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INTERFACE IN COMPOSITE MATERIALS

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Abstract - It is generally accepted that the mechanical properties of composite materials are largely dependent on the interactions at the matrix/filler interface. To cite an exemple, recent work on a model bitumen-silica composite has given insight into the role played by the interface. In this case, the respective influences of interfacial area and degree of matrix/filler interaction on the storage modulus of the composite have been quantitatively established.

Although many factors intervene, clearly the strength of the interface must depend to a large extent on both the number and the nature of the bonds between the two phases.

In cases in which only physical bonds (e.g. Van der Waals) are formed, the interfacial strength may be predicted from the surface characteristics of the two solids in contact. A study of such a system, aluminium/elastomer, has shown the significant contribution of the free surface energies of the two components to mechanical resistance, locus of failure and environment effects.

In many real composite materials, interfacial bonds of a chemical nature must be taken into account. The influence of these chemical bonds will be examined by considering results obtained from polymer/polymer and polymer/glass interfaces.

Despite the general applicability of the conclusions of these interfacial studies, it mustnevertheless not be forgotten that, in certain cases, the properties of the interphase, in the proximity of the interface, are of fundamental importance. It is for this reason that it is of the utmost importance to define tests which enable the direct measurement of the stress-transfer capacity of both interfaces and interphases in composite materials.

INTRODUCTION

Great strides have been made in composite materials technology during these last decades. Such materials display most attractive mechanical properties for a very small weight, and are distinguished by the fact that stress transmission takes place between matrix and reinforcing agent.

Various problems had to be overcome, however, in the development stage, since the performance of these materials is conditioned by the intrinsic properties of the various components and is largely determined by the adhesion, i.e. the interactions between reinforcing agent and matrix. Among the factors governing the performance of a composite, a prominent role is played unquestionably by the adhesion between a fibre, for instance, and a matrix. This phenomenon is related to the intermolecular forces exchanged at the fibre-matrix interface. The governing factors are numerous, since they depend both on the nature, the intensity, the number of interfacial bonds and the surface structure of the components or the interface defects.

The fundamental question which arises, and already prompted many investigations and even disputes, is whether "optimum adhesion" is necessary or essential to achieve good stress transmission and the best possible mechanical and rheological characteristics.

The answer is complex, because a host of parameters of most different origins are mentioned in the literature. They are distributed in three classes : those relevant to reinforcement (nature and composition of the reinforcing agent, roughness, effect of number and size of fibres or fillers), those pertaining to the matrix (rheological properties, ageing, polymerization shrinking) and finally those related to the interface (thickness, friction forces, wetting of the reinforcing agent by the matrix, effect of impurities, and particularly of

water).

The variety of these parameters reveals how difficult it is to set up a unique theory including all factors and leading to an overall understanding of the phenomena.

Clearly, the intrinsic properties of both the reinforcing agent and the matrix play a role in the stress transfer from a material to another one, but it is also apparent that the nature of the interface, its structure and hence its properties, are determining for this exchange and therein lies actually the core of the problem.

To study the factors affecting the "quality" of an interface, one should observe or find out :

- the effect of the interfacial area and the nature of the matrix, together with
- the effect of the bond strengths exchanged, whether physical or chemical.

EFFECT OF THE INTERFACIAL AREA

Fritschy and Papirer recently demonstrated in our laboratory the role played by the interface in a bitumen-silica model composite material (1). They chose this type of material on one hand because bitumens display well-known rheological properties and behave like typical visco-elastic materials and, on the other hand, because bitumens and bitumen-silica composite materials obey just like "conventional" reinforced elastomers Williams, Landel and Ferry's (WLF) time-temperature relationship.

The authors first attempted to verify the empirical relationship suggested by Medalia, expressing tan δ (i.e. the ratio of the loss and storage moduli) in terms of the $\phi\psi$ parameter, where ϕ represents the volume fraction of the filler and ψ the interfacial area between the matrix and the reinforcing agent.

$$\psi = \rho S \phi$$

ρ represents the density of the reinforcing agent and S its surface area, and therfore :

$$\phi\psi = \phi^2 S \rho$$

Fritschy and Papirer provided unambiguous experimental evidence for the simple linear relationship between the storage modulus E' and the parameter $\phi\psi$:

$$E' = E'_o + A\phi\psi$$

E'_o being the storage modulus for the unfilled substance.

