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COMPOSITE BASED ON POLYMETHYLMETHACRYLATE WITH FRACTAL CLUSTERS OF ZrO_2 PARTICLES

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The paper presents new composite material with a three-dimensional fractal structure of ZrO_2 nanostructured microparticles, distributed in a matrix of polymethyl methacrylate (PMMA). The conditions and the method of producing the composite samples are described. The procedure of the sample structure study and mechanical tests are presented. It was found that the resulting composite with a content of ZrO_2 particles from 0.1 to 5 wt % in PMMA matrix possesses better strength properties compared to PMMA without filler: those are a lower coefficient of friction and high wear resistance. The composite can be used to replace PMMA in glazing assembly parts of various technical appliances.

Keywords: polymethylmethacrylate, fractal structure, compression yield strength, nanostructured microparticles of ZrO_2.

Introduction

For glazing mobile equipment polymethyl methacrylate (PMMA) is sometimes used. It is an amorphous thermoplastic with a high degree of transparency (92% of light transmission), resistance to weak acids, alkaline and salt solutions, alcohols, water, oils, greases, fuels, resistance to weathering and UV radiation. PMMA is characterized by high electrical insulating properties, increased (for plastics) tensile strength (up to 80 MPa) and has an operating temperature range from -40 °C to +90 °C [1-3].

For a wider range of applications, it is necessary to improve some properties of PMMA. So, PMMA is a highly flammable material, prone to surface stress cracking. Like all plastics, it has less resistance to surface wear as compared with silicate glass and transparent ceramics and loses its insulating properties at high frequencies. Analysis of physical and mechanical properties of polymer glasses [4-7] suggests that a promising direction to improve the properties and extend the range of application of the PMMA may be the creation of composite materials on its basis.

1. Materials and methods of research

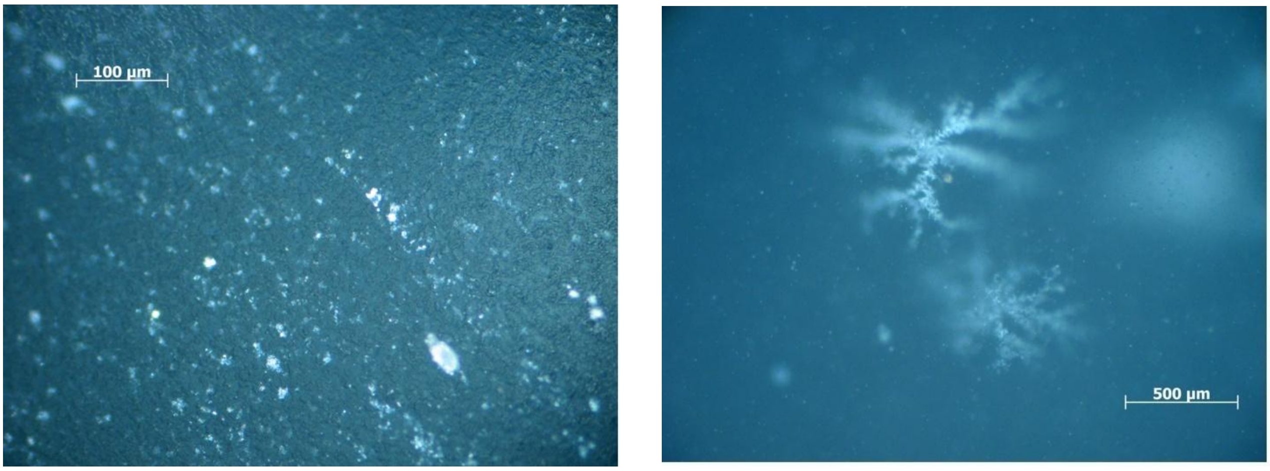
This paper presents a new synthesized composite of PMMA with reinforcing spherical nanostructured ZrO_2 microparticles, and a study of some of its properties in comparison with unfilled PMMA. Spherical particles of ZrO_2 having 0.3÷2 microns diameter, distributed in a transparent matrix of polymethyl methacrylate can increase its wear resistance, electrical- and thermal-insulating properties, resistance to fire, reduce surface damage and, to a certain extent, contribute to laser radiation scattering.

