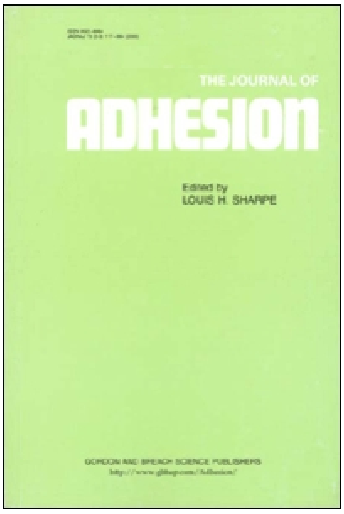

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Some Physico-Chemical Aspects of the Fibre-Matrix Interphase in Composite Materials*

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This paper deals with the influence of interphase formation on the stress transfer capacity of the fibre–matrix interface in single fibre composites and constitutes a brief review of our recent work. This influence is studied through the deviation of the experimental results from a recent theoretical analysis relating the interfacial shear strength to the reversible work of adhesion established between the fibre and the matrix. Two examples of interphases are considered: a transcrystalline layer in carbon fibre–PEEK composites and a pseudo-glassy interphase in carbon fibre–elastomer systems. In the former case, the low transverse mechanical properties of the transcrystalline layer lead to a decrease of the interfacial shear strength, whereas, in the latter case, the glassy behaviour of the interphase explains the improved interfacial stress transfer capacity.

KEY WORDS single fibre composites; interfacial shear strength; reversible energy of adhesion; transcrystalline interphases; elastomeric glassy interphases.

INTRODUCTION

Great attention has recently been devoted to the characterization and control of the fibre–matrix interface or interphase in polymer-based composite materials. It is now considered that the interphase plays a major role in the final performance of the composite and constitutes in fact the third component: while the matrix brings cohesion and the fibres support most of the applied mechanical stresses, the interphase ensures the load transfer. As in other multicomponent materials, interphases in composites are of different origin and exhibit a large range of properties. In

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this paper, which constitutes a brief review of our recent work, two examples of interphases will be considered, the goal being to understand how they influence the stress transfer capacity of the interface and hence the mechanical properties of the composites:

—the first example deals with a "transcrystalline" interphase in carbon fibre–PEEK composites.

—the second one concerns the formation of a pseudo-glassy interphase resulting from strong interactions in carbon fibre–elastomers (EVA, SBR or PUR) systems.

Both thermodynamical and mechanical properties of the interface are measured.

The reversible energy of adhesion, W_o, of the fibre–matrix interface is determined from the surface energies of the solids by using wetting and inverse gas chromatography measurements. W_o is expressed as the sum of London dispersive interactions, W_d, and Lewis acid-base or electron acceptor-donor interactions, W_{ab}, according to the following relationship:[1]

$$W_o = W_d + W_{ab} = (\gamma_f^d \gamma_m^d)^{1/2} - f \cdot \Delta H_{ab}\, n_{ab} \qquad (1)$$

where:

γ^d are the dispersive components of the surface energy of the reinforcing fibre (subscript f) and the polymer matrix (subscript m) respectively,

ΔH_{ab} is the enthalpy of acid-base interactions calculated from the sum of the cross-products of the acceptor and donor coefficients, K_A and K_D, of both the fibre and the matrix,[2,3]

n_{ab} is the population of acid-base pairs or acceptor-donor sites per unit interfacial area. According to Fowkes and Mostafa,[1] n_{ab} should be taken equal to 6×10^{-6} mol·m^{-2}. This value has been recently verified by Nardin and Schultz.[4]

The stress transfer capacity or shear strength of the interface, τ, is measured by a fragmentation test. In this test, a tensile load is applied to model single fibre composites. This load is transmitted from the matrix to the fibre and the fibre breaks into fragments until a limiting size is reached which will allow us to define a critical fragment length, l_c. Although a large controversy exists on the phenomena which are really responsible for this saturation process (interfacial decohesion, plastic deformation . . .), we assume that the interfacial shear strength, τ, can be calculated according to Fraser *et al.*[5] and can also be obtained from the shear lag analysis of Cox:[6]

$$\tau = \frac{d\, \sigma_f(l_c)}{2\, l_c} \qquad (2)$$

where d is the diameter of the fibre and $\sigma_f(l_c)$ is the tensile strength of the fibre at a gauge length equal to l_c. The quantity $\sigma_f(l_c)$ is usually obtained by extrapolation of σ_f measured at higher gauge length.[7] The measurement of the critical length, l_c, is performed either by an acoustic emission measuring device or by an optical microscope.

We have been able to find[4,8] a surprisingly general relationship between the quantities, τ, the interfacial shear strength, W_o, the reversible energy of adhesion and the moduli, E_f and E_m, respectively, of the fibre and the matrix expressed as follows:

$$\tau\left(\frac{E_f}{E_m}\right)^{1/2}=\frac{W_o}{\lambda} \tag{3}$$

We have found experimentally that the coefficient of proportionality, λ, which has the dimension of a length, is equal to 0.5 nm and could, therefore, correspond to a molecular center-to-center distance when only physical interactions are involved between molecules. This is in good agreement with our assumption that only physical interactions are concerned in this domain. Moreover, the fact that a factor $(E_f/E_m)^{1/2}$ is involved in equation (3) has been recently confirmed by Termonia[9] by means of a finite element analysis. In such conditions, the left hand side of equation (3), which is a normalized shear strength of the interface (normalized means that the shear strength is multiplied by a factor $(E_f/E_m)^{1/2}$ allowing all composite systems studied to be compared to each other), can be considered as an adhesive pressure.

