:

$$r = 0.37a\left(\frac{T_0}{T}\right)^{1/4}.$$

Table 1

Dependence of the activation energy (in eV) for semiconductors based on pyrolized composites on pyrolysis temperature and change of g

T_{pyr}, K	Measurement temperature							
	176–192 K		206–230 K		240–280 K		300–430 K	
	E_e*	E_p**	E_e	E_p	E_e	E_p	E_e	E_p
873	0.112	0.108	0.124	0.126	0.181	0.176	0.190	0.186
1173	0.070	0.068	0.078	0.076	0.091	0.087	0.116	0.111
1373	0.044	0.041	0.049	0.048	0.056	0.052	0.065	0.062

 * Experimental results were obtained by Eq. (1).
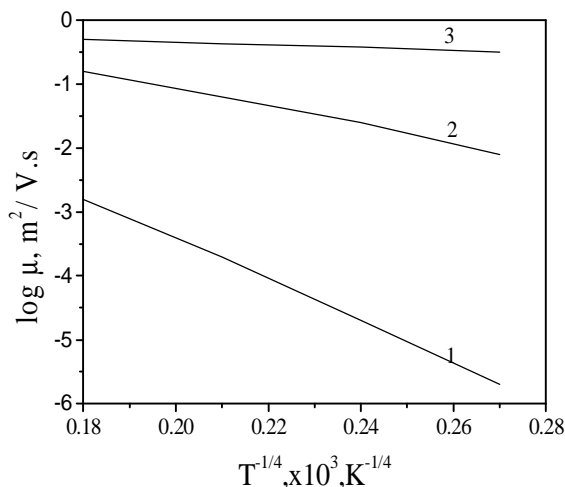 ** The data calculated by Eq. (2).

Fig. 6. Temperature dependence of charge carriers mobility *m* for the ED-20 + PFS + KO-812 + FG composites, pyrolized at 873 (1), 1173 (2) and 1373 K (3), respectively

Fig. 7. Temperature dependence of paramagnetic centers N (1), ESR line width (2) and ESR line assimetry parameter A/B (3) on the pyrolysis temperature for the ED-20 + PFS + KO-812 + FG composites

The dependence of paramagnetic centers concentration in pyrolized polymer composites on pyrolysis temperature has an extreme character (Fig. 7). Curve of the present dependence possesses maximum corresponding to the 900–1000 K range. Change of the ESR absorption line intensity is accompanied by a definite change of its width. In this case, the form and width of the ESR line changes (at constancy of the g-factor) – lines are broadened, and asymmetry of singlet occurs. These changes are more effective for composites pyrolized at rather high temperatures. Maximum on the concentration dependence for paramagnetic centers on pyrolysis temperature is correspondent to the temperature range in which volatile products of pyrolysis are released and polyconjugation systems occur (possessing linear or cyclic structure). Decrease of concentration of the centers above 973 K proceeds due to coupling of a definite amount of unpaired electrons. According to this coupling new chemical structures occur (for example, polyconjugation responsible for electric conductivity increase). Some authors [4] think that this is bound to grafitization of the carbonic skeleton. However, according to X-ray photos absence of the lines characteristic for graphite makes the occurrence of graphite spheres in pyrolysates doubtful.

At higher temperatures of pyrolysis the ESR line width and the asymmetry parameter increase due to the following phenomena. Deepening of thermo-chemical reactions in composites leads to formation of local paramagnetic centers due to thermal decomposition of siloxane chains with further localization of an unpaired electron in oxygen atom, possessing increased affinity to electron. Due to occurren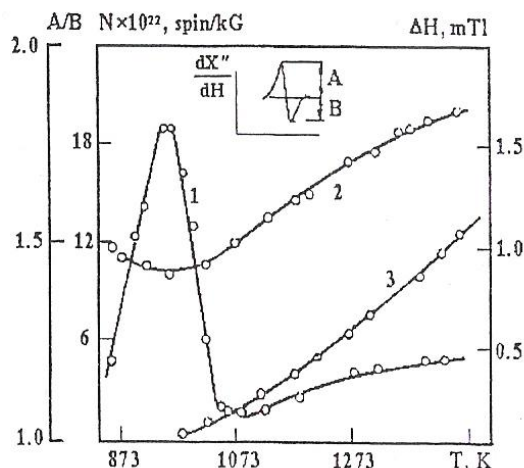ce of the spin-orbital interaction contribution into the spin-hamiltonian the time of spin-spin relaxation, responsible for ESR line broadening, decreases. On the other hand, it is probable to increase the contribution of free charges-current carriers into ESR signal, the ESR line of which is characterized by asymmetry (so called Dayson form [13]).

4. 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 polyconjugation systems is ruled by the jump conductivity mechanism with variable jump length. In this case, its temperature dependence is described by the Mott formulas.

3. Presence of a glassy fiber and polymethyl-silsesquioxane 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.

Acknowledgements

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СТРУКТУРУВАННЯ ТА ЕЛЕКТРОПРОВІДНІСТЬ ПОЛІМЕРНИХ КОМПОЗИТІВ, ПІРОЛІЗОВАНИХ ЗА ВИСОКОЇ ТЕМПЕРАТУРИ

Анотація. *На основі сумішей фенолформаль-дегідної і епоксидної смол створено нові монолітні матеріали в присутності органічних сполук кремнію і скловолокна, відпалених у вакуумі і водневому середо-вищі. Досліджено електропровідні, магнітні та деякі інші властивості синтезованих матеріалів. Експеримен-тально встановлено, що одержані продукти мають напівпровідникові властивості; рівень провідності яких регулюється підбором технологічних умов. Інтенсив-ність і рухливість носіїв заряду зростає з підвищенням температури відпалу. Температурна залежність елект-ропровідності і рухливості зарядів описані за допомогою формул Мотта. Магнітні властивості відпалених матеріалів були досліджені методом ЕСР. Встановлено, що при відпалі утворюються вільні радикали та інші парамагнітні центри. Запропоновано механізм формування провідних кластерів і переносу заряду.*

Ключові слова*: провідність, піроліз, високотем-пературні, структуруючий, електричні властивості.*