To synthesize the composite material, polymethyl methacrylate was used as the matrix; it was obtained through polymerization of a liquid monomer. The filler was a powder of zirconium dioxide (stabilized by cerium), which was synthesized in IMMS RAS using a newly developed technology for non-agglomerated oxide ceramic powders based on ultrasonic pyrolysis [8-9]. Control laboratory samples of PMMA without filler were prepared through block polymerization of methyl methacrylate. Besides, as control samples industrial sheet PMMA of SB-120 brand was used.

Investigation of samples structure was made using an inverted metallographic microscope Carl Zeiss Axiovert 40 in polarized light. The light transmission was evaluated qualitatively using the red laser. Mechanical tests of samples in the form of cylinders were conducted using a universal testing machine Instron 3382 by means of compression method at a loading rate of 0.5 mm/min. Samples of polymerized PMMA and PMMA filled with 0.1 and 5 wt % ZrO_2 powder were studied.

2. Results and discussion

Samples of PMMA are transparent homogeneous material. The composite with 0.1 wt % ZrO_2, despite the use of opaque filler, also has a sufficiently good transparency. Figure 1 (a) shows the surface of the sample. In Figure 1 (b) the focus surface is shifted into the sample to observe the three-dimensional distribution of ZrO_2 particles. ZrO_2 powder in the initial state neither sticks nor agglomerates [8-9]. Samples of the composite with 5 wt % ZrO2 were characterized by low transparency and light microscopy could not be used to study them.



a) b)

Fig. 1. Microstructure of PMMA composite with 0.1% ZrO_2 content

The observed ZrO_2 particles (Figure 1b) are in an orderly manner built in three-dimensional cluster-like fractal structures in the form of dendrites. The average size of these fractal formations is 500 microns. It proves that during the polymerization of PMMA with ZrO_2 nonlinear processes of self-organization took place that led to a complex ordered fractal structure of particles in the PMMA matrix.

Such cluster patterns were previously observed in forming Lichtenberg figures during electrical discharge [10] or "sticky tongues" (clusters) at the interface between two sufficiently immiscible with each other fluids (e.g., water and gelatin [12], paraffin with a dye and without the latter [13]). The formation of these structures refers to the demonstration of multifractal phenomena usually associated with the phenomenon of aggregation limited by diffusion [13]. In accordance with this approach, individual molecules or particles after some random walks "settle" on the aggregate, generating the above-described random fractals [12]. Wandering molecule or particle usually settles near the protuberance of the fractal, not in the depths of the valleys between the dendrite branches, since the probability of transfer to the deep notch is very small. Thus, the probability of growth of dendritic fractal patterns in different parts is different: it is high at protrusions and low in the valleys [13]. In the case of "sticky tongues", the factor controlling growth of stochastic fractal formations is miscibility. At low miscibility (water and sugar solution, water and oil, oil and glycerin), interface tongues are much wider because the surface tension between the two fluids prevents the formation of significant dendrites (large curvature protrusions) [11]. The controlling factor for Lichtenberg figures is the electric potential. The "growth" of the discharge print occurs mainly in the direction of the greatest potential gradient. Deep valleys are well screened that is why there is no growth in them or it is very weak [11, 14]. In this case, the controlling factor of the aggregation limited by diffusion, by analogy with the miscibility and the electric potential, wettability of ZrO_2 particles by liquid PMMA during the polymerization can be assumed. The technology for producing a composite using front polymerization of PMMA has a pronounced directional character. Under conditions of the interaction of the polymerizing system with the external environment, it should lead to the formation of stable regular stochastically self-similar ordered patterns [15]. To describe this phenomenon the term "self-organization" is usually used [16, 17].

