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High-strength and High-modulus Reinforced Plastics

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Studies of the formation, structure, deformation, and fracture of polymeric composite materials reinforced with long fibres are reviewed. The main factors which determine the strength and the elastic modulus of reinforced plastics under short-term static load are discussed.
The bibliography contains 110 references.

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I. INTRODUCTION

Plastics reinforced with an oriented array of long, high-strength, and high-modulus fibres are a new class of polymeric composite materials characterised by a marked anisotropy in physico-mechanical properties, depending on the type of fibres used, their mutual orientation, and the relative content of fibres in the matrix.

Because of the ease of controlling (between wide limits) the strength and the deformability of these materials, as well as some of their physicochemical properties (density, resistance to chemicals and to water, thermal and electrical conductivity, etc.), reinforced plastics can be used as constructional materials for a variety of applications, including highly stressed units and components.

We shall not attempt to discuss the structure, properties, and special features of reinforced plastics of various types, which have been recently reviewed in both Soviet and foreign publications[1-7], and we shall only examine the problems of retaining (or exploiting) the strength and the elastic modulus of the fibres in an oriented layer of reinforced plastic stressed in the direction of the fibres.

It is important to define correctly the initial characteristics of the strength members, i.e. the characteristics of the fibres when first prepared. The direct measurement of the properties of the fibre is complicated by the danger of damaging the sample (mechanically or physicochemically), thus degrading its properties while preparing the measurement samples[8]. These difficulties are most marked in the determination of the strength of the fibres, since in this case the measurements are affected not only by the sample preparation conditions but also by the scale factor, by the strain rate, and by the method of clamping the sample in the tensile tester. The measurement of the elastic modulus is usually straightforward, but in the case of organic fibres it may be influenced by several factors.

With oriented samples carefully prepared under laboratory conditions several workers have obtained characteristics corresponding to the initial properties of the fibres. This success makes it even more important to develop methods of quantitative analysis of the influence of various structural defects in real reinforced plastics on the mechanical properties of the components made from them.

Information on the adhesive strength of the fibre–polymeric matrix system is essential in studies of interactions in this system. Special models have been developed to calculate the adhesive strength, to identify the special features in the formation of the adhesion couple, and to give a quantitative formulation of the effect of the adhesive strength on the behaviour of the plastic under different stress conditions.

In addition to a strong adhesion the polymer matrix should offer a set of elastic and mechanical characteristics which ensures a uniform distribution of the stress over the system of fibres experiencing deformation under load. Theoretical work on this problem has been published both in the Soviet Union and abroad[9-12]. The use of epoxy polymer matrices in composite materials is reviewed by Rozenberg and Oleinik in the present issue of this Journal (see p.164).

The strength and elastic modulus of an oriented material under axially symmetrical load can be increased by increasing the relative content of reinforcing fibres. Therefore one of the problems in the design of reinforced plastics is the production of systems having a high packing density, with a regular hexagonal packing (in the case of fibres with a circular cross-section) and a minimum number of defects.

The materials known as hybrid polymer composites have attracted much attention during the past ten years. By combining within the same composite two or more types of fibre, or more than one matrix, we are able to control the properties of reinforced plastics between much wider limits, and in some cases we can achieve synergetic effects. It is also possible to vary the properties of the material in a prescribed way in the bulk across the cross-section of the item.

Another important area of research is concerned with the phenomena associated with the frontal or the uniform solidification of polymers and composite materials. Studies of stressed and strained states created during the formation, cooling, and storage of the material and of the residual stresses and strains (after relaxation) should lead to improved technological processes for the production of components from reinforced composite materials having the required properties.

We shall not attempt in this review to survey the whole of the current work on the development of high-strength reinforced plastics and on studies of their deformation and fracture and of their behaviour under practical conditions. The discussion will be confined mainly to the aspects developed by Enikolopov and his co-workers.

II. REINFORCED PLASTICS WITH AN ORIENTED STRUCTURE

1. Effect of the Strength and Length Distribution of the Elementary Fibres and Filaments on the Strength of Oriented Reinforced Plastics

One of the main problems in the study of the tensile strength of oriented composite materials is the determination of the initial strength of the fibres. Existing models of fibre structures can be used to calculate the elastic modulus

but are almost useless for predicting the strength characteristics of fibres[13].

The effect of the scale factor on the strength of elementary organic fibres (Vniivlon, Kevlar-49, Terlon) has been studied[14], and it was found that their strength characteristics are adequately described by the statistical theory of strength with a distribution function whose parameters are determined by the structure of the fibre. For Kevlar-49 and Terlon the strength distribution histogram was bimodal, due to the presence of various types of defect associated with the amorphous–crystalline structure of polymers showing a "shish-kebab" morphology[15].

The theory of the strength of a bundle of unattached fibres has been discussed[16] by assuming a Weybull distribution of fibre strengths. The high-grade physico-mechanical characteristics of reinforced plastics are the result of the simultaneous deformation of high-strength fibres interconnected by the polymeric binder. According to the statistical theory of fracture proposed by Rosen[11] the strength of an oriented composite material is equal to that of a bundle of non-interacting fibres of appropriate length (called the ineffective length, l_{ineff}). Experimental studies of the dependence of the strength of the bundle on the scale factor and comparisons with the strength of microscopic samples of plastic based on single fibres or braids (small bundles of fibres connected by the polymeric binder) have confirmed that the strength of a micro-plastic is the same as that of a bundle of unattached fibres of length l_{ineff}. This length can be calculated from the relative hardness of the components (according to Rosen) or from data on the adhesive strength in the fibre–polymer matrix system[17].