The materials used in this investigation were 80/100 bitumen, a residue from distillation (supplied by the Feyzin Refinery of the French S.N.E.A.P. Corporation) and "Aerosil" silicas (supplied by the Degussa Co), consisting of non porous spherical particles, the characteristics of which are shown in Table 1. Samples A 130 to A 380 belong to the same series. R 972 silica was treated with dimethyldichlorosilane, which partly blocks the surface silanol groups. A part of A 300 silica was treated with octamethylcyclotetrasiloxane (D4), thus removing all silanols at the surface. The species O x 50 and MOX 170, which are rich in aluminium, do not exhibit the same properties as the first ones.

Two viscosimeters, Rheovibron DD VII (manufactured by Toyo Measuring Instruments, Japan) and Metravib (supplied by Metravib Corporation, Ecully, France) were used for studying the properties of the composites.

The values of the storage modulus E' measured at 20°C and 15 Hz, as a function of the filling ratio, are shown in Fig. 1. The values of E' are averages determined in a statistical study. As a preliminary, the silicas were agglomerated with water or heptane in the case of varieties R 972 and (A 300 + D4). It is apparent that the composites of the series with increasing surfaces are all situated on the line corresponding to the system bitumen - A 130 silica. On the other hand, the OX 50 and MOX 170 silicas which are richer in aluminium and display more pronounced adsorbing properties than the other samples, are all situated above this line with higher modulus values. E' is, therefore, really dependent on the activity of the reinforcing surface.

TABLE 1. Characteristics of silicas used by Fritschy and Papirer

Silicas	BET surface areas (measure with nitrogen) ($m^2.g^{-1}$)	Approximate diameters of the particles (nm)
A 130	130 ± 25	16
A 150	150 ± 25	-
A 200	200 ± 25	12
A 300	300 ± 30	7
A 380	380 ± 30	7
R 972	120 ± 30	16
OX 50	50 ± 15	40
MOX 170	170 ± 30	15
A 300 (D4)	270	-

Fritschy and Papirer also evaluated the adsorbing capacity of these various modified silicas when placed in carbon tetrachloride solutions of asphaltenes. The quantities chemisorbed were measured by determining the weight losses by pyrolysis at 80°C. Table 2 records the main values by unit of weight and of solid surface. While the first series of silicas seem to exhibit the same adsorbing capacity per unit surface, the same does not hold true for the modified silica series, and the quantity adsorbed is much lower when the number of silanols is decreased.

TABLE 2. Capacity of asphaltene adsorption by silicas, as determined by Fritschy and Papirer

Silicas	$g.g^{-1}$ (± 0,01)	$g.m^{-2}$ (x 10^{-3})
A 130	0,14	1,08
A 150	0,14	0,95
A 200	0,17	0,83
A 300	0,26	0,87
A 380	0,35	0,92
R 972	0,03	0,25
A 300 + D4	0,00	0,00
OX 50	0,08	1,70
MOX 170	0,29	1,70

In this manner, the value of E' is much lower for sample (A-300 + D4), in which case the quantity of bitumen fixed irreversibly by unit surface is almost zero, all silanols being blocked by octamethylcyclotetrasiloxane. Thus, to a deactivated surface corresponds a low value of the modulus.

To sum up, Fig. 1 verifies the relation $E = E'_0 + A\phi\psi$

on one hand because E' increases linearly with the surface area of the reinforcing agent and on the other hand because E' remains constant when the parameter $\phi\psi$ remains constant, i.e. when the volume fraction of filler and the area of the reinforcing agent/matrix interface vary, but in such a way that the product $\phi\psi$ should remain unchanged.

Fig. 1 also shows that the value of the storage modulus E' depends on the activity of the surface of the reinforcing agent and is not devoid of effect on the properties of the interface.

