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Gorbatkina Yulia Arkadievna and
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The monograph is focused on controlling interfacial strength, which is one of the substantial problems of the science of adhesion. The subject of discussion is the interfacial strength in adhesive joints in which the substrates are various fibers and the adhesives are epoxy resins modified with active diluents, rigid-chain thermoplastics, or fine fillers (in particular, nanosized fillers). The change in adhesive strength during the formation of joints (during curing) and under various operating conditions is studied. The dependence of adhesive strength on the introduced plasticizer concentration is analyzed. The existence of synergism of interfacial strength is shown; the factors responsible for the occurrence of the synergism are analyzed; the mechanisms controlling the synergism in the case of using various types of modifiers are revealed. Using the example of the activities of the adhesion research group of the Laboratory of Reinforced Plastics of Semenov Institute of Chemical Physics of the Russian Academy of Sciences, a brief historical review of the origin, development, and formation of a new direction in the science of adhesion—adhesion of polymers to fibers—is given.

The book is intended for a wide audience: researchers, teachers, students, masters, postgraduate students, and all those who are engaged in studying the surface phenomena, the physics and chemistry of polymers (primarily, epoxy resins), and the design and application of composite materials.

TABLE OF CONTENTS

PREFACE

An extensive use of polymer composite materials, in particular, fiber-reinforced plastics, in the middle of the last century has given an impetus to the formation and rapid development of a new direction in the science of adhesion—adhesion of polymers to fibers. The use of these materials in various fields of industry and technology has been increasing every year and thereby has caused an acute necessity in the development of a scientific basis for designing composite materials.

It soon became clear that the properties of fibrous composites and their failure are determined not only by the properties of reinforcing fibers and polymer matrices, but also by the processes that occur at the fiber–matrix interface, because interfacial strength determines the possibility of stress transfer across the interface, i.e., the efficiency of using the strength of the reinforcing (fibrous) filler. To design composites with desired properties and predict changes in these properties, it was necessary to know the behavior of the adhesive strength of the components and the interfacial strength under respective conditions.

A fiber, together with the adjacent polymer layer, constitutes the unit cell of any fiber-reinforced plastic. It was these cells (or rather their models) that began to be used to determine the adhesive strength between the components of fibrous composites.

An adhesive joint is formed on the surface of a fiber immersed into an adhesive layer. The geometry of the joint is characterized by length l, which is determined by the polymer layer thickness, and area S:

$$S = \pi d l,$$

where d is the fiber diameter. The S values generally do not exceed a few square millimeters.

In the 1960s through to the 1980s, adhesion of polymers to fibers was studied in the United States, the Soviet Union, France, Finland, and—later—in Israel and Germany. At that time, an experimental and technical base for measuring the adhesive strength in polymer–fiber joints was largely founded. In those joints, the substrate was fiber segments, i.e., cylindrical objects with a small diameter (7–200 μm).

These "microjoints" differ from other adhesive joints in the shape and size of the specimens. It is their geometry that leads to the fact that the techniques, devices, and facilities required for preparing and testing these joints differ from the respective techniques used to test conventional adhesive joints, in which the substrates are generally flat or slightly curved surfaces with an area of a few tens and a few hundreds of square millimeters.

It should be noted that the foundation of an experimental base for measuring the adhesive strength in fibrous filler–binder systems is a constantly evolving process. The chronology of its development coincides with the chronology of the emergence of new types of fibers and binders.

The development of methods for measuring the adhesive strength (τ) in polymer–fiber systems was accompanied by the accumulation of knowledge about the τ value of various pairs and the laws governing changes in adhesive strength under various conditions for the formation and failure of joints.

This knowledge was primarily required for those who were engaged in the design and use of fibrous composite materials. For engineers and technologists, it was necessary to compare the τ values of different pairs and know how the interfacial strength changes with a change in the temperature–time conditions for the formation of composites and in the operating conditions (with a change in temperature, loading conditions, storage, etc.). Therefore, of all the numerous factors affecting adhesive strength, those that should be known to design required materials were studied first.

As noted above, adhesion of polymers to fibers was studied in many countries; however, the studies conducted at Semenov Institute of Chemical Physics of the USSR Academy of Sciences were particularly regular and systematic. The results obtained by the early 1990s were described in two monographs:

1. Yu. A. Gorbatkina, *Adgezionnaya prochnost' v sisteme polimer-volokno,* Moscow, Khimiya, 1987.
2. Yu. A. Gorbatkina, *Adhesive Strength of Fibre–Polymer Systems,* New York–London–Toronto, Ellis Horwood, 1992.

The second book is a revised and expanded version of the first book. In particular, a chapter on adhesion of linear polymers (polyolefins and heat-resistant linear polymers, such as polysulfones, polyethersulfones, polyetherimides, and polyarylene ether ketones) to fibers was specially written for the second book. To the best of our knowledge, those two monographs still remain the only books entirely focused on the description of the basic laws governing the change in adhesive strength in joints where the substrates are fibers.