However, studies of reinforced plastics have brought to light a number of factors which are incompatible with Rosen's theory: 1) the dispersion of the strength of the fibres and of the micro-plastics is approximately an order of magnitude greater than the calculated value[14]; 2) the strength of the micro-plastics is dependent (albeit slightly) on the length of the sample, and falls off markedly when the standard ring specimen is replaced by real mechanical components and mass-produced items. These discrepancies are due to inhomogeneities and defects in the structure of real materials which are ignored in Rosen's idealised model. Among the most important of these effects is the instability of the properties of the fibres used, for example, in the windings of reinforced plastics.

Detailed studies have been made of the properties of filaments based on organic fibres: the scatter of the elastic moduli was relatively slight (variation coefficient $\nu_E \cong 4\%$), but the strength of the individual fibres within a braid covered a range of 20–25%, with a variation coefficient of 6–12% (depending on the length of the sample). The dispersion of the Weybull parameter β, which describes the effect of the scale factor, was also found to be relatively large[16].

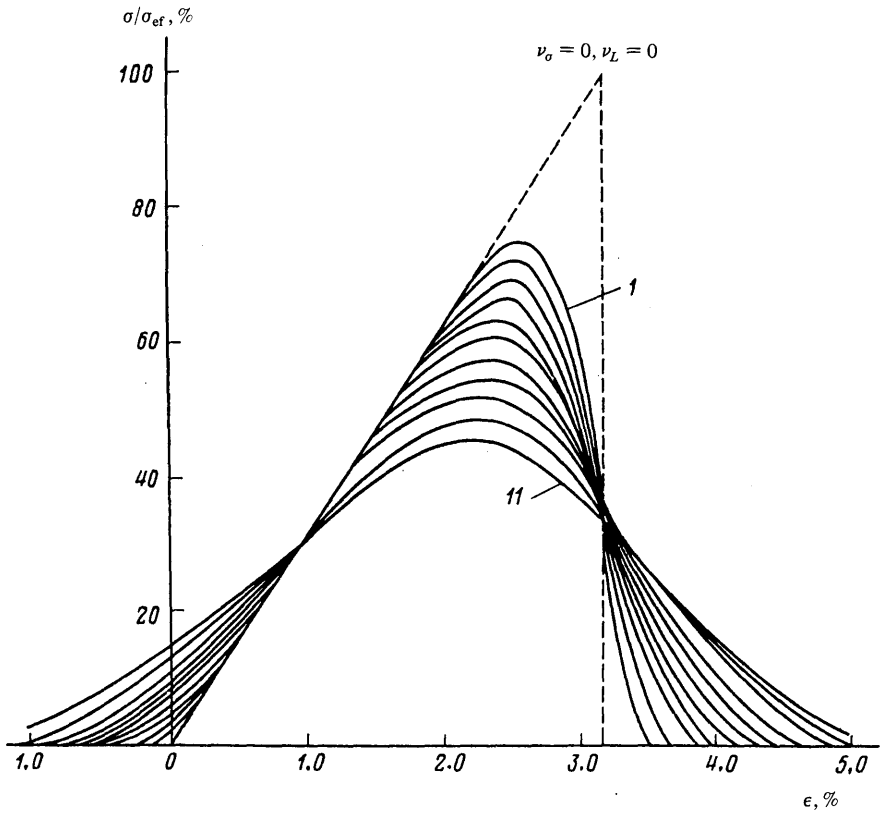


Figure 1. Tensile diagrams ($\sigma/\sigma_{ef}-\varepsilon$) calculated for bundles of organic fibres with different length dispersion: curves *1–11* correspond to variation coefficient of length (ν_L) between 0 and 1% in steps of 0.1%; σ is the strength of the bundle, σ_{ef} is the mean strength of the elementary fibre[18].

The interaction between the elementary fibres in the filaments, resulting from their partial adhesion during the production of the filament or from the twist in the filament, can be described by an appropriate ineffective length (for organic filaments, 20–150 mm), or alternatively by the ratio of the Weybull coefficients for the filament and for the elementary fibre respectively ($\beta_f/\beta_{ef} = 1.3–2.0$). The interaction between the fibres resulting from the presence of the polymer matrix causes l_{ineff} to decrease and β_f/β_{ef} to increase. For a micro-plastic based on Vniivlon filaments and an epoxy polymer matrix $l_{ineff} = 0.1–0.3$ and $\beta_{mp}/\beta_{ef} = 10–20$.

The $\sigma-\varepsilon$ tensile diagrams of the filaments for loads near the maximum for each sample usually include a non-linear region (due to a gradually increasing number of broken fibres, which produces a decrease in the aggregate cross-section of unbroken fibres). Micro-plastics under load break almost instantaneously, and a non-linear portion is not observed in the $\sigma-\varepsilon$ diagram, i.e. their behaviour under load is the same as that of elementary fibres.

However, because of the dispersion in the strength of the filaments themselves, which produces a dispersion in the strength of the resulting micro-plastics, a real reinforced plastic (for example, the ring samples with a uniform orientation) can be treated as a bundle of micro-plastics having different strengths. The breaking of one member of such a system creates a large-scale defect (a stress concentrator), which weakens the structure more markedly than the breaking of an individual fibre. This is one reason for the failure to exploit the initial strength of the elementary fibres in real reinforced plastics (as opposed to micro-plastics).

Another important contribution to the sequential breaking of the elementary fibres in real materials is the dispersion of the length of the fibres in filaments and in braids. Length inequality of the fibres in filaments occurs even at the fibre production stage, due to chemical and thermal fluctuations in the reaction region; dispersion of the length of fibres in braids occurs in the textile filament production processes (spinning and twisting), and also on the reeling machine.

A mathematical model[18] of the breaking of fibre bundles (filaments, or braids) which allows for the dispersion of the fibre length in terms of the variation coefficient ν_L has recently been proposed. The $\sigma-\varepsilon$ tensile diagrams calculated for braids in which ν_L varies from 0 to 1% are shown in Fig.1, and the dependence of the breaking stress of the braids on the parameter ν_L is shown in Fig.2. The broken lines are the tensile diagram for a single fibre or for a bundle with $\nu_\sigma = 0$ and $\nu_L = 0$.