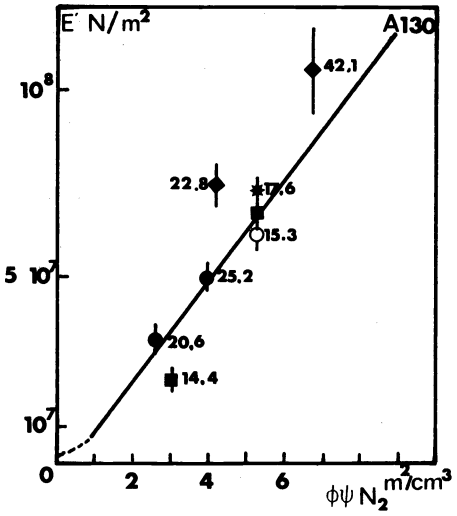

Fig. 1 . Storage modulus of bitumen-silica composites, in terms of the parameters $\phi\psi$, according to Fritschy and Papirer
(✱) A 200, (□) A 300, (○) A 380, (●) R 972, (■) A 300 + D4, (◆) OX 50 and OX 170.

Let us, now, examine the effect of the forces exchanged at the interface, viz. the nature, the intensity and the number of bonds which are to be found therein.

PHYSICAL BONDS

In addition to the intrinsic characteristics of the materials in contact, the "degree of intimacy" appears to be a determining criterion for the exchange of interactions between the reinforcing agent and the matrix. It must be added that the wetting theory of adhesion supposes that, on intimate contact or wetting of the reinforcing agent by the matrix, i.e. when the reversible energy of adhesion of the matrix on the reinforcing agent is higher than, or equal to the energy of cohesion of the matrix, it is possible to bring the surface forces of the materials into action, regardless of their nature. It was shown that the forces of physical interaction, i.e. of the Van der Waals type, are often sufficient to ensure good adhesion if perfect wetting is obtained.

Various attempts have been made at studying the strength of an assembly in terms of the nature and the surface properties of the solids in contact. Schultz and Carré (2) demonstrated recently the contribution of the free surface energies of the two components of an aluminium/elastomer system, to the mechanical strength, the mode of failure of this assembly, and the influence of the surrounding medium.

In a first step, Schultz and Carré's aim was to establish quantitative relationships between the properties of the solids in contact and the failure strength of the assembly. The first requirement of such a study is characterization of the solids in terms of the surface energy.

Since direct measurements of this parameter is not possible in the case of solids, due to motionlessness of atoms and molecules, an indirect method such as the study of solid-liquid interactions, e.g. involving measurement of contact angles, should be resorted to. Two methods were used.

The first one, which is now conventional, is concerned with the contact angles of a series of liquids in the presence of vapour (method with one liquid phase) ; the second one uses the contact angle of a polar liquid (water or formamide), measured on the solid immersed in various hydrocarbons (the two liquids method). The validity of the methods was confirmed by the similarity of the values measured for a series of polymers. Application of the second method to aluminium substrates subjected to various surface treatments allowed, by taking also into account the texture and the porosity, determination of the components of their surface energy and thus provides evidence for the striking effect of surface treatment.

The aluminium samples used by Carré underwent the following surface treatments :

- degreasing with organic solvents : hexane and dimethylformamide (DMF),
- a conversion treatment : an amorphous phosphatization, by reacting with a solution of phosphoric acid, chromic acid and fluoride after alkaline pickling or degreasing.

- an electrochemical treatment, an anodization or anodic oxidation, which gives rises to an almost anhydrous surface film of oxide.

- in a last stage, an anodization followed by a "sealing" treatment achieved by clogging the pores through hydration of the alumina.

The wettability techniques used allow determination of the surface characteristics of aluminium, viz. γ_S^D and γ_S^P, the dispersive and polar components of the surface energy as well as I_{SW}^P, which represents the energy of the polar or non-dispersive interactions between water and the solid. The results shown in Table 3 clearly demonstrate the considerable effect of the nature of the surface treatment. The surface characteristics of the two elastomers used, NBR (butadiene-acrylonitrile copolymer) and SBR (butadiene-styrene copolymer) are also shown in Table 3.

