ELECTRICAL CONDUCTIVITY AND MECHANICAL PROPERTIES OF POLYMER COMPOSITES PYROLYSED AT HIGH TEMPERATURES

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Introduction

Probability of proceeding of necessary chemical reactions in polymer materials increases with temperature (breaks of separate chemical bonds, depolymerization, free radical formation, etc.) [1]. 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 adhere properties of semiconductors to high-molecular compounds.
Effectiveness of formation of the polyconjugation systems increases with temperature, if pyrolysis proceeds in vacuum or in inert atmosphere. ESR signal is one of the signs of polyconjugation appearance in polymer systems [2]. Electrons, delocalized in the conjugation system, are responsible for ESR signal, although 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).
Unique semiconducting properties, excluding very short of them, 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 electrically conducting properties.

Experimental

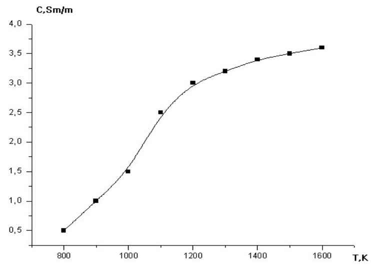
The main aim of the presented work is the obtainning of pyrolized monolythic materials with a wide range of electric conductivity.
Epoxy resin, phenol-formaldehyde resin (novolac), polymethylsilsesquioxane and fiber glass were chosen as the initial substances.
Pyrolysis of mixtures of the components 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. The conductivity of pyrolized samples or pyrolyzates was measured with using 4-contact method. Polarization microscopy technique was used for determination of their microstructure. The paramagnetic properties of pyrolizates were investigated by using of Brukker type ESR spectrometer. The sign and mobility of charge carriers was measured by the Hall effect technique.

Results and discussion

Figure 1 reflects the changes of some electrical and mechanical properties of polymer composites based on epoxy and polyformaldehide resin, polymethylsilsesquioxane and glassy fiber after pyrolysis at temperatures 800-1600K. These dependences are the result of proceeding of deep physicochemical transformations in materials.
At high temperatures silsesquioxanes turn into inorganic glass - three-dimension siloxane cubic structures which react with fiberglass side hydroxyl groups. In this reaction they form covalent bonds with those side groups. Therefore the chemical bonds between clusters of conju-

gated double bonds and glass fibers through Si-O-Si skeleton are formed. Such structures lead to formation of monolithic solids.

a)



b)

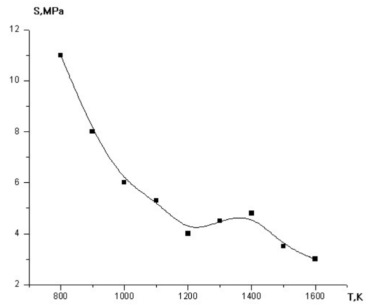


Fig.1 Dependences of the electrical conductivity (a) and proof strength (b) of composites, based on polyformaldehide and epoxy resins. polymethylsilsesquioxane and glassy fiber, on the pyrolysis temperature

Formation of polyconjugated systems is rather probable at pyrolysis of a compound containing phenol-formaldehyde or epoxy resin with inclusion of KO-812 at the glass surface. 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 clusters of polyconjugation and barrier interlayer's between them [3]. The number of charge carriers and their mobility increases with the volume of polyconjugation clusters.

The nature of conductivity of pyrolyzed polymer materials is expressed by investigation of the γ dependence on temperature. It is experimentally established that this dependence satisfactorily is described by Mott law [4]:

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

Where T_0 and γ_0 are constants.

The expression for carrier mobility has analogical character. Thermochemical reactions in composites leads to formation of local paramagnetic centers, due to thermal decomposition of carbon and siloxane chains with further localization of unpaired electrons on the structural defects. It is probable the contribution of free charges-current carriers into ESR signal, which is characterized by asymmetry.

Conclusion

High-temperature treatment of polymer composites (pyrolysis) stimulates processes of formation of covalent bonds between organic and inorganic parts, which leads to formation of monolithic solids and polyconjugation systems.

Charge transfer between these systems is ruled by the jump conductivity mechanism with variable jump length in accordance with Mott formula.

References

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