The dispersion of the length of filaments in braids is usually studied by direct measurement of the filament lengths. No attempt is made to measure the dispersion of the fibre length within the filament. A method of measuring both the dispersion of the fibre length in the filaments and the overall dispersion of the fibre length in the braids was proposed in Ref.18. It relies on an analysis of the non-linear part of the $\sigma-\varepsilon$ tensile diagram for a filament, on the assumption that the non-linearity is due to the sequential involvement of the fibres in the deformation of the filament. The fractional number of fibres under load at a given deformation of the filament can be determined by comparing the measured stress of the filament with the stress calculated by Hooke's law. Differentiating the $\sigma = F(\varepsilon)$ dependence with respect to deformation gives the fibre length distribution curve and the variation coefficient ν_L.

Within a single filament the dispersion of the strength of organic fibres (ν_L) is usually found to be less than 0.12%, and for braids of these filaments it increases to 0.15–0.25%, which can lower the strength of a bundle (or braid) of these filaments by approximately 10% (see Fig.2); an analogous decrease was found in studies of the strength of micro-plastics based on braids in which the length dispersion was artificially modelled by previously applying different loads to the braid. When the problem is put in the elastic formulation a given dispersion of the stress is equivalent to a dispersion of the length of the filaments in the braid: experimental studies of the effect of the modelled dispersion of filament length in braids on the strength of the micro-plastics prepared from them agree very well with calculations (see Fig.2).

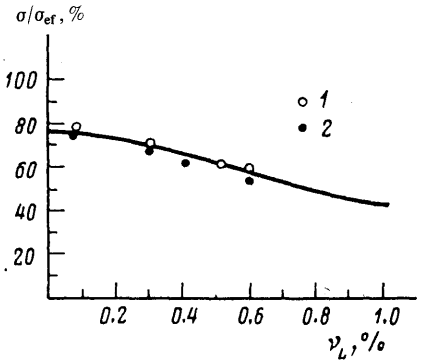


Figure 2. Reduced strength of the bundle of fibres σ/σ_{ef} against the variation coefficient of the length of fibres ν_L; the curve shows the theoretical dependence for a bundle of unattached organic fibres; the experimental points were obtained in tests on bundles or braids (*1*) and on micro-plastics (*2*).[18]

We note that the adverse effect of the dispersion of the length of fibres in filaments or in braids on the strength of reinforced plastics can be most marked in materials based on carbon or boron fibres, whose breaking strain is often less than 1%.[1]

2. Interaction of the Polymer Matrix with the Surface of the Reinforcing Fibres and Effect of the Adhesive Strength on the Mechanical Characteristics of Reinforced Plastics

The properties of composite materials depend not only on those of the components (fibres and matrix) but also on the interactions between the components, and especially on the strength of adhesion at the interface, which determines the effectiveness of the transmission of stresses through the phase boundary.

In spite of the obvious importance of studies of the adhesive strength in the development of reinforced plastics little was known for a long time on the changes in adhesive strength at the fibre–polymer interface: studies of adhesion have been traditionally confined to large-scale samples (prisms, plates, etc.). It was not clear to what extent the results obtained for flat surfaces could be transferred to cylindrical surfaces 10–100 μm in diameter (i.e. in the range of diameters of the fibres used in reinforced plastics). We should also note that for most of the high-strength reinforcing fillers used at present (carbon, organic, boron) the direct measurement of the adhesive strength in the fibre–polymer system is the only way of assessing the strength of

the coupling, since large test samples (plates, prisms, etc.) with the same fibre area cannot be prepared.

The apparatus and procedures which have been developed for preparing polymer–fibre composite samples, the adhesion testers for studying these samples at temperatures between −195 and +200 °C at different loading rates and in different atmospheres, and the new methods of treating the results of experiments on competitive (adhesional and cohesional) breaking processes have allowed the dependence of the adhesive strength in the fibre–polymer system on various factors to be studied systematically. The factors include the cooling and storage conditions, the measurement temperature, the rate of application of the stress, the composition of the binder, the type of fibre, the treatment of the fibre surface, etc.[18–34].

The most characteristic feature of adhesion couples is clearly seen in polymer–fibre systems: a non-uniform distribution of stresses at the interface, resulting from differences in the physico-mechanical characteristics of the components. This produces a strong dependence of the measured adhesion strength on the shape and size of the sample, and we must define the criteria for the most rational choice of numerical values of the adhesion strength. The local adhesion strength τ_{loc} has been proposed as the characteristic least sensitive to geometric factors: this parameter is determined by extrapolating the experimental results to zero length of the adhesion couple[26]. The τ_{loc} value can be used as a measure of the interaction at the interface, and also in studies of the nature of the adhesion and of the mechanism of the adhesion failure[27,28].

Studies of the dependence of the local adhesion strength of epoxy polymers on temperature and hardening rate have shown that under isothermal conditions τ_{loc} varies with the degree of hardening in the same sense as the hardness of the binder, tending towards an asymptotic value[27]. From studies of the kinetics of the development of adhesional strength during hardening it was found that the adhesion of these binders to steel and boron fibres is mainly due to chemical bonds[27].

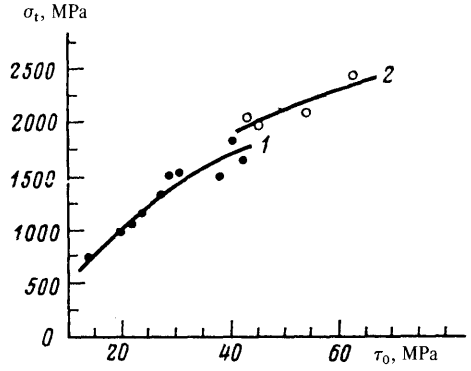


Figure 3. Dependence of the tensile strength of singly oriented glass fibre composites on the adhesion strength of the appropriate polymer–fibre system: *1*) for alkali-free glass fibres, *2*) for fibres of VMP grade[33].