Figure 1 shows that this relationship is perfectly verified when using a great variety of composite systems with glass and carbon fibres and thermosetting and thermoplastic matrices. Although all the results are in remarkable agreement with equation (3), it is clear that this semi-empirical model is oversimplified. Nevertheless, as fully discussed in a paper entirely devoted to its establishment,[4] this model seems to be valid in a large domain insofar as, in particular, the bulk properties of the matrices are not altered near the fibre surface or, in other words, no interphase exhibiting particular properties is formed.

In fact, the goal of the present paper is to study the formation and properties of interphases using this general model. We are going to show that any significant

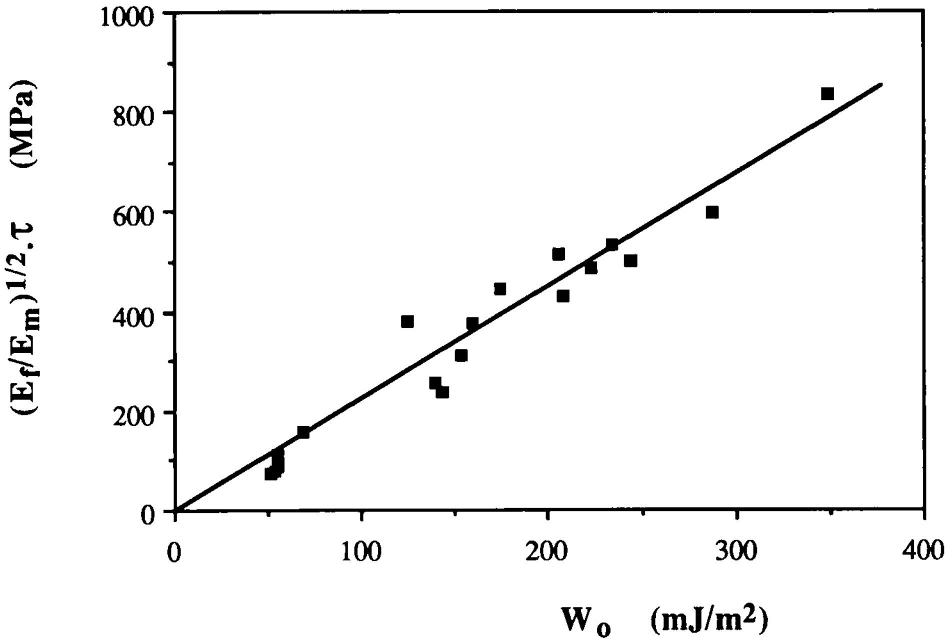

FIGURE 1 Relationship between the normalized shear strength of the interface and the reversible energy of adhesion.

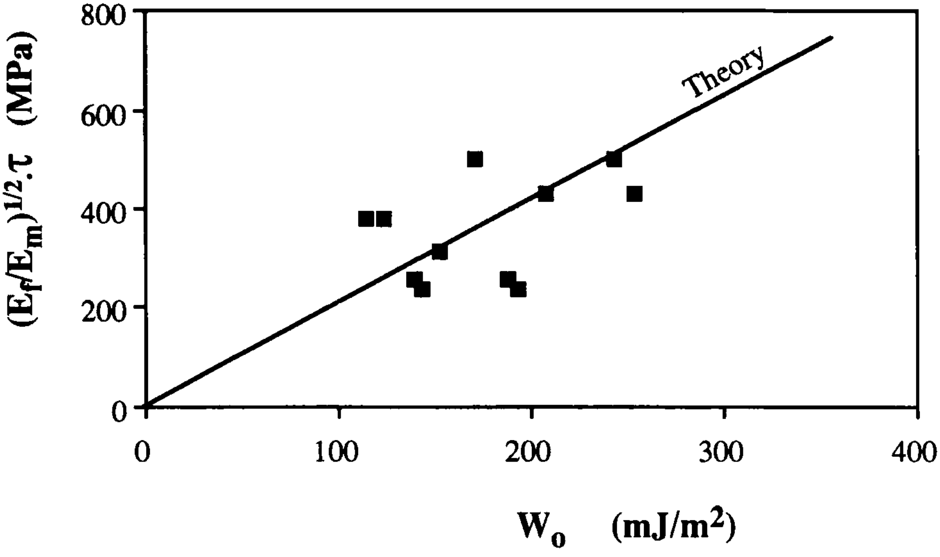

FIGURE 2 Relationship between the normalized shear strength of the interface and the reversible energy of adhesion for carbon fibre–PEEK composites.

deviation from the straight line shown in Figure 1 could be interpreted in terms of the formation of an interphase having a modulus, E_m^*, different from the modulus, E_m, of the bulk matrix. At the same time, the influence on the stress transfer capacity of such boundary layers could be evidenced.

