Shape memory composite materials based on polysiloxane and ultrahigh-molecular-weight polyethylene

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Composites based on polysiloxane (PS) and ultrahigh-molecular-weight polyethylene (UHMWPE) are a new class of materials, including materials of medical designation, that possess, besides bioinertness, a combination of controlled physicomechanical and service characteristics. By changing the ratio of components, the conditions of their preparation, and the modification methods, it is possible to create materials with a gradient of properties and to control their elastic strength characteristics, hardness, and elasticity in a wide range [1]. In spite of the fact that the given materials are not only thermodynamically but in a number of cases also technologically incompatible, methods have been developed for preparing composites based on them [2]. At the same time, detailed analysis of the process of preparation of the composites made it possible to establish new possibilities in the development of materials with special properties, for example shape memory materials.

The composites investigated were based on polysiloxane SKTV-Shch with an average molecular weight of ~7 × 10^5 and UHMWPE of the Gur'ev and Tomsk works with a molecular weight of ~2 × 10^6. Material in the form of a filled composite based on SKTV-Shch with the addition of 15 parts silica and a certain quantity of anticrosslinking additive was also used in order to compare the structures obtained after mixing.

An analysis was made of the structure of composites of UHMWPE and PS with different contents of components, obtained with different mixing conditions. The density of deformation energy was used as a generalising parameter of the external energy action on the system during mixing [3].

The analysis conducted made it possible to establish the following: shape memory is manifested in the given composites on the formation of interpenetrating networks (IPNs). (In spite of certain incorrect usage of the term “interpenetrating networks”, which is generally applied to polymers “synthesised by crosslinking in each other’s presence” [4], below we will refer to the formation of interpenetrating phases of PS and UHMWPE as IPN formation.)

At small concentrations, UHMWPE in PS acts as a dispersed component; with increase in concentration, the UHMWPE particles are sintered, forming an IPN. With further increase in the UHMWPE concentration, continuity of the PS phase is lost, and it becomes dispersed in the UHMWPE. The cohesive force of the phases depends on the surface area of the particles that is wetted by PS, and accordingly on the shape of the UHMWPE particles, the rheological properties of PS, and the technology used to mix the components.

Optical studies of particles of UHMWPE and its blends with PS showed that the UHMWPE particles have a fairly developed surface. This increases considerably the area of interphase contact between the components. At the same time, cavities (air cushions) are formed on the surface of the UHMWPE particles, preventing the flow of PS in them. Ensuring more complete wetting of UHMWPE and PS by raising the temperature is impossible, as UHMWPE does not pass into the viscous flow state with increase in temperature, and the influence
of temperature on the viscosity of PS is extremely weak. For better combination of the components, significant shear stresses are needed, which can be achieved by changing the conditions of preparation of the composites (for example, partial scorching of PS) [2].

Thus, for the development of shape memory materials, it is necessary to ensure a certain ratio of components, combined with a controllable shear stress [5].

Both theoretical and experimental studies have been carried out to find the region of optimum filling of PS with UHMWPE. Mathematical modelling of the process of IPN formation was done using the Monte Carlo method. It was assumed that a specified number of UHMWPE particles of certain diameter were distributed within the PS. The average number of interactions of each UHMWPE particle with neighbouring particles was estimated. Here, the following assumptions were made: the particles have a spherical shape and are distributed regularly; a UHMWPE particle was assumed to be a material point of certain radius, and, consequently, two particles were assumed to be interacting if they were at a distance smaller than their diameter. The nature of the particle size distribution was ignored. In the mathematical model, a series of UHMWPE particle sizes (diameters 0.2, 0.3, 0.4, ..., 1.0 mm) and the content of UHMWPE in PS (10, 20, 30, ..., 100 wt%) were specified. For each specific particle size and UHMWPE content, the average number of interactions between the UHMWPE particles was calculated. After this, dependences were plotted that linked the UHMWPE content and the average number of interactions between the particles. This does not entirely correspond to the real process, as, when the components are mixed, the position of the particles can vary considerably. However, the low reliability of the proposed model will show itself at a high UHMWPE content, i.e. in the region where the IPN breaks down.

As a result of processing the data obtained, with an average number of interactions between the particles of 3, the range of UHMWPE concentrations in which the emergence of an IPN was possible was established (20–60 wt%).

The physicomechanical properties of the composites obtained are illustrated in Figure 1.

To assess the memory effect, the specimen of polymer composite was held in the clamps of a tensile testing machine, elongated by 100% (use was made of a specimen of rectangular shape with a length of the deformed section of 50 mm, a width of 30 mm, and a thickness of 2 mm), after which the compressive force in the specimen was determined. The specimen was then heated and cooled, after which the compressive force was again measured. The results of the given experiment are presented in Figure 2.

When UHMWPE is introduced into PS, before interpenetrating network formation, the compressive stresses in the composite material decrease, and, after the formation of interpenetrating networks, the internal stresses increase, as the Young’s modulus of the UHMWPE is higher than that of PS. From Figure 2a it can be seen that the emergence of an IPN begins at a UHMWPE content of ~20 wt%, which confirms the conclusion drawn from the results of mathematical modelling.

When the composite is heated, melting of the UHMWPE occurs, and compressive stress is created only by the PS (see Figure 2b). After cooling, when UHMWPE again passes into the solid state, some of the internal stresses created by the PS are absorbed by the UHMWPE, and the compressive force in the material falls (see Figure 2c). In the process of subsequent heating, remelting of UHMWPE occurs, and the mechanical stresses created by PS tend to give the specimen its original shape back, again developing considerable force.

The maximum elongation at break (blow ratio) of the composite material is determined by the amount and type of UHMWPE introduced (see Figure 1). Specimens of materials with Gurev UHMWPE (UHMWPE content 35 wt%) break at an elongation of 100%, whereas specimens of composites with Tomsk UHMWPE break at the same elongation at a UHMWPE content of 40–45%. A difference of this kind is due to the UHMWPE particle size. Thus, the diameter of the Gurev and Tomsk UHMWPE particles is 0.05 and 0.3 mm respectively.

A feature of the examined shape memory composites is that they can be manufactured from medical-designation materials and do not contain any additives. PS and UHMWPE have been cleared for application in such a specific region of medicine as endoprosthetics. Owing to shape memory, prostheses can be manufactured on their basis that simulate human organs with a greater approximation than existing polymer products.
The developed materials have another and no less important area of application. This is connected with increasing the operating safety of electrical apparatuses, distributing units, and substations. Among the most important and potentially critical elements of the given devices are the high-voltage insulators. A trend has now been noted worldwide of replacing existing ceramic insulators with polymer insulators, and here the most promising materials for the manufacture of protective coatings are polysiloxanes. However, for Russia, this is a far-off prospect, at least 20–25 years off. At the same time, it is possible to prevent emergencies due to failure of ceramic insulators by equipping them with a heat-shrink sheathing of the developed materials.

REFERENCES

1. V.P. Britov et al., Kauch. i Rezina, No. 6, 1999, p. 8.

Figure 2. Dependence of the nominal stress under 100% elongation (a) before heating, (b) after heating, and (c) after heating and subsequent cooling of specimens of Gurev (1) and Tomsk (2) composites on the UHMWPE content.