

This article was downloaded by:

On: 22 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



The Journal of Adhesion

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713453635>

Interface and Interphase in Carbon Fibre-Styrene Butadiene Rubber (SBR) Composites

M. Nardin^a; A. El Maliki^a; J. Schultz^a

^a Centre de Recherches sur la Physico-Chimie des Surfaces Solides, CNRS, MULHOUSE, France

To cite this Article Nardin, M. , Maliki, A. El and Schultz, J.(1993) 'Interface and Interphase in Carbon Fibre-Styrene Butadiene Rubber (SBR) Composites', *The Journal of Adhesion*, 40: 2, 93 – 106

To link to this Article: DOI: 10.1080/00218469308031276

URL: <http://dx.doi.org/10.1080/00218469308031276>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Interface and Interphase in Carbon Fibre-Styrene Butadiene Rubber (SBR) Composites

M. NARDIN*, A. EL MALIKI and J. SCHULTZ

Centre de Recherches sur la Physico-Chimie des Surfaces Solides, CNRS, 24, Avenue du Président Kennedy, F-68200 MULHOUSE, France

(Received March 10, 1992; in final form July 28, 1992)

The stress transfer capacity of carbon fibre-SBR interfaces is analysed in terms of interfacial shear strength and measured by means of a fragmentation test on single fibre composites. For all the cases studied, the experimental values of the interfacial shear strength are largely higher than theoretically expected. Such a result is explained by the existence near the fibre surface of an interfacial layer in which the polymer chain mobility is greatly reduced. Such an interfacial region of low mobility is pointed out by mechanical spectrometry on unidirectional composites at different fibre contents. This interphase could exhibit a pseudo-glassy behaviour and, in particular, an elastic modulus close to that of the elastomer in its glassy state whatever the temperature.

KEY WORDS fibre-matrix adhesion in composites; stress transfer phenomenon; fragmentation test on single fibre composites; carbon fibre-rubber interface; interphase.

1 INTRODUCTION

Over the past decade, the use of fibre reinforced elastomer composites has been continuously growing, in particular in the paper industry (printing blankets), for example, as well as for automotive and airplane applications. This is mainly due to the fact that new elastomers, especially thermoplastic elastomers, exhibit an outstanding balance of properties vis-a-vis engineering thermoplastics. As for other composite materials (thermosetting or thermoplastic resin-based composites), the fibre-elastomer interface plays a major role in the final and in service performances of composites. However, the literature concerning the mechanical and physical properties of these types of interfaces is surprisingly poor.

The aim of the present study is to analyse the stress transfer capacity of carbon fibre-styrene butadiene rubber (SBR) interfaces in relation to the level of adhesion established between both materials. The choice of SBR is mainly derived from the fact that it is a purely amorphous elastomer. The interfacial stress transfer capacity

*Corresponding author.

is defined in terms of interfacial shear strength measured by means of a fragmentation test on single fibre composites.

A model has been recently proposed¹ to correlate the interfacial shear strength (τ) to the reversible work of adhesion (W) between fibre and matrix in polymer-based composites. In this model, W is defined as the sum of dispersive and Lewis' acid-base interactions (physical interactions) between the fibre and the matrix. For different composite systems, constituted of thermoplastic or thermosetting resins reinforced by glass or carbon fibres, it was shown that τ is related to W as follows:

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

where E_m and E_f are the elastic moduli of the matrix and the fibre, respectively. The coefficient λ is a distance equal to about 0.5 nm and corresponds to a conventional intermolecular centre-to-centre distance involved in physical interactions, such as Van der Waals and acid-base interactions. However, to establish equation (1), it has been assumed that (i) both the fibre and the matrix exhibit a purely elastic behaviour, (ii) a pure elastic stress transfer is involved at the interface and (iii) no interfacial layers exist between the fibre and the matrix.

In the present study concerning rubber-based composites, the three previous assumptions are certainly not fulfilled. In particular, the existence of an interfacial layer, in which the mobility of elastomeric chains is greatly reduced compared with the bulk, was recently evidenced in particulate reinforced rubbers^{2,3} by means of mechanical spectrometry. In fact, this interphase is able to age physically at temperatures above the glass transition temperature of the matrix and then exhibits a pseudo-glassy behaviour. Consequently, an additional goal of this work is to test the validity of the proposed model in the case of elastomeric matrices, in particular if such an interphase is formed.

2 EXPERIMENTAL

The fibres used in this study were untreated, oxidized (electrolytic oxidation) and sized PAN-based high strength carbon fibres (T300 from Soficar), exhibiting an elastic modulus E_f of 236 ± 15 GPa.

Only one type of SBR (BASF 1500), with 23.5% by weight of styrene, was used for the whole study. This rubber was slightly cross-linked by mixing in at 60°C, in a Brabender Plasti-Corder PLE 651 device, 0.45% by weight of dicumyl peroxide (DCP), which totally decomposes in a short time at temperatures above 120°C.

Contrary to previous analyses,^{1,4} we consider that SBR is essentially a non-polar polymer exhibiting a negligible ability to establish acid-base interactions with a carbon fibre surface. The interfacial adhesion energy, W , between both materials is therefore simply assumed equal to the sum of dispersive and polar interactions, according to Owens and Wendt's approach:⁵

$$W = 2(\gamma_f^D \gamma_m^D)^{1/2} + 2(\gamma_f^P \gamma_m^P)^{1/2} \quad (2)$$

where γ^D and γ^P are, respectively, the dispersive and polar components of the surface energy of carbon fibre (subscript f) and SBR matrix (subscript m).