"TRANSCRYSTALLINE" INTERPHASE

Composites made of carbon fibres having received different surface treatments and PEEK (poly-ether-ether-ketone) matrix show[10] a rather large scatter or deviation from the general behaviour given by equation (3), as shown in Figure 2. This has been attributed to the formation of a "transcrystalline" interphase near the fibre surface.[11]

The properties, structure and thickness of this "transcrystalline" interphase depend strongly on the processing conditions. The carbon fibre–PEEK interphase has, therefore, been modified by isothermal crystallisation at temperatures ranging from 320°C to 200°C.[10]

It is shown, in Figure 3, that the shear strength of the interface is modified only for the composite containing the highly-reactive oxidized carbon fibre, no change being observed with the low surface energy untreated carbon fibre. It can be concluded that the "crystalline" interphase and, therefore, the stress transfer depend on the level of interaction between the fibre and the matrix.

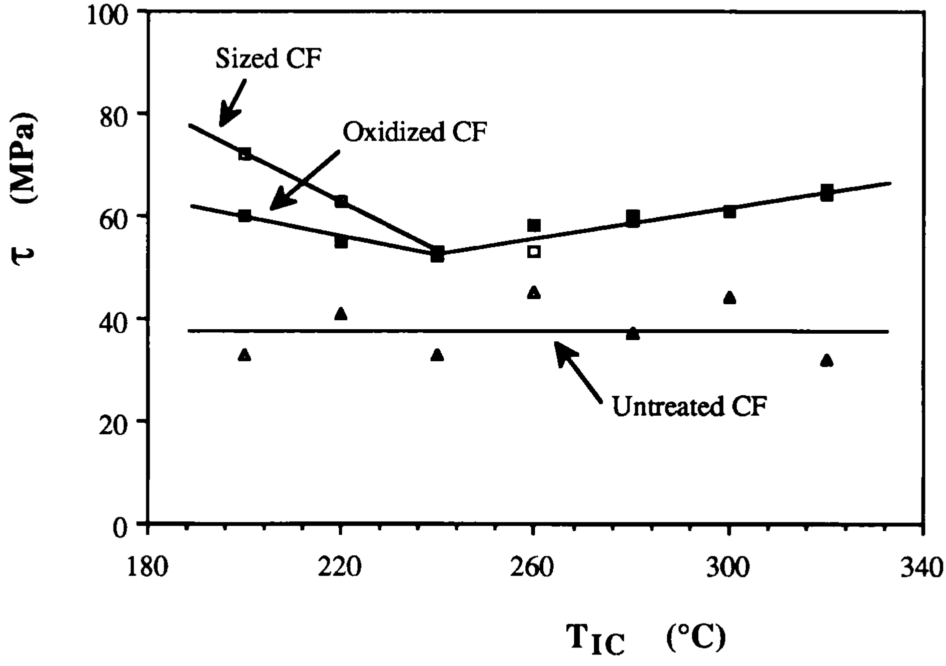

FIGURE 3 Variation of the interfacial shear strength as a function of the isothermal crystallisation temperature in carbon fibre–PEEK composites.

It is also observed that the shear strength is minimum at an isothermal crystallisation temperature of 240°C corresponding to the highest crystallisation rate.[12] It is concluded that the rate of crystallisation of the PEEK matrix is a major factor affecting the stress transfer capacity of the interface. The fast growth of a poorly organized structure or the creation of a highly constrained state of the amorphous phase at high rate of crystallisation could constitute complementary explanations.[11]

Assuming to a first approximation that a transcrystalline interphase is always formed near the fibre surface, it is clear that, during fragmentation, this interphase is subjected to a transverse tensile stress perpendicular to the direction of the crystallites, as schematically shown in Figure 4.

The transverse elastic modulus, E_m^*, of this interphase can be determined from equation (3), assuming that it is still valid as far as the bulk modulus E_m is replaced by E_m^*. The results, reported in Figure 5, show that the values of E_m^* are much smaller (50 to 70%, the lowest value of E_m^* being observed at a temperature corresponding to the highest rate of crystallisation)[12] than those of E_m, determined directly on the pure matrix having followed the same isothermal crystallisation procedure. This fact can be explained in the following way.

Since its crystalline phase is essentially included into randomly-dispersed spherulites, PEEK can be considered as a quasi-isotropic material. From recent measurements[13] of both the elastic modulus, E_m, and the degree of crystallinity, χ_m, of bulk PEEK, it appears experimentally that:

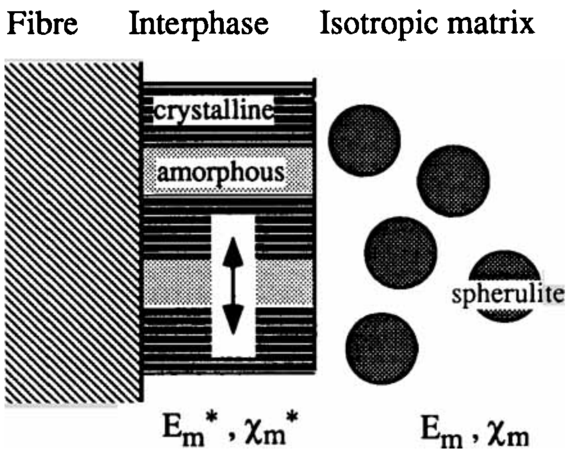

FIGURE 4 Schematic representation of a transcrystalline interphase.