This book is a logical continuation of the two above books. It represents results obtained in studying the adhesive strength of joints composed of a fiber and a binder based on modified epoxy oligomers at the same Laboratory of Reinforced Plastics of Semenov Institute of Chemical Physics of the Russian Academy of Sciences.

The studies were conducted in collaboration with a number of institutions; the authors sincerely thank all those who participated in the studies. The authors are especially grateful to Prof. M.L. Kerber and Prof. I.Yu. Gorbunova (Chair of Technology for Processing Plastics and Elastomers, Mendeleev University of Chemical Technology of Russia). The authors also sincerely thank all those whose work and knowledge contributed to the appearance of this book.

INTRODUCTION

This monograph is focused on studying the adhesion of modified epoxy resins to fibers. In the past two decades, these polymers have been used to design reinforced plastics exhibiting not only high strength and rigidity, but also high fracture toughness (crack resistance), impact resistance, and fairly high post-impact properties. Therefore, in those years, the structure and properties of modified epoxy matrices and composites based on them have been intensively studied.

Since epoxy resins are characterized by an advantageous combination of physicomechanical, dielectric, and chemical properties, they are commonly used in industry, in particular, in the production of reinforced plastics, adhesives, and casting compounds. However, epoxy resins in the cured state are fairly fragile substances. To eliminate this disadvantage and have the possibility of designing structural materials based on epoxy matrices with a desired set of properties, various modifiers (polymers, monomers, fine powders, etc.) are introduced into epoxy oligomers.

Until recently, the problem of crack resistance and impact resistance has been solved by modifying epoxy matrices with low-viscosity rubbers [1–7]. However, this method is fraught with a decrease in the strength and thermal characteristics of the composites. Recently, these problems have been solved by modifying epoxy matrices with flexible- and rigid-chain thermoplastics, dispersed fillers, and active diluents [8–24]. In the most recent years, blends of thermoplastics have also been used to this end [25–27]. The effect of various modifiers on the structure and properties of epoxy resins has been discussed in many reports. The least studied aspect of this problem is the adhesion of modified epoxy resins to solids.

The effect of the introduction of a modifier (minor component) on the interaction of epoxy resins with solids (particularly with fibers) is really an extremely important issue. The adhesive ability of modifiers is typically lower than that of epoxy resins: the adhesive strength of dispersed fillers to solids (with no pressure applied) is almost zero; the strength of the active diluent–solid interface is negligible; joints of heat-resistant rigid-chain thermoplastics with solids are significantly less durable than joints of epoxy resins with solids, even if the adhesive joints are formed under optimum temperature–time conditions (melt casting).

A natural question now arises of whether the introduction of a component with a lower (or even zero) adhesive ability into an epoxy binder will cause a significant decrease in the strength of the modified matrix–solid interface. For fiber-reinforced plastics, it is well known that this decrease leads (in the case of imperfect adhesion) to a deterioration in the physicomechanical characteristics of the composite material [28, 29].

This paper describes results that can provide an answer to the above question.

The measure of adhesion is shear adhesive strength τ, which is determined by pulling a fiber out of a cured binder layer (pull-out method):

$$\tau = F/S,$$

where F is the force required to break the adhesive joint, $S = \pi dl$ is the area of the joint (resin–fiber interfacial area), d is the fiber diameter, and l is the length of the adhesive joint (length of the fiber portion immersed into the polymer).

Composites, the adhesion of which is discussed, are based on epoxy oligomers ED-20 (counterpart of DGEBA) and ED-22. In most cases, measurements are conducted for model samples for which a steel wire with a diameter of 150 μm is used as a support (substrate).

It is extremely convenient to use a high-strength steel wire as a substrate. The lengthwise wire diameter is constant with a high degree of accuracy; the area of the joints changes only with a change in their length l. The average load required to break the wire is 50 N (at a loading speed of 1 N/s). Therefore, steel fiber–epoxy binder joints typically undergo adhesive fracture, even if the area of the joints S achieves 1.5–2.0 mm^2 ($l/d \geq 20$–25). In the absence of samples that underwent cohesive fracture (along the fiber), the measurement accuracy for τ increases, while the time required for conducting the experiment decreases. It is also significant that, using this substrate, it is possible to vary the area of the joints over the widest possible range.

The obtained joints were tested using adhesion meters designed at the Laboratory of Reinforced Plastics of Semenov Institute of Chemical Physics of the Russian Academy of Sciences; the adhesion meters provide measurements under quasistatic and dynamic loading at various temperatures and a constant rate of increase in the force applied to the sample: F; ˙ = const; $\dot{\tau}$ = const.

The sample preparation, testing, and measurement result processing procedures are described in detail in [30, 31]. Some necessary methodological details are given in the Appendices.

