Temperature Dependence of Impact Fracture Energies of Short Glass Fiber–Epoxy and Unsaturated Polyester Composites

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Synopsis

The temperature dependence of the impact fracture energies of composites reinforced with random-planar orientation of short fibers was studied theoretically and experimentally. The theoretical values of the impact fracture energy of these composites is described by the sum of the fracture energy of the matrix and the fibers and the energy necessary to pull out the fibers on the crack surface, taking into consideration the temperature dependence of the critical fiber length and the breaking probability of fibers. The impact fracture energies were studied experimentally for epoxy and unsaturated polyester resins reinforced with random-planar orientation of short glass fibers. The theoretical values of the impact fracture energy were in good agreement with the experimental values. It was found that in any composite, the impact fracture energy of the fibers in a composite mainly contributes to the impact fracture energy of the composite at room temperature. At higher temperatures, fiber pull-out energy is more significant.

INTRODUCTION

Loads working on composites reinforced by short fibers are transferred to the fibers through the fiber–matrix interface. Therefore, the impact fracture energies of composites are influenced greatly by the shear strength at the fiber–matrix interfaces or by the critical fiber length which is dependent upon such shear strength. The impact fracture energies of composites have been discussed thus far on the basis of the energies necessary to pull out the fibers of the fracture surfaces for composites reinforced with unidirectionally oriented short fibers,[1–7] taking the interfacial shear strength into consideration. However, there is practically no study for composites in which the short fibers are randomly oriented two- or three-dimensionally.

The authors have established a method[8,9] to evaluate the critical fiber length for glass fiber–thermosetting resin systems. The temperature dependence of the critical fiber length was studied by using this method, and the temperature dependence of the tensile strength of composites was discussed. The impact fracture energy, like the tensile strength, is influenced by the test temperature. This relationship has not been previously reported.

In this report, the theoretical equations for impact fracture energies of composites reinforced with random-planar orientation of short fibers is derived by first taking the temperature dependence of the critical fiber length and the breaking probability of fiber into consideration. The adequacy of the theoretical equations is discussed based on experimental results for glass fiber–epoxy and glass fiber–unsaturated polyester resin composites.[8,9]

Journal of Applied Polymer Science, Vol. 23, 1679–1691 (1979)

0021-8995/79/0023-1679$01.00

THEORY

When notched test specimens made of composites were subjected to Izod impact tests the fracture propagates locally and rapidly, and the response of each constituent to the applied load does not take place simultaneously. Therefore, the impact fracture energies under such conditions may be derived from a sum of the energies that are contributed by each constituent through different fracture mechanisms from the loading start to the final fracture.

Supposing that u_m and u_f are the fracture energies of the matrix and the fibers, respectively, while u_{po} is the interaction between the matrix and the fibers, i.e., the energy to pull the fibers out of the fracture surface. The impact fracture energy U_c of the composites reinforced by short fibers can be represented by the following equation:

$$U_c = u_m + u_f + u_{po} \tag{1}$$

The fracture energies of each constituent mentioned above will be discussed in detail.

Fracture Energy of Matrix, u_m

General elasticity theory cannot be applied to evaluate the fracture energy of polymers used as the matrix, because they exhibit typical plastic deformation. Therefore, the fracture energy u_m contributed by the matrix during the fracture process of composites may be represented by the following equation using the measured fracture energy and taking the volume fraction of matrix into consideration:

$$u_m = u'_m(1 - v_f) \tag{2}$$

where u'_m and v_f are the fracture energy per unit area of the matrix and the volume fraction of the fibers, respectively.

Fracture Energy of Fiber, u_f

The fiber stresses produced in impact bending fracture of notched samples vary considerably according to their locations. Therefore, the fracture energy u_f contributed by the fibers consists of the elastic deformation energy u_{fi} for the crack initiation at the notch tip and another energy u_{fb}, necessary to break the fibers crossing with the crack surface progressively during the crack propagation.