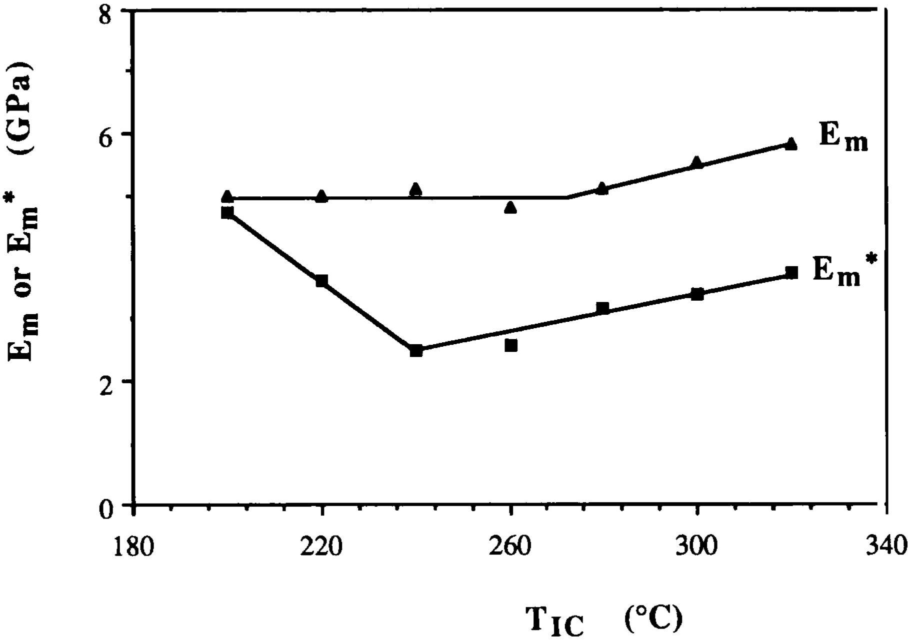

FIGURE 5 Variation of the elastic moduli of the interphase, E_m^*, and of the bulk PEEK matrix, E_m, as a function of isothermal crystallisation temperature.

$$E_m \approx \chi_m E_c + (1 - \chi_m)\, E_a \tag{4}$$

where E_a (1.8 ± 0.4 GPa) and E_c (15 ± 2 GPa) are the elastic moduli of the amorphous and crystalline phases, respectively.

To a first approximation, let us consider the transcrystalline interphase near the fibre surface as a homogeneous stacking of amorphous and crystalline layers (Fig. 4). From a simple, purely elastic, analysis, the Young's modulus, E_m^*, of this interphase in the direction of the fibre axis is related to its degree of crystallinity, χ_m^*, by:

$$E_m^* = \frac{E_c E_a}{(1 - \chi_m^*)\, E_c + \chi_m^*\, E_a} \tag{5}$$

In order to estimate the degree of crystallinity, χ_m^*, inside a transcrystalline interface, it is considered that χ_m^* is close to the content of the crystalline phase in a spherulite. Therefore, since the average value of χ_m is about 25% for most of the processing conditions of PEEK studied,[13] and taking the volume fraction of spherulites in the bulk equal to that of a loose random packing of spheres[14] (*i.e.* about 60%), the values of χ_m^* are found ranging from about 40 to 50%. This is in good agreement with the average value of χ_m^* ($\approx 50 \pm 10\%$) calculated by injecting the values of E_m^* given in Figure 5 into equation (5). Such an agreement confirms the fact that the elastic modulus, E_m^*, of the transcrystalline interphase in the direction of the fibre axis is inferior to E_m in each case, since a simple calculation from equations (4) and (5) shows that the degree of crystallinity, χ_m^*, inside the transcrystalline interphase must be higher than about 75% in order that E_m^* at least equals E_m.

Finally, an important conclusion is that the formation and the properties of such interphases in composites based on crystalline thermoplastic matrices can be controlled by the processing conditions, mainly the rate of crystallisation, but also by adjusting the level of adhesion at the fibre–matrix interface.

PSEUDO-GLASSY INTERPHASE

By testing, dynamically, unidirectional ethylene-vinylacetate (EVA) based composites containing varying amounts of carbon fibres, it is found that the apparent activation energy, corresponding to the glass transition, of EVA in the presence of the reactive oxidized carbon fibre is much higher than in the pure matrix.[15] This was attributed to the formation of an interphase resulting from chains of reduced mobility.[16] High interaction at the interface leads to a polymer layer exhibiting a glassy or pseudo-glassy behaviour as compared with the rubbery behaviour of the pure matrix.

The fragmentation test performed on such single fibre composites shows that results obtained at temperatures below T_g, *i.e.* $-36°C$, obey our general relationship (3) whereas results obtained at temperatures above T_g show that the stress transfer capacity is much higher than theoretically expected (Fig. 6).

