Influence of the composition of composites with binary filling on the physicomechanical properties of polymer films

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ABSTRACT
The effect of fillers – aluminosilicate glass spheres and fullerene C_{60} – on the deformation and strength characteristics of polymer films based on crosslinked sodium polyacrylate is examined. The effect of fullerene on the absorption properties of the polymeric material is shown.

Moisture-absorbing acrylate polymers are widely known and have great practical importance in different areas of industry, medicine, agriculture, and so on [1–3]. They comprise slightly crosslinked polymer networks consisting of units of acrylic derivatives and capable of absorbing a large amount of liquid – up to 2000 g/g per 1 g of dry polymer or more. It must be noted that acrylate moisture superabsorbants possess a considerable shortcoming – low strength, which limits considerably the areas of application of the absorbing materials.

Earlier we investigated films based on copolymers of acrylic acid and 2-methyl-5-vinyltetrazole with fullerene C_{60}. It was shown that the use of fullerene in the composition of tetrazolyl acrylate composites lowers the tensile strength of films insignificantly but increases their relative elongation considerably (\(\varepsilon = 1100\%\)) [4].

Solid dispersed fillers of different nature are introduced into the polymer phase in order to change the physicomechanical, thermal, electrical, and other properties of materials, although, most often, the main task is to improve their deformation and strength characteristics [5]. It is known that in most cases the mechanical strength of polymer composites increases in proportion to the content and degree of dispersion of inorganic filler.

We produced new moisture-absorbing polymer composites with binary filling and investigated their physicomechanical properties. The composites were synthesised in film form by radical polymerisation in an aqueous medium at a temperature of 50°C. A redox system consisting of ammonium persulphate (APS) and tetramethyleneethylenediamine was used as the initiator, while N,N'-methylenebisacrylamide (MBAA) was used as the crosslinking agent. The degree of neutralisation of acrylic acid (AA) was varied in the range \(\alpha = 0.0–0.9\). Polymerisation was conducted with an initial monomer concentration of 22 wt% and a crosslinking agent concentration of 0–0.5 wt% of the AA. The synthesis time of the composite in the aqueous medium was 1.5 h.

Fullerene (F) supplied by the “Ilip” CJSC was introduced into the reaction mixture without preliminary dissolution at the initial stage of synthesis during stirring. As the composite was heterogeneous, the proportion of modifier not entering the composite was determined by the gravimetric method after swelling of the composite in distilled water for 5–7 days.

Aluminosilicate glass spheres (GS) were provided by “Steklovolokno” LLC (Novgorod) and comprised glass particles of 50–200 \(\mu\)m diameter and 300 kg/m\(^3\) density.

The degree of equilibrium swelling was measured by the gravimetric method. The polymerisation procedure and the methods for investigating the reaction products are given in reference [6].

Figure 1 presents the dependence of the tensile
strength of filled polymer films on the concentration of aluminosilicate glass spheres.

With a low filler content in the polymer matrix, the particles of the filler – aluminosilicate glass spheres – are, as it were, crosslinked points of the polymer network arising as a result of the interaction of polymer macromolecules with the surface of the inorganic filler. Increase in the concentration of dispersed phase leads to strengthening of the material owing to the formation of a continuous reinforcing network as a result of the interaction of filler particles with each other [7, 8].

From the literature it is known [9] that the influence of different factors, leading to a non-monotonic change in the strength characteristics during filling, is the reason for the emergence of the so-called concentration effect of inversion of the reinforcing action of fillers: the same filler, depending on its content in the polymer composite, can either weaken or reinforce it. The described effect is observed in the present case. It is possible to speak of a strong interaction between the polymer matrix and the aluminosilicate glass spheres, which can lead both to an increase and to a reduction in the strength properties, depending on the degree of change in the molecular mobility of chains in the surface layers.

Such marked changes in the properties of the polymer composites when even small quantities of inorganic filler are introduced cannot be explained by considering only the interaction between the surface of the filler and individual macromolecules without taking into account the participation of the supermolecular structural formations changing their properties under the action of the filler.

From Figure 1 it can be seen that the maximum tensile strength of acrylate films with binary filling is possessed by films with a glass sphere (GS) concentration of 10 wt%. The concentration maximum can be regarded as the limit of saturation of the adsorption centres on the surface of the filler by macromolecules. With a filler content exceeding this optimum, continuity of the three-dimensional structure is lost. On the basis of conducted investigations, it was shown that composite materials containing 10 wt% aluminosilicate glass spheres have the greatest gelation start time.

Any failure of the polymeric material begins when microdefects or inhomogeneities are present, which results in the emergence of localised stresses far exceeding the average stress within the studied material. High localised stresses lead to an increase in the defect and, consequently, to failure of the polymeric material. As the rate of crack growth depends on the degree of inhomogeneity of the composite material, it is necessary to take into account the influence of the dispersed phase on inhomogeneity not only from the viewpoint of the emergence of macroheterogeneity, governed by the presence of filler particles, but also from the viewpoint of microheterogeneity, determined by the effect of filler on structure formation.

The use of aluminosilicate glass spheres lowers the elongation at break according to the filler concentration, which follows from an examination of Figure 2. Increase in the elongation at break with 19 wt% GS or more can be attributed to the plasticising effect of water contained in the polymer specimens, as these specimens have 10% greater moisture content values.

Table 1 presents the deformation and strength characteristics of the studied moisture-absorbing composite materials.

An examination of Table 1 shows that the introduction of fullerene into the composite lowers the tensile strength of the polymer films but increases their elongation at break. It must be noted that the curves of the dependence of the deformation and strength characteristics on the fullerene concentration are extremal in nature.
Here, the orienting effect of fullerene is most likely felt in the process of polymerisation of AA, as a result of which a more regular and less defective structure is formed.

From Table 1 it is also evident that the introduction of fullerene into the polymer composite increases the absorption capacities of acrylate hydrogels in distilled water.

Fullerene-modified hydrogel films can be recommended for use in non-linear optics, as they are characterised by optical transparency, especially in the swollen state. Of note are the good physicomechanical characteristics of the composite materials, which enable moisture-absorbing materials of prescribed geometric shape to be produced [10].

Thus, the use of fillers makes it possible to modify the initial polymer matrix, which can lead to the creation of moisture-absorbing acrylate materials with specified and specific properties.

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REFERENCES