Work on the dependence of the adhesive strength of polymer–fibre systems on temperature and loading rate has shown that below the glass transition region of the adhesive the local adhesive strength falls off linearly with increase of temperature and increases linearly with the logarithm of the loading rate[28–30]. This suggests that the adhesive failure of components (like their cohesive failure) takes place by a thermal fluctuation mechanism.

Refs.28, 31, and 32 describe a quantitative study of the relationship between the adhesive strength and the strength of the sample under tensile stress, compression, bending, and shear. The parameter used as a measure of the adhesive strength in this work was the quantity τ_0, defined for the final length of the sample, since it is affected by all the forces acting on the elementary cell of the reinforced plastic and therefore it can reflect more accurately than τ_{loc} the conditions of adhesion failure at the interface in real composites.

In oriented glass fibre composites prepared from various binders the tensile strength of the material σ_t increases with the adhesion of the binder to the fibre (see Fig.3). At high values of the adhesive strength we note a tendency for the plot of σ_t against τ_0 to reach a saturation level.

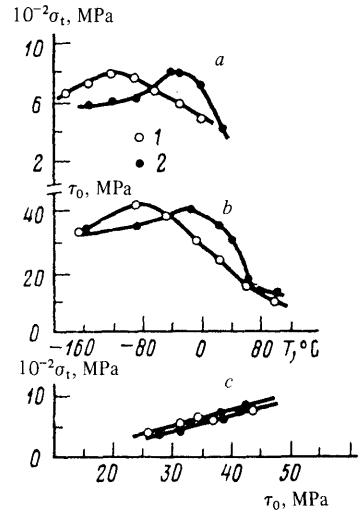


Figure 4. Effect of temperature on (*a*) the tensile strength σ_t of uniformly oriented glass fibre composites and (*b*) the adhesion strength τ_0 of the polymer–fibre system; (*c*) are the correlation curves; the binder is *1*) butvar-phenol, *2*) epoxy-phenol.

Changes in the same sense of the adhesive strength τ_0 and of the strength of the glass fibre composite σ_t are observed also in studies of temperature effects (Fig.4). Since both the strength of the glass filaments and the strength of the binder increase monotonically as the temperature T decreases, the observed correlation between the shape of the σ_t–T and τ_0–T curves suggests that in these composites the weakest member is the phase boundary, and therefore that the fracture of these materials begins at this boundary.

The most meaningful information on the relationship between the adhesion at the interface and the properties of the material is obtained from experiments in which the fibre and the binder material are kept constant, but the adhesion is varied by modifying the surface of the fibrous filler. Work of this type has shown[31,32] that changes in the adhesive interaction are accompanied by corresponding

changes in the strength of composites with a single orientation (both pressed and wound). The changes are in the same sense for all types of test (in tension, shear, compression, and bending, see Fig.5).

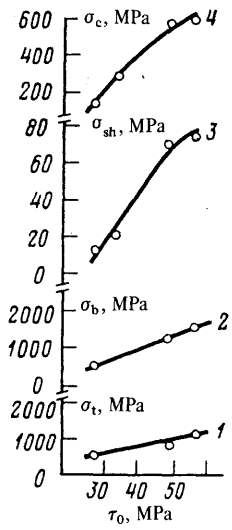


Figure 5. Strength of uniformly oriented glass fibre composites prepared from fibres with a pristine or a modified surface against the adhesion strength; EDT-10 binder, *1*) tension, *2*) bending, *3*) shear, *4*) compression[32].

Thus recent work shows that in glass fibre composites the adhesive strength of the polymer–fibre system is one of the factors mainly responsible for the mechanical characteristics of the material. The fracture of these materials (under tensile load) also reflects the level of adhesion at the interface: we observe a transition from failure at the interface (for small values of τ_0) to fracture by the increase in the number of broken fibres (for large values of τ_0). In the latter case the statistical model of fracture proposed by Rosen is applicable to the glass fibre composite.

In high-strength composites based on organic fibres of the Vniivlon type no correlation is observed between the adhesive strength and the strength of the material: for all the binders examined (covering a range of τ_0 from 40 to 60 MPa) the strength of the material under tension, compression, bending, and shear remained constant. This suggests a fracture mechanism controlled by the weak bond between the fibrils of which the fibre is composed[1].

In glass fibre composites (based on existing binders) a search for methods of modifying the glass surface so as to improve the adhesive strength should yield reinforced materials with enhanced mechanical properties.

In organic fibre composites based on highly oriented fibres of the Vniivlon type surface treatment aimed at strengthening the interaction of the fibre with the binder cannot by itself improve the physico-mechanical properties of the composite, and we must seek to modify the structure so as to enhance the transverse strength of the fibres under tension, i.e. to strengthen the bond between the fibrils.

3. Reinforced Plastics with a High Relative Content of Fibres

One method of raising the strength and the elastic modulus of reinforced plastics is to increase the relative content (by volume) of high-modulus and high-strength fibres, i.e. the reinforcement coefficient K_a. Traditional winding methods give materials containing only 65–70 vol.% of fibres, as compared to the theoretical K_a value of 90.7% for hexagonal close packing of fibres of equal diameter.

Various workers have reported a maximum on the plots of the physico-mechanical properties of reinforced plastics against the relative fibre content, usually in the region of 60–65%.[3,35] We can attribute the decrease in strength of the plastic at high fibre contents to an increase in the porosity of the samples and to the difficulty of producing uniformly thin (less than 1 μm) and yet continuous layers of the polymeric matrix. An indirect confirmation of this conclusion comes from the reported shift of the maximum towards higher values of K_a when the fibre diameter is increased[36].