The surface energy data for the carbon fibres were already measured in a previous study.⁶ Both dispersive and polar components of the surface energy of the matrix are determined by contact angle measurements of liquids, *i.e.* tricresylphosphate (TCP), methylene iodide (CH_2I_2) and water, on SBR sheets at room temperature, by means of a tensiometric method using a DCA 322 (Cahn) apparatus. Calculation of γ_m^D and γ_m^P is based on the Young-Dupré relationship:^{7,8}

$$\gamma_l(1 + \cos\theta) = 2(\gamma_l^D \gamma_m^D)^{1/2} + 2(\gamma_l^P \gamma_m^P)^{1/2} \quad (3)$$

where θ is the contact angle and $\gamma_l (= \gamma_l^D + \gamma_l^P)$ is the surface energy of the liquid. The use of TCP and CH_2I_2 , which are non-polar liquids, leads to the value of γ_m^D , while contact angles of water allowed the determination of γ_m^P according to equation (3).

Single fibre composites for the fragmentation test are prepared in the following way. Two sheets of SBR (0.5 mm thick) are first obtained by moulding (6 MPa pressure) at 90°C for 60 minutes. These sheets are then moulded (10 MPa pressure) on each side of a picture frame, supporting eight parallel carbon fibres, for 60 min. at 150°C to ensure total decomposition of the peroxide in the matrix. Hence, specimens according to ISO 1/2 standards are carefully cut by means of a cutter so that the fibre axis coincides with the axis of the composite as well as possible.

Each sample is then subjected, at a standard cross-head speed of 1 mm/min, (except for some samples for which cross-head speed was varied from 0.5 to 200 mm/min), on an Instron 1195 H tensile testing machine using an environmental chamber enabling temperatures to be varied from -80 to about +60°C (standard conditions : room temperature). Five specimens are tested, corresponding to about 150 to 300 fibre fragments, for each type of measurement. Young's modulus, E_m , of SBR, defined as the tangent at the origin of the stress-strain curves, is measured *versus* temperature in the same experimental conditions. Values of E_m from about -150 to +60°C are also obtained by means of a mechanical Metravib MAK 03 spectrometer at a frequency of 15.6 Hz.

In order to determine the length and the number of fibre fragments during the fragmentation process, different samples of the same type of composite are clamped at different levels of strain on a special frame allowing one to maintain them at the chosen strain and, since SBR is optically transparent, to observe the fibre failures under a Leitz microscope. This procedure leads to the determination of the strain at which a saturation of the fragmentation process occurs. It is worth noting that the fracture strain of SBR was found equal to about 150% at room temperature.

At the end of the fibre fragmentation process, the critical length l_c is defined as 4/3 times the mean fragment length in agreement with Kelly and Tyson.⁹ The interfacial shear strength, τ , is therefore calculated according to the Fraser and Di Benedetto¹⁰ expression:

$$\tau = \frac{d}{2l_c} \sigma_f(l_c) \quad (4)$$

where d and $\sigma_f(l_c)$ are, respectively, the fibre diameter and the fibre tensile strength at a gauge length equal to the critical length l_c . The values of $\sigma_f(l_c)$ are calculated by extrapolation at l_c (of the order of 1 mm) of fibre strength data obtained at higher

gauge lengths, as described previously.¹¹ By combining equations (1) and (4), the critical aspect ratio l_c/d is given by:

$$\frac{l_c}{d} = \frac{\lambda \sigma_f(l_c)}{2W} \left(\frac{E_f}{E_m} \right)^{1/2} \quad (5)$$

It is clear that expressions (4) and (5), based on a purely elastic analysis, may not be well adapted for elastomeric materials such as SBR and this fact will be discussed later.

Sheets (4 mm thickness) of unidirectional oxidized carbon fibre-SBR composites are made from fibre bundles (6K filaments) using the same moulding conditions that were described above. The volume fraction ϕ of fibres is varied from 5 to 30%. Square pieces (14 × 14 mm) are cut in these sheets with a razor blade and then glued on the two plates of the Metravib mechanical spectrometer. As proposed elsewhere,^{2,3} in order to evidence a physical ageing behaviour of the composites at temperatures above the T_g of the matrix, these samples are submitted, in a direction perpendicular to the fibre axis, to a moderate static tensile load of 1.2 N (resulting strain of 1 to 2%) over which is superimposed, periodically, a dynamic deformation (frequency = 15.6 Hz) of very low amplitude (~0.05%). The variation of the storage dynamic modulus E' versus time is recorded for each composite.

Finally, thermal properties, *i.e.* essentially glass transition temperature, T_g , of neat SBR as well as SBR matrix in unidirectional composites with different fibre content ϕ , are determined by differential scanning calorimetry (DSC) using a Mettler TA 3000 apparatus. The DSC spectra are recorded with an increasing temperature rate of 10°C/min.

3 RESULTS AND DISCUSSION

The values of the dispersive and polar components of the surface energy of SBR and carbon fibres as well as the resulting thermodynamic adhesion energy, W , between both materials, calculated from equation (2), are gathered in Table I. As expected, SBR appears to be a poorly polar matrix, which is certainly not able to establish acid-base interactions with carbon fibre surfaces. The lowest value of W is obtained in the presence of sized carbon fibres, mainly due to the fact that the

TABLE I
Values of the dispersive γ^D and polar components γ^P of the surface energy of SBR and carbon fibres (from Ref. 6), and energy of adhesion W between both materials

Materials	γ^D (mJ/m ²)	γ^P (mJ/m ²)	W (mJ/m ²)
SBR	35 ± 3	4.5 ± 0.5	—
untreated fibre	50 ± 8	7 ± 3	95
oxidized fibre	48 ± 10	15 ± 4	98
sized fibre	34 ± 6	13 ± 3	84

