

# ELECTROCONDUCTING THERMOPLASTIC MATERIALS FOAMED IN SUPERCRITICAL CO<sub>2</sub>

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One of the topical problems of modern materials science is the creation of low-density polymeric compositions with new electrophysical and optical properties. Foamed electroconductive materials makes it possible to construct echoless chambers with improved amplitude-frequency characteristics, low mass and dimensions, reduced combustibility, and a rather high electromagnetic radiation absorbability. It was established that foamed electroconductive materials with a pyramid-shaped front surface (to increase the number of rereflections of electromagnetic waves) and with the concentration of absorbing particles increasing in the direction of wave propagation provide a better match between the impedances of the material with that of the external medium. The existent technologies of manufacturing of electroconductive foamed material are based on the following processes: (1) gas released by chemical reactions between the reactants; (2) high-rate stirring of compositions containing surfactant with to stable foams; (3) soaking preliminary foamed compositions with graphite colloid suspensions; and (4) energy input to initiate the release of gases from the foaming components.

A new approach to manufacturing foamed functional materials was developed in connection with the use of supercritical CO<sub>2</sub> (SC-CO<sub>2</sub>) for modifying polymeric and composite materials on the basis of organosilicon rubbers, fluoroplastic, plasticized polyvinylchloride (PVC), and porous polyethylene.

Among the above approaches, a combination of SC-CO<sub>2</sub> with thermal expansion of acid-treated graphites, which expand in the polymer matrix with the release of gases and formation of an electroconductive branched structure, seems to be an promising method.

Modified graphites (MG) were prepared by treating low-ash graphites with a mixture of sulfuric and nitric acids until graphite bisulfate (C<sub>24</sub><sup>+</sup>HSO<sub>4</sub><sup>-</sup> 2.5 H<sub>2</sub>SO<sub>4</sub>) was formed with subsequent washing with water. PVC plastisol compositions were prepared by introducing modified graphite into PVC-dioctylphthalate (DOP) paste at 165°C for 30 min. Differential scanning calorimetry revealed heat effects near 180°C, which were not observed in the absence of NG. This can be explained by thermal expansion of MG in the polymer matrix. As the content of MG in the polymer composition was increased from 2.4 to 19.6 wt %, the mass densities of the thermally expanded (at 250°C for 5 min) samples were 530 and 138 g/l, respectively. Thermomechanical analysis showed that, as the temperature rises, the indenter first plunged into the sample (as it softened) until the foaming of the composition started due to the thermal expansion of MG, after which the of indenter moved in the opposite direction. When PVC plastisol was filled with MG particles, the foamed composition began to conduct electric current due to the formation of an electroconductive branched structure in the polymer matrix. Samples containing 2.4, 4.6, 6.8 wt % MG exhibited no dc electroconductivity. After thermal expansion, the conductivity of these samples was 2.5×10<sup>-6</sup>, 7.7×10<sup>-4</sup>, and 1.7×10<sup>-2</sup> S/cm, respectively.

The possibility of the purposeful formation of porous polymers by varying the pressure and/or the SC-CO<sub>2</sub> temperature during exposure and the decompression rate seem to

be a promising direction. In our opinion, to synthesize a plastisol composite material under SC-CO<sub>2</sub> conditions, it is necessary first to create pores in the sample and then initiate MG thermal expansion under normal or SC-CO<sub>2</sub> conditions. When heated, thermoplastic polymers soften and their viscosity decreases, thereby enhancing CO<sub>2</sub> diffusion into the sample. The preparation of samples by heating in SC-CO<sub>2</sub> with subsequent decompression and cooling of cuvette to a temperature of ~10°C results in the formation of foamed porous samples.

A sample prepared from a mixture a fusible fluoroplastic powder and 33 wt % of modified graphite was subjected to thermal expansion at 300°C for 3 min and then rolled on rotating hot dies to a thickness of 0.32 mm. Upon treatment a SC-CO<sub>2</sub> medium at a pressure of 15 MPa and a temperature of 150°C for 1 h followed by rapid decompression and cooling with water, the sample foamed up to a thickness of 1.7 mm. For SC-CO<sub>2</sub> foamed electroconductive thermoplastic materials, the reflection coefficient at a wavelength of 1 cm was found to be two- to threefold lower.

Thus, we prepared foamed materials on the basis of organosilicon rubbers. We found that, during the thermal expansion of samples produced from low-molecular organosilicon rubber, the sizes of the particles and distances between them change so that eventually electroconductivity arises (see Fig. 1).

