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Study of the structure and physical-chemical properties of polystyrene compositions filled with secondary kaolin

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Abstract. This article discusses the study of the structure and physicochemical properties of polystyrene compositions filled with secondary kaolin. Physicochemical processes were studied by thermo graphic analysis. The article also talks about thermo graphic studies of experimental masses, which made it possible to establish the temperature ranges of exothermic and endothermic effects, the rate of sintering processes and the nature of its course over time. In this article, a study of the thermal conductivity of soot-filled compositions based on polystyrene and polyvinylidene fluoride. Also presented are the experimental results of studies of the dependences of the thermal conductivity of compositions based on polystyrene on the concentration of soot and on temperature. The presence of reversible structural rearrangements in polymer soot-filled compositions was found.

1 Introduction

Today in the world the development of simple, non-scarce, cheap semi-metals and metal glasses used in the electronics industry is growing day by day. In this regard, the development of effective soot-filled composite polymer materials (CPM) and products based on them and other standardized metals, light guides, sensors and various devices based on them, used in the electronics industry, is of particular importance.

Currently, in the world in microelectronics and instrument making for the production of scarce and expensive semimetals, metallic glasses, sensors and various devices based on them, it is of particular importance in the manifestation of certain properties of which belongs to the interfacial layers (IFL) in the polymer-filler system, on the technological At this stage, it is necessary to conduct in-depth studies of the structure and state of the interfacial bond between the filler and the polymer binder, especially those that include ultrasonic dispersion of filler particles in binder media in the technological stages of research.

In the Republic, measures are being taken to obtain CPM for the electronics industry and certain scientific results are being achieved. The Development Strategy of the new Uzbekistan defines important goals, objectives and directions – "...development of technologies for the production of innovative products in areas being transformed into

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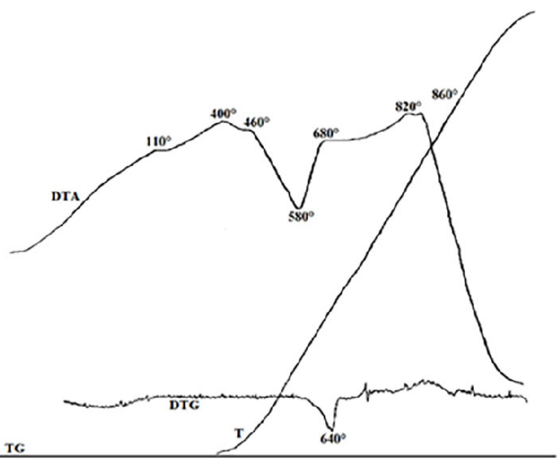
innovation zones that create high-quality products...". In this regard, the development of the composition and technology for producing effective modified CPM and products made from them with special properties and the establishment of optimal technological parameters for the manufacture of light guides, sensors and devices for various purposes from CPM for the electronics industry is relevant and in demand.

2 Materials and methods

The physicochemical processes occurring in the experimental masses during heat treatment were studied by the method of complex thermo graphic analysis. Thermographic studies were carried out on a Hungarian derivatograph of the "Paulic" brand in the temperature range from 20 to 1000°C. A sample of kaolin brought from the Angren ceramics plant was subjected to derivatographic studies. The sample weight was 10-12 mg. Figure 1 shows four curves.



T – temperature measurement; TG – weight changes; DTG – rate of weight change; DTA – changes in heat content

Fig. 1. Thermogram of kaolin from the Angren deposit.

Thermographic studies of experimental masses made it possible to establish the temperature ranges of exothermic and endothermic effects, the rate of sintering processes and the nature of its course over time. The differential curve of the sample under study has two endothermic and two exothermic peaks. The first endothermic effect corresponds to the removal of hygroscopic moisture (110°C). The second, in the temperature range of 460-680°C, is due to the dehydration of kaolin with the subsequent formation of metakaolinite. In the temperature range of 820-850°C, very insignificant peaks are formed, which can be attributed to the possible decomposition of kaolinite into aluminum and silicon oxides [1-3].