Table 3. Surface characteristics of aluminium surfaces and elastomers used by Carré

Surface	γ_S^D (mJ.m^{-2})	I_{SW}^P (mJ.m^{-2})	γ_S^P (mJ.m^{-2})
Water-extrated Al	42	38,7	7
DMF-extracted Al	135	62,5	19
Converted Al	150	18	1,6
Anodized Al	125	95	44
Anodized, sealed Al	41	55,5	15
SBR	29,5	11,5	0,7
NBR	26,5	44	9,5

The irreversible energy of adhesion W_o corresponds to the sum of all interactions between the two materials, and can therefore be written as :

$$W_o = I^D + I^P$$

where I^D and I^P represent the energy of the dispersive and polar interactions. Of course, this relation is valid only when all interactions are of the Van der Waals type.

The Fowkes model allows estimation of I^D between materials 1 and 2 according to

$$I_{12}^D = 2(\gamma_1^D \gamma_2^D)^{1/2}$$

By way of analogy, other researchers used for I_{12}^P the relation

$$I_{12}^P = 2(\gamma_1^P \gamma_2^P)^{1/2}$$

Taking into account the fact that the apparent surface of contact between aluminium and elastomer is not equal to the real surface of contact, notably for anodized aluminium, calculating the reversible energy of adhesion of aluminium/elastomer systems led to the results shown in Table 4.

On the other hand, Schultz and Carré determined the energy of adhesion by directly measuring the resistance to separation of the assembly studied. This test yielded two types of information :

- one is relevant to the numerical value of the force of the energy of failure.

- the other is of quite another kind, and concerns the location of the failure.

Table 4. Reversible energies of adhesion and energy of cohesion of aluminium/elastomer systems, according to Carré

Substrate	Al/SBR		Al/NBR	
	Adhesion E_o mJ/m^2	Cohesion E_o mJ/m^2	Adhesion E_o mJ/m^2	Cohesion E_o mJ/m^2
Al converted	133	60	134	72
Al anodized	130 x $\frac{\text{real surface}}{\text{apparent surf.}}$	60	156 x $\frac{\text{real surface}}{\text{apparent surf.}}$	72
Al anodized sealed	76	60	88	72

Location of the failure

Visual examination proved inadequate to determine the mode of cohesive or interfacial failure, because the residual of one or the other adhering phase is very small. By comparing the wetting of adherends by water, it was shown from measurement of contact angles, that the failure is interfacial for systems consisting of sealed, anodized aluminium, and cohesive for systems consisting of aluminium which underwent conversion and anodization. These results were also confirmed by scanning electron microscopy.

Energy of failure

Measuring the energy of failure as a function of the rate of peeling and the age of the sample, showed a decrease in strength of the assembly in the case of anodized aluminium, probably related to the phenomenon of sealing, as the depth of penetration of the elastomer into the oxide layer modifies, to a considerable extent, the state of the stresses during the peeling. In this case, the mode of failure is cohesive, just as for converted aluminium. On the other hand, for sealed, anodized aluminium, it is primarily interfacial, except at places displaying "cracklings". In the case of anodized aluminium/SBR, very high energies of failure resulting in irreversible straining of the substrate, were observed, thus revealing that the energy dissipated in this case also depends on the bulk properties of the substrate. Finally, the property of aluminium to adhere to SBR and NBR was classified as : anodized Al > sealed, anodized Al > converted Al.

Thus, comparing the reversible energies of adhesion calculated from the surface energies, on the assumption that the only interactions exchanged are Van der Waals bonds, does not allow by itself prediction of the adhering property of aluminium according to its surface treatment. One should also take into account the roughness and porosity factors and the morphology of interfaces which determine the distribution of stresses, and hence the geometry of the surface of failure. The thermodynamic calculations allow, nonetheless, prediction of the location of the failure in the various assemblies.

The model assemblies aluminium/elastomer also provided Carré with a means to study the changes of the properties of interfaces, using liquids which are inert with respect to the viscoelastic properties of the elastomers. Two aspects, one thermodynamic, and the other kinetic, characterize the phenomenon of failure in liquid medium. The results of this study, confirmed by the model which was set up, allowed determination of the dimensions of the domain where the various physico-chemical processes take place, and allowed demonstration of the role played by the interface.

CHEMICAL BONDS

In numerous instances mentioned in the literature, formation of chemical bonds between the reinforcing agent and the matrix, notably through coupling agents, has been advocated by various authors to improve the performance of composite materials.

It should be reminded that, although the formation of chemical bonds at the interface improves very often the performance of composite materials, it does not explain all the properties of a system comprising a reinforcing agent, a coupling agent and a matrix.

