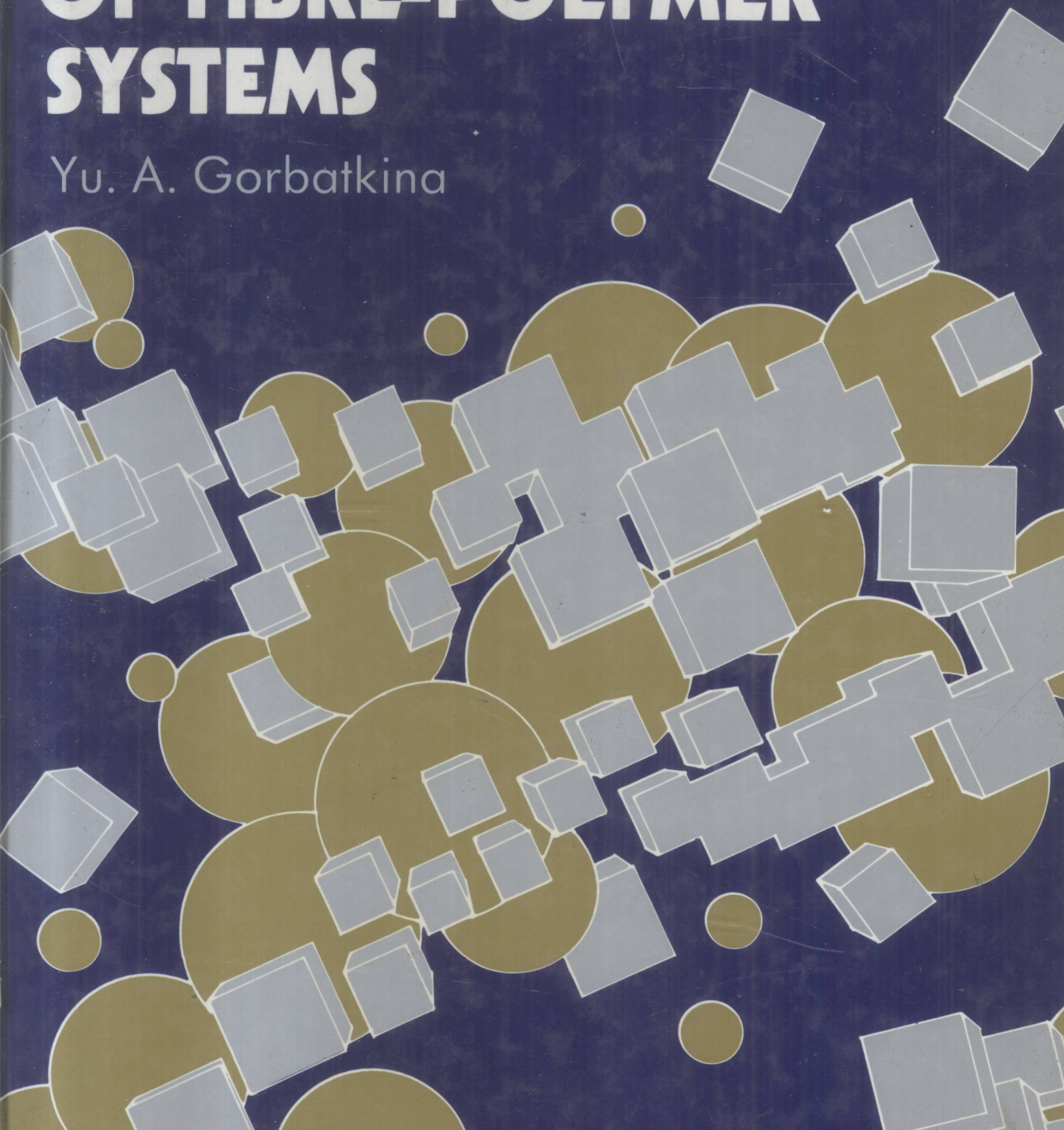


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ADHESIVE STRENGTH OF FIBRE-POLYMER SYSTEMS

Yu. A. Gorbatkina



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ADHESIVE STRENGTH IN FIBRE-POLYMER SYSTEMS

YU. A. GORBATKINA

Institute of Chemical Physics, Academy of Sciences,
Moscow, Russia

Translator:

A. A. BEKNASAROV



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Preface to the English edition

(adapted from that to the Russian edition)

High-strength composite materials, in particular composite materials with polymeric matrices, have been extensively used over the last 20 to 30 years in various branches of industry and technology, including aircraft, automotive and rocket engineering, and ship-building.