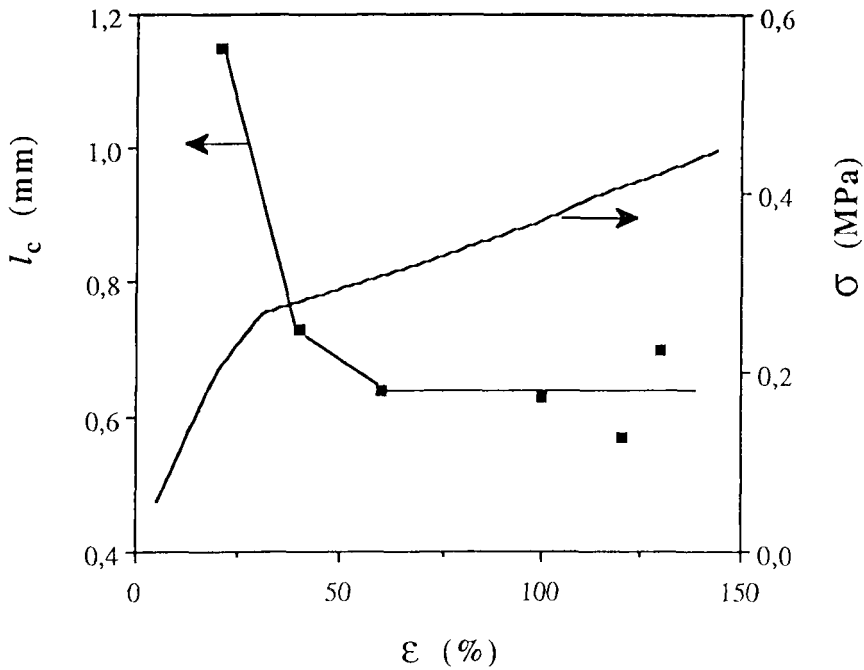


FIGURE 1 Critical length l_c for systems involving untreated carbon fibres at room temperature and tensile stress σ of SBR versus strain ϵ .

dispersive component of the surface energy of this latter is smaller than for other fibres and close to that of a polymer.

In order to determine at which applied strain ϵ the fibre fragmentation process stops, the variation of the critical length l_c versus ϵ for untreated carbon fibre-SBR system is shown in Figure 1, in relation to a typical stress-strain curve of single fibre composites. It appears that l_c reaches a minimum plateau value for ϵ close to 60%, indicating that no additional load can be transferred above this ϵ -value. As shown in Figure 1, this limiting stress transfer value of strain corresponds to the region where the stress-strain curve exhibits a creep-like shape, *i.e.* when a large deformation results from a slowly increasing stress. Therefore, for the whole study, values of l_c will always be determined as a strain considerably higher (130–140% at room temperature) than this limiting value and close to the ultimate tensile strain of the matrix (150% at room temperature) to ensure that the fragmentation process is totally achieved.

Figure 2 shows the relationship between the interfacial shear strength, τ , calculated from equation (4), and the adhesion energy, W , at the interface. It immediately appears that the experimental values of τ are much higher, about 40 times, than those theoretically expected from equation (1). Consequently, in Figure 3, it can be seen that the variations, in logarithmic scales, of the critical aspect ratio l_c/d versus E_f/E_m , for systems involving untreated and oxidized carbon fibres, lie below the theoretical curve corresponding to equation (5). Similar results have already

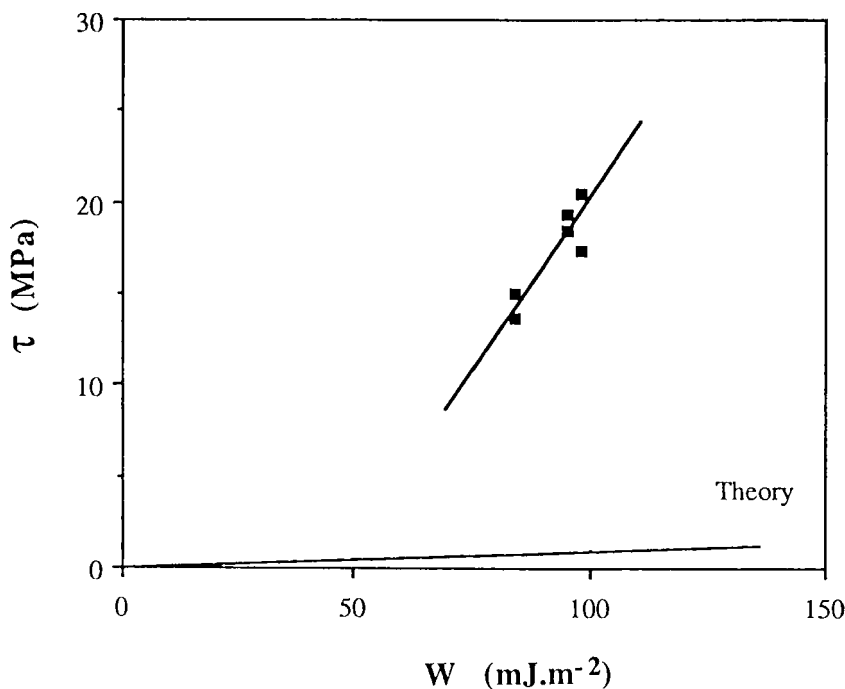


FIGURE 2 Relationship between the interfacial shear strength τ and the energy of adhesion W at room temperature. Comparison with theoretical predictions (equation (1) with $W = 100 \text{ mJ/m}^2$).

been observed on carbon fibre-poly(ethylene-vinylacetate) or glass fibre-polyurethane systems.¹² Such variations were obtained by carrying out fragmentation tests at different temperatures, which mainly affect the elastic modulus E_m of the SBR matrix. Therefore, it is noticed that at temperatures below the T_g ($\sim -50^\circ\text{C}$) of the matrix, the experimental points are located in the near vicinity of the theoretical curve. On the contrary, as already observed previously,¹² at temperatures above the T_g of SBR, it seems that the values of l_c/d are almost kept constant, except at high positive temperatures where they increase again slightly.