The same observations are made for other matrices such as styrene-butadiene copolymer (SBR).[17] Figure 7 again shows an example of the relationship obtained between the interfacial shear strength and the reversible energy of adhesion in the

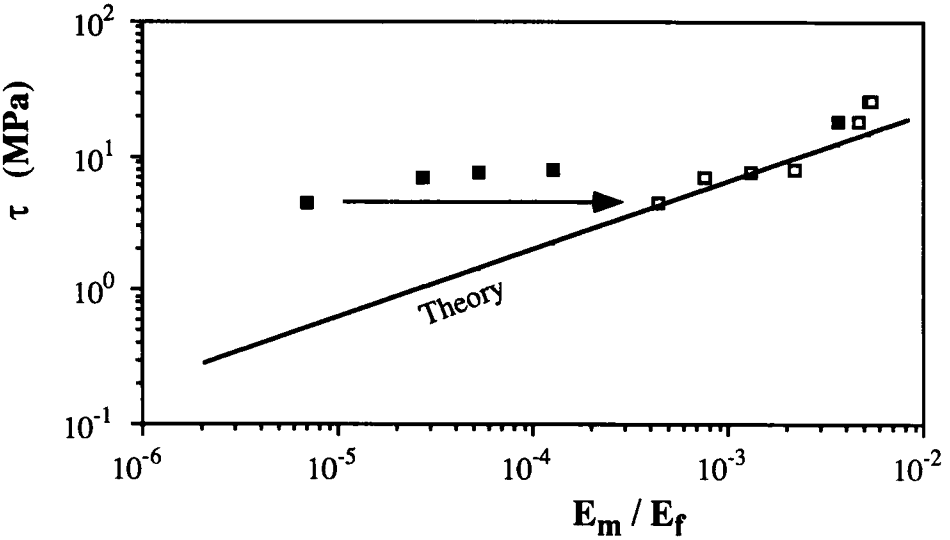

FIGURE 6 Relationship between the interfacial shear strength and the reversible energy of adhesion in the case of oxidized carbon fibre-EVA composites (☐: using E_m^* instead of E_m).

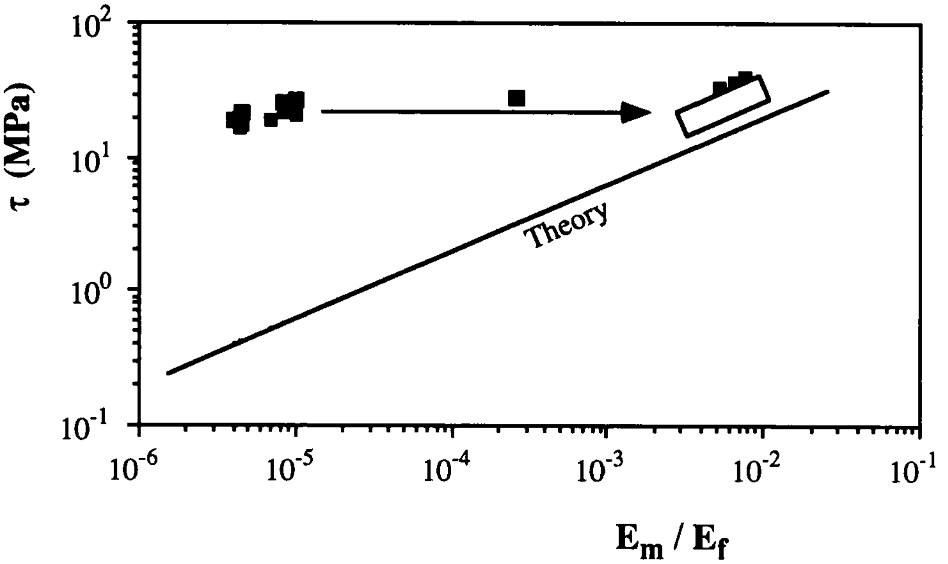

FIGURE 7 Relationship between the interfacial shear strength and the reversible energy of adhesion in the case of untreated and oxidized carbon fibre-SBR composites (☐: using E_m^* instead of E_m).

case of carbon fibre–SBR composites. It is seen that, here again, the stress transfer capacity is considerably higher than expected theoretically.

In both cases, the experimental values of τ are several order of magnitude higher than calculated from equation (3). When plotting τ as a function of the ratio E_m/E_f, in logarithmic scales, equation (3) should lead to a straight line of slope 0.5 (Figs. 6 and 7). It is seen that all the experimental data obtained at different temperatures lead to points lying above this theoretical line, at least when temperatures above T_g of EVA or SBR are considered.

This is attributed to the existence of a glassy interphase. This assumption is verified by replacing, in equation (3), the bulk modulus, E_m, of the matrix at a given temperature by the modulus, E_m^*, of the matrix in its glassy state. As seen in Figures 6 and 7, all the stress transfer values are thus shifted close to the straight line expected on theoretical grounds.

