U.D.C. 667.521/1

Improvement of Resistance of Glass-reinforced Plastics to Water by Means of Hydrophobic Adhesive Compounds

A.I.Mikhal'skii

Hydrophobic adhesives have been widely used to improve the resistance of glass-reinforced plastics to water. They are either applied to the surface of the glass filler, or introduced into the plasticiser or the polymeric binder.
Various mechanisms are discussed and compared, by means of which hydrophobic adhesives influence the properties of glass-filled polymers. The enhancement of the water resistance of the glass-reinforced plastics could result from improved mechanical adhesion between the polymer matrix and the glass, from a more uniform distribution of internal stresses in the boundary layer, from greater cohesive strength of the polymer film on the filler surface, and from increased adhesion between polymer and filler, which is due to the formation of stronger adsorption bonds between them. Special attention is paid to the possible formation of a chemical bond between the hydrophobic adhesive and the glass and silica surface.
A list of 114 references is included.

CONTENTS

I.	Introduction	977
II.	Principles of matching hydrophobic adhesives to polymer systems	978
III.	Procedures for modifying glass-filled polymers with hydrophobic adhesives	978
IV.	Mechanisms by which alkylalkoxysilanes influence the properties of glass-reinforced plastics	981
V.	Reasons for improvement of water resistance of glass-reinforced plastics	983
VI.	Interaction of silicate surfaces with simple analogues of alkylalkoxysilanes	984
VII.	Interaction of glass and silica surface with actual finishes	985

I. Introduction

The main method for producing high-strength materials in modern technology is the reinforcement of polymers with fillers. The working characteristics of the material are determined by the combination of properties of the components and their interaction. Hence the improvement in the physical and mechanical properties of the reinforced polymer is not a consequence solely of the introduction of a high-strength filler into the system. The strengthening effect of the filler depends on a series of mechanical, physical, and chemical phenomena related to the structure of the polymer and the surface properties of the filler. The complex of phenomena occurring in the polymer–filler boundary layer is especially important. Rebinder[1] suggested that the reinforcing action of the filler is due to the transition of the polymer at its interface into a strengthened oriented state. Burov and Andreevskaya[2] discussing the mechanism of the strengthening action of glass fibre in glass-reinforced plastics, considered that the binder, while of low strength in the mass, became considerably stronger in thin films on the filler surface. The founding of Kargin's school of the theory of polymer structure was followed by considerable development of these views. Papers in recent years have extended these concepts to take into account the influence of the filler on the supermolecular structure of the polymer.

Lipatov, who observed the elevation of the glass point of a series of polymers as a function of the filler content[3] and the nature of the solvent for the polymer[4], suggested that reinforcement could be discussed in terms of adsorption. The nature of the solvent, the surface geometry of the filler, and adsorption interaction between the polymer and this surface affect primarily the number of possible conformations of the polymer molecule in the vicinity of the surface. Since this number is considerably diminished under the influence of adsorption forces, polymer molecules in adjacent layers are more loosely packed, while their flexibility is restricted. The glass point is determined by the mobility not only of the chain segments but also of the supermolecular structures. Thus the effect noticed by Lipatov is associated with a sharp limitation on the mobility not of single polymer chains on the filler surface but of the supermolecular structures which they form. Investigation of the dielectric relaxation of filled polymers[5] also shows that interaction with the surface restricts principally the mobility of supermolecular structures, whereas that of the chain segments changes little.

With polyhexanoamide as example Solomoko et al.[6] showed that the presence of a filler improves the mechanical properties of polymer films by changing the size of the spherulites. It is interesting that this process can be controlled in the required direction by surface modification of the filler. For example, two types of Aerosil—the original and an aminated sample—were used in this work[6]. In the former case the polyhexanoamide spherulites decreased in size from 30 to 26 μm on the introduction of 0.1% of the filler, and to 14 μm with 5%. In the latter case a greater decrease in size of the spherulites—to 19 μm—was found at a filler concentration of 0.1%; further increase in concentration did not affect their size. The aminated Aerosil surface shows a greater tendency to interact with the polymer, which leads to a substantial change in the mobility of the macromolecules, and hence in the conditions of formation of the spherulites. It is noteworthy that the mechanical properties of the films are improved only at low filler concentrations (0.1%), i.e. when the strength is influenced only by the morphology of the polymer. At high filler concentrations the mechanical properties of the polymer film deteriorate owing to the appearance of defects in the system.

The strength of a filled polymer is determined in considerable measure by the internal stresses. Lipatov[5,7,8] emphasises in particular that, with increase in the rigidity and the interaction energy of the polymer chain with the filler surface, the system departs further from

equilibrium during hardening of the polymeric binder. This decreases the number of points of contact between the polymer chain and the filler surface, which lowers their adhesive interaction and also causes the appearance of internal stresses, these being especially large in systems having a large surface, e.g. glass-reinforced plastics. Under certain conditions of mechanical constraint the stresses produced in the material during its forming later supplement those caused by its use. For example, the action on a filled polymer of various agents, among which moisture is the most typical under the working conditions of glass-reinforced plastics, will lead to an appreciable deterioration in properties†. This is the more important in that water, because of its high polarity, possesses great competitive power for interactions at the polymer–filler boundary.

Thus a paramount requirement in the production of high-strength polymeric materials which are reliable during operation is to create conditions at the polymer–filler interface which will ensure maximum adaptability of the macromolecular chains to the geometry of the filler surface, an adequate number of points of contact with the latter, and strengthening of adhesion bonds.

II. Principles of Matching Hydrophobic Adhesives to Polymer Systems

A procedure which has proved its value during recent years has been to use hydrophobic adhesives in glass-reinforced plastics filled with thermoplastics and elastomers. Alkylalkoxysilanes containing various functional groups in the organic radical have been most widely used in this connection.

A fairly wide range of such compounds have now been prepared and tested. Many workers[9-21], on examining their efficiency as a function of composition, have shown that the choice of hydrophobic adhesives as modifiers for polymeric materials reinforced with glass fibre must be based on the potentiality for chemical interaction between functional groups of modifier and polymer. General recommendations, supported by practical results, are in effect to use derivatives of vinyl- or methacryloyl-alkoxysilanes for polyester resins and derivatives of amino- or epoxy-alkoxysilanes for epoxide and phenolic resins.

Jellinek and Hanson showed[22] that the primary amino-group in 3-aminopropyltriethoxysilane (A-1100) is involved in cross-linking the epoxy-resin into a network structure. Vanderbilt and Clayton[23] noted the efficiency of unsaturated silanes with elastomers vulcanised in the presence of peroxides, the degree of cross-linking having been raised by the additional use of dienes containing conjugated double bonds. According to these workers the latter were able to bond the organosilicon product on the surface of the glass fibre and the elastomer.

Somewhat different criteria are used to select modifiers for thermoplastic materials reinforced with glass fibre. In the opinion of Plueddemann the decisive factor for the efficiency of a modifier is its compatibility with the polymer[24]. Since chemical interaction of the components is improbable, compatibility is ensured by similarity in polarity. More strongly polar properties of the modifier should have improved the adhesion of polymer to glass. However, Plueddemann showed[24] the presence of a maximum, the strength of the material reaching a limit and then falling with increased polarity of the modifier. An important part is obviously played by the orientation of the organic radicals in the modifier on the surface of the glass, which diminishes the effective polarity of the modifier when deposited on glass.

Plueddemann's hypothesis is supported by the work of Lee[25], who studied the wetting of polysiloxane finishing films on a glass surface, for which he determined the critical surface tension γ_{cr}. The latter was a measure of the polarity of glass surfaces which had been treated with various compounds. It was highest for 3-glycidyloxypropyltrimethoxysilane, and lowest for vinyltrimethoxysilane (42.5 and 25 dyn cm^{-1} respectively). From an examination of a fairly wide range of finishes Lee concluded that the functional groups of the finish are arranged horizontally on the surface. Hence the conformation of the molecules of the finish in the boundary layer are such that its polarity is not determined solely by the type of functional group, since the latter may occupy different positions relative to the surface of the glass.

Sterman and Marsden[26], however, do not exclude chemical interaction between hydrophobic adhesives and thermoplastic materials at the end-groups of the polymer or at free radicals formed by degradation of individual polymer chains during forming. On this hypothesis it is obviously difficult to make a practical recommendation for the choice of modifier. These workers therefore combined the components empirically, after examining a fairly wide range of compounds and assessing them from the change in mechanical and electrical properties of the filled thermoplastic materials produced by the action of water.

III. Procedures for Modifying Glass-filled Polymers with Hydrophobic Adhesives

In the present-day manufacture of glass-reinforced plastics hydrophobic adhesives are applied in three ways—deposition of the modifier from dilute solution on the filler (finishing), incorporation in the lubricant for the glass fibre, and finally direct incorporation in the polymeric binder. Since hydrophobic adhesives were first used as finished, many papers have been published on this technique. They cover optimum recipes for the finishes, temperature schedules for fixing them on the glass surface[27], and the effect of various physicochemical factors on the properties of the resulting materials.

It has been noted above that the choice of modifier is specific to each kind of binder. This has been illustrated[9-15] by actual examples of the use of finishes in glass-reinforced plastics, the properties of the latter being assessed after subjection to moisture. Losev, Aslanova, et al.[13] have examined the effect of ten amino-ethoxysilane finishes, with various substituents attached to the nitrogen atom, on the mechanical properties of a glass-reinforced epoxy-resin, and shown that the water resistance is lowered by replacing an amino-hydrogen atom by e.g. a butyl radical. However, introduction of a second amino-group into an aminoalkylethoxysilane (AGM-3), although it improves the properties of phenol–formaldehyde plastics, has an adverse effect on the properties of the epoxy-resins. This is explained by the greater reactivity of the latter. It probably affects formation of the polymeric structure on the filler surface, which is too active towards the given polymer and hence intensifies the disequilibrium of the system during setting[7].

† The above is not the only reason for the adverse effect of moisture.

The properties of glass-reinforced plastics can be improved, not only by a specific choice of finish, but also by using a mixture of finishes of the same class- Voitsekhovich et al. [14] note that more monolithic glass-reinforced plastics are obtained by using a mixture of di- and tri-ethoxyaminosilanes (ADE-2 and ADE-3). Grinevich [15] showed that a mixture of methyl and vinyl siliconates (GKZh-11 and GKZh-12) is an effective finish for an unsaturated polyester resin, whereas a mixture of vinyl and allyl siliconates (GKZh-12 and GKZh-18) is required for a polyester–polyacrylate resin. The latter improves the mechanical properties of a thermosetting glass-reinforced plastic in the initial state, and reduces the loss in strength after treatment with boiling water to 11%, whereas when vinyltriethoxysilane is used the loss in strength is 32%. After air hardening of the same resin a smaller change in strength is observed on finishing with vinyltriethoxysilane, although the efficiency of a mixture of GKZh-12 and GKZh-18 is maintained because the initial strength is increased. Thus the action of a finish is governed not only by the class of compound to which it belongs but also by peculiarities in its molecular structure and by the composition of the polymeric binder.

