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Optical composites based on porous silica glasses

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Problems of synthesis of composites with different polymer structure fillers are discussed. Time and temperature conditions to get the samples transparent in all visible spectrum region have been found. The preservation of quartzoid skeleton structure of composites is confirmed experimentally by electron microscopy. Peculiarities of some optical, physical and thermomechanical properties connected with pore polymer filler nature have been discovered and their explanations may be based on the type of packing of macromolecules, synthesized inside confined pore volume. For a composite with PMMA filler the radiation strength value is 3–4 times higher than for bulk polymer. So the investigations of pyhsical and mechanical composite parameters have shown that these new lightweight glasslike materials can be employed for optical applications in the range of temperature from 20° C up to 150–170° C without any loss of their properties, in contrast to pure polymers used in optics.

1. Introduction

The composite materials are at present employed in modern branches of advanced technology and are often used instead of homogeneous substances for different practical purposes. The use of polymeric composites as the materials for design have shown that it is possible in this way not only to overcome different polymer disadvantages but to pass to the creation of new materials with unusual properties [1], [2].

Two types of transparent substances are traditionally used for optical applications – quartzlike silica glasses and bulk polymers. Their advantages and shortcomings are apparent. In particular, very good silica glass optical properties are combined with a very high specific gravity. On the other hand, the polymers are usually characterized by a lack of mechanical and chemical tolerance. Though the polymer glasses hold much promise in laser optics communications [3], their extensive practical implementation is limited among other factors by their low radiation strength.

Usually, the homogeneous composition of silica glass and polymers could not be prepared by mixing them in the course of their synthesis or by their melting. So the porous glasses allow the exceptional possibility of creating a new composite material with homogeneous interpenetrating phase structure conforming to the conditions of physical and mechanical properties optimization, according to theoretical considerations [2]. The microporous slica glasses (MPG) are of a great interest to the solution of this problem for the following reasons:

1. Their interconnected pore system is distributed over all volume at random and the low pore size offers freedom for precise agreement of two phase refraction index to eliminate composite light scattering.

2. Highly developed inner surface of silica skeleton is tightly covered by polar OH groups. So the different methods of chemical modifications of these groups [5] can be employed for variation of two phase interaction, one of the controlling factors of composite properties [2].

Recently, silica porous glasses (PG) have attracted considerable attention to polymeric composite creation [6]–[9], in particular to light-sensitive medium [10]–[12]. However, the peculiarities of optical, physical and mechanical properties of this new type of materials are now only at the beginning of their investigation. The relation between these properties and the phase structures was not investigated at all. The problem of silica skeleton structure preservation after the composite synthesis is still to be solved experimentally.

The first results of structure studies of composite MPG-polymer and the results of some optical and mechanical investigations of these transparent composites filled with different nature polymers are presented in this paper.

2. Experimental conditions

For the MPG preparation the liquefying sodium-borosilicate glasses of NK-3 type (4.0 Na_2O·3.8 K_2O·33.2 B_2O_3·59.0 SiO_2, % mol) were employed after heat treatment to trigger phase segregation (500° C, 3 h). The samples (40 × 40 × 6 mm) underwent leaching in 3N HCl solution at 100° C (15 h). Then they were rinsed in distilled water for 7 days (the flush water was changed no less than twice a day), air cooled and heated at 560° C for 1 h. MPG obtained were analysed by BET method using water adsorption-desorption isotherms and their porosity (W_s) was determined by weight method as in [13]. The results are presented in Fig. 1.

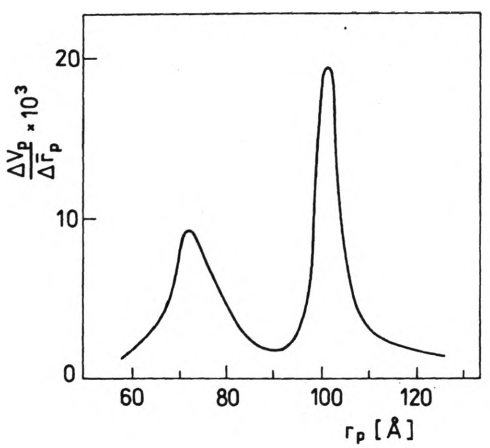

Fig. 1. Pore volume distribution $\left(\frac{\Delta V_p}{\Delta r_p}\right)$ *vs.* radii r_p of MPG (NK-3). $W_s = 0.44 \pm 0.01$ cm³/cm³ (0.34 cm³/g)

Organic monomers – methylmethacrylate (MMA) and styrene (St) – were purified by well-known methods and additionally distilled over CaH_2 in an inert

atmosphere prior to polymerization. Azoisobutyrodinitrile (AIBN) rectified by two-fold crystallization from C_2H_5OH was used as an initiator of a free-radical polymerization at 0.15 wt% concentration.