The same type of experiments, done with carbon fibres/EVA and SBR systems, have also been performed with carbon fibres/polyester-polyurethane or polyether-polyurethane composites and glass/polyether-polyurethane composites. Similar observations have been made and all results are in good agreement with the formation of a glassy interphase in the rubber matrix. This is demonstrated in Figure 8, where the ratio τ_{exp}/τ_{th} is plotted *versus* the square root of the ratio E_m^*/E_m. The term τ_{exp} is the value of the stress transfer observed experimentally, whereas τ_{th} is the value calculated from equation (3), E_m is the modulus of the bulk matrix and E_m^* is the modulus of the matrix in its glassy state. A good correlation is found for the very different composite systems studied.

The existence of such a pseudo-glassy interphase resulting from reduced chain mobility has also been verified by performing creep experiments on unidirectional composites containing a volume fraction of carbon fibres ranging from 5 to 30%.[17] As described by Haidar,[18,19] these composites exhibit a physical ageing behaviour at temperatures above T_g when subjected to a small static deformation of the order of 1 to 2%. The value of the dynamic storage modulus, E′, is measured by superimposing on the static deformation a dynamic deformation of very small amplitude (Fig. 9a).

When the static load is applied, segmental mobility of chains increases (softening) and the dynamic storage modulus, E′, abruptly decreases. Then the chain mobility at room temperature decreases (hardening) resulting in an increase of E′ with time (Fig. 9b). Moreover, it is observed that the rate of hardening increases with the fibre volume fraction showing the determining influence of the interfacial contact area between the polymer and the fibre. This physical ageing effect, observed at temperatures far above the glass transition temperature of the elastomer matrix (T_g (SBR) ≈ -50°C) can be explained only if an interphase of glassy behaviour exists at room temperature. These experiments confirm the existence of an interfacial layer exhibiting a glassy behaviour over a large range of temperatures above T_g and resulting from hindered mobility through strong interactions with the reinforcing fibres.

However, other potential mechanisms have been explored[17] in order to explain the unexpectedly high stress transfer capacity of carbon fibre-elastomer interfaces leading to the observed deviation between theoretical predictions and experimental results.

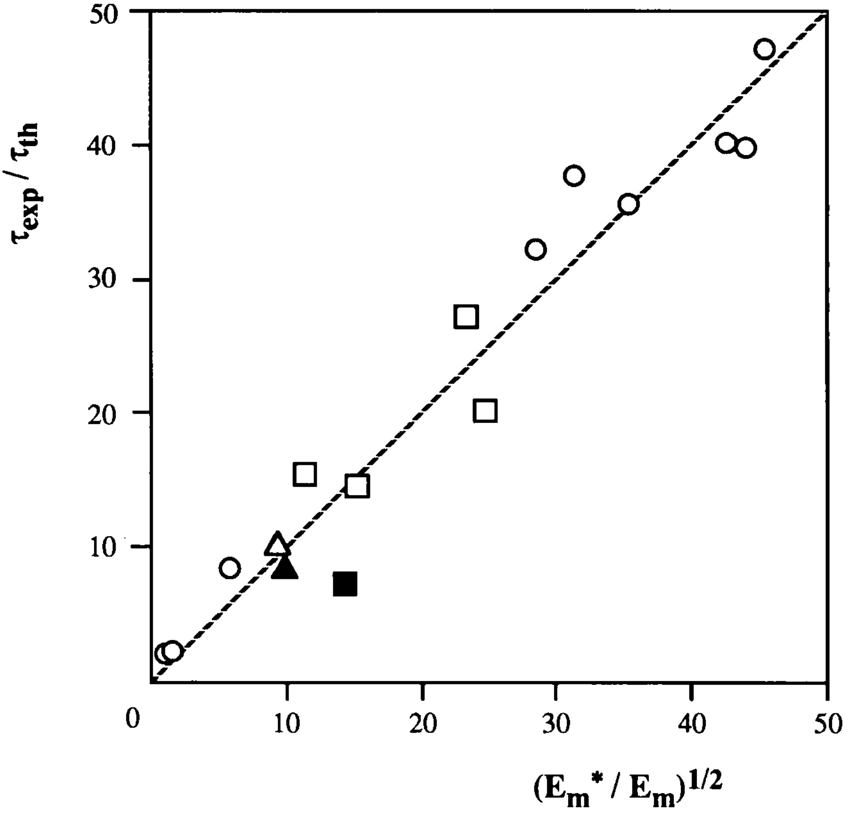

FIGURE 8 τ_{exp}/τ_{th} *vs* $(E_m^*/E_m)^{1/2}$ for different composite systems (oxidized carbon fibre: ○ SBR at different temperatures, ■ EVA, △ polyester-PUR, ▲ polyether-PUR; glass fibre: □ polyether-PUR).

For instance, a possible explanation could be that the reversible energy of adhesion, W_0, is underestimated because chemical bonds are created. The value of W_0 which would be required to fit the theoretical prediction given by equation (3) is of the order of 5000 mJ·m^{-2} which is meaningless.