Nevertheless, a correct choice of finish based on the above principles still does not ensure that it will be efficiently used. Finishing is a technical process, for which conditions must be determined and maintained. Thus the properties of a glass-reinforced plastic will depend on the quantity of finish applied, the conditions of hydrolysis, the pH of the working solution, the temperature at which the finish is fixed on the glass fibre, the duration of this process, and several other factors. Biefeld and Phillips [27] give the temperatures at which finishes are fixed on glass depending on their functionality and the nature of the groups which are likely to interact with the surface. However, technical schedules developed for one finish can by no means always be used for treatment with other finishes [28] even belonging to the same class.

The second method of modification—the use of active lubricants—eliminates several adverse technical factors in the thermochemical treatment of fillers [39-42]. A finish incorporated into the lubricant comes into contact with a clean glass surface, which is freshly formed and therefore more active. The treatment of individual glass fibres avoids the effect of capillary flow of the finish and enables a more uniform film of the alkylalkoxysilane to be obtained on the filler. Furthermore, the introduction into the lubricant of an elastomer or a plasticiser, e.g. dibutyl sebacate, lowers the internal stresses in the surface layer of the binder during setting [23]. The above peculiarities were probably a consequence of the less sharply defined dependence of the strength of the glass-reinforced epoxy–phenolic plastic on the period of immersion in water when an active lubricant containing AGM-3 was used than in the case of thermochemical treatment with AGM-3 finish [29]. It is noteworthy that neither short-period nor long-term tests in air reveal differences in the method of applying AGM-3.

It was shown [29] that the third method of modification—the incorporation of an epoxyalkylalkoxysilane (ES) into the resin—did not have the proper effect: the strength of the glass-reinforced plastic depended quite markedly on the time it was immersed in water. Obviously, no analogy can be drawn here between the first two and the last method of modification with the aim of comparing their efficiency, since the last case involved a finish of a quite different class, containing epoxy-groups instead of amino-groups.

A systematic study of methods for modifying glass-reinforced plastics with hydrophobic adhesives was made by Kiselev and Bodrova [16]. They used a series of binders—phenol–furaldehyde–formaldehyde (FN), resol (BSL), phenol–formaldehyde (VFT), this third resin modified with viniflex, and butyral–phenol (BF-2)—to examine the effect of aminoethoxysilanes (A-1100, AM-2) and an ethoxysilane containing hydroxyl in the organic radical (MR-1), incorporated into the resin, on the stability of glass-reinforced plastics after treatment with water and a highly humid environment. With the optimum content of active additive in the binder glass-reinforced textolites retain 65–90% of their strength after subjection to boiling water for 2 h, whereas the usual value for an unmodified plastic is ~30%. The dielectric characteristics of the glass-reinforced textolites were used to assess the method of modification with aminoethoxysilanes; they showed that the stabilisation effect is most completely developed when the additive is introduced into the resin.

Other papers [17-21] also indicate an improvement in the properties of glass-reinforced plastics when ethoxysilanes are used as modifiers for the binder. The advantages of this method over finishing are firstly that the binder comes into contact with a more uniform surface, which possesses better wetting properties than a surface treated with a finish [34]. The tendency of the molecules of the finish to aggregate [34], especially when applied from aqueous solutions, aggravates the impairment of wetting.

Zisman [35] considers that, even with a small contact angle, individual cavities on the rough surface of a finished glass fibre remain unfilled with resin because of its high viscosity and rapid polymerisation. On the application of a load or of water to the plastic, stress concentrations will arise around each of the cavities, which will impair its properties. Bascom and Romans [36] examined the influence of such microdefects on the strength of a glass-reinforced epoxide plastic and found that, in order to reduce their number, it was necessary to make the wetting angle smaller and improve the technique of impregnation, e.g. by using a variable tension in the filament passing through the impregnating solution.

Further, the distribution of hydrophobic adhesive in the resin–filler system probably has a certain effect on the properties of the glass-reinforced plastic. Thus Kenyon [37] has shown that, in spite of the greater adhesion interaction of an epoxy-resin with glass finished with the product A-1100, the use as finish of 3-glycidyloxypropyltrimethoxysilane (A-187) produces a greater improvement in the mechanical strength of the plastic (Table 1 and diagram). He ascribes this inconsistency to the differing abilities of the finishes to diffuse inside the resin adjacent to the filler surface. This changes the depth of the modified binder near the surface of the filler, which in the present case probably determines the strength of the glass-reinforced plastic.

We shall attempt to compare the processes undergone by the binder in a glass-reinforced plastic modified by a hydrophobic adhesive, using Lipatov's views [5,7,8] on the mechanism of the reinforcing effect of fillers in polymers. Application of a finish to the filler surface increases its tendency to interact with the polymer, since the finish contains groups capable of interacting with the binder. Hence the rate of setting of the resin will be far higher on the finished surface than in bulk. The polymer molecules, having combined with it through the appropriate functional groups, lose their mobility, and are unable to pass into the equilibrium state. The formation of chemical bonds on the surface is then a favourable factor, whereas the strain in the polymer molecules is undoubtedly an adverse

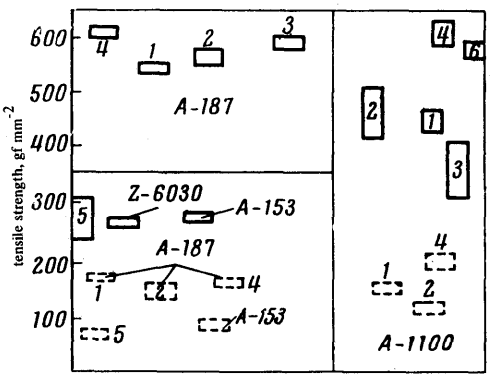
factor. Incorporation of a hydrophobic adhesive into the binder does not influence to such an extent formation of the polymer structure near the filler, so that the system will be closer to equilibrium.

Table 1. Strength of adhesion between Epon 815 resin and glass[37] (in conformity with ASTM D 1344-57).

Surface modifier		Breaking load, kg
brand	chemical name	
—		110
A-153	phenyltriethoxysilane	160
Z-6030	3-methacryloylpropyltrimethoxysilane	200
A-187	3-glycidyloxypropyltrimethoxysilane	297
A-1100	3-aminopropyltriethoxysilane	414
"Inner-layer" modifier + A-1100	—	502

New problems inevitably arise in the modification of binders with active additives[16-20]. Sterman and Marsden[19] studied the effect of several additives on the properties of polyester, epoxide, and phenolic resins containing various powdered fillers (glass, quartz, kaolin, calcium carbonate, etc.). From a comparison of the effect of hydrophobic adhesives when used as finishes and when introduced into the binders (0.5–2%) these workers concluded that the active additive migrates from the bulk of the resin to the surface of the filler, thereby enhancing the stability of the glass-reinforced plastic to the same extent as does the finish. Migration is confirmed by the improved stabilising effect of the additive on the properties of the material when the filled composition is kept until it sets. Immediate setting, for example, will not give the effect observed for some time (19 h). These workers show further that the action of the additive is connected with the presence of the filler (the strength of pure resin mouldings is unaffected by silanes) and depends on its nature. Addition of an active product has no effect on the strength of a composition filled with calcium carbonate, but considerably improves the properties of systems filled with glass, quartz, etc. A necessary condition for an alkoxysilane to be effective is that it should be hydrolysed on the filler surface. Preheating kaolin at 120°C removes most of the water from its surface, so that the mechanical properties of a filled resin become worse. This does not apply to fillers to whose surface water is more firmly bound (glass, quartz). Finally, assessing the influence of the technique of hardening on the properties of plastics modified by addition of a silane, these workers note that the condensation of a finish and its adhesion to the surface are not complete without further heating, continued for a definite time until gelling occurs.

Vanderbilt and Jaruzelsky[18] studied the mechanical properties of butadiene–styrene, polyester, and epoxide resins containing similar fillers, and paid special attention to the choice of optimum quantities of the additives A-1100 and A-172 (vinyltris-2-methoxyethoxysilane) introduced into the resin. The content of these did not exceed 2% on that of the filler, 4.6% based on the binder. These workers showed that, when quartz was used as filler, the optimum content of the silane was 0.5–1% on the filler. The additive has different effects on the properties of different resins: the strength of butadiene–styrene mouldings, which are weak in the original state, is increased several times; whereas the increase for epoxy-mouldings, which possess greater strength, is small. It is considered[18,38] that the epoxy-resin contains functional groups which tend to interact with the original surface of the filler to form stable bonds, and these ensure quite good mechanical properties for the plastic independently of the presence of a silane. The butadiene–styrene resin is unable to form such bonds, and therefore the action of an added hydrophobic adhesive, which promotes interaction of the resin with the filler surface, is shown in a sharp increase in strength.



Strength of Epon 815 resin filled with finished glass microspheres: —) in the dry state; --) after immersion in boiling water for 24 h. Finishing process: 1) finish dissolved in hexane; 2) finish dissolved in acetone; 3) finish dissolved in CCl_4; 4) "inner-layer" modifier applied before finishing[37]; 5) finish absent; 6) filler absent.

A different situation is found after filled mouldings have been subjected to boiling water for 7 days: the strength indices of the unmodified butadiene–styrene resin remain at the same level, whereas those of the epoxy-resin are substantially diminished. The presence of a hydrophobic adhesive then produces an increase in strength: as a result of modification the strength of a specimen after the treatment with water has increased several times. This was explained by the different amounts of water absorbed by the resins—3% for the expoxy-resin, 0.3% for the butadiene–styrene resin.

The above workers[18] confirm for calcium carbonate other data[19] showing that a filler containing on the surface neither water nor groups capable of hydrolysing an ethoxysilane produces no change in strength of mouldings as a result of their modification. No effect is produced by adding to the resin–calcium carbonate system the product A-172 which has previously been hydrolysed with water. Noting the necessity for at least partial hydrolysis of the additive introduced into the binder for a glass-reinforced plastic, Vanderbilt and Jaruzelsky consider

that the amount of water needed is present in actual resins: even the "driest" butadiene–styrene resin contains 0.04% of water.

The interaction of moisture in the binder FN with the added aminoethoxysilane AM-2 was studied by Kiselev and Bodrova[16] using the Karl Fischer method. With not more than 2% of additive the moisture content decreases, after which it increases somewhat owing to the accumulation of water formed presumably by the condensation of silanols, which are products of the hydrolysis of AM-2. The additive content corresponding to the minimum on the curve is the optimum content for the given resin, but it will vary somewhat on passing to other batches. Apart from correct choice of the concentration of the hydrophobic adhesive in the resin, the possibility that it may affect the setting of the binder must be taken into account; this aspect is ignored in most papers.

In conclusion it must be noted that there are several practical reasons, in addition to the above considerations, for the greater efficiency of the use of additives rather than finishes. Elimination of a finishing stage, requiring special equipment, from the industrial production of glass-reinforced plastics simplifies the process and makes it far more economic. Furthermore, glass cloth containing a finish or an active lubricant on the surface is unsuitable for prolonged storage after impregnation with the binder, since premature setting of the resin takes place as a consequence of the high surface concentration of modifier on the cloth. Impregnation of glass cloth with a modified binder does not have such a great effect on its viability.