Polymerization took place in glassy ampoules with the inserted MPG samples joined to a two-outlet glass apparatus allowing us to perform all necessary manipulations either in inert gas (Ar) environment or under vacuum. Ampoules were heated in the ring microfurnace at 150–180° C for 2–3 hours to remove absorbed ambient moisture, while the whole system was evacuated down to $P_{res} = 1.3 \times 10^{-2}$. Then the system was filled with Ar, and AIBN monomer solution was poured into ampoule joined to the second outlet. After solution degasation (3 times for complete removal of dissolved oxygen) the system was filled with Ar once more, the cock was shut off and all apparatus was cut from vacuum line. In the Ar environment, AIBN monomer solution was poured into the ampoules containing MPG and the ampoule was sealed. The following regime for fabrication of transparent fault-free composite samples was elaborated:

25° C – 48 h and 24 h for MMA and St, respectively,

30–60° C – raising temperature at 5° C/h rate and curing the ampoule for 4–5 hours after each rise.

The sample annealing was done at 120° C to minimize unbounded monomer content and remove inner stress, induced by liquid monomer hardening.

For the polymer content analysis of composites we used organic compounds capability to decompose into volatile compounds when heated up to 600–650° C. Quartzoid skeleton neither changes the weight in the course of heating nor melts down at this condition [14]. Complete removal of polymer phase was performed in the course of composite MPG-polymer samples heating up to 650° C in the ring furnace and holding them at this temperature for 3–4 hours. Polymer phase amount was detected by weight method with error margin not exceeding 0.1% (Tab. 1). Reproducibility of experimental results was not worse than 0.5% for fragments of one and the same sample and 1% for different samples.

Table 1. Polymer phase content in composite filled with PMMA

MPG		Polymer phase, content (β), % wt		Extent of pore filling with PMMA, %
Type	Porosity	Calculation	Experiment	
NK-3	0.34	28.80	27.50	⩾98.70

UV absorption spectra were measured with Carry-14 spectrophotometer.

The structure investigation both of MPG samples and of the composites synthesized on their basis was carried out with the use of electron microscope (EM-125K, Russia). The method of platinum-carbon replica was used. The surfaces for these investigations were shaped by the manner of the sample breaking in air just before the depositing of replica materials in vacuum. In this case the surface etching was not made. These investigations were also carried out at the magnification

(140–160 thousand times) for the replica method to reveal all possible microstructure details. An LTIPCh-7 laser ($\lambda = 1.06$ μm) was used to measure the radiation strength.The diameter of the light spot having a close-to-Gaussian energy distribution was about 20 μm. The relative error in determining the breakdown threshold did not exceed 5%.

The microhardness was determined on the PMT-3 instrument using the Vickers system, with a sample subjected to a load of 0.1 kG for a period of 45–50 s.

The values of Young's modulus E and bending strength σ were found from stress-strain curves resulting from bending experiments on a universal testing machine "Instron". The traverse speed was 0.5 mm/min. The samples were cut out as bars of the sizes of $24 \times 24 \times 2$ mm having all sides polished. The distance between supports was 20 mm. The temperature increase was stepwise, the duration of each step being 10 minutes.

3. Results and discussion

The main problem in the synthesis of transparent composite samples was to get rid of the absorbed water on the surface of the quartzoid skeleton and to avoid the gel-effect abrupt manifestation in the course of the monomer polymerization. The thing is that the polymerization rate increases in the presence of the silica according to some data [15]. For this reason the autoacceleration appearance and the monomer coming to the boil at the beginning of polymerization process is to be expected. As MMA-monomer in bulk polymerization always demonstrates more pronounced gel-effect than St monomer [16], the different elaborated regimes for two monomers show its obvious manifestation in the case of polymerization in pore volume of MPG. When we tried to decrease the polymerization time at 25° C up to 10–15 hours and up to 20–30 hours (for MMA and St, respectively), we noticed the appearance of composite sample non-transparency even at this temperature. This effect was also pronounced when the porous sample pre-treatment temperature was below 100–120° C. Most likely the composite sample non-transparency manifestation is determined by the presence of physically absorbed water on skeleton surface as its main quantity may be disposed off from surface only at temperature higher than 120° C [5]. The non-transparent composite samples have the lower polymer content than transparent ones as it follows from weigth measurements.