The τ value determined in experiments depends on many factors. It was shown [28, 32, 33] that five of them can be considered as the main factors, namely, the energy of interfacial bonds, the number of these bonds, the interface imperfection, the value of residual stresses acting in the interfacial joint, and the structure of the near-surface (interfacial) layers.

To elucidate the effect of modification on the interfacial strength, it is necessary to analyze how each of the above factors changes upon the addition of a modifier (minor component) to epoxy resin. Accordingly, it is necessary to know these changes (measure them in experiments or determine them by some methods).

The energy of bonds acting across the interface is determined by the nature of the adhesive and the substrate.

The number of interfacial bonds is determined by the number of active sites on the substrate surface and the degree of involvement of these sites in the interaction with the adhesive. The last-mentioned parameter depends on the degree of wetting of the substrate by the adhesive. The higher the number of discontinuities, various defects, and air bubbles arising from interfacial wetting, the smaller the number of active sites capable of interacting with the adhesive.

Interface imperfection is also primarily determined by the ability of the adhesive to wet the substrate. Defects arising from poor interfacial wetting of the formed joint subsequently (upon loading) become stress concentrators, i.e., a source of decrease in the adhesive strength. Thus, from this point of view, a high degree of wetting is a necessary condition for a high interfacial strength.

The residual stresses acting at the fiber–polymer interface arise during the formation of the joint and the subsequent cooling of it from the formation (curing) temperature to test temperature T. They depend on the difference in the mechanical and thermal characteristics of the adhesive couple components and on the difference between the test temperature T and the glass transition temperature of the adhesive T_g, i.e., to a first approximation, on the $\Delta T = T_g - T$ value.

The structure of near-surface layers determines the mechanisms of nucleation, development, and propagation of defects (cracks) responsible for the fracture of adhesive joints and, accordingly, for their interfacial strength. The structure of a polymer adhesive in the bulk and in the layers adjacent to the interface is formed during curing. In this case, one of the main questions is whether the structure of the adhesive after curing is single-phase or heterophase.

It is clear from the above that, to elucidate the dependence of the factors that determine the measured τ value on the nature and amount of the modifier, it is necessary to study a number of characteristics of the adhesive in the liquid state, during curing, and in the solid state (after curing). It is necessary to know how the modification affects the equilibrium contact angles, which characterize the wetting ability of the adhesive; the rheological characteristics of the adhesive before and during curing, i.e., primarily, the temperature–time and concentration dependences of viscosity; the glass transition temperature of the adhesive; and the behavior of the σ–ε diagrams. These parameters can be used to determine the magnitudes of the elastic moduli, which are required for estimating the residual stresses, and detect the development of inelastic (particularly plastic) deformations in the matrix upon the addition of a modifier, data on which make it possible to discuss the fracture process in the matrices and their adhesive joints. In addition, it is necessary to know changes in the thermal expansion coefficients, which are also used in the assessment of residual stresses, and changes in the structure of the blend matrix upon the addition of a minor component. To reveal the last-mentioned changes, it is necessary to study the absorbance during curing, construct phase diagrams, and subject the structure to electron microscopy and X-ray diffraction analyses.

To the best of our knowledge, the full-range studies have not been performed for any system. The studies of the adhesion of polysulfone-modified epoxy resins were the fullest, the closest to the "ideal."

The following can be added to the above. The main aim of modification of epoxy matrices is the formation of composites with improved physicomechanical characteristics, in particular, with a higher impact resistance and crack resistance. Therefore, it is only natural that studies of the properties of matrices and the fiber–matrix interface should be combined with studies of the properties of composites based on these matrices. Only in this case it is possible to determine whether the selected type of modification is advantageous. The determination of correlations between the properties of composites and the properties of matrices (bulk and surface) provides a targeted control of the properties of the composites. This means that the studies mentioned above should be supplemented by a study of the physicomechanical characteristics of composites based on blend matrices.

However, this range of issues is beyond the scope of this manuscript, in which we confine ourselves to the description of the effect of modification on the interfacial strength and the mechanisms governing the changes caused by the modification.

These issues are discussed in Chapters 1–3. In addition, Chapter 4 describes results on the further development of the pull-out method, which is the main method used to study the interfacial strength in polymer–fiber joints.

LIST OF ABBREVIATIONS

CNT - carbon nanotubes
DADPS - 4,4’-diaminodiphenyl sulphone
DMA - dynamic mechanical analysis
DMAA - dimethylacetamid
GEG - diethylene glycol
FS - fluorinated surfactants
FCNT - functionalized CNT
PAEK - polyarylene ether ketone
PSK - polysulphone adhesive
PS - polysulphone
PEI - polyetherimide
PEPA - polyethylene polyamine
TEAT - triethanolamine titanate
ShF - shungite filler