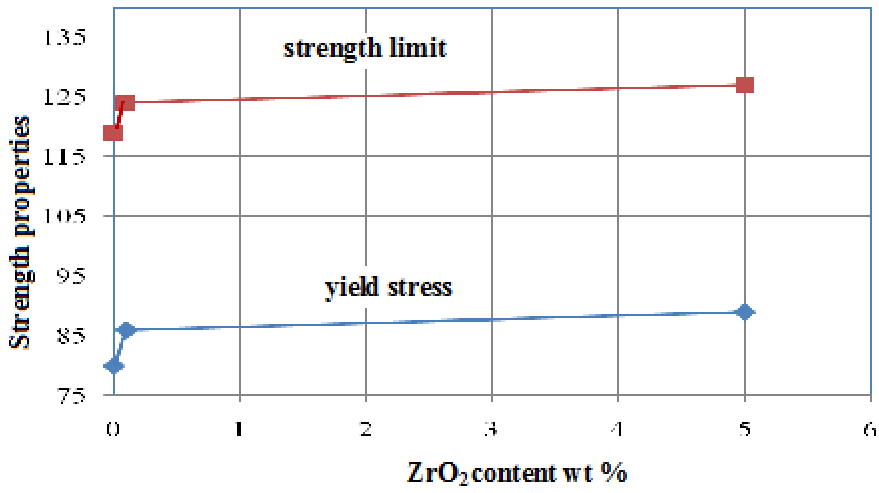


Fig. 2. Strength characteristics change depending on the amount of ZrO_2 filler

Resulting from compressive tests of samples, their mechanical properties are shown in Figure 2. A view of the typical compression curve is shown in Figure 3. The strength of the PMMA matrix averaged 119 MPa. Minor addition of ZrO_2 (0.1 wt %) led to an average increase in the strength limit of 3%, and addition of 5 wt % ZrO2 to a 5% increase. The yield stress changed similarly. Type of deformation curve, depending on the content of ZrO_2 does not change. Figure 2 shows that a marked improvement in the mechanical properties is observed at very low doses of ZrO_2 (0.5 wt %). Further increase in the filler content does not lead to a significant change in strength characteristics.

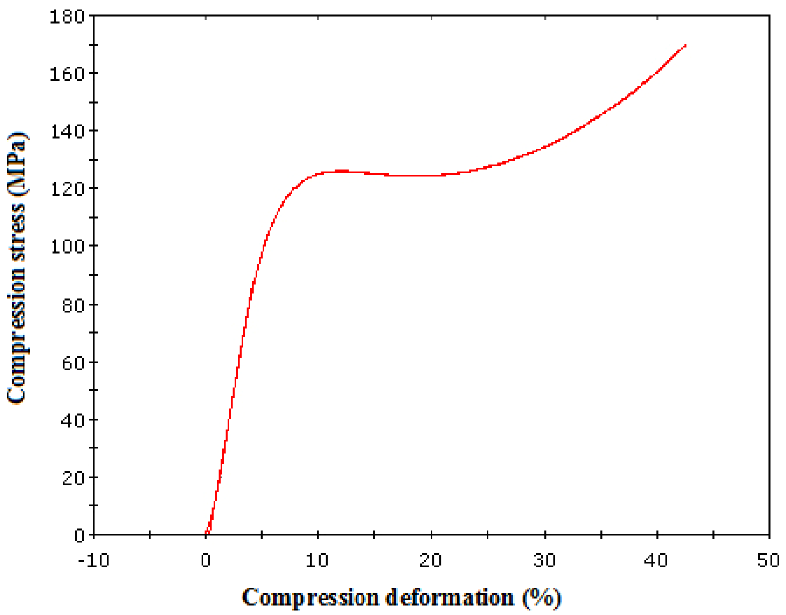


Fig. 3. Deformation curve of the PMMA sample containing 0,1% ZrO_2 at a static compression test

Conclusion

A new composite of PMMA with reinforcing spherical nanostructured microparticles of ZrO_2 was obtained. It may be used to replace PMMA in glazing items of various facilities, for example, airplanes and helicopters, to protect against abrasive effect of gravel-sand dust, thermal and aerodynamic heating or for reducing human exposure to high-intensity light (including laser).

The optimum content of ZrO_2 aerosol powder in PMMA matrix is 0.1 wt %. Such composites at almost complete preservation of the transparency to the human eye compared with the conventional PMMA possess high strength characteristics (7-11%).

It was found that during polymerization of PMMA with the addition of ZrO_2 powders processes of structural self-organization took place. They lead to the production of composite having complex structures in the form of three-dimensional dendritic fractal patterns.

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