Hence, it can be first concluded that our model works well for systems involving the rubber matrix when the matrix is in its glassy state and, on the contrary, fails to explain the results obtained at temperatures higher than the glass transition temperature of the rubber.

To explain such a discrepancy between theoretical predictions and experimental results, several assumptions can be made:

- (i) The value of W is underestimated for the systems considered. According to equation (1), higher values of W could explain the experimental values of τ .
- (ii) The analytic approach, based on a purely elastic interfacial stress transfer proposed by Cox,¹³ is totally inadequate. Therefore, inelastic deformations have to be taken into account; in particular, after an interfacial rupture has

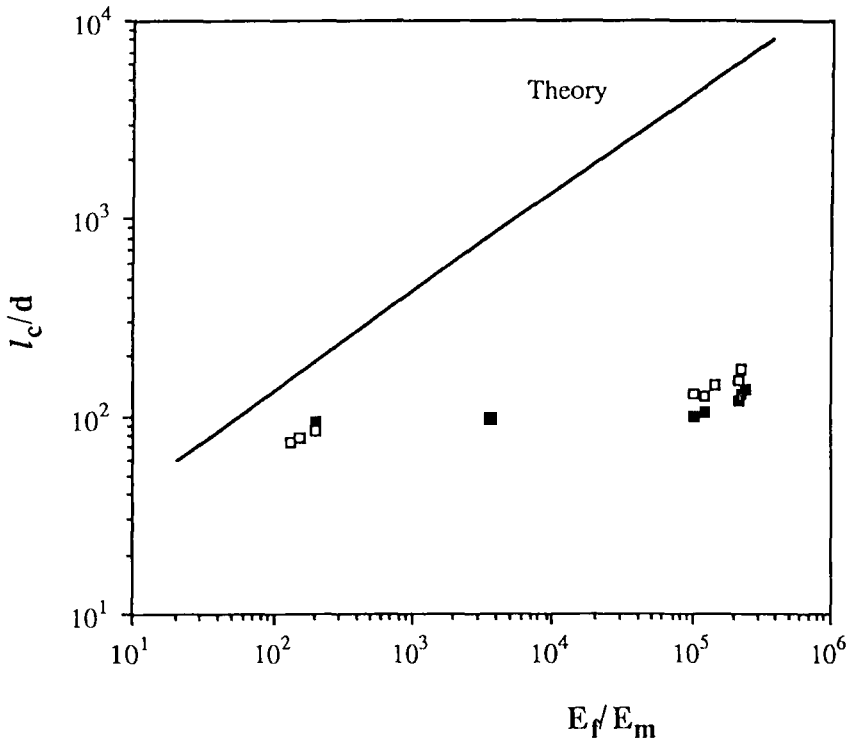


FIGURE 3 Variation of the critical aspect ratio l_c/d versus E_f/E_m in logarithmic scales for untreated (■) and oxidized (□) carbon fibres.

occurred, a friction phenomenon between fibre and matrix as recently proposed by Gent and Liu.¹⁴

- (iii) The influence of hysteretic losses in the bulk matrix, due to the viscoelastic behaviour of SBR in its rubbery state, has to be considered. Such a behaviour could lead to a large increase of the measured interfacial shear strength. By analogy with the rheological model of adhesion first proposed by Gent and Schultz,¹⁵ it can be assumed that the experimental shear strength, τ_{exp} , is related to the theoretical resistance, τ_{th} , (equation (1)) as follows:

$$\tau_{exp} = \tau_{th} \phi(v, T) \tag{6}$$

where ϕ is a viscoelastic term, obeying time-temperature equivalence according to Williams-Landel-Ferry,¹⁶ and thus depending on strain rate (v) and temperature (T) at which the fragmentation test is performed. As mentioned above, the value of ϕ should be equal to about 40 for a cross-head speed of 1 mm/min at room temperature.

- (iv) The existence of an interfacial layer, which exhibits physical and mechanical properties completely different from the bulk SBR, should be assumed. In

particular, an interphase constituted of elastomeric chains of reduced mobility near the fibre surface, as proposed elsewhere² for particulate reinforced rubber, can be invoked.

The four previous assumptions are now examined in turn.

First, an underestimation of W cannot explain the discrepancy observed, since the W -value required to verify the model according to equation (1) would be of the order of 5000 mJ/m^2 , for the given conditions. Obviously, such a high value has no physical meaning.

Let us examine now the second assumption concerning the validity of the micro-mechanical approach. First, it has to be mentioned, according to Netravali *et al.*,¹⁷ that the critical length, l_c , is not necessarily equal to $4/3$ times the mean fragment length, the multiplying factor being between about 1 and 1.5. It is clear that such a scatter affects the values of τ but cannot explain why these values are so high.