PRINCIPAL SYMBOLS

A – surface activity of surfactants
C – the amount of injected modifier (relative to the weight of resin) (concentration)
d – fibre diameter (substrate)
D – dispersion of adhesive strength value
E_{ben} – modulus of elasticity under bending
E_t – tensile modulus
F – force required to break an adhesive joint
G – polymer shear modulus
k – sensitivity of the interface to the rate of application of an external load
K – relative sensitivity of the interface to the rate of application of an external load
l – adhesive joint length
MM– molecular mass
n – total number of test specimens
n_τ – number of joints fractured adhesively
n_σ – number of joints fractured cohesively
Q – heat flow
r – radius of the fibre, the adhesion of which is determined by
S – area of adhesive joint
S_{sp} – specific surface area of dispersed fillers
t_c – time of cure
t_f – time during which adhesion joints are fabricated
T_f – temperature at which adhesive joints are fabricated
W – water absorption
α – coefficient of linear expansion
α_h – degree of resin hardening
β – conversion of reactive groups
G_m – maximum adsorption of surfactant
H_l – limiting surfactant adsorption
η_{red} – reduced viscosity
θ – contact angle
ρ – substance density
σ – surface tension of polymers

σ_c – composite strength
σ_{res} – residual stress
τ – shear adhesive strength in fibre-polymer system
τ_0 – adhesion strength of control joints (not exposed to the test factor)
τ_t – adhesion strength of joints that have been in a liquid for a time t
τ_T – temperature residual stresses
τ_{loc} – local adhesive strength
τ_{res} – residual stresses acting at the polymer-fibre interface
τ_{exp} – experimentally measured adhesive strength

CHAPTER ONE

EFFECT OF THE NATURE AND AMOUNT OF THE MODIFIER ON THE ADHESIVE STRENGTH OF EPOXY–FIBER JOINTS

1.1. Adhesion of Epoxy Resins Modified with Active Diluents

Epoxy oligomers are modified with active diluents to decrease the viscosity, improve the processing characteristics of the original (liquid) compositions and increase the elasticity of the cured resins.

The commonly used active diluents are aliphatic epoxy resins, i.e., glycidic esters of polyhydric alcohols characterized by a low molecular mass, a high content of epoxy groups, and a low viscosity. They are involved in the formation of epoxy oligomers and included in their structure.

Let us consider how the adhesive ability of the ED-20 epoxy oligomer changes after modifying it with diethylene glycol diglycidyl ether DEG-1, which is a widely available and commonly used active diluent.

The variation in the strength of ED-20+triethanolamine titanate (TEAT)–steel wire joints upon the addition of DEG-1 into to the resin is shown in Fig. 1-1. Note, first of all, that the base of the studied compositions—unmodified resin ED-20—interacts with a wire to form one of the strongest (compared with other epoxy resins) interfaces (Fig. 1.1). The adhesive strength of the minor component—DEG-1—with the same wire is 30–50 times lower. However, the addition of it into the resin at concentrations of $C \leq 50$ wt % leads to an increase in the interfacial strength, rather than to a decrease in it: the τ–S curve of the ED-20+TEAT system is localized below the τ–S curves of the ED-20+TEAT+DEG-1 systems for joints of all sizes. Figure 1.1 shows this effect for an adhesive containing 50 wt % DEG-1. (All adhesive strength values given in this chapter were obtained at room temperature and a loading rate of $\dot{F} = 1$ N/s).

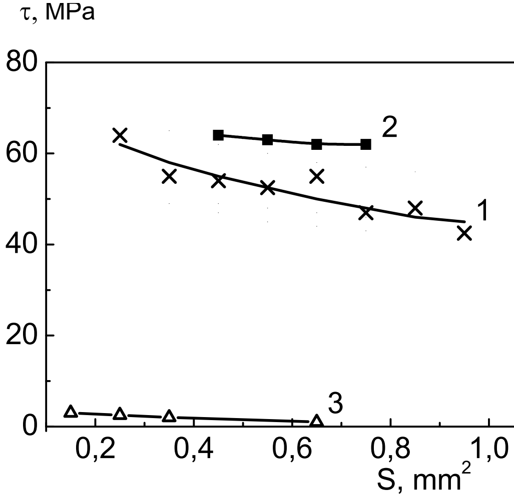

Fig. 1-1. Dependence of adhesive strength τ on the area of joints *S* for ED-20+TEAT+DEG-1–steel wire systems (*d* = 150 μm) at various DEG-1 concentrations in the matrix (*C* (%): (*1*) 0, (*2*) 50, and (*3*) pure DEG-1).
Data on plotting the τ–S curves are given in A1.

The same figure (Fig. 1-1) clearly shows that the τ values depend on the size of the joint; they monotonously and nonlinearly decrease with increasing *S*. This decrease in τ is a common phenomenon. It is observed for joints of thermosetting and thermoplastic polymers with fibers of any nature and any diameter, if the measurements were conducted at temperatures *T* below the glass transition temperature of the polymer T_g: $T < T_g$. It is known [30, 31, 34–46] that the behavior of the dependence represents a nonuniform distribution of tangential stresses—both external (applied) and “internal” residual (primarily thermally induced) stresses existing in the joints before their loading and, as was noted in the Introduction, arising during the preparation of the specimens and their cooling to test temperature *T*—at the fiber–polymer interface.