In view of the above facts the incorporation of hydrophobic adhesives in the polymeric binder is the most economical prodedure for modifying glass-reinforced plastics to improve their resistance to water.

IV. Mechanisms by which Alkylalkoxysilanes Influence the Properties of Glass-reinforced Plastics

It has been noted above that the incorporation of hydrophobic adhesives into the binder involves their migration on the filler surface, just as finishing involves diffusion of the finish into the bulk of the resin. Thus some common phenomena are observed in glass–resin–alkyloxysilane systems, independently of the method of introducing this last component. We have noted individual differences above. Now let us examine possible mechanisms by which the finish influences the properties of glass-reinforced plastics, assuming to a first approximation that they are applicable to any of the modification procedures.

The properties of filled systems are not determined solely by those of their separate components—polymer and filler. Processes occurring at the interface between the two phases acquire great importance[1-8], especially with systems having a large surface (glass-reinforced plastics). It is here that the greatest effect of modification by a hydrophobic adhesive must be expected. Several authors discuss the role of the finish in terms of mechanical "swaging" of the fibre by the binder and the friction arising between them. In fact, the coefficient of linear expansion α_t of polymeric binders is more than ten times that of glass fibre‡, so that after the material has set and cooled the glass fibres are firmly held in the polymer matrix. In this case physical contact—pressure and friction—governs interaction of the components. Landsman and Klunder[39] consider that water, penetrating into a glass-reinforced polyester plastic, has a lubricating effect on the contact surface between resin and glass, and diminishes the friction between the components. They support their conclusion by the fact that the strength of the plastic, although dropping greatly under the influence of water, is almost completely restored after drying. Vašta and Zvonař[40] and also Skupin[41], while sharing this view, consider that the role of the finish is to restrict access of water to the surface of the fibres, so that the friction between the components varies to a less extent.

In effect these workers[40,41] consider only one of the properties of the finish, which is rendering the glass surface hydrophobic. However, as shown above, the choice of finish is not entirely determined by this property. In particular, Clark and Plueddemann[21], by treating glass cloth initially with chlorosilane and then with Z-6030 finish (3-trimethoxysilylpropyl methacrylate), obtained from a polyester resin a plastic possessing high water-repellency but low strength in both dry and wet states. Application of the finish Z-6030 to the surface of the original glass cloth considerably improved the mechanical properties of the glass-reinforced plastic. Replacement of the active additives AM-2 and MR-1 in the binder FN by methyltriethoxysilane[16] resulted in a deterioration in the properties of the glass-reinforced plastic, although methyltriethoxysilane tends to make the glass more water-repellent.

There is no doubt about the mechanical adhesion between filler and binder in a glass-reinforced plastic[40-42]. However, the behaviour of the system is determined probably not so much by its magnitude as by the uniformity of distribution of the stresses which arise. The part played by the finish must evidently be appraised on these lines, with the effect of the mechanical "swaging" of the fibres on the properties of the glass-reinforced plastics taken into account. It is obviously for this reason that some authors regard the finish as an interlayer, which diminishes the internal stresses in the plastic. This opinion is held in particular by Hooper[43], who considers that the presence of the finish lowers the interfacial tension during forming of the system. Erickson et al.[44] assume that the finish changes the adsorptive power of the glass surface, leading e.g. to preferential adsorption of the hardener in the surface layer. As a result of this, thin polymer films adjacent to the glass surface acquire a different structure and different properties. These workers[44] consider that their elasticity increases, so that the stresses in the boundary layer become smaller.

The above views[43,44], however, have not found practical confirmation by other investigators, and to some extent even contradict the latter. Hooper[43], when discussing the decrease in internal stresses in a filled plastic due to the deformability of the layer of finish, does not consider the effect of modifying the surface on the formation of adjacent polymeric structures, which according to Lipatov[7] will be less in equilibrium and more strained on interaction with the filler surface. The views of Erickson et al.[44] also contradict the position of Lipatov, who, considering the effect of the interface on the structure of three-dimensional polymers[45], has shown that a filler increases the effective density of the polymer network as a result of the appearance of additional branch points on interaction with the surface.

Thus great caution must be exercised in speaking of an increase in the elasticity of a hardened polymer in the

‡ For example, glass E has $\alpha_t = 4.8 \times 10^{-6}$ deg^{-1}, while the corresponding value for polyester resins is $(80-150) \times 10^{-6}$ deg^{-1}.

boundary layer. It is not in vain that Kenyon[37] has used, together with finishes, the so called "inner-layer modifier"§, which was applied to finished glass particles. This artefact on the surface of the filler in a polymer film possesses enhanced elasticity and improves the strength characteristics of the glass-reinforced plastic in dry and wet states (Table 1). Furthermore, the presence of the "inner-layer modifier" led to an increase in the strength of the plastic with increase in the bulk content of filler, which was not observed in its absence. These facts indicate efficient plasticisation of the binder directly adjacent to the filler surface, and show that the layer of finish on the glass most probably does not produce a relaxation of internal stresses which are due to the effect of the filler surface on the formation of polymeric structures. For the same reason plasticising additives have an appreciable effect in active lubricants[33].

Trostyanskaya and Poimanov[46-48] take a different view of the decrease in internal stresses under the influence of a finish in a glass-reinforced plastic. They consider that the hydrate sheath of the glass, while inhibiting hardening (e.g. in the case of phenol–formaldehyde resins), changes the density of the hardenable resin as the distance from the interface increases, which intensifies the internal stresses in the plastic. Treatment of the glass fibre with finishes (MR-1, AM-2, etc.) eliminates the action of the hydrate sheath of the glass and results in a more uniform setting of the binder, which improves the properties of the glass-reinforced plastic.

The possibility has been discussed above that adhesion between glass fibre and binder may be accomplished by mechanical "swaging". This is only one of the factors determining the strength of a reinforced plastic. Another factor, which in the opinion of most investigators is more important, is the formation of strong adhesive bonds between polymer and filler. The action of finishes has been discussed in detail from this point of view by Andreevskaya and her coworkers[49-51], and also by several other authors[52-55]. The presence of a finish on the surface of the glass fibre was shown to strengthen adhesion between the hardened resin and the glass. The investigations were made[49-55] on models representing the interaction of the components in actual glass-reinforced plastics, and in several cases the laws deduced were confirmed by the results of mechanical tests on such a plastic[49]. The increase in adhesion interaction between binder and finished glass surface was explained[49-56] by formation of a chemical bond between finish and resin during hardening of the latter.

Spectroscopic analysis has in fact shown changes in the structural constitution of the compositions studied. Thus Nikonova[52,53] has observed a decrease in intensity of the 1600 cm^{-1} band, corresponding to vibrations of the vinyl group in the finish, during the setting of a polyester resin in the presence of vinylalkoxysilane (GVS-9). Wende and Gähde[57,58] examined the infrared spectra of glass cloth treated with vinyltrichlorosilane, followed by methyl methacrylate in the presence of benzoyl peroxide. From the variation in intensity of the 3060-cm^{-1} band, which is also associated with vibrations of the vinyl group, they showed that ~67% of surface vinyl groups are involved in copolymerisation with methyl methacrylate. Other methods of investigation also indicate reaction between the polymer resin and the finish. Consideration of the thermal deformation and the elastic properties of phenol–formaldehyde and urea–formaldehyde resins reveals[17,55,56] that the introduction of alkylalkoxysilanes—AM-2 and MR-1 [17,56], AGM-9 and ES [55] —leads to the formation of a denser network in the hardened polymer. This was regarded as due to chemical interaction between resin and finish.

Thus it can be accepted on the basis of a number of investigations[53-59] that the increase in strength of adhesion between polymeric resins and a finished glass surface is due to the formation of a chemical bond between the binder and the layer of finish. Hence it is not fortuitous that different finishes have different effects on the adhesion of the binder to a glass fibre. For example, AGM-9 and ES increase the strength of adhesion between a glass fibre and a urea resin[54] to about 130 kgf cm^{-2}, whereas AGM-3 increases it to 56 kgf cm^{-2} (compared with 29 kgf cm^{-2} for the original glass fibre). In tests on aluminium borosilicate and basalt fibres[50] finish AM-2 increases the strength of adhesion by 30% in the case of an epoxy–phenol binder (480 instead of 366 kgf cm^{-2}), and by 20% with a butyral–phenolic binder (e.g. 260 instead of 216 kgf cm^{-2}).

Besides the chemical composition of the binder and the character of the glass surface, internal stresses at the polymer–filler interface influence the adhesive strength, these arising from defects in the glass surface and from the shrinkage of the binder when it sets. The contribution made by these stresses to the adhesive strength is especially great with large shrinkages of the binder, and can be diminished with a uniform distribution of stress over the interface. The lubricant (a paraffin emulsion) has a characteristic effect on the adhesion of glass fibre to various resins[50]. The presence of a lubricant lowers the surface energy of the glass and also avoids the formation of any specific bonds with the binder. Thus application of a lubricant would be expected to be accompanied by a decrease in adhesive strength, as has been observed[50] for an epoxy-resin (258 instead of 303 kgf cm^{-2}), the shrinkage of which does not exceed 3%. With modifications of a polyester resin having larger shrinkages (5.8–8.5%) the presence of a lubricant on the glass increased the adhesive strength from 110 to 134 kgf cm^{-2}. The ability of a plastic paraffin layer to "resorb" surface tensions makes a larger contribution to the change in adhesive strength than does change in the nature of the glass surface. This suggests that surface tensions in the polymer–filler system influence its properties. The action of a finish was not assessed from this point of view[50]. However, the results obtained have something in common wtth data[33,37] showing that a plasticiser in an active lubricant has a favourable effect on the properties of glass-reinforced plastics.

The properties of reinforced materials depend not only on the forces of adhesion between binder and glass fibre—mechanical or physicochemical in character—but also on the cohesive strength of the components. Tikhomirov[60], in particular, regards this as the decisive factor. He employed in his discussions the concept of a critical contact surface, at which the "aggregate" strength of the adhesive bonds between each individual fibre and the polymer matrix is equivalent to the tensile strength of the fibre. The ratio of the breaking load of the glass fibre to its strength of adhesion to the polyester resin gives a value of 0.025 mm^2 for the critical contact surface, which corresponds to a fibre length of ~0.5 mm. Thus accord-

§ The "inner-layer modifier" was the same epoxy-resin from which the glass-reinforced plastic had been obtained, but it contained a polyester plasticiser. As a result the modulus of elasticity of the resin on the surface of the finished glass could be lowered by a factor of 8.

ing to Tikhomirov it is sufficient to ensure in a glass-reinforced plastic complete contact between binder and fibre for a length of 0.5 mm in order that fracture of the material will be determined by the strength of the fibres. Further increase in adhesive strength will bring no advantage. Since the fibres normally used are longer than 30 mm, efforts to increase adhesion are not justified in all cases[60]. Discussing problems of the surface modification of the filler, this worker considers it incorrect to explain the strengthening of materials[49-55] by increase in the adhesion interaction with the polymer, which is not the cause of the improvement in strength but merely accompanies it. He refers[60] to Rebinder's work[1], and explains reinforcement as an increase in the cohesive strength of the binder in thin films on the modified glass surface. In fact the finish, by reacting chemically with the resin[52,53,55-58] and also raising the interaction energy of the latter with the filler, changes the properties of the binder in the glass-reinforced plastic in conformity with the views of Lipatov[7]. However, the question posed by Tikhomirov of the unjustified increase in adhesion interaction in glass-reinforced plastics must be regarded as debatable.