At present, any theoretical analysis on interfacial stress transfer in composite materials cannot explain the results obtained in the present study, even those specially focused on elastomer-based composites. For example, Gent and Liu¹⁴ have recently proposed an energy approach based on the fact that during the fragmentation test interfacial decohesion primarily occurs and then stress transfer is mainly carried out by friction between fibre and rubber. Their analysis leads to the following expression of the force, f , required for the fragmentation phenomenon in single fibre composite and allows the estimation of G_a , the interfacial fracture energy:

$$f = \pi dk \frac{l_c}{2} + (2\pi AdE_m G_a)^{1/2} \quad (7)$$

where A is the cross sectional area of the sample, and k a parameter equal to the product of the friction coefficient μ and the normal pressure p at the interface. Gent and Liu have studied model composites constituted of glass fibres or glass rods embedded in silicone resins for which k is kept almost constant ($\sim 0.5 \text{ MPa}$). Consistent results were, therefore, obtained in good agreement with those of pull-out experiments on the same systems and peeling energy on silicone-glass sheet assemblies. Nevertheless, they observed that the force at which fibre breaking occurs is almost constant at each step of the fragmentation process in good agreement with a unique frictional phenomenon. On the contrary, we have noticed that an increasing force is required to achieve the fragmentation of carbon fibre in the SBR matrix. Moreover, a rapid calculation based on equation (7), taking $A = 6 \text{ mm}^2$, $l_c \approx 1 \text{ mm}$, $d \approx 7 \text{ }\mu\text{m}$, $E_m \approx 1 \text{ MPa}$, $k \approx 0.5 \text{ MPa}$ (Gent and Liu's value) and $f \approx 1.8 \text{ N}$ at the end of the fragmentation process (Figure 1), shows that the first term of the right-hand side of equation (7), corresponding to friction loading, is negligible and leads to an estimated value of G_a of about 13 kJ/m^2 . This value is three to ten times higher than the cohesive energy of SBR¹⁸ and, therefore, has no physical meaning.

In order to determine the importance of a viscoelastic effect on the experimental values of the interfacial shear strength τ , a few fragmentation experiments were performed at different strain rates and temperatures. Figure 4 shows that, for the system involving untreated carbon fibres at room temperature, τ is not dependent

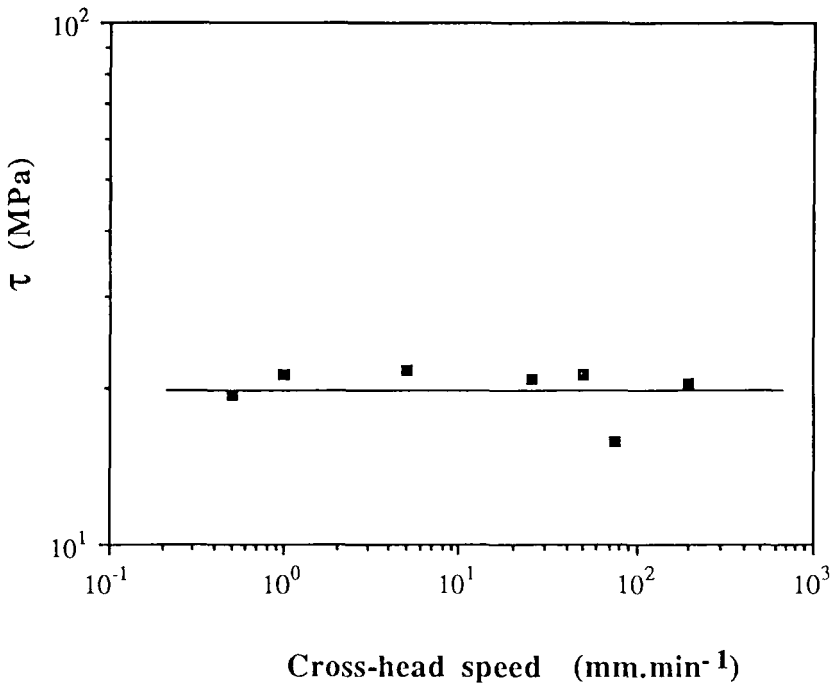


FIGURE 4 Interfacial shear strength τ for untreated carbon fibre systems at room temperature *versus* cross-head speed used during the fragmentation test.

on the cross-head speed applied during the fragmentation test. Therefore, to a first approximation, it can be concluded that hysteretic losses have no influence on the critical length, l_c , which is a morphological quantity, although these losses actually exist in the bulk matrix during the fragmentation experiment. This indicates that a viscoelastic effect can be rejected. However, Figure 5 shows that τ is a temperature-dependent quantity for untreated and oxidized carbon fibre-SBR composites (cross-head speed = 1 mm/min). Moreover, at a temperature, T , above the T_g of the matrix, τ linearly decreases with T for both cases. This decrease can be interpreted in terms of surface energy gradient *versus* temperature, as will be seen in the next section, rather than being related to a viscoelastic effect.

Finally, before attempting to analyse an eventual effect of an interfacial layer on the stress transfer phenomenon, such an interphase has first to be pointed out by appropriate experiments. This is carried out by creep measurements on unidirectional oxidized carbon fibre-SBR composites, as proposed in another study^{2,3} and described in the experimental section. The dynamic storage modulus E' of the composites, for volume fraction φ greater than 5%, is found first to decrease suddenly when the static load is applied. This corresponds to a softening phenomenon related to an increase of segmental mobility of the polymer chains. Afterwards, a linear increase of E' *versus* time is observed on a logarithmic scale. This is illustrated in Figure 6 for a composite with a fibre volume fraction φ equal to