With an increase in the amount of the active diluent introduced into the matrix, the τ(*S*) dependence becomes less pronounced; this relationship seems only natural. In fact, the DEG-1 diethylene glycol used to modify the epoxy matrix has a plasticization effect: the introduction of it leads to a decrease in T_g (Fig. 1-2). Since the interfacial residual stress value is proportional, to a first approximation, to $\Delta T = T_g - T$ (in our case $T \approx$ 20°C), with a decrease in T_g, the ΔT value becomes lower, the residual stresses decrease, and their distribution becomes more uniform. It is this factor that leads to a more gently sloping τ–*S* dependence.

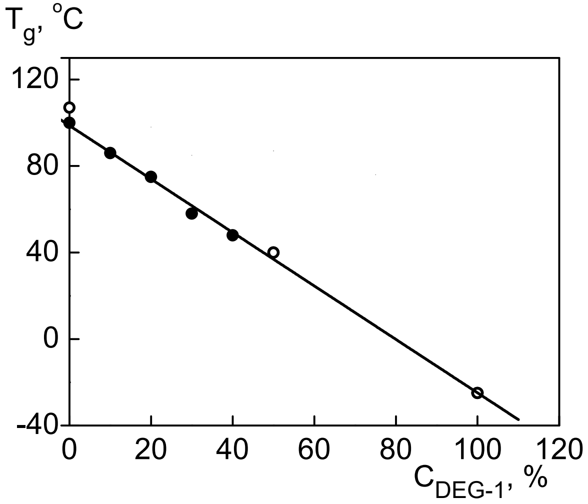

Fig. 1-2. Variation in glass transition temperature T_g after modifying the ED-20 epoxy resin with diethylene glycol diglycidyl ether DEG-1. The T_g values are determined: (•) from thermomechanical curves and (o) by the DSC method.

The concentration dependence of the adhesive strength of the studied joints (at $l/d \geq 6$) is described by a curve with a weakly pronounced maximum (Fig. 1-3), which is observed at a diluent content of 40–50%. The increase in the τ values at the maximum (relative to the adhesive strength of the unmodified resin) is 15–20%. Figure 1-3 also shows the concentration dependence recorded after introducing the DEG-1 active diluent into the ED-16 epoxy resin cured at room temperature with polyethylene polyamine (PEPA); the τ–*C* dependence is also described by a curve with a maximum, and the maximum is also observed at large amounts of the diluent (~40 wt %).

Thus, the plasticization of the ED-20 resin, which exhibits a high adhesive ability, with diethylene glycol, which is a component with an extremely low adhesive ability, does not decrease the adhesive strength in joints with fibers; in a certain concentration range, the plasticization even increases this parameter. In other words, upon the introduction of the DEG-1 active diluent into ED-20, the synergistic effect of adhesive strength is observed.

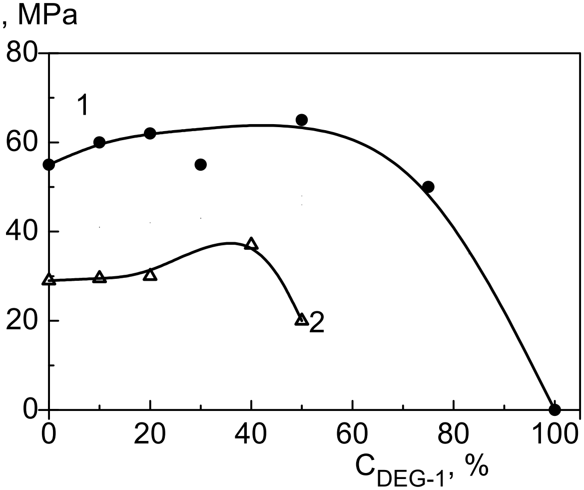

Fig. 1-3. Dependence of adhesive strength τ of modified epoxy binder–steel wire joints *(d* = 150 μm) on the amount of the DEG-1 active diluent:
(*1*) ED-20+TEAT+DEG-1 at $S = 0.55$ mm^2 ($l/d \approx 7.5$) and
(*2*) ED-16+PEPA+DEG-1 at $S = 0.95$ mm^2 ($l/d \approx 13$).

The following question now arises: what are the causes of this effect? To answer it, we will consider how factors responsible for the measured adhesive strength value change during plasticization.

DEG-1 is an active diluent capable of incorporating into the polymer chain. The use of it does not change the nature of the bonds acting at the adhesive–fiber interface. The introduction of DEG-1 leads to an extremely effective decrease in viscosity (η): upon the addition of 20% DEG-1 into the ED-20 resin, the η values decrease by almost 2 orders of magnitude (Fig. 1-4).