In connection with Tikhomirov's concept[60] of increasing the cohesive strength of the filler to strengthen the polymeric material we must consider several papers[61-64] which report an increase in the strength of glass produced by applying an organosilicon film to its surface. Removal of adsorbed water from the surface will obviously be of no little importance here, since it affects the surface tension, and the strength will increase in conformity with Griffiths' equation

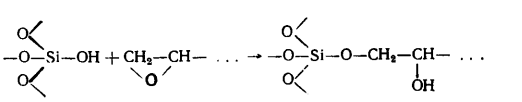
$$\sigma^2 = \frac{2\gamma E}{\pi a}$$

where σ is the tensile strength of the glass, γ its surface tension, E the Young's modulus, and a the depth of the cracks.

Outwater and Ozaltin[61] showed that treatment with the finishes A-1100 and A-172 increases the initial strength of glass by about 18%, and boiling diminishes it by a smaller amount. Thus a finish can have a favourable effect on the cohesive strength of both polymer and filler. For the present it is difficult to say whether this is decisive.

V. Reasons for Improvement of Water Resistance of Glass-reinforced Plastics

Hydrophobic adhesives have found application in glass-reinforced plastics not so much because they improve the properties of the latter in the initial state as because of the high stability conferred to the action of moisture. The question arises as to how finishes, by increasing the strength of adhesion between resin and glass, are able to maintain it at a high level after the plastic has been kept in water. Being highly polar, water is able to destroy adsorption bonds at the resin–glass interface—both weak dispersion bonds (of energy not exceeding 1–2 kcal mole^{-1}) and polarisation bonds—and then the still stronger hydrogen bonds (5–10 kcal mole^{-1}). Furthermore, water is able to break down chemical bonds which are unstable to hydrolysis. For example, an epoxy-resin is capable of forming a chemical bond with a glass surface[38]:



(I)

However, the resulting C–O–Si bond is hydrolytically unstable.

Zisman[35] examined the specific effects of finishes on the susceptibility of glass-reinforced plastics to the action of water, and discussed two possible causes—change in the ability of water to penetrate the plastic when a finish was used, and the formation of hydrolytically stable chemical bonds at the resin–glass boundary.

Three molecular diffusion processes—through the mass of polymer, along the glass–polymer interface, and finally through any protective film on the glass at sites not covered by the resin—underlie the mechanism of the penetration of water into a glass-reinforced plastic. The permeability of the glass-reinforced plastic to water changes with modification of the properties of the polymer and the glass surface. Intermolecular (cohesive) interaction of the polymer plays some part in this: increase in such interaction impedes diffusion of water between the macromolecules. Thus the cohesive strength of various films on glass, including those formed by the polymer or the finish, determines the rate of the diffusion process, which will also depend on the hydrophilic character of the surface. In this respect the action of the finish is in effect to produce on the glass a highly cohesive layer which is not readily wetted by water. Zisman remarks, however, that on this basis finishing will have a large effect when the whole surface of the glass fibres is made water-repellent and the angle of wetting is ~90°, since only then does the ability of water to penetrate the system by capillarity become insignificant.

With regard to the role of chemical bonds Zisman notes that intermolecular physical forces are sufficient to obtain a high-strength glass-reinforced plastic; these develop with good wetting and filling of the cracks in the glass by the binder, i.e. with a sufficient area of contact. This is consistent with Tikhomirov's views[60]. However, Zisman[35] and Dean[38] consider that formation of a chemical bond between resin and glass is desirable in cases in which the stability of the plastic to the action of a corrosive medium must be raised. Dean[38] states that, among all the forces acting between an ionic solid (glass) and a resin, only covalent bonds (50–100 kcal mole^{-1}) are not weakened by the action of water. A large number of chemical bonds is not required to strengthen the material; moreover, it is undesirable, since according to Dean their purpose at the interface is to ensure the simultaneous operation of the far weaker van der Waals forces. For steric reasons chemical bonds possess low mobility, and the presence a large number of them lead to strain in the surface layer of polymer.

Furthermore, the decrease in strength of glass-reinforced plastics after being kept in water is in some measure due to plasticisation of the binder. Whereas Zisman and Dean completely ignore this aspect, Pohl[65] assigns paramount importance to it. He determined the dynamic bending modulus of elasticity of a glass-reinforced plastic and the torsional modulus of rigidity, and attributed[65] variation in the former to destruction of adhesion bonds between resin and filler and change in the latter to plasticisation of the binder.

The investigation was made on a glass-reinforced polyester plastic with vinyltrichlorosilane and the product A-172 as finishes. Pohl showed that keeping the plastic in boiling water produced a more marked change in the dynamic modulus of rigidity than in the modulus of elasticity. The stabilising effect of the finish shows far more clearly in shear tests. Thus he assumes that the action of water on a glass-reinforced plastic is determined

primarily by its plasticising ability, and he draws an analogy between water and acetone, towards the action of the latter of which the finish was also useful. This investigation[65] was made essentially on a single material (a glass-reinforced polyester plastic), and it is therefore difficult to transfer the author's confidently expressed point of view to other systems, the action of water on which may develop differently, e.g. as a consequence of a change in the chemical composition of the resins and of their specific properties in general.

Clark and Plueddemann[21] and also Vanderbilt[66] assume that a layer of finish, chemically combined with the resin, reacts with the glass by means of bonds which readily tend to recombine, as a result of which the finish moves, as it were, along the surface of the glass, relieving local stresses. Hydrogen bonds and single siloxane bonds are considered[21] as possibilities, the latter formed by interaction of surface hydroxysilyl groups of the glass with alkoxyl or hydroxysilyl groups of the finish. The authors assume that single -Si-O-Si- bonds are capable of recombination, while hydrogen bonds prevent removal of the finish by water. Although the latter statement cannot be accepted[35,38], the contribution of hydrogen bonds to strengthening at the resin-finish-glass boundary is not open to doubt. The view[21] that local stresses are "relieved" by a layer of finish has much in common with Hooper's ideas[43], which we have already discussed.

Thus the question arises of the nature of the bonds between glass and finish. Arguments are given[53,57,58] in support of a chemical (siloxane) bond formed by interaction of alkoxy- and hydroxy-groups of the finish with surface hydroxyls of the glass or silica. If this mechanism is accepted, it is easy to explain the improved resistance to water of glass-reinforced plastics modified with hydrophobic adhesives, since the -Si-O-Si- bond is stable to hydrolysis.

VI. Interaction of Silicate Surfaces with Simple Analogues of Alkylalkoxysilanes

Before analysing this work let us consider, as the closest model to glass, the chemistry of a silica surface and its interaction with certain silanes. The hydroxyl coating on silica includes[67,68] various types of hydroxy-groups—isolated or free, 5.2-5.4 Å or at least 3.1 Å apart; paired hydroxyls linked by a hydrogen bond, the distance between them being 2.52-2.60 Å; and groups of three or four hydrogen-bonded hydroxyls—and is accompanied by a polymolecular film of water the main adsorption centres of which are either bound hydroxyls and coordinatively unsaturated silicon atoms (sites with groups of three or four bound hydroxyls)[68-71] or free hydroxy-groups[72,73]. It has been estimated[67] that on an Aerosil surface containing no adsorbed water the concentration of free hydroxyls per 100 Å^2 is 2.6, and that of bound hydroxyls 2.2.

Formation of a hydrogen bond between hydroxy-groups on a silica surface affects their properties. Firstly, they show far less tendency to any kind of interaction—specific adsorption or chemisorption—with organic compounds[67,72]; secondly, they are more liable to removal from the silica surface on heat-treatment[71,74], as a result of which some of the bound hydroxyls become free hydroxyls.

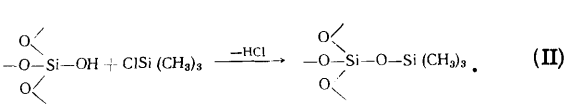
In the infrared absorption spectra of SiO_2 (silica, Aerosil, porous glass) vibrations of the O-H bond in free hydroxyls are represented by a narrow band at 3750-3745 cm^{-1} [67,69,71], and those in bound hydroxyls by a broad band in the range 3750-3000 cm^{-1} [67], after which O-H vibrations of adsorbed water molecules occupy the range 3750-2800 cm^{-1} in the case of silica[72]. In glasses undergoing crystallisation all the above bands are displaced to lower frequencies[75,76]: e.g. a band at 3500-3640 cm^{-1} corresponds to vibrations of free hydroxyls. Furthermore, new bands may appear[75] owing to formation of the strongest hydrogen bonds between hydroxyls in glasses having a low silica content (e.g. below 62%).

The mechanism of the interaction between certain substances and a silica surface can be assessed from the change in intensity of the vibrational bands corresponding to the different types of hydroxy-groups. In particular Kiselev and his coworkers[67,72,77] have shown that the adsorption of aromatic compounds (benzene, toluene, etc.) and of alcohols (methanol, ethanol) produces a sharp drop in intensity of the absorption band due to free hydroxyls. Furthermore, removal of the latter from the surface diminishes its ability to adsorb such compounds. The intensity of the 3750-cm^{-1} band decreases even at low surface coverage with alcohol molecules, whereas the intensity of the band due to bound hydroxyls does not change at all[72]. Hence only free surface hydroxyls are involved in the specific adsorption of alcohols. Sidorov[71] considers that bound hydroxyls are involved in this process at or above 550°C. However, this temperature is so high that in practice all bound hydroxy-groups are removed, the surface being enriched with free hydroxyls[67,74,78].

The weakening and complete disappearance of the band due to free hydroxyls when the Aerosil is treated with alcohols indicates[72] the occurrence of alkoxylation on the silica surface, i.e. the formation of surface Si-O-C bonds. Ease of alkoxylation of silica with alcohols was probably one of the reasons for the concept of chemical reaction between a silica surface and complicated hydroxy- and alkoxy-derivatives, including finishes.

A number of papers have been published on the interaction of Aerosil[67,79-83], silica gel[78,84], glass fibre[57,58,85], and microporous glass[86] with alkylchlorosilanes. Davydov et al.[67] showed that treatment of Aerosil with trimethylchlorosilane results in disappearance of the band due to free hydroxyls (3750 cm^{-1}) but leaves that due to bound hydroxyls unchanged. This phenomenon was explained by two causes—firstly energetic (a certain amount of energy is required to rupture the hydrogen bond of surface hydroxyls, but the heat of reaction with trimethylchlorosilane is only 11 kcal mole^{-1}), and secondly steric hindrance (the areas occupied by one trimethylsilyl group and one free hydroxyl together with one bound hydroxyl are roughly equal: i.e. the remaining chlorosilane molecules are unable to approach the bound hydroxyls after the more active free hydroxyls have reacted).

