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Effect of the Content of Unmodified Nanosilica with Varied Specific Surface Area on Physicomechanical Properties and Swelling of Epoxy Composites

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Abstract—Strength characteristics of polyepoxy formulations with different contents and dispersities of Aerosil nanosilica were studied. The effect of silica on the swelling of epoxy-polymeric composite in water was examined.

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Nanodispersed silica (NS) of the Aerosil type is a highly dispersed powder with spherical nanosize primary particles susceptible to self-aggregation. As is known, NS is capable of self-organization of its structures in polymeric matrices and affects the structure of polymeric chains, which makes it possible to improve the strength, thixotropic, and other properties of polymers. Therefore, NS is used as a filler and thickener of industrial epoxy resins in manufacture of joint fillers, glues, filled floors, and glass-reinforced plastics [1–3]. Its most readily accessible unmodified forms are frequently used in these processes. Both in practical use and in scientific studies, the problem of the influence exerted by the physical characteristics of Aerosils (specific surface area, physically adsorbed water, aggregation capacity, etc.) is frequently disregarded. In particular, not only the concentration, but also the dispersity of silica should affect the basic characteristics of the composite. Information about the nature of this influence arouses permanent interest [4–13].

In this study, we examined the possibility of controlling the physicomechanical properties and water absorption of epoxy composites by varying the concentration and specific surface area of unmodified Aerosil.

EXPERIMENTAL

Experiments were performed with an epoxy polymer based on ED-20 resin (manufactured by Ufakhimprom) with varied content of silicas A-50, A-100, A-175, A-300, and A-455 (manufactured by the Institute of Surface Chemistry, National Academy of Sciences of Ukraine; the number is the specific surface area in square meters per gram), cured by introduction of 12.5 wt % polyethylenepolyamine (PEPA) at room temperature with aftercure at 110°C for 3 h. The composites were tested in accordance with GOST (State Standard) for compression (GOST 4651–68, stubs 12 mm in diameter and 15 mm high), bending (GOST 4848–71, 2 × 25 × 80 mm plates), and shearing (GOST 17 302–71, 30-mm overlap of 10-mm-wide glass-reinforced plastic plates, layer thickness not exceeding 1 mm). The measurement error was 1–2% for compression tests and 5–10% for shearing and bending tests. Separately, the swelling of composite samples (10 × 5 × 2 mm plates) in water in the course of 100 days was studied. The swelling was evaluated by the gain in mass. Samples 1 cm in diameter and 2–3 mm thick were placed in test tubes with water. After each withdrawal, the samples were thoroughly dried with a lignin blanket and were allowed to stay for 40–50 min before weighing under normal conditions (18–22°C). Atomic-force microscopy (AFM) and scanning electron microscopy (SEM) were used to obtain images of the samples by the standard procedure. IR reflection spectra of pure powders of epoxy polymers were measured with a Nicolett instrument (USA–EU) without addition of potassium bromide.

It can be seen from the results obtained (Fig. 1) that, in some cases, minor additions of NS noticeably

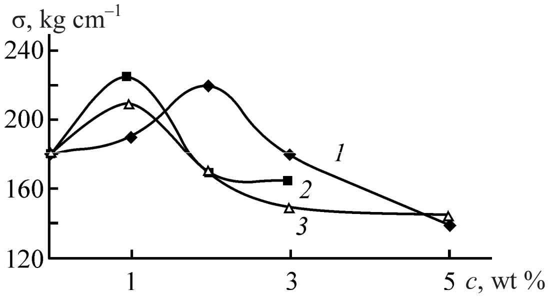

Fig. 1. Shearing strength σ of composites filled with Aerosils with different specific surface areas. (*c*) Aerosil content. (*1*) A-100, (*2*) A-175, and (*3*) A-455.

affect the physicomechanical properties of the epoxy polymer. The strongest reinforcing effect is observed for the shearing strength σ (with the composite in the form of a thin layer between plates). In the range 1–2 wt % filler, this parameter may grow by 15–25%. Further increase in the Aerosil concentration results in that σ falls. It can be concluded that its concentration strongly affects the shearing strength of the epoxy polymer in the form of a thin layer.

At the same time, the compression and bending strengths change only slightly for bulk (~1 cm^3) samples in their filling with silica. It can be seen from the table that, at best (for A-50 and A-100 NS), the increase in the compression strength does not exceed 5–10%. This weak effect is only observed within a narrow range near 1 wt %, in agreement with published data [6, 7]. Analysis of the results obtained and published data [4–12] suggests that the effect of composite strengthening upon NS introduction becomes weaker as the sample thickness grows. Possibly, this occurs because of the multiplication of bulk macroscopic defects, e.g., microcracks, heterogeneities, and air bubbles.