A decrease in viscosity accelerates the spreading of the compositions over the surface of solids and contributes to a decrease in the interfacial imperfection. However, the wetting ability of the unmodified ED-20 resin is fairly high; for example, the equilibrium contact angles θ formed by ED-20 on glass fibers do not exceed 12°. Modifying leads to as low decrease in θ as 2°[1]. Therefore, the resin–fiber contact areas in all ED-20+TEAT+DEG-1 systems can be considered the maximum possible and

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[1] The measurements were conducted by the Shcherbakov–Ryazantsev method [47, 48]; the θ values were calculated from the parameters of small droplets deposited directly on the fibers.

almost identical. This means that the modifying of the ED-20 oligomer with the DEG-1 active diluent should not lead to an increase in the number of bonds established at the interface during curing and a significant decrease in the interfacial imperfection. Accordingly these factors cannot be responsible for an increase in the adhesive strength.

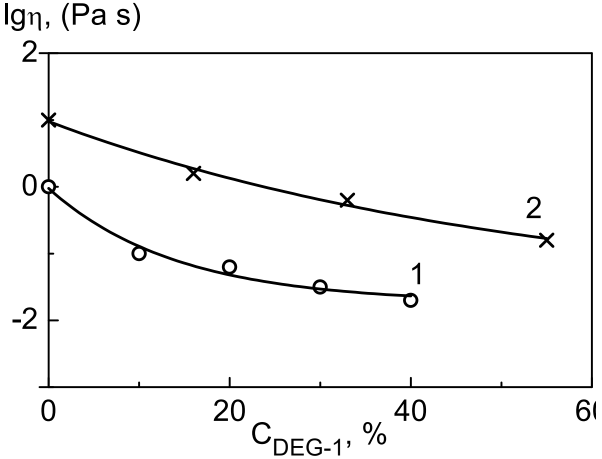

Fig. 1-4. Dependence of the logarithm of viscosity lgη of epoxy compositions on amount *C* of the introduced active diluent: (*1*) ED-20+DEG-1+TEAT and (*2*) ED-16+DEG-1+TEAT.

The ED-20+DEG-1+TEAT systems do not undergo phase separation during curing and remain single-phase after curing at any DEG-1 concentration. This finding is evidenced by the almost linear decrease in the glass transition temperature upon the introduction of diethylene glycol into ED-20 (Fig. 1-2), the study of the thermal degradation of cured polymers [49], and the transparency of the cured specimens. Therefore, there is no reason to attribute the increase in the measured adhesive strength values to a change in the structure and properties of the near-surface layers and, hence, to a change in the failure mechanisms.

Thus, the key factor determining the change in τ upon modifying should apparently be considered the change in the residual stresses τ_{res} existing at the interface. As noted above, the τ_{res} value is proportional, to a first approximation, to the difference $\Delta T = T_g - T$, which, in the case under consideration, where all measurements were conducted at room temperature, decreases with an increase in the amount of DEG-1 introduced into the resin. Accordingly, the τ_{res} values should decrease, and their distribution should become more uniform; it is these effects that were observed in experiments (Fig. 1-1).

A decrease in τ_{res} leads to a gradual increase in the adhesive strength of the joint of the studied compositions with fibers (Fig. 1-3) to fairly large *C* values of $\cong$ 50 wt %.

However, a decrease (narrowing) of the ΔT range also means that the measurement temperature approaches the glass transition temperature of the binder, while the adhesive strength decreases (similar to the cohesive strength of the polymers).

When the DEG-1 content in the ED-20+DEG-1+TEAT system achieves 50 wt %, the glass transition temperature approaches room temperature. At higher DEG-1 concentrations, the compositions are in the rubberlike state and the adhesive strength values above T_g decrease by several dozen times.

Thus, upon modifying the ED-20 epoxy oligomer with the DEG-1 active diluent, the maximum in the concentration dependence of the adhesive strength arises from the plasticization of the epoxy binder. Plasticization leads to the following: first, a decrease in the interfacial residual stresses and, second, the approximation of the measurement temperature to the region of transition of the binder from the glassy state to the rubberlike state. The superposition of these two competing processes leads to the appearance of a maximum in the concentration dependence of the adhesive strength and the synergistic effect of the interfacial strength.

1.2. Adhesion of Epoxy Resins Modified with Heat-Resistant Thermoplastics

The modifying of epoxy resins with heat-resistant thermoplastics, which is commonly used at present, provides the formation of polymer blends exhibiting a high crack and impact resistance without deteriorating their heat resistance. Polysulfones (PSFs) [10–15, 50–57], polyethersulfones [16, 17, 58–60], polyether ketones [61, 62], polyetherimides (PEIs) [8, 9, 63–69], and other thermoplastics are added to epoxy resins [70–83]. The maximum amount of the introduced thermoplastic usually does not exceed 20–25%, because thermoplastics significantly increase the viscosity of epoxy compositions; at a higher content of thermoplastics in the blend, they become unprocessable.