On the other hand, it is not obvious that a significant exchange of chemical bonds at the interface between a matrix and a reinforcing agent imparts maximum mechanical strength to this composite material.

To quote an exemple, Gent (3) demonstrated the effect of the number of interfacial chemical bonds between a glass surface and an elastomer on the failure strength.

The glass surfaces were treated with a mixture of vinyl- and ethylsilane. It is known that only the vinylsilane groups react with polybutadiene according to a radical reaction. The failure strength data plotted in Fig. 2 clearly show that adhesion increases proportionally to the quantity of vinylsilane used for treatment.

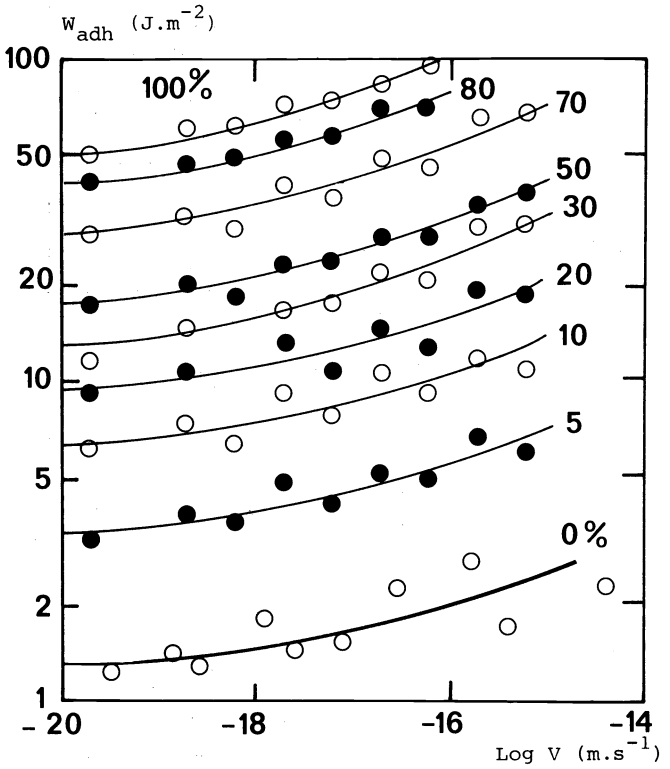

Fig. 2. Energy of adhesion vs. separation rate of glass-polybutadiene assembly, according to Gent.

At very low speed and high temperature, i.e. under conditions approximating equilibrium, the value of the energy required for failure passes from 1 J/m^2 in the case when only ethylsilane groups are deposited on the glass, so that no covalent bonds are formed with the elastomer, to a value of 40 J/m^2 when all chemical groups are vinylsilanes. This factor 40 may be related to the difference in intensity between covalent and dispersive bonding. This difference in peeling energy for these two cases is, however, higher by a factor of ca 20 than that calculated from the dispersive components of the surface energies and the energies of dissociation of the covalent bonds. This difference was assigned to the polymeric character of the elastomer. As a matter of fact, numerous polymeric chains must be subjected to stress before detaching the substrate, thus demonstration that performance of a composite material comprising a long chain polymeric matrix is better than that achieved with a more rigid or more highly crosslinked material. The decrease in failure strength of the glass-polybutadiene system with the crosslinking degree of the elastomer has also been verified by Gent.

Other interesting information with reference to the effect of chemical bonds on the properties of an assembly was contributed by Schultz and Delescluse (4), who developed a new method allowing investigation of the process of chemical adhesion, without modification of the characteristics of the materials assembled.

The phenomena have been assigned, as in the case of Gent's investigations, to the formation of covalent bonds at the interface, according to a radical process initiated by decomposition of a peroxide.

For a model assembly polyethylene/polyethylene (PE/PE), it was possible to calculate the number of covalent bonds created at the interface from values of the degree of swelling in a solvent. Fig. 3 shows that the peeling energy of the PE/PE assembly is directly proportional to the number of chemical bonds created at the interface. In certain cases this

energy may even be higher than the energy of cohesion of the materials.

Similar conclusions were obtained by Gent for model systems of polybutadiene assemblies, linked by covalent bonds generated through decomposition of dicumylperoxide via a radical mechanism.