All the composite samples, synthesized in experimental conditions have high transmission over the entire visible region of the spectrum according to Fig. 2. The higher transmission of MPG-based composites (curves 2 and 3) compared to that of the basic MPG (curve 4) indicates that polymer filling the pore volume eliminates light scattering. The lower transmittance of composite MPG-PSt (curve 3) relative to this value of composite MPG-PMMA (curve 2) can be explained by the proper absorption of PSt in UV-region and, probably, by too large a difference between refractive indices of PSt and silica skeleton [13], [16]. So it is clear that PMMA glass (curve 1) is more transparent in the far UV than composite MPG-PMMA becuase of the silicate phase presence in it.

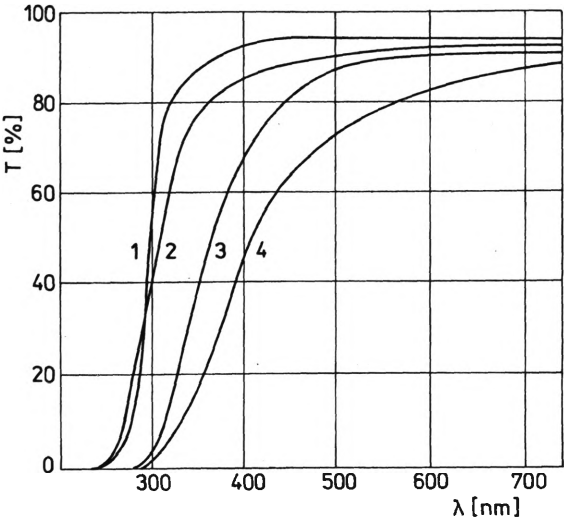

Fig. 2. Transmission spectra of bulk PMMA (1), MPG filled with PMMA (2) or PSt (3) and pure MPG (4). Sample thickness 2 mm

An analysis of the structures of composite MPG-PMMA sample and of MPG sample by electron microscopy shows "secondary" silica particles of about the same size as in the basic MPG and none of the details that might suggest the destruction of the silica skeleton. So the experimental conditions we used for the synthesis of composite samples permit us to avoid the negative effect of the polymerizing monomer shrinkage.

The microstructure of the composite is clearly seen in the electron micrographs taken at high magnification (×160000). One can definitely conclude from their analysis that there are no discontinuities in the form of microvoids at the interface between the silica and polymer phases. This agrees with the supposition we made from analysing the relief on the fractured surface that PMMA firmly adheres to the silica walls of the pores. This adhesion may be associated with the interaction of polar carbonyl groups in PMMA with hydroxyl groups on the surface of the silica skeleton and on "secondary" silica globules present in rather high concentration; according to JANOWSKI and HEYER [17], it is from 4 to 7 groups per nm^2.

The weight fraction of PMMA in composite samples (β, Tab. 1) has been calculated assuming that PMMA has a density of 1.19 g/cm^3 [18] and its proximity to experimental values testifies about practically a whole filling of the pore volume by the polymer. A small difference in these values is most probably related to a rather great number of ultramicropores present inside the silica skeleton ($\tilde{r}_p$ = 5–10 Å), in which macromolecules cannot be formed for steric reasons.

As for the values of volume radiation strength q_v, this parameter is much smaller for porous matrix as compared with monolith silica glass K8 usually employed in optical element technology (Tab. 2). The bulk polymers also have very low laser beam resistance, especially SR-39 now to be widely used in ophtalmology. But the

radiation strength of MPG-PMMA composite exceeds the q_v values of bulk PMMA and of MPG by a factor of at least 3–4 and approaches the value of K8 glass. We have checked experimentally that this effect cannot be explained by the influence of the polymer molecular mass [19], measuring the characteristic viscosity of bulk PMMA and polymer removed from the composite. In our opinion, one reason for this effect may be associated with the high degree of purity of PMMA that fills the quartzoid skeleton pores, since the mechanical impurities do cause a high lowering of the q_v value for polymeric materials [3]. The porous glasses used to synthesize the composite "filtrate" the monomer through the holes having a diameter of the order of 15–20 nm, whereas the finest filters based on nuclear membranes, used to obtain PMMA for optical purposes [20], have pore dimensions of the order of 150 nm. On the other hand, the radiation strength of the composite is supposed to be determined primarily by the strength of the quartzoid skeleton itself, which has a larger value of q_v than the polymers [20]. However, a replacement of the organic filler for the same silica porous base and for the same degree of the pore filling causes a significant change in the level of q_v (see Tab. 2). Both polymers – PMMA and PSt – are transparent in near IR spectral region for the experimental conditions employed. These facts indicate an increase in the radiation strength of PMMA as a filler of porous quartzoid compared to PSt. It may be connected with a few factors determined, for example, by the interaction of composite two phase and/or by the special inner structure of polymer synthesized into pore volume.