The highest strength and rigidity are exhibited by fibre-reinforced plastics. Their properties depend significantly not only on the properties of the fibrous filler and matrix but also on the mutual interaction between these components, especially on the interfacial adhesion strength, since it is precisely this parameter which determines the efficiency of stress transfer across the interface. Therefore, for the properties of composites to be monitored in a chosen direction, it is necessary to know the adhesion of the binders to the fillers and its variation under the influence of various factors.

The processes that occur at the surface depend to a considerable extent on its state. Therefore, in order to judge the effect of adhesion on the physicomachanical characteristics of a reinforced material, one must study the adhesion of real binders to real fillers, i.e. to the fibres which are used in the fabrication of reinforced plastics, with a particular geometrical and energy state of their surface in the material.

The adhesion capacity of rigid polymers is mostly evaluated from their adhesive strength. Determinations of adhesive strength are mainly carried out on macro-sized specimens. To do this, flat surfaces are glued together, the bonded area being equal to tens and hundreds of square millimetres. It is well known, however, that the strength value depends on the size of the test specimens. Naturally, there are no grounds for expecting that the adhesive strength established for flat surfaces will be similar to that for cylindrical surfaces with a diameter of 1–100 μm (which is typically the diameter of fibres used in the manufacture of composites). It should also be noted that for most high-strength reinforcing fibrous fillers currently employed (carbon, boron, organic, silicon carbide) it is impossible to prepare bulky specimens (in the form of plates, prisms, etc.) with a surface identical to that of fibres. Therefore, the direct determination of adhe-

sive strength in a fibre-matrix system is the only way to evaluate the strength of adhesion to these fillers.

A fibre, together with its adjacent adhesive layer, is the elemental unit of any fibrous composite. Therefore, in order to realize as closely as possible the conditions which exist in a reinforced system, one should study adhesive strength exactly in such an elemental unit, i.e. in the fibre-polymer system. The study of adhesive strength on micro-sized samples requires very small quantities of either of the components, which is especially important in the determination of the adhesion of novel binders and also of the adhesion to new types of fibre.

The present book is devoted to the study of the adhesive strength of joints with fibres used as substrates. Investigations of such joints have been carried out in the USA, France and Finland, but a more detailed and systematic study of fibre-polymer systems has been conducted in the Reinforced-Plastics Laboratory of the Institute of Chemical Physics of the USSR Academy of Sciences. Most experimental results described in the book have been obtained in our laboratory over the last two decades, and our most recent data appear in this English edition.

Investigations of adhesive strength were started in our laboratory for the simple reason that the designers of composite materials—engineers and technologists—were faced with the need to compare the strengths of bonding of various adhesive-adherend combinations and to know the dependence of adhesive strength on various factors—the type and composition of adhesives, type of fibre, service temperature, storage conditions, etc. Therefore, the book is concerned primarily with the behaviour of adhesive strength in systems used for the fabrication of high-strength composite materials. Of the numerous factors that influence adhesion, priority is given in the book to those which play a significant role in the fabrication, storage and application of fibre composites.

The English edition of this monograph is a revised and enlarged edition of the book published previously in Russian and containing new material.

The inclusion of the material in this English version will enable the reader to follow more readily the correlations between the adhesive strength, on the one hand, and the strength of polymers and fibre composites, on the other. Another feature is the presentation of data on the adhesive strength of fibre-thermoplastic matrix joints.