Elastic Deformation Energy of Fiber, u_{fi}

The energy u_{fi} contributed by the fibers until a crack is initiated at the notch tip in the Izod impact test may be determined as elastic deformation energy of a cantilever beam. In general, the elastic deformation energy u_b per unit area of the cantilever beam can be given by the bending theory as follows:

$$u_b = \frac{\sigma_{\max}^2 D}{18E} \tag{3}$$

where $\sigma_{\max}$, E, and D are the maximum stress, Young's modulus, and the distance

from the notch tip to the hammer impact point, respectively. Therefore, in the Izod impact test, the elastic deformation energy per unit area contributed by the fibers u_{fi} can be determined as follows, taking the volume fraction of fiber into consideration:

$$u_{fi} = \frac{\sigma_f^2 D}{18E_f} v_f \tag{4}$$

where σ_f is the tensile strength of fiber, E_f is Young's modulus of the fiber, and D is the distance from the notch tip to the hammer impact point.

In composites reinforced by short fibers, the applied loads are transferred to the fibers through the fiber–matrix interfaces. Therefore, assuming that the shear strength at the fiber–matrix interface is constant,[10] the average stress $\bar{\sigma}_f$ along the overall fiber length, prior to the fiber breaking, is given by the following equations:

$$\begin{aligned} \bar{\sigma}_f &= \left(1 - \frac{l_c}{2L}\right)\sigma_f \qquad L \geqq l_c \\ \bar{\sigma}_f &= \left(\frac{L}{2l_c}\right)\sigma_f \qquad L < l_c \end{aligned} \tag{5}$$

where σ_f is the tensile strength of the fiber, L is the fiber length, and l_c is the critical fiber length. Thus, a uniform stress does not occur along the overall fiber length when the stress of the fiber reaches the stress level of tensile strength σ_f and the average stress $\bar{\sigma}_f$ is lower than the tensile strength σ_f. Therefore, the deformation energy u_{fi} of fiber in the composite reinforced by short fibers can be given as follows, taking the average stress $\bar{\sigma}_f$ of eq. (5) into consideration:

$$\begin{aligned} u_{fi} &= \frac{\left(1 - \frac{l_c}{2L}\right)^2 \sigma_f^2 D v_f}{18E_f} \qquad L \geqq l_c \\ u_{fi} &= \frac{\left(\frac{L}{2l_c}\right)^2 \sigma_f^2 D v_f}{18E_f} \qquad L < l_c \end{aligned} \tag{6}$$

Energy to Break Fibers Crossing with the Crack Surface, u_{fb}

If the embedded length of the fibers measured from the crack surface is longer than $l_c/2$, they tend to break in the composites reinforced by unidirectionally oriented short fibers. Therefore, the breaking probability at the crack surface of fibers with random-planar orientation is determined first to obtain the energy necessary for the fiber breaking.

The fibers inclined by an angle θ to the applied load at the crack tip are subjected to an applied load as shown in Figure 1(a); therefore, the fibers at the crack tip are stretched in the direction inclined by θ to the applied load, Figure 1(b). When the fiber stress reaches its tensile strength σ_f, the effective stress component σ_θ to pull the fibers out of the matrix is

$$\sigma_\theta = \sigma_f \cos\theta \tag{7}$$

Assuming that the shear strength τ at the fiber–matrix interface is constant,[10]

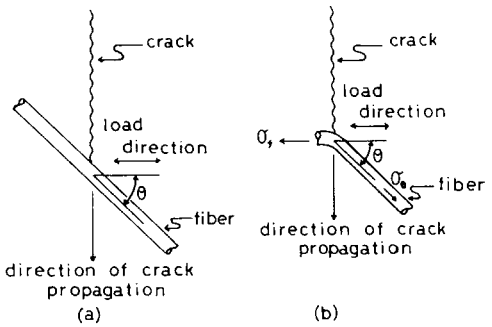

Fig. 1. Schematic representation of the state of a fiber at the crack tip.

the fibers embedded longer than l_θ will tend to break during crack propagation according to the force equilibrium relation

$$l_\theta = \frac{\sigma_f d \cos\theta}{4\tau} \tag{8}$$

Furthermore, $l_c = \sigma_f d/2\tau$.[10] Then,

$$l_\theta = \frac{l_c}{2}\cos\theta \tag{9}$$

Therefore, the average length $\bar{l}_\theta$ necessary to break the fibers with random-planar orientation at the crack surface is given as follows:

$$\bar{l}_\theta = \frac{\int_0^{\pi/2} l_\theta d\theta}{\int_0^{\pi/2} d\theta} = \frac{l_c}{\pi} \tag{10}$$