The technological difficulties which prevent the incorporation of a high density of fine fibres are due mainly to the friction between the fibres during the formation of the material, which opposes their redistribution into the optimal hexagonal configuration. Furthermore, the dispersion of the fibre diameters lowers the theoretical limit of packing density (except for some special relationships between average fibre diameters in the case of a bimodal distribution).

To overcome these difficultes we must first of all optimise the structural order of the reeled element consisting of filaments or braids, i.e. create a close packing at the stage preceding the fixing of the positions of the filaments. Equally important is the achievement of a uniform distribution of the polymeric binder between the fibres[37]. This is done by repeated steeping of the filaments and braids in the binder during the winding of oriented reinforced plastics, by stretching them by friction (without slippage) on tensioning pulleys, and by forming an ordered, thin tape from a number of filaments or braids in a special profiling stacker. Some workers have applied ultrasonic vibrations to the stacker in order to lower the friction and to achieve a closer packing of the filaments in the tape, as well as a uniform penetration of the binder into the fibrous material. These new technological processes have given ring samples of glass or organic fibre composites in a single orientation containing up to 85 vol.% of fibres, i.e. approaching the theoretical limit, coupled with a negligibly small porosity of the samples (less than 1%).

When thermoplastic organic fibres are used the fibre content of the reinforced composite can be as high as 90 to 100 vol.%.[38,39] These high packing densities are achieved through irreversible thermal deformation of the fibres normally to their axis, which changes the fibre cross-section from a circular to an arbitrary shape, imposed by the contact with the neighbouring fibres. To prepare these maximally reinforced organic fibre composites the technological parameters must be chosen so as to retain as far as possible the initial strength and stiffness of the fibres in spite of their thermal deformation. A strong bond between the profiled fibres can be obtained from the self-adhesion forces (by direct interaction of the fibres) or by interposing thin layers of binder between the fibres.

If the porosity is kept to a minimum (less than 1%) the elastic modulus E and the tensile strength of the samples show a linear increase (as required by the additivity principle) up to the highest volume contents of fibres of different types. These results are illustrated (Fig.6) by plots (in relative units) of the characteristics of glass fibre reinforced plastics based on fibres 9–11 μm in diameter and an epoxy-diane binder. Increasing the fibre content of the glass fibre

composites increases their strength under compression more markedly than under tension: this is explained by the specific effect of the close-packed array of fibres, which prevents the loss of strength.

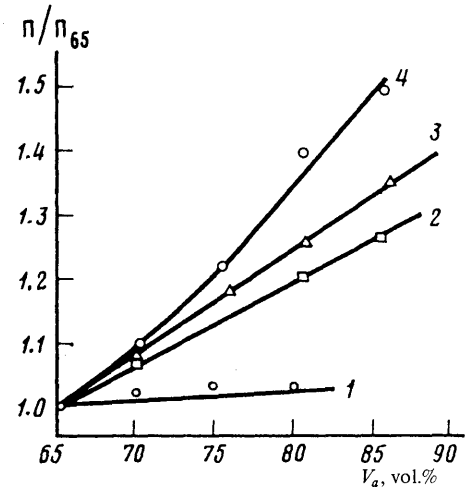


Figure 6. Effect of the fibre content by volume on the physico-mechanical characteristics of glass reinforced composites; П is a characteristic of the glass fibre composite for any value of the fibre content V_a, $П_{65}$ is the same characteristic for a 65% fibre content, *1*) τ_{sh}, *2*) σ_t, *3*) *E*, *4*) σ_c.[37]

4. Hybrid Polymeric Composite Materials

The preparation of hybrid polymeric composite materials (HPCM) by combining two or more types of reinforcing fibre (glass, organic, carbon, or boron) is a promising area of research in materials science, because of the prospect of controlling the properties of these materials between much wider limits.

The most important influence on the physico-mechanical behaviour of HPCM (especially under tension) is from the difference in the limiting deformations of the fibres present in the material. Organic–glass and carbon–boron plastics have been studied as HPCM based on fibres with similar deformation characteristics. The physico-mechanical properties of these materials are exactly described by the additivity principle.

An entirely different behaviour is observed in studies of HPCM containing fibres with substantially different deformation properties. In HPCM with alternate reinforcing elements having a low linear density or with alternate layers less than 0.1 mm thick the different fibres in carbon–organic, carbon–glass, boron–glass, and boron–organic composites do not break simultaneously under tension. Fig.7 shows as an example the tensile diagrams of carbon–glass composites with different ratios of carbon to glass fibres. In the initial region *I* (Fig.7) the carbon and the glass fibres are being deformed together. At a relative deformation of 0.7–1.0% we observe the fracture of samples containing more than the critical amount of carbon fibres (25 vol.%, curves *1* and *2*). At lower contents of carbon fibres this deformation does not cause breaking. In region *II* (Fig.7) curves *4* and *5* are non-linear, indicating the gradual breaking of the long carbon fibres into progressively shorter lengths. The presence of a "quasi-plastic" region (*II*) in the tensile diagram of the HPCM gives an increased breakdown energy, impact strength, and fatigue and dynamic strength in these materials. Beyond this region the almost linear region *III* extends up to the limiting deformation of 3–4%. On increasing the content of glass fibres the deformation at break of the carbon fibres in carbon–glass composites increases from 0.7 to 1.5%. This synergistic effect is apparently due to the repeated breaking of the carbon fibres into progressively shorter pieces, and to the avoidance of macroscopic cracks and premature failure of the material in glass fibre composites.

