Epoxy polymer adhesive properties in the presence of fine powder silicas with modified surfaces

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The introduction of fine powder silicas with modified surfaces into epoxy polymers was investigated. An increase in adhesive and cohesive properties was obtained. The greatest efficiency (up to 110% relative growth of adhesive strength) can be achieved by the introduction of butosil, a filler with a hydrophobic surface, and by the introduction of titanoaerosils obtained by the combined high-temperature hydrolysis of titanium and silicon chloride vapours. The mechanisms of these observed effects are discussed. The most probable causes are the decreasing inner concentration and increasing cohesive interaction as a result of macromolecular chain packing stimulated by the filler surface.

1. Introduction
The problems of polymer adhesion (coatings, glues, etc.) to a solid surface are receiving constant attention [1–5]. The main means of enhancing adhesive interaction is by chemical modification of the surface or polymer, thus providing strong intermolecular or chemical interaction at the phase boundary. At present, structural methods of polymer reinforcement are also being developed, among which are methods of introduction of different organic and inorganic modifiers [5].

In the present work, the effect of the introduction of fine powder silica fillers (aerosils) on the adhesive properties of the epoxy polymer were investigated. The fillers are distinguished by different specific surface areas, the state of the microparticle surface (silica modified by organic and inorganic substances) and by the method of surface modification (combined high-temperature hydrolysis or molecular deposition). The choice of the composite is due, on the one hand, to the wide field of application of epoxy adhesives and, on the other hand, to the unique possibility of varying the parameters of a filler based on synthetic silica [6].

2. Experimental procedure
The composites were prepared from the epoxy oligomer based on bisphenol A with $M = 400$, which was cured with 10 parts by weight polyethylenepolyamine. In order to obtain a hydrophobic and organophylic silica surface the hydroxyl groups were substituted by different organic compounds. Samples of titanoaerosils were obtained by molecular deposition of titanium oxide and by combined high-temperature hydrolysis of vapours of titanium and silicon chloride. Table I gives a list of the fillers used and their characteristics.

After deposition on the metallic surfaces, and after forming an adhesive layer, the composites were cured at room temperature (25 °C) for 24 h, and then thermally treated at 80 °C for 3 h and 120 °C for 0 h.

The adhesive strength was estimated by normal breaking of adhesive steel joints. The experimental procedure corresponded to conventional requirements [7].

3. Results and discussion
Fig. 1 shows the experimental data of epoxide-to-metal adhesive strength measurements. The epoxides have different contents and type of chemically modified fillers. The introduction of fine powder additives, in all cases, influences the adhesive strength. This influence is weak for aerosils A 175 and A-300 and is more significant for chemically-modified silicas. An optimal concentration of filler exists at which adhesive strength is maximum, increasing in comparison with that of the coating without a filler by 50%–100%.

The dependency of the adhesive strength of epoxides on the non-modified silica concentration (Fig. 1a) has a visible maximum in the region of 4 mass parts for A-300 and 6 mass parts for A-175, and the absolute values of strength obtained are equal.

TABLE I Specific square of surface, S, structure and concentration of inoculating groups, a, for the silicas investigated

Grades of silica	Structure of surface	S $(10^{-3}$ $m^2\,kg^{-1})$	a $(mmol\,g^{-1})$
Aerosil, A-175	$\equiv Si-OH-$	175	0.30–0.35[a]
Aerosil, A-300	$\equiv Si-OH-$	300	0.60
Titanoaerosils, TS-5[c]	$\equiv Si-O-Ti\equiv$	235	0.05[b]
TS-20		210	0.20
TAS-9		215	0.09
TAS-20		108	0.20
TAS-36		90	0.36
Aerosil, modified by diethyleneglycol, ADEG	$\equiv Si-O-CH_2-CH_2-OH$	300	0.70–0.00
Aminoethoxyaerosil, AEA	$\equiv Si-O-CH_2-CH_2-NH_2$ $\underset{\mid}{O-C_2H_5}$	300	0.70
Aminopropylaerosil, APA	$\equiv Si-O-\underset{\mid}{Si}-O-(CH_2)_3-NH_2$ $O-C_2H_5$	300	0.50
Butosil, B-2	$\equiv Si-O-(CH_2)_3-CH_3$	300	0.70