From the appearance, in the infrared spectra of silica modifications treated with trimethylchlorosilane[85,86], of bands in the region of C-H-stretching vibrations (2970 cm^{-1}) and their preservation after the solvent has been washed off and the sample subjected to prolonged vacuum treatment, it was concluded that the chemical reaction



(II)

took place on the silica surface. This is the only possible reaction involving an alkylated monochlorosilane on the silica surface which will yield an alkylated silyl coating. A side-reaction is hydrolysis of the trimethylchlorosilane followed by condensation to a dimer, but the resulting hexamethyldisiloxane is easily removed by vacuum treatment. An equally unambiguous interpretation can be given to the treatment of Aerosil with dimethyl chlorosilane[83], which contains only one functional group (chloro) capable of chemical reaction.

The properties of a trimethylsilyl coating on silica have been studied by adsorption[79-81,84], chromatographic[78,84], and mass-spectrometric[87] methods. Borisenko, Kiselev, et al.[84] showed that the most uniform trimethylsilyl surface coating is formed by treating silica gel with trimethylchlorosilane in the absence of traces of water (dry silica gel and the silane were sealed in an ampoule) at a high temperature. The defects in the coating permit only the small molecules of acetone to penetrate to the residual surface hydroxyls. These defects are inaccessible to the larger benzene molecules, which tend to interact specifically with a silica surface[77]. The decrease in the retention volumes of benzene on the surface by a factor of 50 and the lowering of the heat of adsorption from 11 to 6 kcal mole^{-1} as a result of its trimethylsilylation[84] suggest that the actual nature of the adsorption process has changed: whereas specific adsorption of benzene is observed on hydroxylated silica, the adsorption on a trimethylsilylated surface is non-specific. The results indicate not only a fundamental change in the surface properties of the silica but also complete shielding of the residual hydroxyls by the trimethylsilyl coating (under the given conditions of treatment), which excludes any interaction whatever with substances whose molecules are not smaller than those of benzene. This is confirmed by comparing the areas occupied by a trimethylsilyl group, a free hydroxyl, and a bound hydroxy-group[67].

Different results were obtained[84] when silica gel was treated with dimethyldichlorosilane: the retention volume of benzene changed roughly tenfold in comparison with the original surface. However, this ratio was poorly reproducible because the dimethyldichlorosilane formed a polymer, polydimethylsiloxane. This was considered[84] to impair the uniformity of the alkylsilyl coating. The great influence of secondary processes on the character and degree of modification of the silica surface becomes still more evident when it is remembered that dimethyldichlorosilane interacts with two types of surface hydroxyls: besides the free hydroxy-groups some of the bound hydroxyls react with the chlorine atoms[67], so that the silica surface should have undergone more profound changes than on treatment with trimethylchlorosilane. However, this does not occur[84], for the reaction analogous to (II) is not the sole reaction.

Burushkina, Chuiko, et al.[82] have used methylvinyldichlorosilane to make a detailed study of the interaction of a dichlorosilane with an Aerosil surface. Treatment of the Aerosil with the vapour at various temperatures (20–400°C) was assessed from the change in intensity of a series of bands in the infrared spectrum of the modified Aerosil. The effects of temperature, duration of treatment, and preliminary dehydration of the Aerosil were noted. Thus evacuating the Aerosil at 200°C before treatment increased the number of silyl groups grafted to the surface. Their number successively decreased on passing to the higher temperatures of 400° and 500°C. The increase was attributed to the freeing of hydroxysilyl groups perturbed by a hydrogen bond. This obviously implies the rupture of hydrogen bonds between surface hydroxyls and adsorbed water molecules. The decrease was caused by loss of a proportion of the surface hydroxysilyl groups and hence a decrease in the active centres. Since only bound hydroxyls are removed at 400–500°C [67,71,74], not only free but also bound hydroxyls are involved in the reaction of methylvinyldichlorosilane with the silica surface. The rate curves[82] enable this process to be interpreted as chemisorption, with hydroxysilyl groups regarded as reactive centres. The experimental conditions excluded formation of the polysiloxane polymer, so that systematic examination of chemical interaction on the surface was possible.

VII. Interaction of Glass and Silica Surface with Actual Finishes

Methods of studying the reactions of simple organic silanes have been used to investigate the interaction of actual finishes with a silica surface[53,57,58,88-91]. The infrared spectrum of a finished glass fibre contains new bands[53,57,58] belonging to the finish—stretching vibrations of C–H in the range 3000–2800 cm^{-1} [53] and vibrations of the vinyl group at 3070–3055 cm^{-1} [57,58]—which are not appreciably affected by prolonged (at least 30 h) rinsing of the glass fibre with the solvent, subsequent vacuum treatment (0.001 mmHg at 200°C for 2 h), and boiling in a weak alkali (0.5% ammonia solution for 2 h) [53]. The stability of the grafted groups is regarded[53,57,58] as proof of the formation of a chemical bond between finish and glass, since no other bonds are able to retain the layer of finish on the surface under such severe conditions. The most probable reaction in these systems will occur between halogeno-, hydroxy-, and alkoxy-groups in the finish and hydroxysilyl groups in the glass. On the basis of this scheme the authors conclude that a siloxane bond may be formed at the finish–glass boundary.

This conclusion was fully substantiated by a study of the interaction between trimethylchlorosilane and a silica surface[86]. The compounds used in the above researches[53,57,58]—finish GVS-9, vinyltrichlorosilane, vinyltriethoxysilane in its original state and partly hydrolysed—are multifunctiona: GVS-9 contains three ethoxyethoxy-groups attached to the silicon atom, and the others contain three halogeno-, ethoxy-, or hydroxy-groups. The experimental method, which ultimately simulated the behaviour of a finish on the surface of an actual filler, in no way excluded any additional reactions due to hydrolysis and condensation of the compounds used. Since all the finishes[53,57,58] were terfunctional, they might give rise to network polysiloxanes.

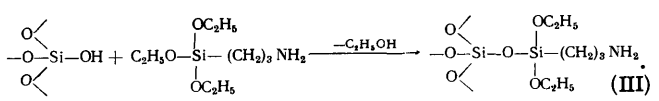
Wende and Gähde[57,58] showed that treating glass cloth with a chlorinated vinylsilane results in the formation of a grafted compound which is stable in a vacuum at 300°C (for 1 h). Treatment with an ethoxy-derivative gives no band at 3060 cm^{-1} in the infrared spectrum of the glass cloth which had been subsequently heated at 100°C. However, partial hydrolysis of the vinyltriethoxysilane results in the appearance of a band due to vinyl groups, although it is far weaker than for treatment with vinyltrichlorosilane. The authors interpret their observations in terms of the different abilities of chloro-, hydroxy-, and ethoxy-groups to form a chemical bond with the glass surface. They do not dwell on the complete consistency of this pattern with the ability of the compounds to polymerise: chloro-substituents are easily hydrolysed even in the air, whereas particular conditions are needed with alkoxy-groups, so

that hydrolysis of the ethoxysilane was necessary before application to the glass surface. This process is accelerated in alkaline medium, and it is probably for this reason that Nikonova[53] finds that finishes graft to an alkaline glass fibre to a greater extent than to an alkali-free glass fibre. Conversion of even the small proportion of finish molecules into a network polysiloxane and adsorption of the latter on the glass fibre will result in the formation on the glass surface of a polymer which firstly is insoluble, since it has a network structure, and secondly is thermostable, like all polysiloxanes. The structural groups which the authors observed in the infrared spectra are present both in the initial finish and in the polymer formed from it. Thus their results[53,57,58] leave no doubt as to the formation on the glass surface of grafted compounds which are stable to various agencies, but these results in no way determine the nature of the compounds or the character of the interaction with the surface. In our view the unequivocal conclusion that an Si–O–Si bond is formed between finish and glass is unjustified with the given experimental method.

More thorough spectroscopic investigations have been made[88-91] at the Pisarzhevskii Institute of Physical Chemistry of the Ukrainian SSR Academy of Sciences. The experimental conditions simulated less closely the finishing of a glass filler, but permitted a deeper insight into its mechanism. The test materials were 3-aminopropyltriethoxysilane and Aerosil, the former is widely employed as a finish, and the latter is a convenient form of silica for spectroscopic investigations. Conditions of treatment were varied widely: Aerosil was modified with the 3-aminopropyltriethoxysilane both as the vapour (at 20–150°C) and as dilute solutions in benzene (at 20–80°C). Determinations were made of the statistical exchange capacity (SEC) to characterise the concentration of groups grafted to the surface. Besides the C–H-stretching vibrations (3000–2800 cm^{-1}), the antisymmetric (3367 cm^{-1}) and symmetric (3288 cm^{-1}) N–H vibrations of the primary amino-group[88,89] and the O–H vibrations of the surface hydroxyls were examined in the infrared spectra of the modified Aerosils.

The main conclusions on the mechanism by which a finish adds to a silica surface were based on the insolubility and great thermal stability of the grafted compound in a vacuum (300°C at 10^{-4} mmHg), the weakening and complete disappearance of the band due to free surface hydroxyls (3750 cm^{-1}) with increase in the statistical exchange capacity of the specimens[88,89], and finally the decrease in the concentration of ethoxy-groups in the surface compound[90]. In the last case the calculation was made from determinations of carbon in the specimens: the concentration of ethoxy-groups was found by subtracting the carbon in propyl groups from the total carbon content, the number of propyl groups having been calculated from the concentration of amino-groups.

Results are presented[90] showing that increase in the statistical exchange capacity of the specimens is accompanied by a change in the ratio of amino-groups to ethoxyl from 1 : 2 to 1 : 1. Since the theoretical ratio for the initial substance in 1 : 3, it is obvious that the molecules of the finish lose some of their ethoxy-groups during transformation on the surface. On the basis of the observations[88,89] the surface reaction is given as



Thus, although additional information has been obtained on the nature of structural groups on the Aerosil surface, the same conclusion is reached as before[53,57,58] on the formation of a siloxane bond. The fundamental possibility of the formation of a cross-linked polysiloxane from 3-aminopropyltriethoxysilane is not considered, nor is its tendency to hydrolysis under the treatment conditions discussed.

Nevertheless, this process is of interest if only because it leads to a decrease in the ethoxyl content of the grafted layer, and hence should be considered in interpreting the results[90]. Furthermore, the absence of the 3750-cm^{-1} band in the spectra of the modified Aerosil is not unequivocal evidence that free surface hydroxyls are involved in reaction (III), since other O–H vibrational bands were observed, e.g. at 3690 cm^{-1} [89]. This band is due to bound hydroxyls[67], and its presence may imply conversion of free into bound hydroxyls as a consequence of specific adsorption of the compound on the surface. It was obviously in this connection that the hydroxyl concentration of the Aerosil was determined[90] by deuterium exchange and mass spectrometry, and compared with the content of amino-groups on the Aerosil surface. This revealed that increase in the statistical exchange capacity to a particular value was accompanied by a decrease in the content of hydroxy-groups. Further increase in the concentration of amino-groups by a factor of 2.5 produces almost no change in the hydroxyl content of the surface (Table 2). Thus the question arises of incomplete realisation of the proposed reaction mechanism (III).