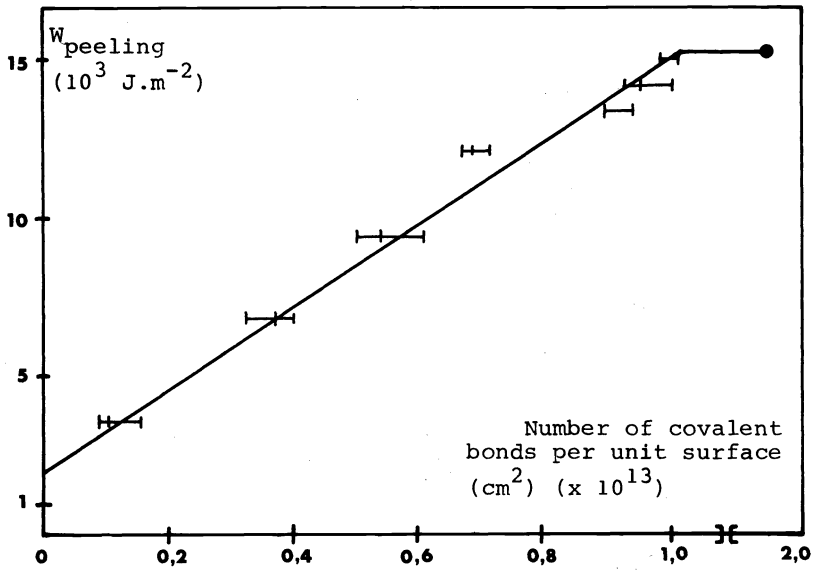

Fig. 3. Energy of adhesion vs. number of covalent bonds generated at PE/PE interface, according to Schultz and Delescluse.

Gent recalls, however, that the increase in peroxide quantity deposited on the surface causes an increase in the energy required for rupturing the system only in the case of low concentrations. In fact, the number of long chains decreases above a certain quantity of crosslinking agent, the molecular sequences are shorter, thus requiring shorter extension prior to break.

As was shown by various studies, investigation of the properties of the interface, however, must in certain cases be extended to that of the interphase. By way of example, Bikerman showed that the failure of an assembly never occurs at the interface of two solids (Ref. 5). He inferred therefrom that the strength of such a system is by no means dependent on the only interactions exchanged at the interface, but only on the volumic properties of the solids in contact. To account for the seemingly interfacial failure frequently observed, i.e. at the time of the "pull-out" of the fibres of a composite, he invokes the presence of a "low-cohesion interfacial layer".

Bikerman describes several classes of low-cohesion interfacial layers which consist of air, low molecular weight fractions or of products arising from reaction between the elements of the system.

Although Bikerman's analysis is questionable, the fact remains that numerous phenomena observed experimentally can be explained by this theory, thus confirming in these cases, the role played by the interphase rather than by the interface alone.

It is apparent from these examples that the behaviour of the interface of composite materials can in no way be derived from a single explanation.

In fact, the studies concerned with interfaces have been roughly divided into two fields : surface chemistry and micromechanics, depending on the authors and the speciality in which they are working, whereas in fact these two fields cannot be separated or partly left out of consideration.

THE TRANSMISSION OF STRESSES

The achievement of high mechanical strength composite materials is conditioned by the force actually transmitted to the fibres. Great interest is therefore attached to understand how the stress imposed on the materials is distributed on each fibre.

Until recent years, the main attention of the authors has been directed to measuring the shear strength of composites with unidirectional reinforcing agent. One of the first studies was concerned with the bending of a beam on backing pieces. The major disadvantage of such a system is that shear stress distribution is not easy to determine. Other methods were used for test pieces with varied shapes (parallelipipedal, trapezoidal, curved, dumbbells with holes in extremities), for compression and tensile tests.

The most recent method, based on research work by Fraser, Ancker, Di Benedetto (6, 7), and taken up again by Miwa (8), is concerned with tensile tests performed on samples containing a monofilament. This single test allows at the same time investigation of the distribution of structure defects in the fibre, the intensity of interaction exchange between reinforcing agent and matrix, and of stress transmission at the interface.