[a] Concentration of silanol groups.
[b] Mass fraction of titanium dioxide.
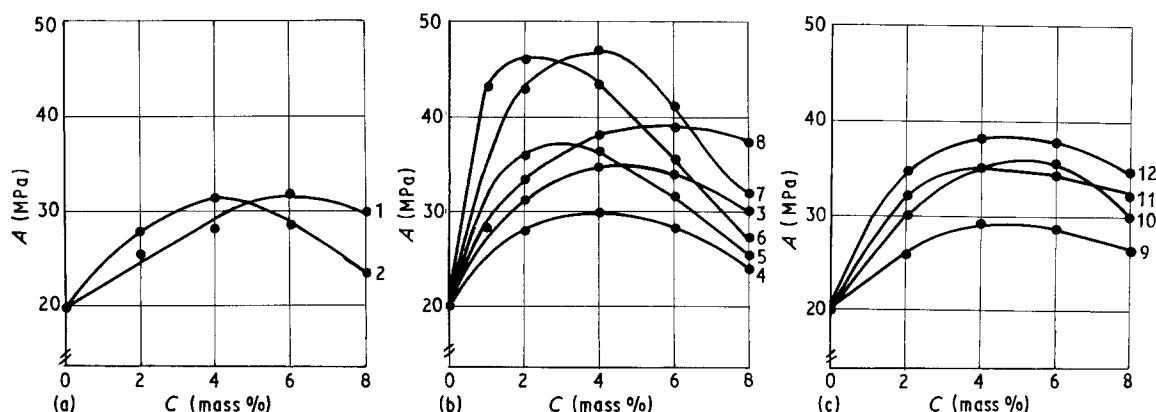[c] TS-5, TS-20 – molecular deposition method.

Figure 1 Dependence of adhesive strength as normal breaking strength, A, on the fine powder silicas content: (a) original silicas 1-A-175, 2-A-300; (b) titanoaerosils 3-TS-5, 4-TS-20, 5-TAS-9, 6-TAS-20, 7-TAG-30, 8-TiO, (c) silicas, chemically modified with organic compounds 9-ADEG, 10-AEA, 11-APA, 12-B-2.

Fig. 1b shows the anologous dependency for titanoaerosils. From the behaviour of the curves obtained, the following points can be made. The titanoaerosils obtained by the molecular deposition technique have low adhesive power values compared with non-modified silicas, and the maximum value of strength decreases with increasing titanium oxide content on the surface. The titanoaerosils obtained by the combined high-temperature hydrolysis technique give a maximum value of adhesion. The maximum value of strength is in the region of small concentration (2–4 mass %) and its absolute value increases with increasing titanium dioxide content. For comparison, the dependency of composite adhesive strength on pure titanium dioxide concentration is shown in Fig. 1b; a medium value of strength is seen in comparison with TAS- and TS-filled epoxides.

In the third group, there is a dependency of composite adhesive strength on the concentration of silicas modified with organic compounds (Fig. 1c) to obtain lyophobic (butosil D 2), luophyllic (ADEG) and amino-containing (APA, AEA) surfaces. In spite of

considerable differences in surface states, as shown in Fig. 1c, the character of concentration dependencies varies only slightly. Only the variation of adhesive strength maximum (in the region of 4–6 mass %) can be noted. According to their effect, the modified silicas may be grouped B-2 > AEA, APA > ADEG.

The results obtained can be explained with the help of the known conception about the formation of a polymer surface layer near a filler particle with properties different from those of the matrix. The formation mechanism and boundary-layer structure, however, are the subjects of present discussion [1, 2, 5]. It is supposed that different chemical states existed on the surface, and thus the potentional of a chemical reaction occurring during the hardening process can change the structure of forming network and hence the physico-chemical properties of the polymer. This supposition in this work is in an agreement with current opinion on the role of "weak" boundary layers in adhesive interaction [8], and the importance of surface energy in interface layer formation [9]. As previously illustrated for urethane polymer [6], the
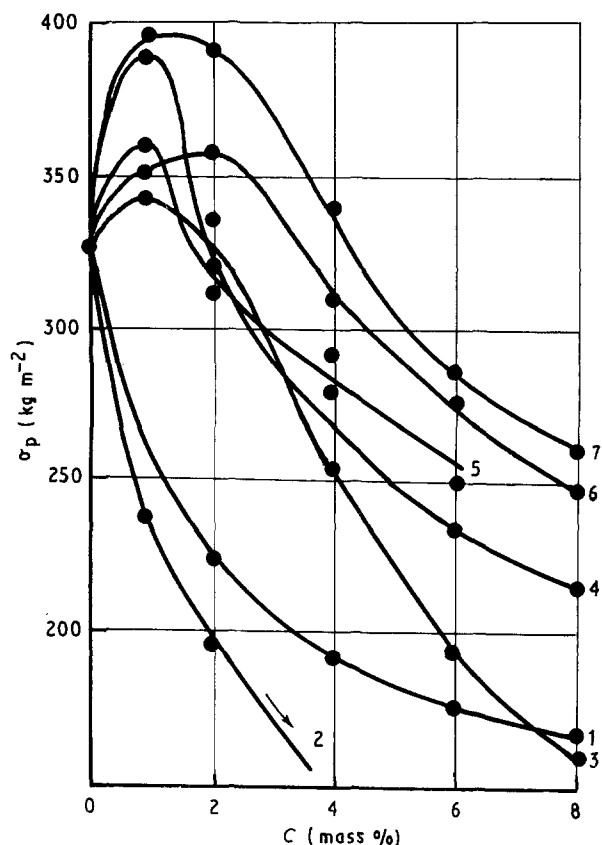
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Figure 2 Dependence of tensile strength, σ_p, of the epoxy composite on fine powder filler content: 1, A-175; 2, A-300; 3, ADEG; 4, AEA; 5, APA; 6, B-2; 7, TAS-2.