Hence, the breaking probability $P(b)$ of the fibers with random-planar orientation is given as follows:

$$P(b) = \frac{L - 2\bar{l}_\theta}{L} = \left(1 - \frac{2l_c}{\pi L}\right) \tag{11}$$

The above equation suggests that whole fibers are pulled out without breaking when the filled fiber length L satisfies the condition $L < 2l_c/\tau$. When $L \geqq 2l_c/\tau$, the pulling-out probability $P(p)$ of the fibers is given as follows:

$$P(p) = \frac{2\bar{l}_\theta}{L} = \frac{2l_c}{\pi L} \tag{12}$$

Now we turn our attention to the energy to break the fibers crossing the crack surface. The fibers positioned at the crack tip are subjected to stress along not only the crack surface but also the fiber length direction. The stress distribution along the fiber lengths just before the fiber breaks[10] is shown in Figure 2. The stress transferable to the fiber σ_x at a distance x along the fiber from the crack surface is given as follows:

$$\sigma_x = \frac{2\sigma_f}{l_c}\left(\frac{l_c}{2} - x\right) \tag{13}$$

The fiber stress becomes zero at $x = l_c/2$ from the crack surface.

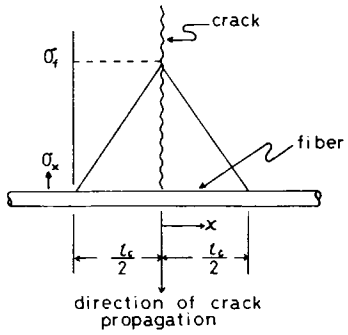

Fig. 2. Schematic representation of the stress distribution of a fiber at the crack tip.

In general, the elastic deformation energy u_o of the fibers (length L and diameter d) subjected to tensile stresses is given as follows:

$$u_o = \frac{\sigma^2 \pi d^2 L}{8E_f} \tag{14}$$

where σ and E_f are the fiber stress applied and the Young's modulus of the fiber, respectively.

Therefore, the elastic deformation energy u necessary to break the fibers crossing the crack surface is determined from eqs. (13) and (14), taking into consideration that the fibers are strained on both crack surfaces:

$$u = 2\frac{\pi d^2}{8E_f}\int_0^{l_c/2} \frac{4\sigma_f^2}{l_c^2}\left(\frac{l_c}{2} - x\right)^2 dx = \frac{\pi d^2 \sigma_f^2 l_c}{24E_f} \tag{15}$$

The energy obtained above is the energy necessary to break a single fiber. Assuming that there are n fibers per unit area, the number of fibers n can be related to the area fraction of fibers A_f as follows:

$$\frac{1}{4}\pi d^2 n = A_f \tag{16}$$

On the other hand, the stereological theory shows that the area fraction A_f is equal to the volume fraction v_f[11]; therefore, the number of fibers n can be represented as follows:

$$n = \frac{4v_f}{\pi d^2} \tag{17}$$

When the fibers are in random-planar orientation, the energy u_{fb} per unit area necessary to break the fibers found in the crack surface can be determined from eqs. (11), (15), and (17), taking the breaking probability of fibers into consideration:

$$\begin{aligned} u_{fb} &= \frac{\sigma_f^2 l_c v_f}{6E_f}\left(1 - \frac{2l_c}{\pi L}\right) \qquad L \geqq \frac{2}{\pi} l_c \\ u_{fb} &= 0 \qquad L < \frac{2}{\pi} l_c \end{aligned} \tag{18}$$

It should be noted here that the fracture energy of fibers crossing the crack surface is calculated repeatedly in eqs. (6) and (18). Therefore, the energy u_{fb}

should be reduced by the deformation energy accumulated by fibers crossing the crack surface and breaking during crack propagation. This occurs until the crack is initiated. The latter energy term is small and is therefore neglected in this report.