Table 2. Mass-spectrometric analysis of aminoalkylated Aerosils after deuterium exchange[90].

Conditioning temp., °C	SEC after conditioning (15 h), mmole g^{-1}	Duration of exchange, h	Total exchangeable centres on surface, mmoles g^{-1}	Quantity of centres, mmoles g^{-1} for the groups	
				NH_2	OH
200	0.14	2	1.49	0.28	1.21
200	0.39	2	1.51	0.78	0.73
200	0.57	2	1.52	1.14	0.38
200	0.93	3	2.20	1.86	0.34
200	1.41	3	3.18	2.82	0.36

How is it possible to graft 2.82 millimoles of amino-group per gramme to the silica surface if, after a concentration of 1.14 mole NH_2 g^{-1} has been reached, surface hydroxyls are not involved in the process? An obvious answer is to postulate that molecules of the finish can undergo independent transformation with the formation of polymeric derivatives on the Aerosil surface, but it is difficult to assess the relative proportions of these processes. It is hardly possible to check them from the variation in the ethoxyl content, since transformation of the finish—whether etherification on the surface (scheme III) or the cocondensation of molecules—involves the liberation of ethanol, which interacts readily with a silica surface[79-81]. After treatment of Aerosil with 3-aminopropyltriethoxysilane vapour at 150°C a band appeared in the infrared spectrum[90] at 2985 cm^{-1}, which corresponds to antisymmetric vibrations of the methyl group in the presence of a C_2H_5–O bond. Thus, an additional possibility is ethoxylation of the surface, which probably accompanies[90] the main processes, and under favourable

conditions will become increasingly dominant. The absence of the 2985-cm^{-1} band with the other Aerosil modifications may not be complete proof of the absence of ethoxylation, since the concentration of grafted ethoxy-groups is probably small, and a strong band due to C–H-stretching vibrations (2935 cm^{-1}) is superimposed on their characteristic band (2985 cm^{-1}).

Consequently interaction between the silica surface and ethanol, which is a product of the hydrolysis and the condensation of the ethoxysilane, should lead both to a decrease in the concentration of surface hydroxyls and to a change (decrease) in the ratio of amino- to ethoxy-groups in the grafted compound. The experimental results, including those in Table 2, are interpreted[90] solely as a consequence of condensation of the ethoxy-groups of the silane with hydroxysilyl groups of the silica. In our view, however, all the observed phenomena may be due also to other processes—firstly hydrolysis and condensation of the terfunctional finish into a cross-linked polymer adsorbed on the silica surface, and secondly ethoxylation of the Aerosil surface by ethanol liberated in the first process. The unequivocal conclusion that a chemical bond is formed between finish and silica surface is open to doubt, since the phenomena observed by these workers can be explained by other processes.

An interesting investigation was made by Tertykh, Chuiko, et al.[91] on the part played by amino-groups in the reaction between 3-aminopropyltriethoxysilane and an Aerosil surface. This group was characterised by two absorption bands—at 3380 and 3305 cm^{-1}—which were displaced to shorter wavelengths by vacuum treatment at 450°C, their frequencies becoming respectively 3500 and 3425 cm^{-1}. This substantial shift in the bands was explained by breakdown of the hydrogen bond between the primary amino-groups in the finish and the free hydroxyls on the silica. This bond is quite stable, since it is destroyed only after vacuum treatment at 450°C, when the hydroxyls hydrogen-bonded to amino-groups were split off, i.e. when "removal of one of the components of the hydrogen-bonded complex" takes place. As long as the complex does not break down, the aminoalkylated Aerosil is not involved in specific adsorption interaction with methanol and acetone. After destruction of the complex these compounds are adsorbed on the surface, which results in broadening of the 3425-cm^{-1} band.

The results[91] show that the amino-group of the finish is able to interact with the silica surface with formation of a fairly stable bond. At present, of course, this conclusion applies only to 3-aminopropyltriethoxysilane, for other amino-alkoxysilanes have not been studied from this point of view. An analogous investigation would enable us not only to establish the possibility of interaction between finishes and a silica surface through the amino-groups but also to ascertain the effect of substituents attached to the nitrogen atom on its tendency to surface reaction.

It has been shown[92] that analogues of real finishes—aminoalkylethoxysilanes containing one ethoxy-group—do in fact react chemically with a silica surface. This is proved by the preservation of bands due to CH-stretching vibrations in the spectrum of the Aerosil after extraction and high-temperature vacuum treatment. Formation of any thermostable derivatives of the aminoalkylsilane not grafted to the surface was excluded by the monofunctionality of the agent. The use of model compounds led to the conclusion[92] that chemical reaction is possible between an ethoxy-group in the aminoalkylsilane and the surface hydroxyls of Aerosil.

It is difficult to say to what extent this process occurs with finishes containing two or three ethoxy-groups and showing a tendency to more complicated reactions. Since these compounds have proved effective for practical application, it would be of great interest to examine their tendency to polymerisation in contact with a glass surface and determine the contribution of this process to the general pattern of transformation of the finish on the surface.

---o0o---

The above review was written at the beginning of 1969. While it was being prepared for publication a considerable number of papers appeared on improvements to the application of hydrophobic adhesives in polymeric materials and on extensions to their field of use[93–97]. It has been proposed[93,94] that finishes and active additives should be employed not only in glass-reinforced plastics but also in glues, sizes, coatings, and moulding compositions. New modifiers have appeared which improve adhesion in filled polymers, e.g. finishes based on modified epoxy-resins[98] and novel organosilicon compounds containing nitrogen[99].

Hydrophobic adhesives find application in the most recent and promising types of composite materials, e.g. in a glass-reinforced plastic based on a thermostable polyimide resin[100] and in carbon-reinforced plastics[101]. The properties have been described[100] of glass-reinforced plastics based on a polyimide binder obtained from the dianhydride of benzophenone-3,3′,4,4′-tetracarboxylic acid and *m*-phenylenediamine. Glass cloth S-994 was used as filler, with its surface modified three ways: it was subjected to heat-treatment; it was finished with product A-1100 after heat-treatment; and it was treated with product HTS during stretching of the glass fibres. The presence of the modifier on the glass cloth produced a sharp increase in the water resistance of the material: 90–99% of its bending strength was maintained after immersion in boiling water for 2 h, whereas a glass-reinforced plastic based on the heat-treated glass cloth retained only 45% of the initial strength. A second, no less important point is the sharp increase in the initial strength of the glass-reinforced polyimide plastic resulting from modification of the filler with products A-1100 and HTS: the bending strength of the material in the dry state was changed from 2140 to 3060–3670 kg cm^{-2}. Thus there is no doubt about the prospects for modifying glass-reinforced polyimide plastics with a finish to raise their initial strength and their resistance to water. However, the problem arises of preserving the strength of the material at high temperatures, since thermal stability remains a primary requirement of such plastics. Finishing a glass cloth with product A-1100 has an adverse effect on the strength of the material during its thermal aging at 316°C, while the use of product HTS leads to a sharp deterioration in the strength indices after aging at this temperature for 300 h. Research workers will probably direct their efforts towards developing methods for stabilising glass-reinforced polyimide plastics which will enable the heat resistance of the material to be maintained while its water resistance is improved.

Alkylalkoxysilanes have hitherto been used in polymeric materials filled with glass, silica, quartz, etc. However, Harris et al.[101] have found an effective method of applying hydrophobic adhesives in carbon-reinforced plastics. They have been able to strengthen a carbon-reinforced polyester plastic considerably by applying alkoxysilanes containing epoxy-groups in the organic radical (A-186 and

A-187) to the surface of carbon fibre previously immersed in boiling 70% nitric acid for 2 h. The strength of the plastic is already increased by the use of oxidised fibres, but their finishing leads to further increases in tensile strength (from 56.6 to 63.7 kgf mm^{-2}), bending strength (47.5 to 53.0 kgf mm^{-2}), and shearing strength (2.52 to 2.77 kgf mm^{-2}). The shear tests indicate that the strengthening of the material due to oxidation and finishing of the carbon fibres is 35% (2.77 compared with 2.06 kgf mm^{-2}). In order to achieve the same improvement solely by oxidising the carbon fibres in boiling nitric acid, the time of immersion would have to be increased from 2 to 24 h. Preliminary oxidation of carbon fibres in aqueous medium is regarded as yielding surface hydroxyls, and the interaction with the silane finish occurs by a mechanism analogous to that observed with glass-reinforced plastics. On studying the fracture of specimens by scanning electronic stereoscopy, however, peculiarities were noted[101] in the detachment of the finished carbon-fibre surface from the mass of the binder. A layer of finish or binder usually remains on the finished glass surface[37]. The surface of a carbon fibre torn from a polymer matrix, however, contained no trace of finish and was entirely similar to an unfinished surface. The explanation given[101] is that the finish bonds more strongly to the binder than to the carbon fibre.

Thus hydrophobic adhesives are beginning to be used, not only in new types of resins, but also in combination with new forms of filler. Hence the interest of research workers in the chemistry of the interaction between these modifiers and various kinds of surfaces is not accidental. Broun, Korolev, et al.[102] used the infrared spectra to estimate the content of grafted groups on the surface of titanium dioxide (anatase, rutile), and showed[103] that, unlike silica, the same number of trimethylsilyl groups are grafted on independently of whether the surface is treated with trimethylchlorosilane or trimethylethoxysilane. Furthermore, these workers observed the formation of carboxylates on a titanium dioxide surface treated with trimethylchloro- and trimethylacetoxysilanes.

Information on the interaction of simple alkylalkoxysilanes with a silica surface has been extended. The relative activities of trimethyl-ethoxy-, -acetoxy-, and -chloro-silanes and their firmness of retention on silica have been characterised[103] by the surface concentrations of grafted trimethylsilyl groups. In the spectrum of Aerosil treated with dimethoxydimethylsilane vapour[104] the band due to C–H vibrations in the trimethylsilyl group (at 2965 cm^{-1}) was accompanied by a band at 2953 cm^{-1}, both of which remained after vacuum treatment of the specimen at 450°C. The appearance of a band at 2853 cm^{-1} is explained[104] by the grafting of methoxy-groups to the silica surface. In fact the spectrum of Aerosil which has been treated with methanol contains a band at 2857 cm^{-1}. Thus this work[104] has shown that the main reaction between dimethoxydimethylsilane and silica—analogous to scheme (III)—is accompanied by a secondary reaction, in which the methanol liberated reacts with surface hydroxyls. The possibility of such interaction has been discussed above (Section VII), and this paper[104] supplies experimental confirmation.

Johanson et al.[105,106] labelled organosilanes with carbon-14 to examine their interaction with silica and alkali free glass surfaces. They found that trimethylchlorosilane was adsorbed on the glass than on silica, On immersion of the glass in boiling water or on exchange with unlabelled trimethylchlorosilane molecules, however, the number of primarily adsorbed molecules greatly diminished. This suggested that the interaction of trimethylchlorosilane with glass is not confined to chemical reaction with surface hydroxyls, but includes adsorption interaction of additional molecules of the substance with surface metal ions. In contrast to trimethylchlorosilane, trimethylsilanol is easily removed from a silica surface. From this it is assumed that trimethylsilanol adds to a silica surface by means of hydrogen bonds between its own hydroxyl and those of the silica. By using ammonia as catalyst for the silanol condensation, however, these workers were able to prevent the adsorbed trimethylsilanol molecules from exchanging with those in the solution. After desorption the silica retained 90% of the grafted molecules, instead of the 20% observed in the absence of ammonia. Thus a transition from a hydrogen bond to a chemical bond between the compound and the silica surface was accomplished.