Compression and bending strength of composites filled with Aerosils with different specific surface areas

c, wt %	Compression strength, kg cm^{-2}				Bending strength, 10^4 kg cm^{-2}	
	A-50	A-100	A-300	A-455	A-100	A-300
0	1300	1300	1300	1300	3.3	3.3
0.1	–	–	–	–	3.4	3.3
0.5	–	–	–	–	2.9	3.0
0.7	–	–	–	–	2.8	–
1.0	1430	1340	1340	1310	2.6	3.0
1.5	–	–	–	–	2.9	–
2.0	–	1330	1300	1260	–	–
3.0	–	1360	1300	1300	–	–
5.0	–	1360	1300	1220	3.1	–

The most stable enhancing influence is exerted on the strength characteristics under study by NS with small specific surface area (with large particles): A-50, A-100, and A-175 Aerosils (see table, Fig. 1). Aerosils with large specific surface affect the strength parameters of the composite only slightly. This can be attributed to the observed effect of increasing self-aggregation and agglomeration capacity of NS at its larger specific surface area. It is also probable that, in this case, its negative effect not only on the homogeneity of the composite, but also on the structure (defect formation, loosening) of the polymer network is enhanced. It is noteworthy that the effect of an Aerosil is weakened (but not eliminated) upon modification of its surface with silanes and other organic substances (which may lead to loss of clear meaning by the notion of the specific surface area of an Aerosil).

Swelling curves are shown in Fig. 2. The negative value of the degree of smelling, *q* (%), near the beginning of the process reflects the rapid washing out that occurs immediately after a sample is submerged in water. The effect of silica on the composite swelling can be assessed as rather unambiguous. Introduction of Aerosils leads, on the whole, to a decrease in the rate and degree of swelling in water in all stages of the process. For all the composites studied (>20 samples), the swelling is 1.5–2.0%. It follows from Fig. 2 that structural changes occur even at small fillings (1 wt %). As the degree of filling grows, penetration of water molecules into the polymer network becomes increasingly difficult, which is possibly due to densification of the polymeric network upon introduction of nanoparticles. This is confirmed by SEM studies: According to Fig. 3, even upon introduction of 1 wt % Aerosil, the number of pores on the polymer surface decreases dramatically (cf. Fig. 3a).

The effect of the specific surface area on the swelling process can be estimated as comparatively insignificant. At the same time, Aerosils can be conditionally divided into two groups as regards their influence on swelling: low- and high-dispersed. As seen from Fig. 2, for the low-dispersed A-50 and A-100 (and, to a certain extent, for A-175), low concentrations (~1 wt%) of a filler do not exert any significant influence. In these cases, the swelling curves for 0 and 1 wt %