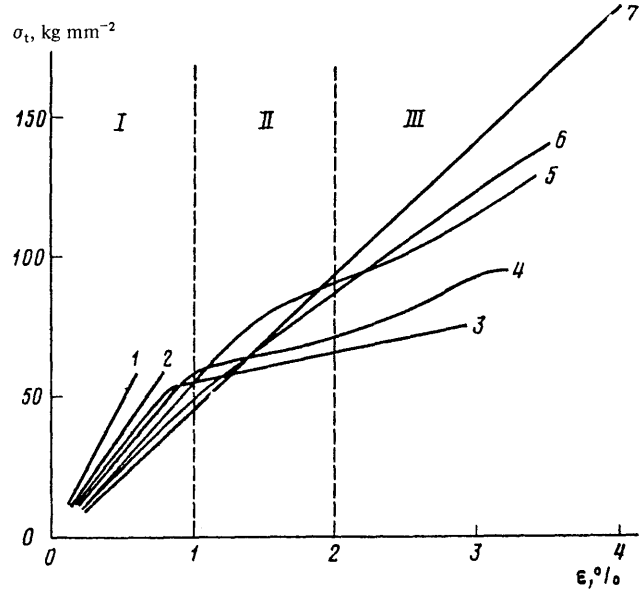


Figure 7. Tensile diagrams for uniformly oriented ring samples of carbon and glass fibre composites with different ratios by volume of carbon and glass fibre contents (%): *1*) 100:0, *2*) 78:22, *3*) 58:42, *4*) 41:59, *5*) 26:74, *6*) 12:88, *7*) 0:100.[52]

Under compression the dependence of the strength on the content of fibres with different elastic moduli is almost linear in HPCM. The elastic modulus stays linear after repeated (up to 10 times) load applications. This means that the carbon and the organic fibres when present in a matrix of glass and boron fibre composites can retain their strength at deformations (and therefore also at stresses) 2–3 times greater than in the simple carbon and organic fibre composites. These synergetic effects allow us to increase the elastic modulus of glass or organic fibre composites by small additions of carbon fibres, and to increase the compressive strength of carbon fibre composites by combining carbon and glass fibres.

An interesting possibility in the development of HPCM is the production of components with variable properties by varying the relative amount of different fibres in different parts of the article. This feature should allow us to control

the stress field in mechanical components both during assembly and in service. It should also be possible to solve the inverse of the traditional problem, i.e. given the most favourable stress field in the component, determine the required material structure. The effectiveness of this approach has been demonstrated for thick-walled vessels under external or internal pressure. Hybrid composite materials have attracted a great deal of interest in both the Soviet and the foreign scientific literature[40-48], but the reported experimental results are not always easy to compare because of the failure on the part of authors to quote the parameters of the material structure, the extent to which the components are kept discrete in the hybrid material, and the relative configuration of the reinforcing elements. The results reported by Phillips[46,47] appear to be the closest to ours[44,45].

We should note that although the theory of the construction and of the behaviour of hybrid composites is still in its early stages these materials have already been widely used in practical applications ranging from aviation components to sports equipment[48].

III. DEFORMATION AND FRACTURE OF MATERIALS WITH COMPLEX REINFORCEMENT

Recent component designs rely on multi-layer polymeric composite materials (PCM) with different and often complex patterns for the orientation of the reinforcing elements. The choice of reinforcement, of binder, and of orientations is determined by the function of the component and by its conditions of service. Materials having identical reinforcing elements and binders and differing only in the pattern of the reinforcement are entirely different materials as regards their mechanical properties. We therefore need theoretical models of the PCM to predict their behaviour with different orientation schemes of the reinforcement from a minimum of experimental information.

Studies of this type have been reported for glass, carbon, and organic fibre composites prepared by the winding method and for hybrid materials based on glass and carbon fibres[49-66].

Tube samples are used for experimental studies of the mechanical behaviour of materials produced by the winding method with complex reinforcement patterns. Special test methods had to be developed for tubular PCM samples under different loading conditions[49,61-63], because there are no standard test methods for this sample geometry.

Purely phenomenological studies of strength as a function of the angle of the reinforcement[57] have shown that in both carbon and glass composites the shear strength can be described by a formula which follows from the Gol'denblat–Kopnov strength criterion. Hence the calculation requires a knowledge of three experimental values of the torsional strength for three known winding angles[64].

A simpler dependence of the strength on the reinforcement angle was obtained[56] from a different phenomenological criterion, which allows for the structure of the material by formulating the failure condition for the plane where fracture is most likely. This criterion gave formulae for the dependence of the strength under uniaxial extension and of the torsional strength on the reinforcement angle in terms of the strength observed experimentally (under the same loading conditions) for a single, arbitrarily chosen winding angle. These theoretical formulae are satisfactorily consistent with experimental curves for glass and carbon fibre composites with winding angles of $\pm 20° \leq \alpha \leq \pm 80°$.[63] The results of experiments on the mechanical behaviour of carbon fibre composites under shear, together with data on the influence of various factors on the shear characteristics, have been used to design new types of component with a weight saving of up to 20%.[64,65,67]

The latest technological method of preparing multi-layer PCM relies on the use of a monolithic packet of uniformly oriented reinforcing layers which is itself oriented in different directions. The mechanical properties of multi-layer PCM are largely determined by those of the uniformly oriented reinforcing material. Hence it is relevant to examine theoretical models of the PCM able to predict the strength and the deformation behaviour of the multi-layer material from experimental data on the elasticity and strength of the uniformly oriented material. Both Soviet and foreign publications describe various models of this type which allow for a number of effects accompanying the deformation and fracture of the PCM and ignored in the purely phenomenological approach based on the linear elasticity theory of isotropic solids[68-75].

Experimental studies of the breaking of glass and carbon reinforced PCM have shown that the ultimate failure of these materials is preceded by various impairments (peeling, cracking) which do not exhaust the load bearing the capacity of the composite. It is important to know the types of stress and the stages in loading responsible for the appearance of these initial impairments as well as those responsible for the ultimate mechanical failure.