It has been shown[105], with hexamethyldisilazane as example, that adsorbed water has a vigorous effect on the transformation of organosiloxanes in contact with a glass surface. For this purpose the water adsorbed on glass was replaced by ^3H_2O, and the variation in its amount during reaction with hexamethyldisilazane was followed. It was established that water causes conversion into trimethylsilanol, which in the presence of the ammonia liberated forms a chemical bond with the glass.

Daley and Rodriguez[107] pay great attention to the hydrolysis of finishes on a glass surface. In their opinion this process precedes interaction of actual finishes with the surface, and its extent affects the properties of glass-reinforced plastics. They checked the hydrolysis of vinyltriethoxysilane (A-151), hydroxypropyltrimethoxysilane (A-174), and pentyltrimethoxysilane (Y-2815) from the variation in intensity of the chromatographic peak of the unhydrolysed finish on contact with glass. Hydrolysis of the finishes was catalysed by alkali-metal ions in the glass, which had an especially marked effect on A-151, whose relatively small molecules most easily approached the surface ions[107]. Glass was finished with the product A-151 under various conditions: (i) particles of glass were merely introduced into a solution of the finish; (ii) acetic acid was added initially, and then the glass; and (iii) the glass was added, and only then was the solution acidified. Hydrolysis of the finish occurred to the greatest extent in case (ii), its completeness being shown in the mechanical properties of polystyrene filled with the finished glass. The polymer had its highest bending strength (510 kgf cm^{-2}) when it contained glass particles finished in the absence of acid, i.e. when hydrolysis of the finish was insufficiently advanced. When hydrolysis was most complete, the strength of the filled polymer had its minimum value (440 kgf cm^{-2}). The explanation given[107] is that the finish, hydrolysed by acetic acid, is deposited on the glass surface only after some delay. This probably involves formation on the glass of a layer of finish, which results in less effective interaction between polymer and filler.

Recent papers[108–110] have examined the adsorption of water on silica, and its effect on the wetting and adhesion of silicate surfaces[111]; others have assessed the destructive effect of water on glass-reinforced plastics and the possibility of diminishing it by means of hydrophobic adhesives[112–114]. The opinion is expressed[112] that water breaks the bonds at the boundary between polyester resin and glass by leaching substances of low molecular weight out of the resin, so that the binder shrinks. Eakins assumes[113] that in general the action of water on glass-reinforced plastics consists in penetrating the material

and increasing the rigidity of the layer of resin on the surface of the glass. This diminishes the ability of the surface layer of polymer to relieve the stresses arising on the formation of cracks and their extension to the filler surface. Furthermore water, by rupturing hydrolytically unstable bonds between glass and resin, disturbs the closeness of packing of binder macromolecules in the surface layer, which permits access of water to the rest of the material. It is considered[112,113] that the use of finishes diminishes the destructive action of water on glass-filled polymers.

Garanina, Semenova, et al.[114] have shown that the properties of a glass-reinforced plastic, in both dry and wet states, can be improved by slightly drying the glass cloth at 80°C for 1.5 h before production of the material. Such removal of water from the filler surface lowers the number and size of microdefects (pores) in the material. These observations are especially significant when it is remembered that the application to glass cloth of most finishes, e.g. aminoalkylethoxysilanes[114], considerably increases the amount of water adsorbed on the glass surface.

REFERENCES

1. P. A. Rebinder, Dokl. Akad. Nauk SSSR, 49, 354 (1945).
2. A. K. Burov and G. D. Andreevskaya, "Steklovoloknistye Anizotropnye Struktury" (Anistropic Glass-fibre Structures), Izd. Akad. Nauk SSSR, Moscow, 1952.
3. Yu. S. Lipatov, Vysokomol. Soed., 5, 290 (1963).
4. Yu. S. Lipatov and Ya. B. Vasilenko, in "Adgeziya Polimerov" (Adhesion of Polymers), Izd. Akad. Nauk SSSR, 1963, p. 113.
5. Yu. S. Lipatov, Paper at the Seventeenth Conference on Macromolecular Compounds, Moscow State University, 1969.
6. V. P. Solomko, T. A. Molokoedova, I. A. Uskov, and T. V. Polichkovskaya, Vysokomol. Soed., 9A, 40 (1967).
7. Yu. S. Lipatov, "Fiziko-khimiya Napolnennykh Polimerov" (Physical Chemistry of Filled Polymers), Naukova Dumka, Kiev, 1967.
8. Yu. S. Lipatov, in "Napoliniteli Polimernykh Materialov" (Fillers for Polymeric Materials), Izd. MDNTP, 1969, p. 9.
9. V. V. Bodrova, I. V. Drogaleva, B. A. Kiselev, A. Ya. Korolev, N. S. Leznov, and Ya. I. Mindlin, Plast. Massy, No. 3, 30 (1963).
10. Ya. D. Avrasin, A. Ya. Korolev, Ya. I. Mindlin, I. V. Drogaleva, and A. I. Prigoreva, Plast. Massy, No. 7, 31 (1960).
11. N. J. DeLollis, Adhesives Age, 11, 21 (1968).
12. V. I. Alksne, K. P. Grinevich, and I. Kh. Yakobson, Mekhanika Polimerov, 787 (1967).
13. V. B. Losev, M. S. Aslanova, N. Ya. Voitsekhovich, Yu. V. Meitin, and G. E. Fridman, Plast. Massy, No. 10, 61 (1967).
14. N. Ya. Voitsekhovich, Ya. I. Mindlin, V. V. Borodashkina, and A. I. Krivonosov, Plast. Massy, No. 7, 44 (1968).
15. K. P. Grinevich, in "Proizvodstvo i Primenenie Kremniiorganicheskikh Soedinenii" (Production and Application of Organosilicon Compounds), Izd. MDNTP, 1964, Part 1, p. 88.
16. B. A. Kiselev and V. V. Bodrova, Plast. Massy, No. 8, 36 (1963).
17. B. A. Kiselev, A. I. Mikhal'skii, V. V. Bodrova, and N. G. Korbut, in "Fiziko-khimiya i Mekhanika Orientirovannykh Stekloplastikov" (Physical Chemistry and Mechanics of Glass-reinforced Oriented Plastics), Nauka, Moscow, 1967, p. 30.
18. B. M. Vanderbilt and J. J. Jaruzelsky, SPE Trans., 2, 363 (1962).
19. S. Sterman and J. G. Marsden, Mod. Plast., 40, 125 (1963).
20. M. C. Polniaszek, Adhesives Age, 11, 25 (1968).
21. H. Clark and E. Plueddemann, Mod. Plast., 40, 133 (1963).
22. M. H. Jellinek and N. D. Hanson, Mod. Plast., 35, 178 (1958).
23. B. M. Vanderbilt and R. E. Clayton, Rubber Chem. Technol., 38, 379 (1965).
24. E. P. Plueddemann, Proc. 20th Anniversary Tech., Conf. SPI Reinforced Plast. Div., Chicago, 1965.
25. L. H. Lee, J. Colloid Interface Sci., 27, 751 (1968).
26. S. Sterman and J. G. Marsden, Polymer Eng. Sci., 6, 97 (1966).
27. L. P. Biefeld and T. E. Phillips, Ind. Eng. Chem., 45, 1281 (1963).
28. Z. I. Bronshtein, Plast. Massy, No. 4, 27 (1962).
29. V. A. Bershtein and L. V. Petrova, Plast. Massy, No. 11, 57 (1965).
30. N. N. Kryuchkov, in "Primenenie Stekloplastikov v Mashinostroenii" (Application of Glass-reinforced Plastics in Mechanical Engineering), Izd. MDNTP, 1963, p. 25.
31. Yu. V. Meitin, "Issledovanie Khimicheskoi Modifikatsii Steklyannykh Volokon i Polucheniya Novykh Vidov Pryamykh Zamaslivatelei dlya Ikh Proizvodstva" (Investigation of the Chemical Modification of Glass Fibres and the Preparation of New Types of Direct Lubricants for Their Production), Candidate's Thesis, Moscow Institute of Chemical Technology, Moscow, 1968.
32. W. J. Eakins, US P. 3 369 926 (1968).
33. S. A. Shreiner, P. I. Zubov, and T. A. Volkova, Vysokomol. Soed., 4, 1714 (1962).
34. M. Hagedorn, Kunststoffe, 52, 605 (1962).
35. W. Zisman, Khim. Tekhnol. Polimerov, No. 2, 39 (1966).
36. W. D. Bascom and J. B. Romans, Ind. Eng. Chem. Prod. Res. Development, 7, 172 (1968).
37. A. S. Kenyon, J. Colloid Interface Sci., 27, 761 (1968).
38. R. Dean, Khim. Tekhnol. Polimerov, No. 5, 124 (1966).
39. P. Landsman and J. Klunder, Kunststoffe, 54, 791 (1964).
40. M. Vašta and V. Zvonař, Plast. Hmoty a Kaucuk, 1, 261 (1964).
41. L. Skupin, Plast. Hmoty a Kaucuk, 1, 269 (1964).
42. Kh. T. Korten, "Razrushenie Armirovannykh Plastikov" (Breakdown of Reinforced Plastics), Khimiya, Moscow, 1967.
43. R. C. Hooper, Annual SPI Conf., 11, Sec. 8B (1956).
44. P. W. Erickson, A. Volpe, and E. R. Cooper, Mod. Plast., 41, 141 (1964).
45. Yu. S. Lipatov, Vysokomol. Soed., 10A, 2737 (1968).
46. A. M. Poimanov, "Issledovanie Fiziko-khimicheskikh Yavlenii, proiskhodyashchikh na Granitse Steklovolokno-svyazuyushchee i Vliyanie Ikh na Prochnost' Stekloplastikov" (Investigation of Physicochemical Phenomena occurring at Boundary between Glass Fibre and Binder, and Their Effect on the Strength