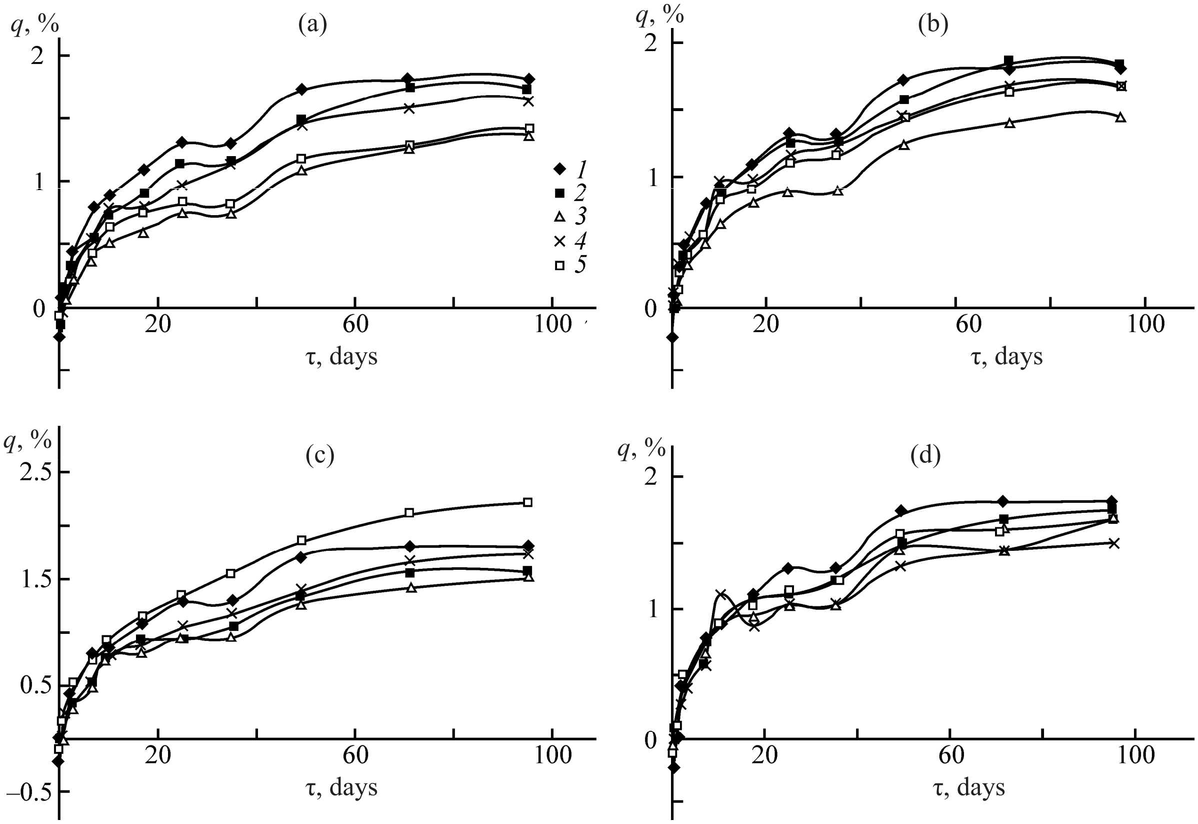

Fig. 2. Degree of swelling in water, q, of epoxy polymers with Aerosils with different specific surface areas vs. time τ. (a) A-100, (b) A-175, (c) A-300, and (d) A-455. Degree of filling, %: (*1*) 0, (*2*) 1, (*3*) 5, (*4*) 10, and (*5*) 20.

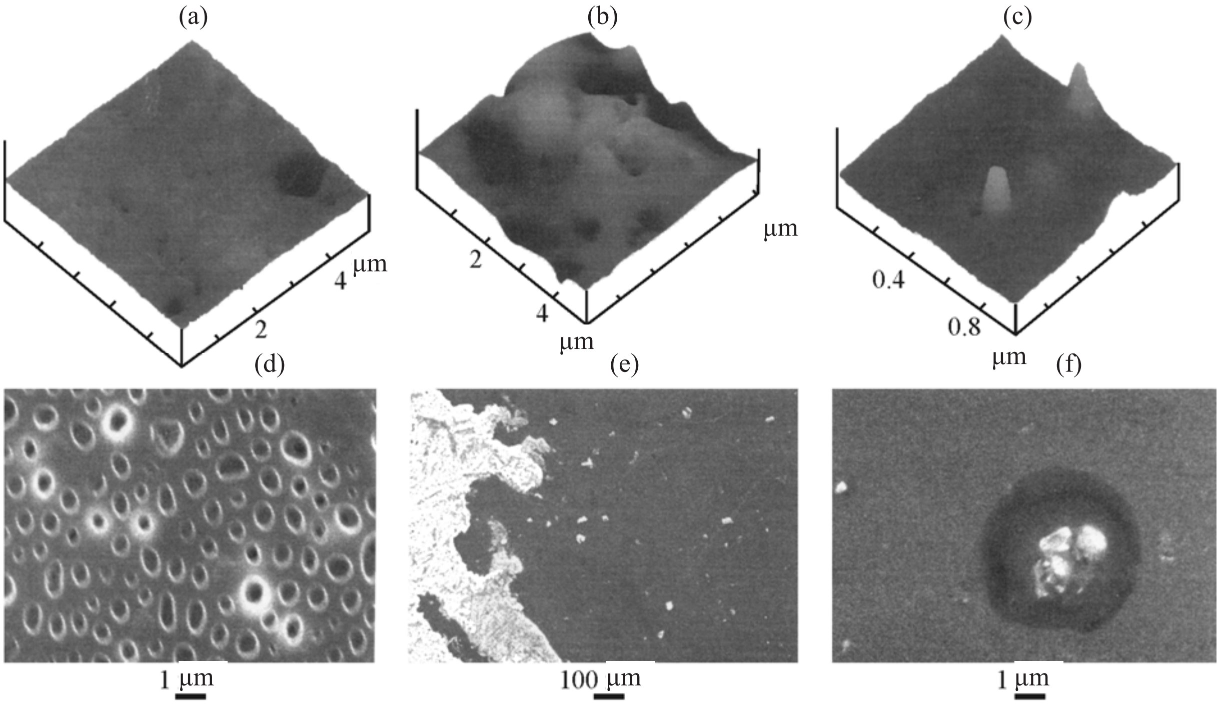

Fig. 3. AFM images of the surface of a film of an epoxy polymer (a) unfilled and (b, c) filled with 3.5 wt % A-300 Aerosil, and also SEM images of a film of an epoxy polymer (d) unfilled and (e, f) filled with 1 wt % A-100 Aerosil.