By combining theoretical models which allow for the layer structure of the material with the maximum stress criteria, and by comparing calculations with experimental results, the principles which determine the breaking of glass reinforced plastics under axial compression, extension, and torsion have been determined for various regions of winding angles[76]. The cause of the disintegration of the binder during the initial deformation and of the final failure of the material under axial extension and torsion has been identified (for different types of glass and carbon fibre reinforced plastics) by using a phenomenological model of the structure of a multi-layer PCM [74] in which a uniformly oriented monolayer is treated as the basic element. By generalising experimental data and various models of the deformation of uniformly oriented composite materials Zinov'ev and Tarakanov[74] have developed a generalised model of the deformation of a uniformly oriented monolayer within a packet of layers which assumes that the matrix of the mechanical characteristics of the uniformly oriented material can have one of eight possible values, depending on the magnitude and sign of the components of the stress tensor and on the sign of the deformation increments. An algorithm for computer calculations was developed from this model. The validity of the results was confirmed by the agreement between theoretical and experimental tensile diagrams[76,77]. It was also shown[69,70] that the torsional fracture of carbon and glass reinforced plastics is induced by compressive stresses along the fibres except in the glass fibre composites with a winding angle $\alpha = \pm 45°$, which break as a result of tensile stresses in a layer at right angles to the fibres. The disjoining stresses in this layer are also responsible for the breaking of glass fibre composites with angles $\alpha = \pm 60°$ and $\pm 75°$ under uniaxial extension. In a glass fibre composite with $\alpha = \pm 45°$ under uniaxial tensile stress the formation of cracks leading to the loss of load bearing capacity is caused by shear stresses. Samples with $\alpha = \pm 45°$ have the highest deformability: their tangential modulus (i.e. the slope of the finite part of the deformation curve) is small on the experimental diagrams and zero on the theoretical. According to this model after the loss of continuity the deformation grows at constant load (assumed to be equal to the limiting load); the proposed algorithm can be used also for loads higher than this limit. In the final stages of deformation we

find a marked increase in the tangential modulus due to the change in the reinforcement angle produced by the deformation, but this does not cause the fibres to break. In glass fibre composites with $\alpha = \pm 60°$ and $\pm 75°$ there is no increase in the tangential modulus, though a high deformability and an increase in deformation at practically constant load are again observed.

Torsional deformation of glass and carbon fibre composites with angles $\alpha = \pm 60°$ and $\pm 75°$ reveals disintegration of the binder as a result of disjoining stresses acting at right angles to the fibres, and of tangential stresses acting along the fibres. The causes of the large-scale failure of the material defined by the criteria given in Refs.74 and 76 for the various winding angles are effectively the same. Because of the special behaviour of $\alpha = \pm 45°$ materials under simple types of load their mechanical behaviour has to be studied with different types of complex loading approximating those experienced by composite materials under field conditions.

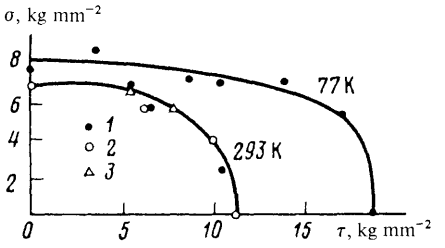


Figure 8. Breaking diagram for an organic fibre plastic at room temperature and at low temperature: *1*) torsion + tension, *2*) proportional deformation, *3*) tension + torsion[78].

Tubular samples of organic and glass fibre composites have been studied[78] for $\alpha = \pm 45°$ and the same epoxy binder under linear deformation conditions under simultaneous axial (tensile) load and torsional moment and with a complex load application curve: tension was used to bring the sample to a prescribed value of σ_i, and torsion was then applied to break the sample at the stress τ_i. The experiment was then repeated in the opposite sequence: a torsional moment was applied to bring the sample to a stress close to τ_i, and then the sample was broken under tension. Breaking diagrams for organic fibre composites loaded in different ways at room temperature and by the complex loading trajectory at low temperature (77 K) are shown in Fig.8. It was found that the experimental values of strength lie on the same breaking diagram for all types of load application. A decrease in temperature produces a marked increase in the strength of organic fibre composites, especially under shear.

IV. PHYSICO-MECHANICAL PHENOMENA IN THE POLYMER FORMATION AND REINFORCEMENT PROCESSES

In this Section we shall review the studies of mechanical phenomena in frontal and in uniform solidification processes, in the heat treatment of polymeric and composite materials, and in their practical applications. Studies of the mechanism of formation of defects and of residual stresses and deformations will also be discussed. The ultimate aim of this group of investigations is to develop favourable technological processes for the large-scale production of thick-walled monolithic components from polymeric or composite materials[79,108,109].

Studies of the chemical kinetics of the solidification of these components have shown[80-86] that the process can be frontal, i.e. spatially non-uniform. Therefore it is important to study the mechanical phenomena accompanying the frontal solidification of articles made from polymers and from reinforced plastics, since defects may be formed or residual stresses may be created.

The problem was solved by postulating[84-90,93] a two-step solidification front, with steps in the liquid and the solid state. This model allows most of the solutions to be obtained in a closed form clearly related to the physical nature of the phenomena and suitable for analysis[93]. Two limiting models were developed for composites: one in which the reinforcing fibres are fully immersed in the liquid binder and a capillary model in which the filler can form a system of capillaries.

By solving various problems in the mechanics of deformation and in hydrodynamics, and by using experimental results, it has been shown that defects can take the form of discontinuities or of residual stresses during frontal solidification[93,94].

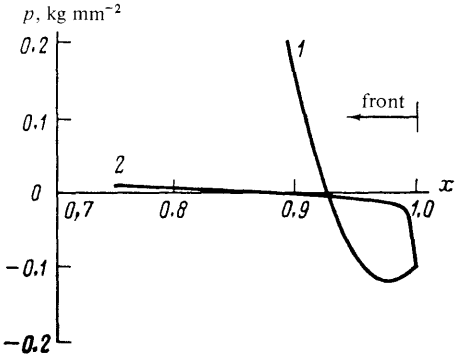


Figure 9. Changes in pressure ahead of the solidification front for a cylinder of reinforced plastic on an elastic mandrel as a function of the position of the front: *1*) stiff mandrel, *2*) stiffness of mandrel reduced by two orders of magnitude; p is the pressure ahead of the front, $x = r/R$ where r is the coordinate of the front and R is the radius of the outer surface of the shell[93].