Another possibility would question the validity of the micromechanical approach applied to a rubbery matrix. Again, no theoretical analysis, even those focused on elastomer-based composites, can explain our data. For instance, Gent and Liu[20] assume that interfacial decohesion first occurs and that the stress transfer during the fragmentation test is, therefore, mainly carried out by friction between the fibre and the elastomer. Such a frictional phenomenon leads to a breaking force of the fibre which should be constant at each step of the fragmentation process. On the contrary, in our case, it is observed that an increasing force is required to achieve the fragmentation of the carbon fibre in the SBR matrix. Moreover, it is shown[17] that the interfacial fracture energy calculated by assuming a frictional phenomenon to occur would be roughly ten times higher than the cohesive energy of SBR, which again has no physical meaning.

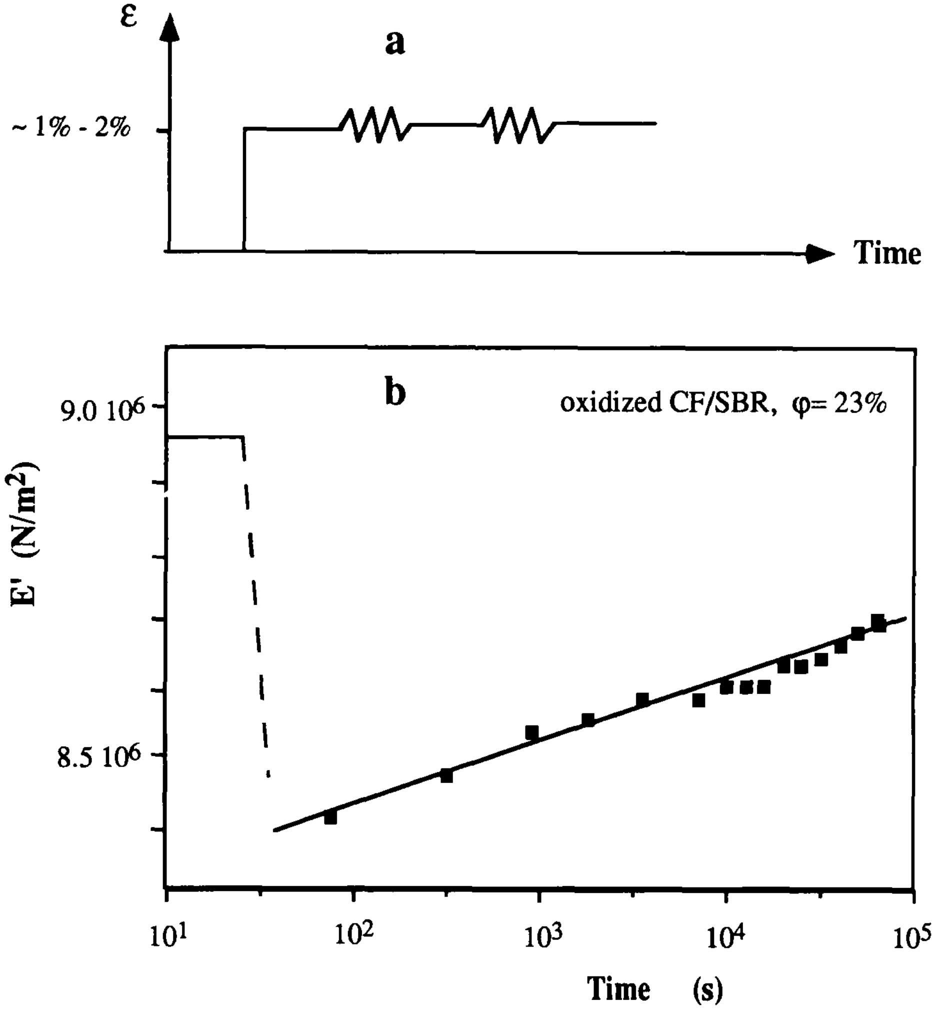

FIGURE 9 a: Schematical representation of creep measurements for determining ageing behaviour, b: Experimental variation of E′ *vs* time during ageing.

Finally, the influence of hysteretic losses due to the viscoelastic character of the matrix has also been carefully considered.[17] It is shown in Figure 10 that the shear strength of the interface, τ, does not depend on the rate of deformation of the single fibre composite samples during fragmentation. It does, however, depend on temperature (Fig. 11) but this effect can quantitatively be accounted for by the thermal variations of surface and interfacial energies. The slope of the τ *vs* T variation of the order of -0.09 MPa K^{-1} is found by differentiating equation (3) with respect to temperature:

$$\frac{\partial\tau}{\partial T}=\frac{1}{\lambda}\left(\frac{E_m^*}{E_f}\right)^{1/2}\frac{\partial W}{\partial T}$$