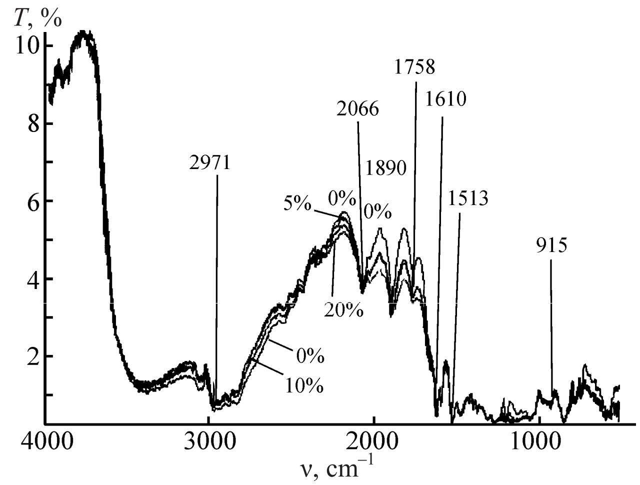

Fig. 4. IR spectra of epoxy polymers filled with 0, 5, 10, and 20 wt % A-100 Aerosil. (*T*) Transmission and (ν) wavenumber.

are very close. For the group of highly dispersed A-300 and A-455, 1 wt % of a filler has a more pronounced effect (Fig. 2).

For the low-dispersed group of Aerosils, the differences in the degree of swelling, dependent on the filler concentration, may be as large as 0.4–0.6%, i.e., approximately up to a quarter of the average degree of swelling. For the Aerosils of the highly dispersed group, these differences are substantially smaller, within the range 0.2–0.4%.

Thus, as the specific surface area of Aerosils decreases, the effect of their concentration on the swelling becomes more pronounced, with the differences in the degree of swelling being considerably less dependent on the NS concentration for highly dispersed Aerosils.

As an additional specific feature of the influence exerted by highly dispersed Aerosils can be regarded the faster saturation period, within 50–60 days. For low-dispersed aerosils, this time is substantially longer. Hence follows that the NSs of the highly dispersed group affect the composite structure to a somewhat lesser extent, whereas low-dispersed Aerosils change it so that the penetration of solvent molecules occurs during a longer time.

It was a priori assumed that there should be a more or less simple relationship between the NS concentration and degree of swelling. It was found that, most frequently, this dependence is not linear or, at least, monotonic. For example, a rather clearly pronounced correlation between the decreasing degree of swelling and increasing NS concentration is observed only for A-455 Aerosil with the largest specific surface area (i.e., smallest particles). In the other cases, the swelling nonlinearly depends on the Aerosil content and decreases near 5 wt % (Fig. 2). This means that, irrespective of the specific surface area of an NS, at its certain concentrations it can form a specific structure characterized by an increased density of the polymer network.

According to IR data (Fig. 4), introduction of unmodified NS does not change the chemical nature of the epoxy composite. All the absorption bands characteristic of epoxy polymers and (in most cases) their intensities remain unchanged even at high degrees of filling (Fig. 4). The band at 915 cm^{-1}, characteristic of oxirane groups of the epoxy resin, is almost not observed, which points to a high conversion of the composite in all cases. No changes are revealed in the intensity of the band at 1605–1610 cm^{-1}, which is standard for epoxy polymers and is characteristic of stretching vibrations ν(CH–CH) of benzene rings. True, a certain decrease is observed in the intensity of overlapping bands in the region 3100–3500 cm^{-1}, characteristic of OH groups of the polymer and adsorbed water. This may indicate that their number slightly decreases upon filling. It is noteworthy that, even at an Aerosil content of 20 wt %, its characteristic absorption band at 3750 cm^{-1}, associated with vibrations of isolated surface OH groups, is not observed. This may point to a strong physicochemical interaction (hydrogen bonds) of these groups with fragments of the polymer chain, which results in that this band disappears, or, more precisely, is shifted to lower wavelengths, to the region 3100–3500 cm^{-1} difficult for band assignment.