Energy to Pull Out Fibers, u_{po}

Kelly[4] and Cottrell[5] proposed that the energy $(u_{po})_{\parallel}$ per unit area necessary to pull out the fibers in fracture processes of composites reinforced with unidirectionally oriented short fibers can be given by the following equations:

$$\begin{aligned} (u_{po})_{\parallel} &= \frac{\tau l_c^2 v_f}{6d} \qquad L \geqq l_c \\ (u_{po})_{\parallel} &= \frac{\tau L^2 v_f}{6d} \qquad L < l_c \end{aligned} \tag{19}$$

where τ is the shear strength at the fiber–matrix interface; l_c is the critical fiber length; L, d and v_f are the length, the diameter, and the volume fraction of fiber, respectively.

When the fibers are in random-planar orientation, eq. (19) can be multiplied by the pulling-out probability of the fibers at the crack surface defined by eq. (12); and the pulling-out energy u_{po} per unit area can be given by the following equations:

$$\begin{aligned} u_{po} &= \frac{\tau l_c^2 v_f}{6d} \cdot \frac{2l_c}{\pi L} \qquad L \geqq \frac{2}{\pi} l_c \\ u_{po} &= \frac{\tau L^2 v_f}{6d} \qquad L < \frac{2}{\pi} l_c \end{aligned} \tag{20}$$

The impact fracture energy U_c per unit area of the notched specimens made of composites reinforced with random-planar orientation of short fibers can be obtained by introducing eqs. (2), (6), (18), and (20) into eq. (1):

$$\begin{aligned} U_c &= u_m'(1 - v_f) + \frac{\bar{\sigma}_f^2 D v_f}{18E_f} + \frac{\sigma_f^2 l_c v_f}{6E_f}\left(1 - \frac{2l_c}{\pi L}\right) + \frac{\tau l_c^2 v_f}{6d}\left(\frac{2l_c}{\pi L}\right) \qquad L \geqq \frac{2}{\pi} l_c \\ U_c &= u_m'(1 - v_f) + \frac{\bar{\sigma}_f^2 D v_f}{18E_f} + \frac{\tau L^2 v_f}{6d} \qquad L < \frac{2}{\pi} l_c \end{aligned} \tag{21}$$

where

$$\begin{aligned} \bar{\sigma}_f &= \left(1 - \frac{l_c}{2L}\right)\sigma_f \qquad L \geqq l_c \\ \bar{\sigma}_f &= \left(\frac{L}{2l_c}\right)\sigma_f \qquad L < l_c \end{aligned}$$

EXPERIMENTAL

The glass fibers, the epoxy resin, and the unsaturated polyester resin used in preparation of the specimens are the same as those described in the preceding reports.[8,9] The composites reinforced with random-planar orientation of short

fibers are prepared as reported before.[8,9] Namely, glass fibers in roving form are bundled with the use of a 4% aqueous solution of PVA, dried for two days, and cut into short fibers of uniform length by a constant-length cutter. After cutting, the short fibers are suspended in a large amount of distilled water and then allowed to settle gently on a filter paper placed at the bottom of the vessel. The water is removed by pressing at a suitable pressure. The fibers are then dried at 80°C for 24 hr. In this manner it is possible to obtain a mat in which the short fibers are oriented random-planarly and yet distributed uniformly.

To prepare specimens differing in the bonding strength at the interface, the random mats are immersed for 48 hr separately in a 3% toluene solution of a silane-type coupling agent (KBM 403, Shinetsu Chemical) and a 6% toluene solution of a releasing agent (KS 707, Shinetsu Chemical) and dried first at room temperature and finally for 8 hr at 70°C.

The fiber length distribution of the glass fibers randomly extracted from the mat is shown in Figure 3. It was noted that the glass fibers were uniform in length and suffered virtually no damage in subsequent treatments. The mean fiber length $\bar{L}$ is 3.47 mm. The following experiments were all carried out on fibers of this length.

For preparing the resin mixtures, 100 parts of the epoxy resin (Epikote 828, Mitsubishi Yuka) and 100 parts of the unsaturated polyester resin (Rigolac 2004 WM-2, Showa Kobunshi) are mixed with 10 parts of an amine-type curing agent (S-cure 661, Nihon Kayaku) and 2 parts of the curing catalyst MEKPO (Parmek N, Nihon Yushi), respectively. These mixtures are stirred thoroughly and then degassed under vacuum for about 20 min.