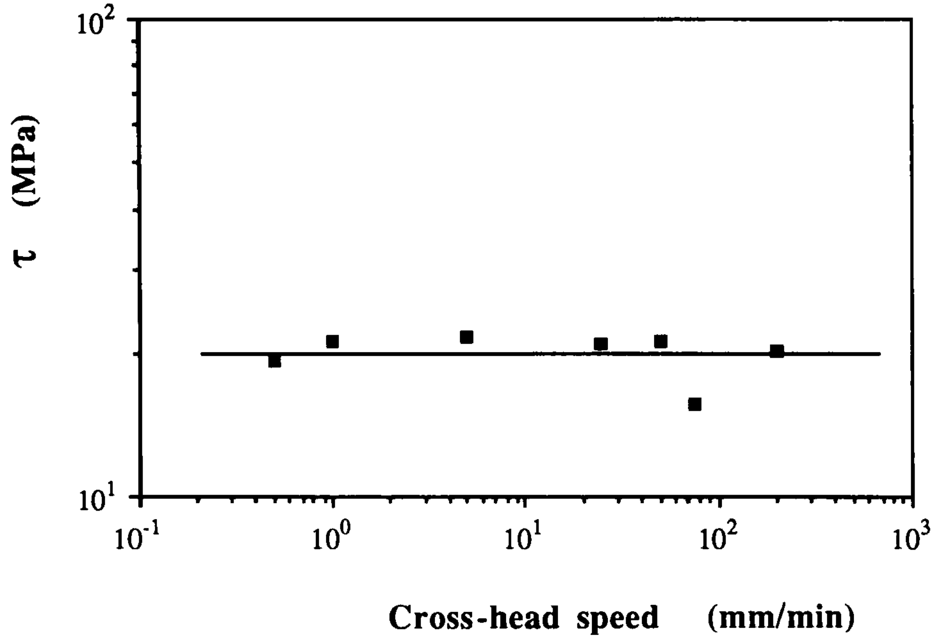

FIGURE 10 Variation of the interfacial shear strength with the strain rate during fragmentation of carbon fibre–SBR composites.

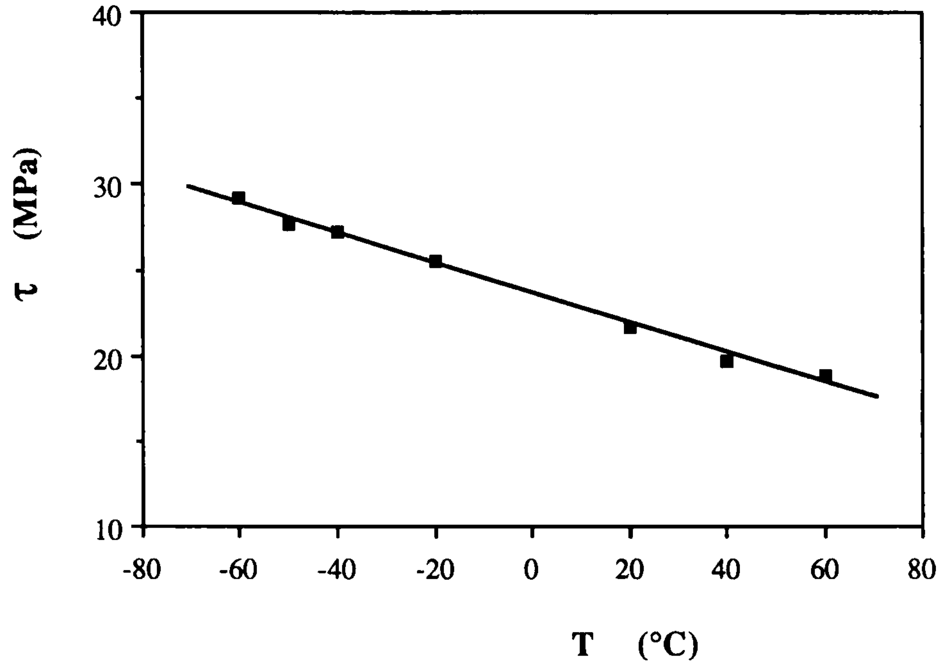

FIGURE 11 Variation of the interfacial shear strength with the temperature during fragmentation of carbon fibre–SBR composites.

assuming that E_m^* is constant with temperature and that the thermal variation of surface energy is about -0.1 mJ·m^{-2}·K^{-1}. The influence of a purely viscoelastic effect on the fragmentation process can, therefore, be disregarded.

It is, therefore, concluded that the high values of the interfacial shear strength of carbon fibre–elastomer composites are explained by the creation near the fibre surface of an interphase in which the polymer chain mobility is drastically reduced compared with the bulk matrix. Again, this effect depends strongly on the level of interaction between the fibre and the matrix as could be checked by using fibres and matrices of different surface energy.

CONCLUSION

The formation of interphases in composite materials plays a very important role since interphases can affect considerably the load transfer capacity of the interface.

In carbon fibre–PEEK composites, a "transcrystalline" layer is formed, the properties of which are controlled by both the level of the fibre-matrix adhesion and the rate of crystallisation of the matrix. The low transverse mechanical characteristics of this layer explain the decrease of the interfacial shear strength.

In fibre–elastomer composites, the interphase results from a decrease of mobility of the polymer chains near the interface due to strong adsorption. The glassy behaviour of this boundary layer explains the improved stress transfer capacity of the interface.

All these results also demonstrate that our general model relating the stress transfer capacity of the interface and the reversible energy of adhesion still remains valid when interfacial layers are formed, inasmuch as the mechanical properties of these interphases are taken into account in place of those of the bulk matrix.

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