3 Results and discussion

It is known that many types of filler, including kaolin, can reduce the consumption of binding materials and reduce the cost of plastic, and this can increase the mechanical strength and some dielectric characteristics of composites. The scientific concept has also been known since the early 70s, according to which fillers, usually mechanically mixed with other components, do not enter into chemical interaction with them. In this work, using structural studies using IR (infrared) and EPR (electron paramagnetic resonance) spectroscopic methods of kaolin-filled PS (polystyrene) composites, the following will be shown:

- Firstly, contrary to prevailing ideas, the formation of a chemical bond between the components of composites in their interfacial layers;
- Secondly, the new magnetic properties exhibited by these composites will be analyzed.

The last circumstance is a very important fact, since modern magnetic engineering requires new non-traditional materials with controlled properties. The very fact that it is possible to acquire some magnetism in PS films after filling with kaolin is not surprising. The fact is that kaolin, which is an aluminum silicate, always contains impurities that have more or less magnetism, for example, iron oxide, calcium and magnesium silicates, etc. Another important thing for us was whether it is possible to purposefully control the magnetic state of the prepared materials. In our particular case, the PS chosen for the dispersion of kaolin particles in the binding medium was ultrasonic dispersion for a certain time in a solution of the polymer in benzene, followed by hot pressing of the mixed components.

It is convenient to begin the analysis of the structural and macro properties of composites obtained in this way with the interpretation of EPR spectroscopic studies. The result of an EPR study in air at room temperature for PS filled with kaolin in an amount of V_1=0,06 is presented in Figure 2. The results of experimental and calculated data on paramagnetic parameters for this and other composites are presented in Table 1.

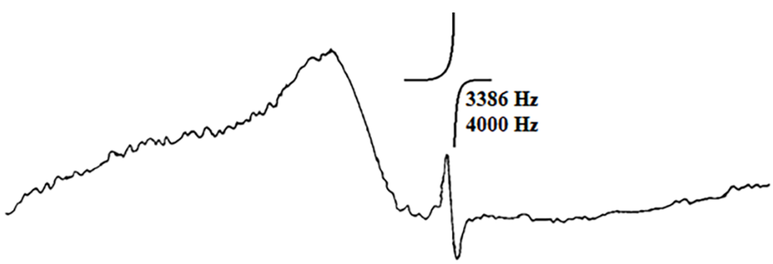


Fig. 2. EPR spectrum of PS+kaolin composite (0,06).

As can be seen from Figure 2, against the background of a general and fairly wide (ΔH_{PP}=800 Oe) signal, two independent and very different in width (ΔH_{PP}=320 Oe and ΔH_{PP}=20 Oe) singlet signals stand out. Judging by the large width, the value of the resonating magnetic field (H_{0x}=3048 Oe) and the fact that the amounts of PMC (paramagnetic center) from this particular signal have a direct correlation with the concentration of the filler, we can assume the inorganic nature of the PMC responsible for the signal with ΔH_{PP}=320. Whereas a signal with ΔH_{PP}=20 Oe with a resonating magnetic field (H_{0x}=3048 Oe) is more likely to be of an organic nature. This assumption can also be supported by the fact that the amount of PMC (Im'/m) decreases with increasing content of filler V_1 (Table 1). The signal of organic origin does not change its EPR line width with a change in the amount of filler, which gives grounds to assume that the nature of the PMC from this component is the same for all the studied composites. The decrease in HPP and (Im'/m)2 and the increase in (Im'/m) with increasing filler concentration can be interpreted in favor of the possibility of a certain connection between these individual PMC [4-6].