The experimental results described here have been mainly obtained by the pull-out technique, which makes reliable comparisons possible. This is very important since the experimentally-derived values of strength (for polymers themselves and their adhesive joints) always depend on the measuring technique and experimental details (in particular, on the shape and size of specimens). Accordingly, comparison of results obtained by a variety of techniques often appears to be less convincing.

The data presented in the book refer largely to adhesives and fibres used in the fabrication of composite materials in Russia. However, it is not the absolute values of the quantities measured which are of interest, but the establishment of general relationships. These relationships are normally of general validity. The data obtained can be used for the analysis and prediction of changes in the properties of similar systems brought about under the influence of the same factors. For example, the book cites many data on the adhesive strength of joints composed of the resin EDT-10 and various fibres. This resin consists of the epoxy oligomer ED-20 (an analogue of DGEBA), diethylene glycol and

triethanolamine titanate, the latter being the curing agent). It is a typical representative of the family of resins used world-wide and based on the diglycidyl ether of Bisphenol A (DGEBA) and the relationships found for it can be extended to all similar matrices.

In concluding this preface, I wish to express my deep gratitude to the translator, Artavaz A Beknazarov, who has put much effort into the translation of the book into English and who has patiently and painstakingly gone through the difficult job of inserting the numerous corrections and additions made by the author during preparation of the manuscript. I also wish to thank those institutions and firms engaged in the design, production and application of fibre composites with whom I have enjoyed a close and successful collaboration. Finally, I wish to thank the Publishers, Ellis Horwood Limited of England, and Professor T. J. Kemp of Warwick University, who have given me guidance and advice and the opportunity to enlarge the first edition of the book and thereby to bring the content up to date as far as possible.

November, 1991
Moscow

Yu. A. Gorbatkina

Abbreviations

ABV	Bakelite (trade name (tn))
AER	Aliphatic epoxy resin
AG-4	Phenol-formaldehyde compound (tn)
AGM-3	Aminosilane (tn)
AGM-9	Aminosilane, γ -aminopropyl triethoxysilane (tn)
B-1	Polysiloxane (tn)
BF	Butvar-phenolic adhesives (tn)
BSL	Resol composition (tn)
DADPS	4, 4'-Diaminodiphenyl sulphone
DAP	Diaminopyridine
DEG-1	Diethylene glycol (tn)
DGER	Diglycidyl ether of epoxy resorcinol
DMDCS	Dimethyldichlorosilane
E-40	Epoxy resin (tn)
E-181	Diepoxide resin (tn)
EA	Diepoxide resin (tn)
ED-16	DGEBA-based epoxy resin (tn)
EDF	Epoxy chlorine-containing adhesive (tn)
EFB-3	Epoxy phenolbutyral resin (tn)
EKhD	Epoxy chlorine-containing adhesive (tn)
EKT-15E	Epoxyaniline (tn)
ETP	Epoxy triphenolic resin
ETsT-1	Epoxycyanuric adhesive (tn)
EC-15	Resin based on cyanuric acid and epichlorohydrin (tn)
FGE	Furylglycidyl ether
FN	Novolac composition (tn)
GMA	Glycidyl methacrylate
HDPE	High-density polyethylene
HTS	Sizing agent (tn)

IF	Bakelite (tn)
K-115	Epoxy compound (tn)
K-21	Silicone sizing agent (tn)
LDPE	Low-density polyethylene
MDF-2	Polyester acrylate (tn)
MTHPA	Methyltetrahydrophthalic anhydride
PAFO	Phenolanilinoformaldehyde oligomer
PAIS	Polyamidoimide adhesive (tn)
PC	Polycarbonate
<i>m</i> -PDA	<i>m</i> -Phenylene diamine
PEPA	Polyethylene polyamine
PMPS	Polymethylphenylsiloxane
PN-1	Polyester resin (tn)
PP	Polypropylene
PPS	Poly(phenylene sulphide)
PPSS	Poly(phenylene sulphidesulphone)
PS	Polysulphone
PVA	Poly(vinyl acetals)
PVB	Poly(vinyl butyral)
PVBC	Polyvinyl butyralcrotonal
PVFE	Polyvinyl formalethylal
PVBF	Polyvinyl butyralfurfural
SF-342	Resol resin (tn)
SP-6	Polyimide resin (tn)
TEA	Triethanolamine
TEAT	Triethanolamine titanate
TEG-1	Triethyleneglycol (tn)
UP-637	Epoxy resorcinol (tn)
V-550P	Vinilkid-550P (tn)
VFT	Resol composition (tn)
VM-1	Analogue of S-glass (tn)
VMP	Analogue of S-glass (tn)
VNIIVLON	Organic fibre (tn)