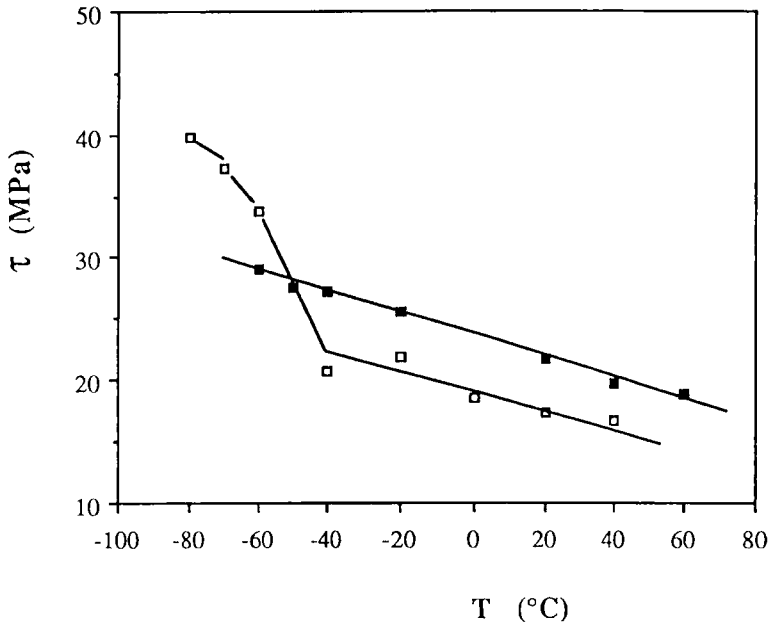


FIGURE 5 Interfacial shear strength τ for untreated (■) and oxidized (□) carbon fibre systems *versus* temperature T.

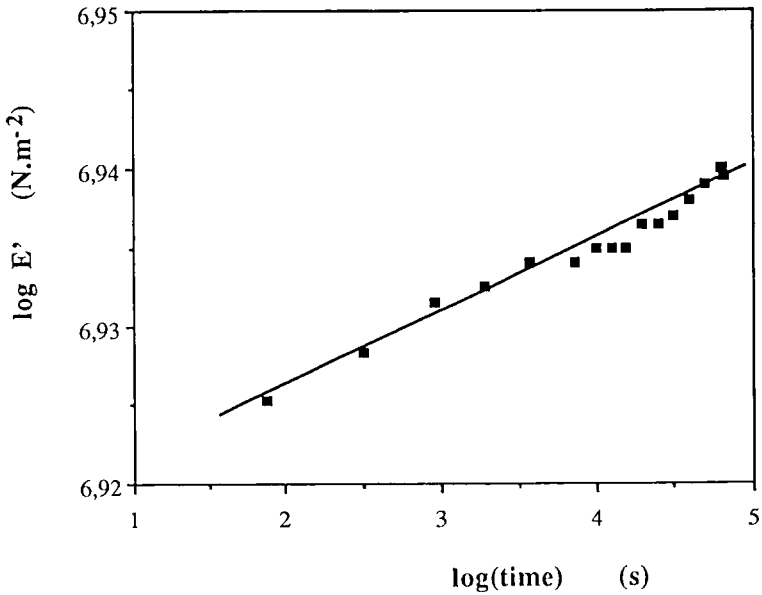


FIGURE 6 Dynamic storage modulus E' *versus* time in logarithmic scales for unidirectional oxidized carbon fibre-SBR composites (fibre volume fraction=23%) subjected to a tensile load of 1.2 N.

Downloaded At: 13:47 22 January 2011

23%. This increase results from a physical ageing phenomenon (decrease of the mobility of macromolecular chains) at room temperature, *i.e.* far above the glass transition temperature ($\sim -50^{\circ}\text{C}$) of SBR. Such a physical ageing process can only be attributed to the existence, near the fibre surface, of an interfacial region exhibiting a pseudo-glassy behaviour in a large range of temperature, and maybe whatever the temperature, as presumed in another work.² The slope, v_p , of the straight line $\log E'$ versus $\log(\text{time})$ can, therefore, be considered as the rate of hardening of the interphase. It is clear that the physico-chemical interactions between carbon fibre and SBR at the interface, essentially London's interactions as seen above, are able strongly to reduce the mobility of the elastomeric macromolecules in the neighbourhood of the fibre surface. A precise analysis of DSC spectra for all the composites studied does not reveal any modification of the glass transition zone of bulk SBR, altering either the intrinsic value of T_g or the width of the temperature range of the whole transition. This could confirm that such a "glassy" interphase, if it actually exists, does not exhibit a glass transition.

Figure 7 shows that the rate of physical ageing, v_p , increases with the fibre volume fraction, ϕ , in the composites. The scatter in the results is certainly due to an actual fibre volume fraction in the small specimens subjected to the test different from the mean value of ϕ in the laminates. This increase indicates that v_p clearly depends on the interfacial surface area and then is in agreement with the existence of an interfacial SBR layer of reduced mobility.