The data obtained suggest that regions of denser macromolecule packing, e.g., in the adsorption and orientation layer that is near-surface with respect to Aerosil particles, and a framework constituted by filler particles are formed in the filled composite [8–14]. At the same time, various defects impairing the strength characteristics are also formed. An important role in the weakening of the reinforcement effect as a result of filling may also be played by nonoptimal aggregation (e.g., clustering, rather than framework formation) and combination of particle aggregates in the polymer. The latter is frequently observed visually and is confirmed by microscopic data (Fig. 3), which can serve to make some conclusions about the structure of the epoxy composites. For example, the AFM image (Fig. 3c) clearly shows "islets" of aggregated silica. It can be seen in smaller-scale images (Figs. 3a and 3b) that pores become coarser and sparser as a result of filling. The same effect is observed in the SEM image: Figures 3d and 3f show that pores become coarser and less in number, and islets of silica aggregates may appear in the pores. On the whole, Aerosil can form, even at small degrees of filling (1 wt %), large bodies of the intrinsic phase neighboring the polymer phase, which, in turn, includes small Aerosil aggregates (Fig. 3e).

CONCLUSIONS

(1) Addition of unmodified silica affects the strength of polymers in different ways, depending on the silica concentration and a parameter under study. A weak tendency toward an increase in the strength parameters is observed at 1–2 wt % content of Aerosil, as well as a tendency toward weakening of the effect of Aerosil on the strength parameters with its increasing specific surface area (as a result of a higher self-aggregation capacity). At the same time, introduction of nanodispersed silicas of the Aerosil type can improve the shearing strength (substantially, by 15–25%) and compression strength (insignificantly, by up to 5–10%).

(2) Changing the Aerosil concentration noticeably affects the swelling of filled epoxy polymers. In the range up to 20 wt %, filling with unmodified Aerosil makes the degree of swelling lower, with the decrease at concentrations of ~5 wt % being the most pronounced. Irrespective of their specific surface area, silicas affect the swelling in similar ways, but low-dispersed silicas (conventionally up to 200 $m^2 g^{-1}$) exert a stronger influence on the swelling (and, consequently, on the structure) of the epoxy polymer than do highly dispersed silicas.

(3) The IR spectra demonstrate that no chemical changes occur in the epoxy polymer upon introduction of unmodified Aerosils. Together with the AFM and SEM images obtained, this fact suggests that filling with unmodified nanosilica substantially changes only the physical conditions of structuring in the composite.

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REFERENCES

1. Trofimov, N.N., Patrusov, V.P., and Shatskaya, K.A., *Plast. Massy*, 2005, no. 5, pp. 13–16.
2. *Handbook of Fillers and Reinforcements for Plastics*, Katz, H.S. and Milewski, J.V., Eds., New York: Van Nostrand Reinhold, 1978.
3. TEKNOS Epoxy Systems for Tank Coatings, *TEK*, 2007, no. 3 (99), p. 84.
4. Park, J.H. and Jana, S.C., *Polymer*, 2003, vol. 44, no. 7, pp. 2091–2100.
5. Mathias, L.J. and McGowen, J.A., *Polym. Composites*, 1997, vol. 18, no. 3, pp. 332–347.
6. Kim, W.G. and Ryu, J.H., *J. Appl. Polym. Sci.*, 1997, vol. 65, no. 10, pp. 1975–1982.
7. Zheng, Y., Zheng, Yi., and Rong, R., *Mater. Lett.*, 2003, no. 57, pp. 2940–2944.
8. Sumenkova, O.D., Osipchuk, V.S., Lebedeva, E.D., and Kononova, O.A., *Plast. Massy*, 2001, no. 3, pp. 35–37.
9. Malakhova, I.V., Bol'bukh, Yu.M., Tertykh, V.A., and Shiichuk, A.V., in *Trudy 11-i konferentsii po vysokomolekulyarnym soedineniyam* (Proc. 11th Conf. on Macromolecular Compounds), Dnepropetrovsk (Ukraine): Ukr. Derzh. Khimiko-Tekhnol. Univ., 2007, p. 148.
10. Skladanyuk, R.V. and Zakordonskii, V.P., *Vysokomol. Soedin., Ser. A*, 2005, vol. 47, no. 1, pp. 34–43.
11. Dupanov, V.O. and Ponomarenko, O.M., Abstracts of Papers, *Vseukrainskaya konferentsiya "Nanomaterialy v khimii, biologii, meditsine"* (All-Ukraine Conf. "Nanomaterials in Chemistry, Biology, and Medicine"), Kiev, 2006, pp. 11–12.
12. Gorshunov, A.V., Thermal Properties of Modified Epoxy Polymers, *Cand. Sci. Dissertation*, Kiev, 2007.
13. Sultanaev, R.M., *Plast. Massy*, 1992, no. 2, pp. 21–24.
14. *Khimiya poverkhnosti kremnezema* (Chemistry of Silica Surface), Chuiko, A.A., Ed., Kiev, 2001.