When the test piece is stretched beyond the elastic limit of the matrix, the monofilament breaks and the length of the fragments decreases as the load increases. The theoretical length of the longest fragments is equal to the critical length ℓ_c defined as the length for which the tensile load reaches the value which causes rupture of the fibre at half length.

In actual fact, the distribution must correspond to fragment lengths comprised between ℓ_c and $\frac{\ell_c}{2}$.

Equating the shearing forces and the breaking strength yields the relationship :

$$2\pi r \, \ell\tau = \pi r^2 \, \sigma$$

r being the radius of the fibre,
ℓ its length,
τ the shearing force,
σ the breaking strength of the fibre.

If the stress reaches the value σ, the fibre breaks in two fragments of length $\frac{\ell_c}{2}$ and hence :

$$\ell_c \simeq \frac{d\sigma}{2\tau}$$

d being the diameter of the fibre.

It is apparent, therefore, that the distribution of the lengths is directly related to the distribution of the breaking strengths and to the transmission of stresses at the fibre-matrix interface. In actual practice, this test consists in computer simulation of the tensile process of the matrix-monofibre sample, which determines the length of the fibres and their distribution. The function of distribution is represented as :

$$f(\ell) = \frac{3d}{8\tau} \, m \, \sigma_o^{-1} \left(\frac{\sigma - \sigma_c}{\sigma_o}\right)^{m-1} \exp\left\{-\left(\frac{\sigma - \sigma_c}{\sigma_o}\right)^{m}\right\}$$

where σ_c, σ_o and m are three parameters relevant to the mathematical model of the fibre strengths, according to a Weibull distribution. The value of the shear strength τ at the interface is estimated so that the $f(\ell)$ distribution calculated should correlate best with that determined experimentally.

An example of data recently found by Schultz and Simon (9) is shown in Fig. 4. The tensile tests were performed on test pieces consisting of glass fibres (untreated and silane treated) and a polyethylene matrix. The cumulative distribution of the fragments for the silane treated glass plotted against the ℓ/d ratios is narrower than that of the untreated glass, thus demonstrating a higher capacity of stress transfer at the polyethylene-silane treated fibre interface.

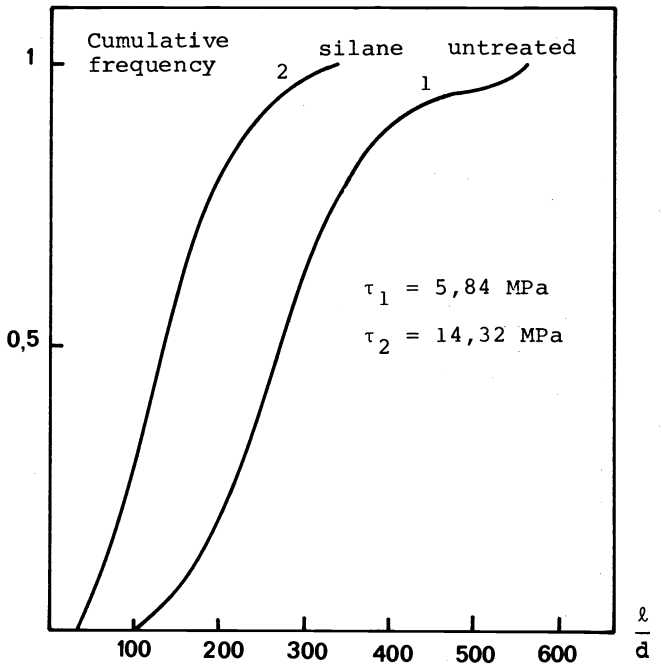

Fig. 4. Distribution curve of ℓ/d for a glass fibre, according to Schultz and Simon

In summary, the data yielded by this test lead to the calculation of the value of parameter τ which measures the capacity of stress transfer at the fibre-matrix interface. This method also provides a means for investigating the effect of the surface treatment of fibres by measuring the breaking strength and length of a given fibre. This technique should allow optimization of the properties of a composite materials, by correlating the parameters measured with other properties of the composite, such as strength, failure, impact strength or fatigue strength.

In spite of the tremendous theoretical and experimental work devoted to the understanding of interface behaviour, we are far from a perfect understanding but nevertheless significant progress to this aim has been made and we hope that it will continue.

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