In the initial state, rigid-chain linear polymers are solid substances that exist in the form of powders, granules, films, etc. To provide the formation of adhesive joints with solids (particularly fibers), thermoplastics should be converted into a melt capable of wetting the surface of the substrate. Without applying pressure, this effect can be achieved only at fairly high temperatures and fairly long contact times between the adhesive and the substrate.

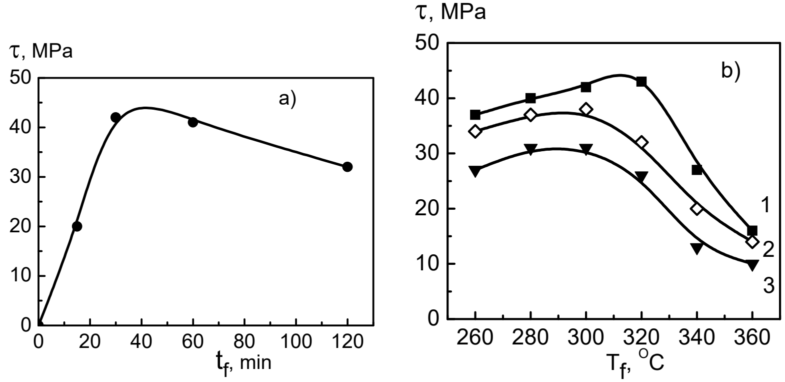

Fig. 1-5. Effect of (a) time t_f and (b) temperature T_f of formation on the adhesive strength of PSF–steel wire joints (wire diameter of $d = 150$ μm):
(a) $T_f = 300$°C and $S = 0.55$ mm^2 and (b) $t_f = 1$ h and $S =$ (*1*) 0.55, (*2*) 0.75,
(b) and (*3*) 1.05 mm^2.

A typical example is shown in Fig. 1-5. Here, the interfacial strength of PSF–steel wire pairs under different temperature–time conditions for the formation of adhesive joints is shown. It is evident that, for this couple, joints with maximum interfacial strengths can be formed at temperatures of 300–320°C and contact times of 30–60 min. Below 260°C, a high-quality interface (without pores and discontinuities) cannot be formed for the following reasons: a homogeneous polymer melt is not formed below this temperature; wetting, which is a necessary condition for adhesion, does not occur; and, accordingly, bonds between the fiber and the polymer are hardly formed.

In the case of using epoxy resin–PSF blends as matrices of fibrous composites, they are usually cured at temperatures of 160–200°C. In this case, fiber–epoxy resin bonds are formed at the interface; as follows from the above, fiber–PSF bonds cannot be formed. The same is true of other epoxy resin–heat-resistant thermoplastic blends (epoxy resin–PEI, epoxy resin–poly(arylene ether ketone) (PAEK), etc.).

Thus, to modify epoxy resins with rigid-chain thermoplastics, the component added to the resin should exhibit adhesive ability that is really close to zero under the temperature–time conditions used to cure the epoxy resins.

Accordingly, to use epoxy resin–heat-resistant thermoplastic blends as binders in the production of reinforced plastics (primarily those based on continuous fibrous fillers), it was necessary to elucidate the laws governing the change in their adhesive properties during modifying and the mechanisms that control them.

Figures 1-6 and 1-7 show the effect of the modifying of epoxy resin with a typical representative of heat-resistant rigid-chain thermoplastics—PSF PSK-1—on the interfacial strength of the ED-20 resin–steel wire joints. It is evident (Fig. 1-6) that the scale dependences of the adhesive strength τ–S of epoxy resin–PSF blends are described, as usual, by monotonically descending curves. The addition of PSF leads to an increase in the interfacial strength; moreover, in the studied concentration range, the increase is nonmonotonic: the τ values of the 5% epoxy resin–PSF blends are very close to the τ values of the unmodified resin, and the curve describing the τ–S dependence for the blend with 20% PSK-1 is close to the curve of the 10% blend. The maximum amount (20 wt %) of the introduced modifier is limited to the viscosity of the resulting polymer blend and the possibility of preparing joints with a well-formed interface, which is associated with the viscosity.

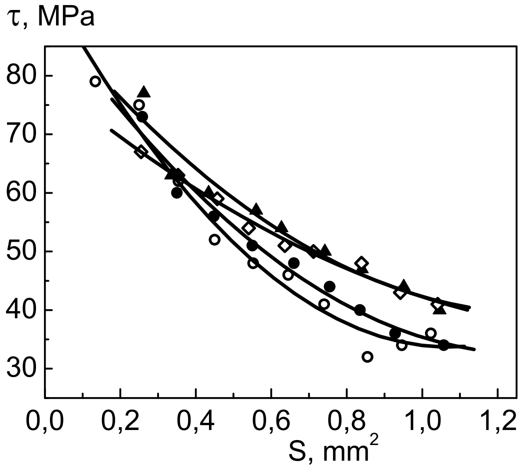

Fig. 1-6. Dependence of adhesive strength τ on the area of joints S for ED-20+TEAT+PSK-1–steel wire systems (d = 150 μm) on the PSK-1 content in the matrix (C, %): (o) 0, (•) 5, (▲) 10, and (◊) 20. Conditions for the preparation and curing of blends are given in A2.