Fig.9 shows a plot of the changes in pressure ahead of the solidification front in a thick-walled cylindrical shell of reinforced plastic: the front is moving from the outer surface ($x = 1$) towards the mandrel, and the binder is liquid ahead of the front. The fall in pressure ahead of the front to zero or even to "negative" values (i.e. to isotropic expansion stresses) suggests the possibility of slippages or breaks in the continuity of the liquid binder, and the formation of holes and pores (curve *1*); a decrease in the hardness of the mandrel by two orders of magnitude largely avoids the danger of defect formation (curve *2*).

A similar approach can be used to analyse the mechanical phenomena in polymers and in reinforced plastics during a frontal liquid–solid transition, and also in other systems (e.g. liquid–polycrystal, liquid–monocrystal, adhesive–substrate, etc.).

The next stage in the formation of components is heat treatment. This usually consists in cooling the article from the solidification temperature to the storage or application temperature, though additional heat treatment is sometimes applied in order to modify some of the properties of the material. Furthermore, materials and components are often used under conditions of variable temperature, which cause thermal stresses.

The mechanism of formation and development of thermal stresses in polymers was studied with samples consisting of amorphous polymers, both linear [poly(methyl methacrylate)] and with a network structure (epoxy resin)[91-93]. The dependence of the thermal stresses in amorphous polymers on the rate of change of temperature, the quasi-irreversibility of the stresses associated with cyclic changes in temperature, and the increase in stress during isothermal relaxation processes have been demonstrated experimentally and justified theoretically[91-93]. For polymers all these processes are strongly non-linear[93].

Problems of thermal stresses in polymers and reinforced plastics can be solved theoretically by using the full system of equations from classical mechanics which describes the stressed and the strained state, and also the functional relationship between the components of the stress and deformation tensors and time. Phenomenological relationships of the heredity equation type are most widely used. So far little work has been done on the use of physical non-linear coupling equations to describe thermal and residual stresses. A non-linear physical generalisation of the Aleksandrov–Gurevich–Lazurkin equation has been used[93,100] as the coupling equation to describe thermal stresses and relaxation phenomena in polymers by allowing for the first two terms in the spectrum of relaxation times and for the temperature dependence of the elastic and relaxation constants. The validity of this coupling equation in non-isothermal processes has been demonstrated[93] by comparing theoretical results with experimental data.

It has been shown[93-99] that the additional heat treatment applied to amorphous polymers to improve their strength and their relaxation time and to stabilise their properties allows the frozen (residual) bulk and linear deformations produced by the solidification and cooling of the polymer to relax. The influence of frozen linear highly elastic deformations has been used to explain the "well" and "hump" effects on the dilatometric curves of polymers.

Cracks or weaknesses in articles made from reinforced plastics can appear not only during solidification and cooling but also during subsequent storage under static conditions. To account for this phenomenon the thermal stresses and the relaxation phenomena have been studied[93,100,101] in components made from reinforced plastics. A theoretical model of anisotropic materials was developed to explain the relaxation behaviour of the polymer matrix and its interaction with the filler, and a coupling equation for the reinforced plastic under non-isothermal conditions was obtained. This equation is outwardly similar to the Aleksandrov–Gurevich–Lazurkin equation for homogeneous isotropic polymers, but in this case the highly elastic deformation has a different meaning, since it is explicitly temperature-dependent, suggesting interactions between the matrix and the filler[93, 100,101]. Relaxation phenomena in relatively thin articles (for example, made from glass fibre composites) can produce dangerous radial tensile stresses during isothermal storage, thus increasing the probability of crack formation at this stage[100,101]. In thick cylinders relaxation effects cause a substantial decrease in stress during the cooling and storage stages[101].

The influence of residual stresses and deformations on the mechanical behaviour of reinforced plastics and adhesives has been studied with the aid of discrete models of the reinforced plastic[102-107]. This required the development of an approximate theory of the boundary layer, applicable to contact problems in the mechanics of composites. The approach relied essentially on the postulated presence of an intermediate (boundary) layer between the adhesive and the substrate. Its main advantage is the possibility of obtaining "elastic" solutions in a closed form, accurately satisfying all the boundary conditions. Residual stresses created in the model by a layer of polymer during solidification, cooling, swelling, etc. can easily be calculated. This theory can explain the dependence of the measured mean strength of some model reinforced plastics (for example, glues and adhesives) on the geometry and on the experimental conditions (length and area of the joint, thickness of the layer of binder, fibre diameter, stiffness of the adhesive and of the substrate, degree of solidification, shrinkage, measurement temperature, etc.). Methods of calculating correctly the true strength of these composites have been proposed[105-107].

The problem of optimising the cooling conditions of thick-walled articles made of reinforced plastics by the winding method has been examined as a practical application of the theory of thermal stresses. In the formulation of the problem realistic account was taken of the possibilities offered by industrial production plant[110]. The method chosen to avoid crack formation was to use a non-uniform temperature field during the solidification and cooling of the sample[108-110]. This is a problem in non-linear programming with restrictions: the main difficulty in its solution is the non-linearity of the restrictions on the calculated radial stresses at each point in space and time[110].

The effect of various parameters of the problem on the final result has been analysed. A general feature of all the optimisation regimes obtained for articles made from typical reinforced plastics is the more rapid cooling of the outer than of the inner surface. Most of the regimes are monotonic, a very convenient feature in practice. In comparison to the traditional regimes they offer a saving in time of a factor of 4 or better, and they allow the construction of monolithic articles with a wall thickness 5–6 times greater than previously.

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