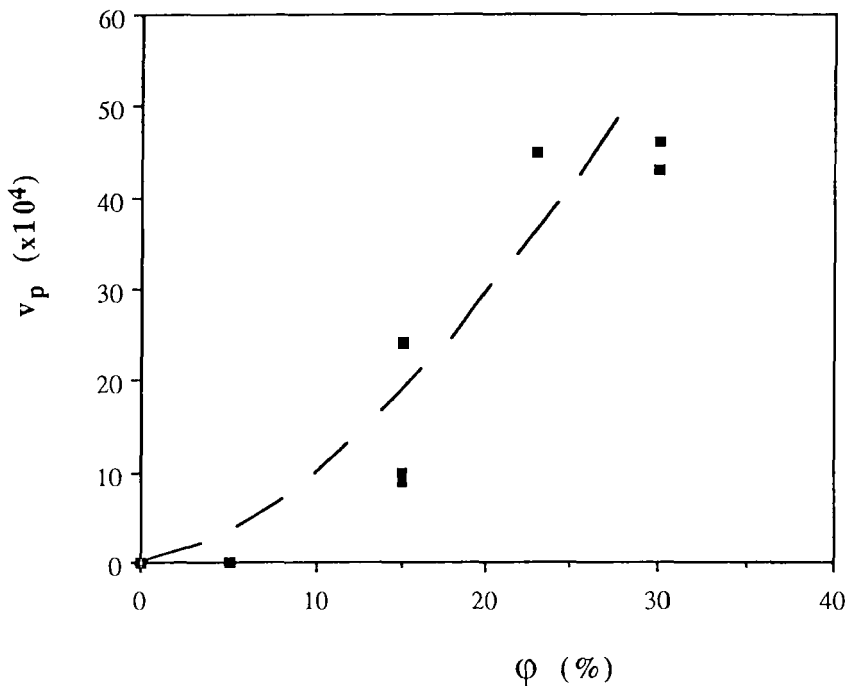


FIGURE 7 Physical ageing rate v_p versus fibre volume fraction ϕ of unidirectional oxidized carbon fibre-SBR composites subjected to a tensile load of 1.2 N.

To determine the influence of such an interphase on the stress transfer phenomenon at the fibre-matrix interface, it can first be assumed that the elastic modulus E_i of this interphase has to be taken into account in equation (1) in place of the Young's modulus, E_m , of the bulk matrix:

$$\tau = \left\{ \frac{E_i}{E_f} \right\}^{1/2} \frac{W}{\lambda} \quad (8)$$

This assumption is based on a recent theoretical study,¹⁹ which analyses the transfer of load through an interphase or a fibre coating using a finite element technique. It is shown (see in particular Figure 5 in Ref. 19) that the normalized load, L , carried by the fibre fragments in the presence of an interfacial layer is related to the elastic modulus, E_i , of this layer as follows:

$$L \equiv \left\{ \frac{E_i}{E_m} \right\}^\alpha \quad (9)$$

where the exponent α ranges from about 0.4 to 0.6 (mean value $\sim 1/2$) depending on the level of fibre-matrix adhesion. Hence, to a first approximation, the combination of equations (1) and (9) leads to equation (8). Consequently, a calculation of E_i can be performed according to equation (8) and the experimental values of τ and W . It is, therefore, found that $E_i = 2.0 \pm 0.4$ GPa. It is worth noting that E_i is about 2000 times higher than the modulus E_m of the bulk SBR at room temperature. However, this estimated value of E_i is equivalent to the elastic modulus of SBR in its glassy state (2.0 ± 0.1 GPa) as shown in Figure 8, where the variation of E_m is plotted against temperature. Such a close agreement clearly could confirm the existence of a "glassy" interphase and the strong influence of this latter on the level of stress transfer at the fibre-matrix interface in elastomer-based composites. It seems also to indicate that our model corresponding to equation (1) remains valid in the presence of an interfacial layer insofar as the mechanical properties of this layer are taken into account in place of those of the bulk matrix.

Finally, considering to a first approximation that E_i stays constant whatever the temperature, the linear decrease of the interfacial shear strength τ versus temperature (Figure 5) can simply be explained by the gradient, $\partial W / \partial T$, of the adhesion energy, W , as follows:

$$\frac{\partial \tau}{\partial T} = \frac{1}{\lambda} \left\{ \frac{E_i}{E_f} \right\}^{1/2} \frac{\partial W}{\partial T} \quad (10)$$

The quantity $\partial W / \partial T$ can be estimated equal to about -0.4 to -0.5 $\text{mJ} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$ according to equation (2) and taking $\partial \gamma / \partial T \sim -0.1$ $\text{mJ} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$. Consequently, for $E_i = 2$ GPa, the theoretical value of $\partial \tau / \partial T$ is found equal to about -0.07 to -0.09 $\text{MPa} \cdot \text{K}^{-1}$, whereas its experimental value is close to -0.09 $\text{MPa} \cdot \text{K}^{-1}$. This agreement is an additional support in favour of the existence, near the fibre surface, of an interfacial layer exhibiting a "pseudo-glassy" behaviour whatever the temperature.

Finally, it has to be mentioned that the thickness of such an interphase is not taken into account as a parameter in our approach. The length scale of the interfacial layer is certainly small (a few nanometers) and should depend on the magnitude of the interfacial physico-chemical interactions, in other words on the value of W . On

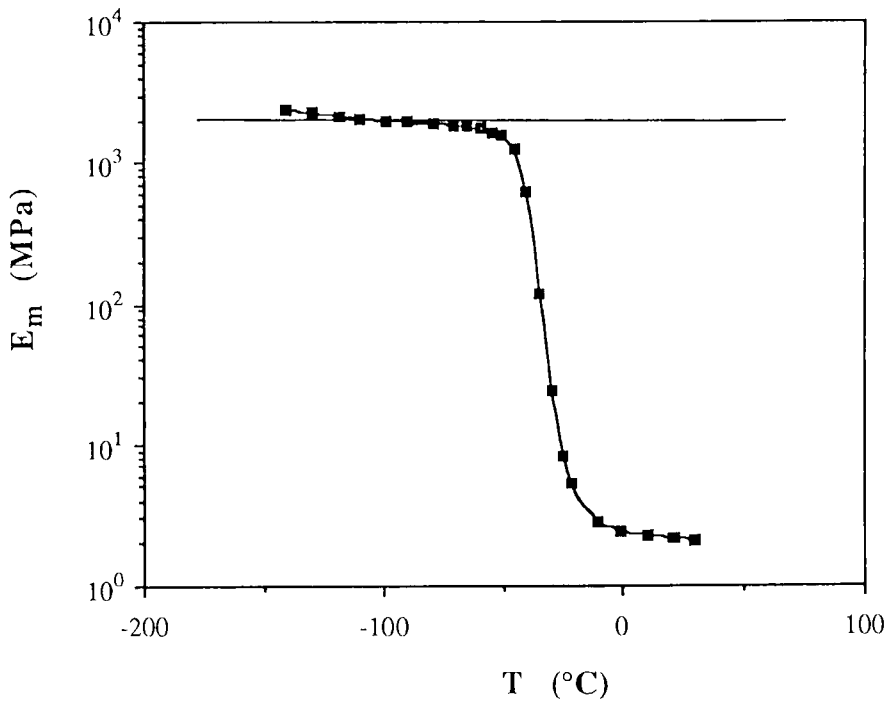


FIGURE 8 Elastic modulus E_m of the bulk SBR *versus* temperature T .