Table 2. Values of the volume radiation strength q_v of homogeneous and composite optical materials

Material		Silica glasses K8 monolith	MPG (NK-3)	Bulk polymers PMMA	PSt	*SR-39	Composites MPG-PMMA	MPG-PSt
q_v	W/cm² $\times 10^{-11}$	2	0.7–0.8	0.4	0.5	0.2	1.5–1.6	0.5–06
	**Relative	1.0	0.35	0.2	0.25	0.1	0.75–0.80	0.25–0.30

* SR-39 – polycarbonate.

** The q_v values for K8 glass is taken to be 1.0.

So it was assumed earlier that improved thermostability of polymer phase in microporous glass-PMMA composite was achieved by the strong adhesion between macromolecules and silica surface. The destruction of PMMA in composite begins at much higher temperature than that of bulk polymer [6]. The results of our investigations of the composite thermomechanical properties, presented in Fig. 3, show not only the increase in thermostability of composites with different polymer fillers, but also the essential growth of the glass transition temperature T_g for polymer fillers (curves 4, 5), as compared with known data [21] for bulk polymers (curves 1, 2). Though the value of Young's modulus E of MPG is found to be constant in a wide temperature range (curve 3), the temperature dependencies of E values for both composites possess some specific features. The E values of composites (curves 4, 5) are much higher than those of MPG (curve 3) in spite of

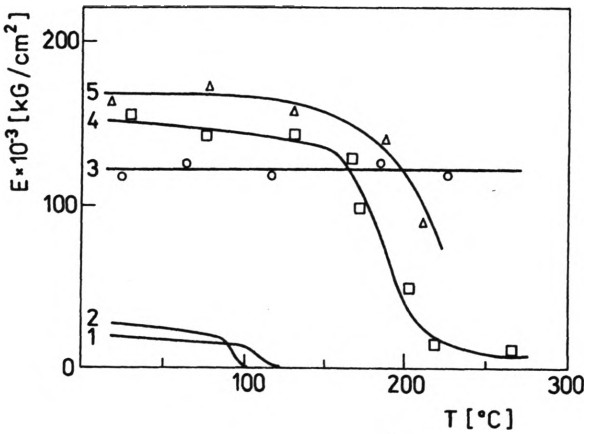

Fig. 3. Temperature dependencies of Young's modulus E for samples: 1 – bulk PMMA, 2 – bulk PSt, 3 – MPG (NK-3), 4 – MPG-PMMA, 5 – MPG-PSt

polymers themselves being much less rigid than silica glass. No additivity of E corresponding to MPG and polymers is observed in the case of the composites. The aggregation state of composites as a whole remains steadily in a wide temperature range up to 150–170° C.

At these temperatures the samples of both composites collapse. The immediate origin of the latter may be a sharp growth of temperature expansion coefficient of polymer fillers.

Table 3. Physical and mechanical properties of composites based on microporous glass (MPG) as compared with these of optical homogeneous materials

Properties	Homogeneous materials				Composite materials	
	Silica glass (K8)	Porous glass (NK-3)	Bulk PMMAS	Bulk PSt	MPG-PMMA	MPG-St
Bending strength σ kG/cm²	–	280	1420	–	900	820
Microhardness H, kG/mm²	940	120–130	20	–	260	230
Density g/cm³	2.3	–	1.19	1.05	1.65	1.60

In our opinion, the improved thermomechanical properties of composite cannot be explained only by one factor – interaction of the two phases, as it was done in [6] for the polymer phase thermostability. The E values of the composite filled with PSt (curve 3) are higher than these of PMMA-based composite (curve 4), though the PSt is less polar polymer than PMMA and its adhesion

must be lower on the quartzoid skeleton surface. Taking into account all our experimental data (see Tab. 2 and Fig. 3), it is possible to conclude that the specific composite properties based on MPG are caused by many factors. We assume that one of them may be the unusual "architecture" of the macromolecule packing in confined pore volume.

Mechanical and physical properties of composite MPG-polymer are in competition with those of traditional optics applied materials (Tab. 3). The values of the bending strength are very high though the silica skeleton is very fragile. The MPG-polymer composites exceed homogeneous PMMA and PSt by a factor of more than 10 in terms of microhardness values. This makes it possible to polish mechanically the composite samples using the technology employed for optical glasses. Thus, after grinding and polishing of the MPG-PMMA composite glass, the optical quality parameters of the surface have the following values: fourth-class surface finish, $N = 1$ and $\Delta N = 0.2$. Low values of density show that these new composite materials can be employed for different optical lightweight element preparation.

4. Conclusions

We hope that the hybrid of quartzoid glasses and organic polymers can stimulate the development of modern optics. The main advantages of these lightweight materials are the high stability to the laser beam action, good thermomechanical properties and low enough thermal expansion coefficient [10]. Further studies of new type quartzoid glass-polymer composites with different structures are of a great importance.

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