The nonmonotonic change in adhesive strength is clearly seen in Fig. 1-7: the concentration dependences of τ of ED-20+PSK-1+TEAT–steel wire joints are described by curves with a maximum. The behavior of the τ–C curves is almost independent of the specimen size ($l/d \geq 6$–8). In all the cases, a maximum is observed after the addition of 10–12% PSK-1 into the matrix; the increase in τ values at the maximum achieves 25–40% (relative to the value of the unmodified ED-20 resin).

Thus, the addition of small amounts of rigid-chain linear PSF PSK-1 to the ED-20 epoxy resin leads to the occurrence of the synergistic effect of adhesive strength: in a certain concentration range, the adhesive ability of the resulting blend is higher than the adhesive ability of the sum of the components.

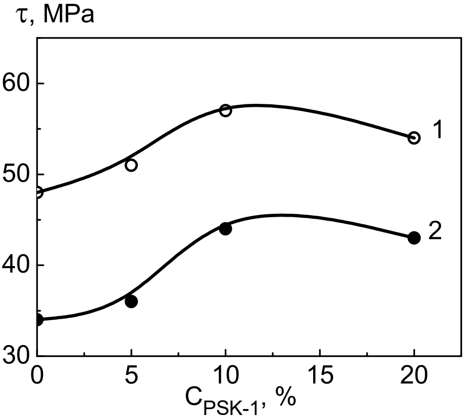

Fig. 1-7. Dependence of adhesive strength τ in the ED-20+TEAT+PSK-1–steel wire system (d = 150 μm) on the PSK-1 modifier concentration C. Area of adhesive joints S = (*1*) 0.55 and (*2*) 0.95 mm^2.

The modifying of ED-20 with PSF makes it possible to prepare binders providing the same high adhesion to fibers as in the case of modifying the resin with the DEG-1 active diluent, i.e., binders, whose adhesive ability is not inferior to that of the best epoxy compositions (see Figs. 1-1 and 1-6).

Earlier, it was repeatedly shown [28, 30, 31, 85–87] that, if the change in the adhesive strength under the action of a particular factor is determined mostly by the matrix, then the relationships established in the case of using a steel wire as a substrate are preserved for adhesion to fibers of a different chemical nature (with a high surface energy). The results obtained for the studied blends confirm these conclusions.

Figures 1-8 and 1-9 show the effect of the amount of the introduced PSF on the interfacial strength for blends interacting with glass and polyamide (capron) fibers (dependences are obtained from the τ–S curves similar to those shown in Fig. 1-6); the figures suggest that the nature of the fiber significantly affects the strength level of the resulting joints. Epoxy resin–PSF blends form extremely strong joints with glass fibers; these joints are not inferior to joints with a steel wire (if the τ values are measured for specimens of comparable geometry, see Table 1-1). In the joints with polyamide fibers, the adhesive strength is significantly lower than that with steel and glass fibers. Apparently, this fact is attributed to the lower surface energy of capron fibers.

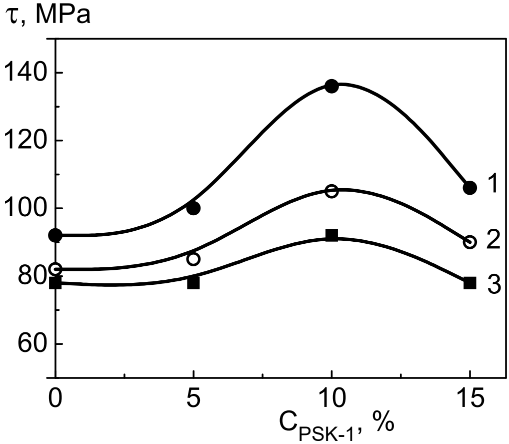

Fig. 1-8. Dependence of adhesive strength τ in the ED-20+TEAT+PSK-1–glass fiber system (d = 13–30 μm) on the PSK-1 modifier concentration C. Area of adhesive joints S = (*1*) 2×10^{-3}, (*2*) 3×10^{-3}, and (*3*) 4×10^{-3} mm^2. The loading rate is 10^{-3} N/s.

Table 1-1. Geometric dimensions of the joints (at *l*/*d* ≅ 7) and the adhesive strength of the ED-20+TEAT–fiber systems

Fibers	Fiber diameter *d*, μm	Length of joint *l*, μm	Area of joint *S*, mm^2	τ, MPa
Steel	150	1000	0.55	50
Glass	~30	200	0.01	55
Polyamide (capron)	200	1400	0.95	10