Another approach to producing electroconductive composites consists in the formation in SC-CO<sub>2</sub> of polypyrrole from the gas and liquid phases in porous polymers, in paper samples, and organosilicon rubbers containing FeCl<sub>3</sub>. In the first case, pyrrole-2-carboxylic acid decompose to yield pyrrole (at 20 MPa and 75°C), which, in turn, polymerizes under the action of FeCl<sub>3</sub>. To modify organosilicon rubbers, samples containing from 2 to 30 wt % FeCl<sub>3</sub> wt % pyrrole-2-carboxylic acid were placed into a reactor and added CO<sub>2</sub> to a supercritical pressure. As a result, samples with conductivities of 10<sup>-4</sup>–10<sup>-6</sup> S/cm. Upon modification in SC-CO<sub>2</sub>, optically transparent fluoroplastic films turned white. Changes in the reflection spectra of fluoroplastic films within 250–450 nm are associated with the formation of microscopic pores in the material. The materials synthesized were examined using acoustic microscopy.

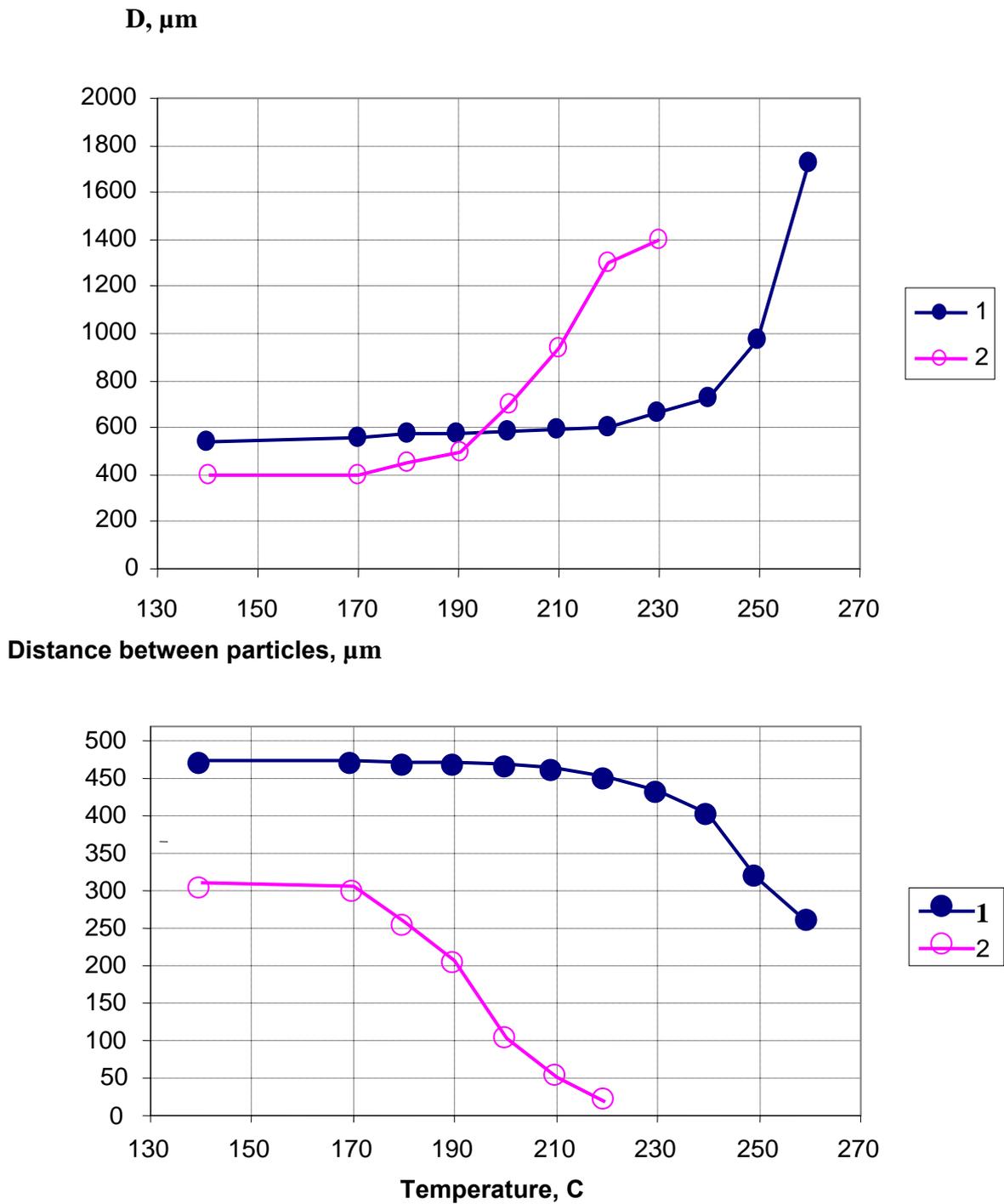


Fig. 1. Dependence of the mean diameter  $D$  of the MG particles and mean distances between the particles on the temperature of heating for SKTN-A low-molecular rubber containing 6 wt % with (1) and without (2) curing catalyst.