the other hand, it is conceivable that the thickness of the interphase should affect the level of stress transfer at the fibre-matrix interface. This constitutes a weak point in our analysis.

4 CONCLUSION

The present study was devoted to the determination of the stress transfer capacity of carbon fibre-SBR interfaces by means of a fragmentation test on single fibre composites. It is shown that the shear strength τ of such interfaces is much higher than theoretically expected by a model recently proposed in a previous work¹ and relating τ to the interfacial thermodynamic properties, *i.e.* the adhesion energy calculated from physical interactions between carbon fibre and SBR. It is first evidenced that the hysteretic losses of bulk SBR during the fragmentation test are not responsible for such a discrepancy between theory and experimental results. On the contrary, the high values of the interfacial shear strength are very well explained by the existence near the fibre surface of an interphase in which the polymer chain mobility is strongly reduced compared with the bulk matrix. Effectively, as stated elsewhere^{2,3} and as observed by creep experiments at moderate applied load, such an interfacial layer could be able to age physically at temperatures far above the

glass transition temperature of SBR and, consequently, exhibit a pseudo-glassy behaviour over the whole range of temperatures studied. It is clear that the mechanical properties of this layer should be completely different from those of the bulk matrix and play a major role in the stress transfer phenomenon. Considering, to a first approximation, that the model relating micromechanical properties to thermodynamic aspects of interfaces remains valid under such conditions, the elastic modulus of the interfacial layer can be estimated and is found equal to that of SBR in its glassy state regardless of the temperature, in good agreement with the expected glassy behaviour of this layer. The variation of the interfacial shear strength *versus* temperature confirms this assumption. Therefore, it can be concluded that, to a first approximation, our model could be able to explain the level of stress transfer at carbon fibre-SBR interfaces in the presence of an interphase of reduced mobility, insofar as the mechanical properties of this interphase are taken into account in place of those of the bulk matrix. Nevertheless, it is conceivable that the thickness of such an interphase could play a role in the stress transfer phenomenon between the matrix and the fibre, but this parameter is not taken into account in our approach.

Acknowledgements

The authors wish to thank Dr. B. Haidar and Mr. H. Salah-Derradji, both of the CNRS of Mulhouse, for their kind help and fruitful discussions concerning physical ageing measurements.

References

1. M. Nardin and J. Schultz, *Comptes Rendus Acad. Sci. Paris*, **t. 311, Série II**, 613 (1990).
2. B. Haidar, *Proc. Rubber Div. Meetings, ACS Symp.*, Las Vegas (NV, USA), May 29–June 1 (1990).
3. B. Haidar, in *Interfacial Phenomena in Composite Materials, IPCM'91*, I. Verpoest and F. Jones, Eds. (Butterworth-Heinemann Ltd, Oxford, 1990), p. 145.
4. M. Nardin, E. M. Asloun and J. Schultz, *Surface Interface Analysis* **17**, 485 (1991).
5. D. K. Owens and R. C. Wendt, *J. Appl. Polym. Sci.* **13**, 1740 (1969).
6. J. Schultz, L. Lavielle and H. Simon, *Proc. Intern. Symp. on Science and New Applications of Carbon Fibers* (Toyohashi, Japan, 1984), p. 125.
7. T. Young, *Phil. Trans. Roy. Soc.* **95**, 65 (1805).
8. A. Dupré, in *Théorie mécanique de la chaleur* (Gauthier-Villars, Paris, 1869), p. 369.
9. A. Kelly and W. R. Tyson, *J. Mech. Phys. Solids* **13**, 329 (1965).
10. W. A. Fraser, F. H. Ancker and A. T. Di Benedetto, *Proc. 30th Annual Technical Conf.*, SPI/Reinf. Composite Institute, section 22-A (1975).
11. E. M. Asloun, J.-B. Donnet, G. Guilpain, M. Nardin and J. Schultz, *J. Mater. Sci.* **24**, 3504 (1989).
12. E. M. Asloun, M. Nardin and J. Schultz, *J. Mater. Sci.* **24**, 1835 (1989).
13. H. L. Cox, *British J. Appl. Phys.* **3**, 72 (1952).
14. A. N. Gent and G. L. Liu, *J. Mater. Sci.* **26**, 2467 (1991).
15. A. N. Gent and J. Schultz, *J. Adhesion* **3**, 281 (1972).
16. M. L. Williams, R. F. Landel and J. D. Ferry, *J. Amer. Chem. Soc.* **77**, 3701 (1955).
17. A. N. Netravali, R. B. Henstenburg, S. L. Phoenix and A. Schwartz, *Polym. Composites* **10**, 226 (1989).
18. H. W. Greensmith and A. G. Thomas, *J. Polym. Sci.* **18**, 189 (1955).
19. Y. Termonia, *J. Mater. Sci.* **25**, 103 (1990).