Principal symbols

C	Concentration
D	Gap diameter in the grip for testing fibre-polymer joints
d	Fibre diameter
d_{av}	Average fibre diameter
E	Tensile modulus
E_f	Tensile modulus of fibre
E_m	Tensile modulus of resin (matrix)
E_c	Tensile modulus of composite
F	Externally applied force
h	Thickness of composite specimen
G	Relative rigidity
L	Span length (in a three-point scheme of determination of interlaminar shear strength of composites)
L/h	Span-to-depth ratio
ℓ	Length of adhesive-bonded joints
ℓ_{av}	Average length of adhesive joints
n	Total number of test specimens
n_τ	Number of joints fractured adhesively
n_σ	Number of joints fractured cohesively (across the fibre)
n_r	Number of joints fractured within the resin
r	Fibre radius
S	Area of adhesive joint
S_{av}	Average area of adhesive joint
S_{sp}	Specific fibre surface
T	Temperature at which measurements are made
T_c	Cure temperature
T_{max}	Temperature at which a maximum is observed in the τ v. T curve
T_g	Glass-transition temperature

xvi **Principal symbols**

T_f	Temperature at which joints are fabricated
t	Loading time
t_c	Time of cure
t_{age}	Ageing time
t_f	Time during which joints are fabricated
U_o	Activation energy of fracture process
α	Degree of conversion of reactive groups (degree of cure)
α_o	Degree of cure at which adhesive strength can be measured
α_{max}	Degree of cure at which a maximum appears in the τ v. α or τ v. t_c curves
α_{∞}	Maximum possible degree of cure at a given temperature
α_{in}	Degree of cure by the ageing time
ϵ (or ϵ_m)	Relative elongation of adhesive
η	Viscosity
ρ	Density
σ	Strength
σ_f	Tensile strength of fibre
σ_m or $\sigma_{t,m}$	Tensile strength of matrix
σ_c or $\sigma_{t,c}$	Tensile strength of composite
σ_{com} or $\sigma_{com,c}$	Compressive strength of composite
σ_b or $\sigma_{b,c}$	Bending strength of composite
τ	Shear adhesive strength
τ_o	True adhesive strength
τ_{exp}	Value of adhesive strength measured experimentally
τ	Value of adhesive strength with competing fracture processes
τ_{loc}	Local adhesive strength
τ_{max}	Value of adhesive strength at the maximum of the τ v. t_c or τ v. α plots
τ	Rate of stress growth upon loading of adhesive joint
τ_{sh}	Shear strength of composite
τ_{ILSS}	Shear strength of composite measured with a three-point loading scheme
τ_T	Temperature tangential residual stresses at fibre–matrix interface
τ_{Tmax}	Maximum temperature residual stresses
ϕ	Bulk content of fibre in composite



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1

Measurement of adhesive strength in fibre-polymer systems

In a study of the adhesion on macro-size specimens the measure of adhesion forces between adhesive and substrate in a case where the contacting substances are in the solid or rubbery state is the adhesive strength or the specific work of adhesion. In the former case, adhesion is assessed by the stress required to separate the components and in the latter, by the work needed for separating (peeling off) the adhesive from the substrate.