of Glass-reinforced Plastics), Candidate's Thesis, MATI, Moscow, 1965.
47. E. B. Trostyanskaya and A. M. Poimanov, Mekhanika Polimerov, No. 3, 8 (1965).
48. E. B. Trostyanskaya, A. M. Poimanov, and Yu. N. Kazanskii, Mekhanika Polimerov, No. 1, 26 (1965).
49. G. D. Andreevskaya, Mekhanika Polimerov, No. 1, 93 (1965).
50. G. D. Andreevskaya, Yu. A. Gorbatkina, V. G. Ivanova-Mumzhieva, and E. E. Zaborovskaya, in "Struktura, Sostav, Svoistva i Formovanie Steklyannykh Volokon" (Structure, Composition, Properties, and Forming of Glass Fibres), Moscow, 1968, Part 1, p. 159.
51. G. D. Andreevskaya, "Vysokoprochnye Orientirovannye Stekloplastiki" (High-strength Oriented Glass-reinforced Plastics), Nauka, Moscow, 1966.
52. S. N. Nikonova, L. I. Golubenkova, A. N. Shabadash, and M. S. Akutin, Plast. Massy, No. 3, 45 (1966).
53. S. N. Nikonova, "Izuchenie Fiziko-khimicheskikh Protsessov na Granitse Steklo–Appret–Svyazuyushchee v Stekloplastikakh" (Study of Physicochemical Processes at Glass–Finish–Binder Boundary in Glass-reinforced Plastics), Candidate's Thesis, NIFKhI, Moscow, 1967.
54. A. I. Krivonosov, M. S. Akutin, S. N. Nikonova, E. A. Lashkova, and L. I. Golubenkova, Mekhanika Polimerov, No. 6, 1119 (1968).
55. A. I. Krivonosov, "Metod Polucheniya Stekloplastikov na Osnove Karbamidnykh Oligomerov" (Preparation of Glass-reinforced Plastics from Urea Oligomers), Candidate's Thesis, Moscow Institute of Chemical Technology, Moscow, 1968.
56. G. D. Andreevskaya, Yu. A. Gorbatkina, N. B. Guseva, B. A. Kiselev, A. I. Mikhal'skii, and V. N. Stepanova, Vysokomol. Soed., 7, 1254 (1965).
56a. M. S. Akutin and A. I. Krivonosov, Trudy Moscow. Khim.-tekhnol. Inst. Mendeleeva, No. 57, 133 (1968).
57. A. Wende and I. Gähde, I Internazionale Tagung über Glasfaserverstärkte Kunststoffe und Epoxydharze, Berlin, 1965.
58. I. Gähde and A. Wende, Plaste und Kautschuk, 13, 22 (1966).
59. H. H. Reinsch, Maschinenmarkt, 74, 1656 (1968).
60. V. B. Tikhomirov, Dokl. Akad. Nauk SSSR, 167, 867 (1966).
61. J. O. Outwater and O. Ozaltin, SPE Trans., 2, 321 (1962).
62. S. I. Sil'vestrovich, M. I. Oganesova, and A. Ya. Karyakin, Dokl. Akad. Nauk SSSR, 178, 156 (1968).
63. V. A. Rydbov, N. I. Borisova, E. N. Kulikova, and G. S. Kalugina, Steklo i Keramika, No. 4, 4 (1967).
64. S. Reichel, Plaste und Kautschuk, 15, 501 (1968).
65. G. Pohl, Plaste und Kautschuk, 13, 16 (1966).
66. B. M. Vanderbilt, Mod. Plast., 37, 125 (1959).
67. V. Ya. Davydov, L. T. Zhuravlev, and A. V. Kiselev, Zhur. Fiz. Khim., 38, 2047 (1964) [Russ. J. Phys. Chem., No. 8 (1964)].
68. V. I. Kvlividze, Dokl. Akad. Nauk SSSR, 157, 158 (1964).
69. G. D. Chukin and L. A. Ignat'eva, Zhur. Prikl. Spektrosk., 8, 872 (1968).
70. G. A. Bugnina and V. V. Serpinskii, Izv. Akad. Nauk SSSR, Ser. Khim., 731 (1966).
71. A. G. Sidorov, Optika i Spektrosk., 8, 806 (1960).
72. V. Ya. Davydov and A. V. Kiselev, Kolloid. Zhur., 30, 353 (1968).
73. G. A. Galkin and A. V. Kiselev, Zhur. Fiz. Khim., 42, 1470 (1968) [Russ. J. Phys. Chem., No. 6 (1968)].
74. S. I. Kol'tsov and V. B. Aleskovskii, Zhur. Fiz. Khim., 41, 665 (1967) [Russ. J. Phys. Chem., No. 3 (1967)].
75. O. A. Troitskii and S. Z. Shmurak, Zhur. Fiz. Khim., 40, 1310 (1966) [Russ. J. Phys. Chem., No. 6 (1966)].
76. S. Horst, Glass Ind., 47, 670 (1966).
77. G. A. Galkin, A. V. Kiselev, and V. I. Lygin, Kinetika i Kataliz, 5, 935 (1964).
78. A. V. Kiselev, Yu. S. Nikitin, V. K. Chuikina, and K. D. Shcherbakova, Zhur. Fiz. Khim., 40, 140 (1966) [Russ. J. Phys. Chem., No. 1 (1966)].
79. A. V. Kiselev, N. V. Kovaleva, A. Ya. Korolev, and K. D. Shcherbakova, Dokl. Akad. Nauk SSSR, 124, 617 (1959).
80. I. Yu. Babkin, V. S. Vasil'eva, I. N. Drogaleva, A. V. Kiselev, A. Ya. Korolev, and K. D. Shcherbakova, Dokl. Akad. Nauk SSSR, 129, 131 (1959).
81. I. Yu. Babkin, A. V. Kiselev, and A. Ya. Korolev, Dokl. Akad. Nauk SSSR, 136, 373 (1961).
82. T. N. Burushkina, A. A. Chuiko, N. V. Khaber, and L. V. Manchenko, Teor. Eksper. Khim., 4, 570 (1968).
83. A. A. Chuiko, V. A. Tertykh, V. A. Khranovskii, Yu. P. Egorov, and L. M. Roev, Teor. Eksper. Khim., 2, 247 (1966).
84. I, V. Borisenko, A. V. Kiselev, R. S. Petrova, V. K. Chuikina, and K. D. Shcherbakova, Zhur. Fiz. Khim., 39, 2685 (1965) [Russ. J. Phys. Chem., No. 11 (1965)].
85. S. N. Nikonova, L. I. Golubenkova, A. N. Shabadash, and M. S. Akutin, Plast. Massy, No. 2, 27 (1966).
86. L. I. Golubenkova, A. N. Shabadash, S. N. Nikonova, and M. S. Akutin, Vysokomol. Soed., 4, 1354 (1962).
87. L. T. Zhuravlev, A. V. Kiselev, and V. P. Naidina, Zhur. Fiz. Khim., 42, 2269 (1968) [Russ. J. Phys. Chem., No. 9 (1968)].
88. V. A. Tertykh, T. N. Burushkina, and A. A. Chuiko, in "Modifikatsiya Svoistv Polimerov i Polimernykh Materialov" (Modification of the Properties of Polymers and Polymeric Materials), Naukova Dumka, Kiev, 1965, p. 85.
89. A. A. Chuiko, V. A. Tertykh, G. E. Plavnik, and I. E. Neimark, Kolloid. Zhur., 27, 903 (1965).
90. V. A. Tertykh, A. A. Agzamkhodzhaev, A. A. Chuiko, and L. T. Zhuravlev, Izv. Akad. Nauk SSSR, Ser. Khim., 1739 (1968).
91. V. A. Tertykh, A. A. Chuiko, V. A. Khranovskii, and I. E. Neimark, Zhur. Fiz. Khim., 42, 1758 (1968) [Russ. J. Phys. Chem., No. 7 (1968)].
92. Yu. V. Zherdev, A. Ya. Korolev, Ya. I. Mindlin, and T. V. Men'kova, Kolloid. Zhur., 31, 201 (1969).
93. C. Kirchner, Adhäsion, 257 (1969).
94. H. Marwitz, Adhäsion, 122 (1970).
95. M. S. Aslanova, Yu. V. Meitin, and N. Ya. Voitsekhovich, in "Proizvodstvo, Pererabotka i Primenenie Stekloplastikov" (Production, Processing, and Application of Glass-reinforced Plastics), Izd. LDNTP, Leningrad, 1969, p. 3.
96. B. Gleeson, Plastics and Polymers, 37, 45 (1969).
97. B. A. Kiselev, S. E. Artemenko, N. L. Zhikhareva, B. N. Zakharov, L. G. Glukhova, and V. P. Anufrieva, Plast. Massy, No. 12, 36 (1969).
98. G. E. Eilerman and J. A. Sanguigne, B. P. 1 140 004 (1969); C. A., 70, No. 14, 22 (1969).
99. V. B. Losev, "Sintez i Issledovanie Nekotorykh Kremniiorganicheskikh Azotsoderzhashchikh

Soedinenii" (Synthesis and Investigation of some Nitrogen-containing Organosilicon Compounds), Candidate's Thesis, Latvian SSR Academy of Sciences, Section of Chemical and Biological Sciences, 1969.
100. J. H. Freeman, L. W. Frost, G. M. Bower, E. J. Traynor, H. A. Burgman, and C. R. Ruffing, Polymer Eng. Sci., 9, 56 (1969).
101. B. Harris, P. W. R. Beaumont, and A. Rosen, J. Mater. Sci., 4, 432 (1969).
102. E. V. Broun, A. Ya. Korolev, L. M. Vinogradova, R. M. Artamonova, and T. V. Men'kova, Dokl. Akad. Nauk SSSR, 187, 1047 (1969).
103. E. V. Broun, A. Ya. Korolev, L. M. Vinogradova, R. M. Artamonova, and T. V. Men'kova, Zhur. Fiz. Khim., 44, 797 (1970) [Russ. J. Phys. Chem., No. 4 (1970)].
104. A. F. Gusein-Zade, Z. N. Nudel'man, A. M. Garber, F. A. Galil-Ogly, E. E. Rostovtseva, and A. I. Malyshev, Kauchuk i Rezina, No. 1, 6 (1970).
105. O. K. Johanson, F. O. Stark, G. E. Vogel, R. M. Lacefield, R. H. Baney, and O. L. Flaningam, "Interfaces and Composites", Symposium, 71st Annual Meeting A. S. T. M., San Francisco, 1968; Philadelphia, Pa., 1969, p. 168.
106. F. O. Stark, O. K. Johanson, G. E. Vogel, R. G. Chaffee, and R. M. Lacefield, J. Phys. Chem., 72, 2750 (1968).
107. L. R. Daley and F. Rodriguez, Polymer Eng. Sci., 9, 428 (1969).
108. G. A. Galkin, A. V. Kiselev, and V. I. Lygin, Zhur. Fiz. Khim., 43, 1992 (1969) [Russ. J. Phys. Chem., No. 8 (1969)].
109. J. Erkelens and B. G. Linsen, J. Colloid Interface Sci., 29, 464 (1969).
110. R. E. Dei, A. V. Kiselev, B. V. Kuznetsov, and Yu. S. Nikitin, Kinetika i Kataliz, 10, 646 (1969).
111. M. K. Bernett and W. A. Zisman, J. Colloid Interface Sci., 29, 413 (1969).
112. K. H. G. Ashbee and R. C. Wyatt, Proc. Roy. Soc., A 312, 533 (1969).
113. W. J. Eakins, "Interfaces and Composites", Symposium, 71st Annual Meeting A. S. T. M., San Francisco, 1968; Philadelphia, Pa., 1969, p. 137.
114. S. D. Garanina, G. P. Semenova, Yu. V. Zherdev, and A. Ya. Korolev, Plast. Massy, No. 10, 48 (1969).