Sapphire (Al_2O_3) or silicon oxide (SiO_2) themselves cannot be responsible for the left-handed component of the EPR signal in our experiments. Most likely, Fe_3^+ is responsible for the manifestation of this component of the EPR signal, because it is valent iron that can produce such a broad EPR line at room temperature. If this is indeed the case, then it is very important to clarify the question of what environment this iron signals in. A comparative analysis of our results shows the following result. This signal is not a consequence of the manifestation of Fe_3^+ paramagnetic, neither in the Si environment nor in SiO_2. The first is possible at microwave frequency 8.4 GHz only at a temperature of 2ºK. According to [7-10] Fe_3^+ in SiO_2 at room temperature exhibits an EPR signal with two characteristic (D=-0,0777 and F=-0,02 cm^{-1}) spin Hamiltonians, whereas in all our experiments only one spin Hamiltonian is distinguished.

Further, the left component of the overall EPR signal of composites cannot be a consequence of paramagnetic either in the environment, only Al_2O_3, or in any combination, only Fe:Al. According to studies, EPR signals for the following combinations Fe:Al=80; 200 and 300 appears only at very low temperatures -4ºK; 90ºK and 20ºK temperatures. Fe_3^+ in natural sapphire at room temperature exhibits an EPR signal with two (D=0,188 and a=0,0281 cm^{-1}) spin Hamiltonians, neither of which corresponds to the data from our experiments (see Table 1). This signal is also not a consequence of Fe_3^+ in TiO_2 (TiO_2 can be present in kaolin in the range of 0,4-1,2%), because in this combination the EPR signal has three spin Hamiltonians (D=0,0309; a=0,0099 and F=0,0308 cm^{-1}), neither of which corresponds to our data. And finally, this signal cannot be a consequence of Fe_3^+ in CaO (CaO can be present in kaolin within the range of about 0,8%), since the EPR signal from such a combination should appear at a liquid nitrogen temperature of 77ºK or at even lower temperatures, for example, at 20ºK.

Table 1. Concentration dependence of some paramagnetic parameters of PS+ kaolin composites.

V_1	a, E	D, MHz	D, sm^{-1}	ΔH_{PP}, E	ΔH_{PP1}, E	ΔH_{PP2}, E	$(Im'/m)_1$	$(Im'/m)_2$
0.02	945	2646	0.0882	1250	550	20	1.05	1.85
0.04	450	1260	0.042	800	300	20	1.04	1.45
0.06	410	1148	0.0382	800	320	20	2.33	1.46
0.08	467	1307.6	0.0435	720	400	20	5.9	1.05

The spin Hamiltonian 0.0882 cm^{-1} from our experiment for the case of PS with kaolin V_1=0,02 practically coincides with 0.083 cm^{-1} Fe_3^+ in $Al[(CH_3CO)_2CH_3]_3$ at room temperature.

4 Conclusion

If such a coincidence is not a random event, then it can:

- Firstly, to point out the events that is so significant from the point of view of the formation of new compounds that occur due to the ultrasonic dispersion of filler particles in the PS binding medium;
- Secondly, to become a point of contention for further explanation of all structural features emerging from EPR experiments of these composites. Before drawing any further conclusions, it is advisable to turn to the IR spectroscopy data of these materials.
- In conclusion, we can say that the subject of research is to determine the change in the pattern of the structure of MPS depending on the content and ratio of the PS polymer and filler - kaolin, introduced into the composition, as well as to determine the pattern of the influence of soot and kaolin on the physico-chemical properties of the developed composite polymer materials.
- In the research work, EPR spectroscopy was used to study the structure of the polymer-filler interfacial layer. The physicochemical and physicomechanical properties of the polymer compositions were determined using well-known standard methods.

- The scientific novelty of the study is as follows:
- justified the creation of modified import-substituting and export-oriented composite polymer materials based on PS and kaolin, replacing semi-metals, metal glasses and light guides based on them, used in various devices in the electronics industry;
- technological methods used in the production of the composite have established patterns of changes in the structure of the interphase layer of filled CMs depending on their content and ratio;
- kaolin significantly affects the structure and physicochemical properties of polystyrene CM, so the developed composite does not have layers that would allow the layer to be characterized as ferromagnetic.

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