The only types of mechanical test that can be carried out for the determination of the adhesive strength of fibre-polymer systems are shear and torsion tests. The tear-off test cannot be used for such systems since it is practically impossible to determine adhesive strength upon breaking of a butt joint, and upon detachment of fibres in cross-ply joints it is impossible to determine, with sufficient accuracy, the area of contact. The measurement of adhesive strength in torsion is not widespread. In order to determine the strength of bonding between polymers and fibres, use is almost always made of samples shown in Fig. 1.1. An adhesive joint is formed on the surface of a fibre embedded in the adhesive layer. The joint geometry is characterized by the length ℓ , which is determined by the polymer layer thickness, and by the area $S = \pi d\ell$, where d is the fibre diameter. (The quantity S may also be called the area of contact.) Upon failure of specimens, one measures the force F required to pull out the fibre from the adhesive layer, i.e. the shear adhesive strength is determined. The adhesive strength of each test specimen is calculated from the formula

$$\tau = F/S \quad (1.1)$$

A very important problem is the meaning of the value of adhesive strength as determined with the aid of this formula. In order for formula (1.1) to be strictly satisfied and, accordingly, in order to obtain the absolute value of τ , the following requirements must be met: (1) the cross-section of the fibre must be circular; (2) the diameter of the fibre portion embedded in the matrix must be constant; (3) the fibre must be coated uniformly

by the polymer; (4) the apparent and true areas of contact between fibre and polymer must be equal; (5) the tangential stresses must be constant at the fibre-polymer interface.

The requirement of the uniform distribution (constancy) of stresses in fibre-polymer joints is not satisfied, as a rule. For this reason, the value of adhesive strength determined by dividing the force by the area characterizes a certain averaged value of τ and is therefore a conditional quantity, like most of the quantities used for strength evaluations.

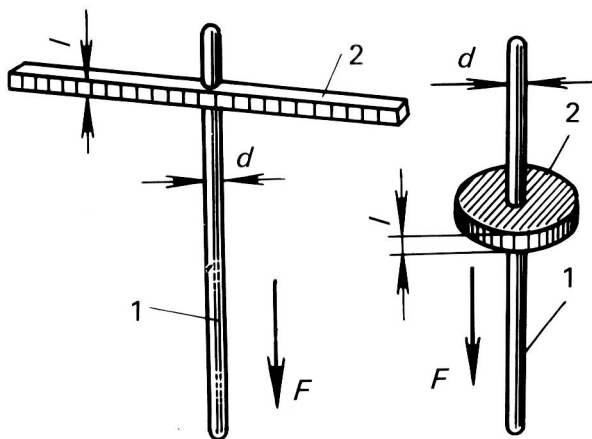


Fig. 1.1.1. Specimens for determination of shear adhesive strength in fibre-polymer joints: (1) fibre of diameter d ; (2) polymer layer of thickness l .

The character of the distribution of stresses operating at the interface will be considered in Chapter 3, where it will be shown that the use of these 'conditional' values of τ allows one to determine the local value of adhesive strength τ_{loc} , which is the 'true' value of τ characteristic of a given fibre-polymer combination. The fulfilment of the other prerequisites of formula (1.1) depends on the fibre preparation technique and on the fibre surface topography, and will be discussed below.

1.1 PREPARATION AND TESTING OF SPECIMENS

The main problem in the fabrication of fibre-polymer joints is to provide a sufficiently small joint area. Indeed, if the contact surface between fibre and polymer is too large, the adhesive forces will predominate over the cohesive forces, and when a load is applied, there will occur a break of the fibre rather than its pull-out from the adhesive. This refers to any type of fibre: glass, carbon, boron, mineral, metallic, synthetic, and textile. In any case, the fibre must be embedded in the polymer to a sufficiently small length, which depends on the type of fibre and adhesive, the diameter of the fibre and its surface condition, i.e. on the fibre strength and bonding strength. This length may vary from tens and hundreds of microns to a few millimetres.

Like cohesive strength, the adhesive strength of joints is a statistical quantity, and in order to determine it one has to test in each case several dozen specimens at least.