It is well known that amino-cured epoxy composites are characterized by the presence of a strong inner strain [12] which is the source of deformation microcracks. The free volume introduced by the silica surface can cause molecular mobility growth near the phase boundary, stimulate the process of denser macromolecular chain packing and a system transition to a more equilibrium state [13]. With a certain filler content there occurs a transition beyond the critical point of packing density [12] and the loosening action begins to prevail due to accumulate defects on the surface. The given process displays itself especially strongly for hydrophyllic aerosils A-175 and A-300, where there is the strongest concentration of surface defects due to the degrading action of water desorption during thermal treatment of the composite. The concurrence between the structural relaxation and the "weakening" action of the phase boundary possibly defines the position and value of the adhesive maximum. So breaking, known as adhesion analysis, occurs in the volume of the polymer, and according to other authors [4, 8, 10], increasing adhesive interaction may be correlated with cohesive strength.

The growth of cohesive interaction in systems modified with silicas is illustrated by the dependence of breaking strength on filler concentration (Fig. 2). It can be seen in Fig. 2 that a good correlation of adhesive and cohesive properties is really observed.

This assumption allows a satisfactory explanation to be obtained for the increasing optimal value of concentration with decreasing specific surface area of filler (A-175 and A-300, TAS-20 and TAS-36), and the best adhesive parametres for the composite containing an aerosil modified with butyl alcohol. The mobile non-polar substituting group does not limit intermolecular regrouping possibilities, and the hydrophobic properties of the butosil surface produce a decrease in the rate of surface defect accumulation with filler content growth.

In spite of some decrease in specific surface area for titanoaerosils (combined hydrolysis), the best adhesive characteristics were obtained for the epoxides modified with this type of highly dispersive filler. It should also be noted that the titanoaerosils were well impregnated with epoxy oligomer and well dispersed in the system with the highest level of filling (without visible separation and coagulation). This set of properties may be associated with the presence of Brensted acid centres on the titanoaerosil surface [14], which contributes to the increase in intermolecular interaction and polymer filler-bridge formation. No strong characteristics of amino-containing silicas, for which possible chemical bond formation cannot be excluded, can result from inappropriate conditions for composite preparation process.

affinity of a surface to the components of the reactive system defines the migration of a low molecular fraction from the polymer volume to the filler boundary. This selective absorption results in the formation of a less-defective polymer matrix, designed for greater external load. The observed increase of adhesive strength can be explained with the help of the depletion of the polymer layer by low molecular impurities, which react with the metal substrate. The extreme character of the dependence of adhesion on filler content confirms this assumption, because according to the given model [6], the saturation of the filler surface with absorbing fractions occurs at an extreme point.

However, many experimental results on silica-modified epoxide adhesion are difficult to explain using the selective interaction model [6, 8–11]. The main difficulty lies in the absence of an explicit effect of the surface state on the adhesive property variation. As can be seen from Table I, the state of the surface of the silicas introduced into the epoxy polymer is characterized by a great number of properties: hydrophobic and organophyllic coating degree, degree of surface group polarity, formation, concentration and activity of surface acid centres (in the case of titanoaerisils). This effect probably indicates that an increase in adhesive properties is caused by the presence of silica with a developed surface rather than by the chemical state of the surface. Hence the physico-sorption phenomena and chemical-bond formation in the interphase layer are not the most important factors.

4. Conclusion

The introduction of fine powder silica filler induces an increase in the adhesive properties of amino-cured epoxy composites. The greatest efficiency (up to 110% relative growth of adhesive strength) can be achieved by the introduction of butosil, a filler with a hydrophobic surface, and titanoaerosils obtained by the

combined high-temperature hydrolysis of titanium and silicon chloride vapours. The most probable mechanism of adhesive interaction growth is a decrease in the inner concentration and an increase in cohesive interaction as a result of macromolecular chain packing stimulated by the filler surface. The selective adsorption of low molecular weight impurities and intermolecular interaction at the phase boundary, as can be concluded from the given experiments, define the effect of the second order for the filler with an organophyllic surface. This mechanism, however, can define the additional increase adhesiveness and strength, when the epoxy composites are filled with titanoaerosils.

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