The random mats are then evacuated thoroughly to remove the air entrapped in the fiber mats, and the resin mixture as prepared above is poured into the apparatus so that the mats can be impregnated fully. Thereafter, atmospheric pressure is gradually applied to expedite impregnation of the resin mixture. The impregnated mats are then cured at 65°C for 17 hr and postcured at 140°C for 5 hr. The composite is then allowed to cool to room temperature at a cooling rate of 0.5°C/min. This procedure enables preparation of bubble-free resins

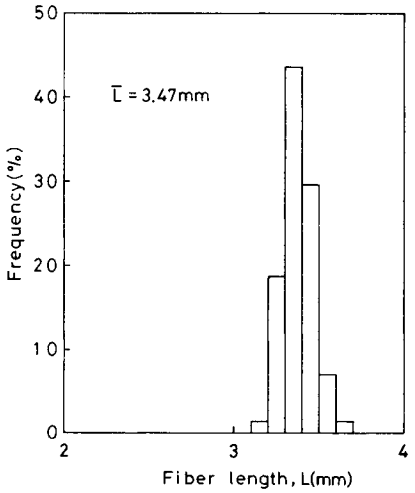

Fig. 3. Distribution of glass fiber length.

reinforced with random-planar orientation of short fibers. The volume fraction of the glass fibers can be controlled by pressing the mat before impregnation. The volume fraction in this experiment is set at 15.5% for the epoxy resin composite and at 17.4% for the unsaturated polyester resin composite.

The test specimens are cut from the composites prepared as above in accordance with JIS 7110 and submitted to an Izod impact testing machine (Toyo Seiki Seisakusho) to determine the impact fracture energy. The measuring temperature is changed at 20°C steps from 20°C to 120°C. The specimens are provided with a V-notch perpendicular to the fiber orientation plane. Five to ten specimens are used for each temperature level tested.

RESULTS AND DISCUSSION

The relationship between impact fracture energies and temperature is shown in Figures 4 and 5 respectively for the epoxy resin system and the unsaturated polyester resin system. The results for the pure matrix are also shown in these figures. In any composite, regardless of the nature of interfacial treatment, the impact fracture energy is nearly the same at temperature ranges lower than 60°C; however, it tends to increase with increasing temperature above 60°C. This tendency is most obvious in the epoxy resin system. In the pure matrix, the epoxy resin has an impact fracture energy three times greater than that of the unsaturated polyester resin.

The scanning electron photomicrographs of the fracture surfaces of these composites are shown in Figures 6 and 7. As seen in Figures 6(a) and 6(b), in the fracture surfaces obtained at room temperature, regardless of the nature of the interfacial treatment, the fiber length protruding from the fracture surfaces is rather short and the composites are fractured mainly under the breaking process of the fibers. On the other hand, at higher temperatures, the specimen treated with the coupling agent shows adhesion of the resin phase over nearly the whole surface of the glass fiber, as shown in Figure 7(a). The fiber is prac-

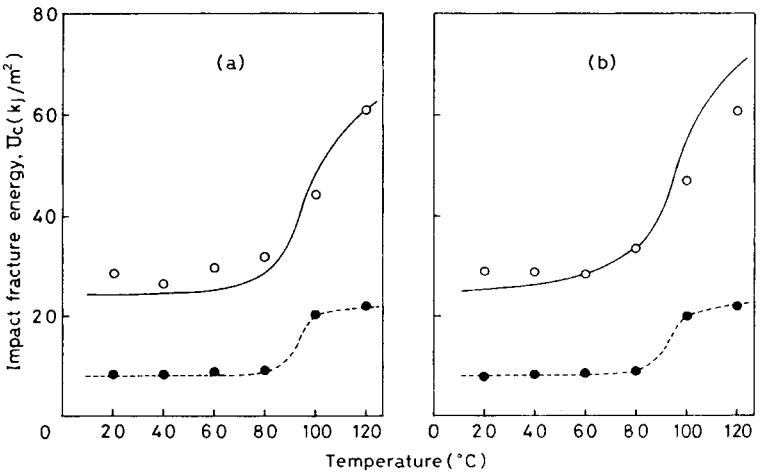

Fig. 4. Relation between temperature and impact fracture energy for the epoxy resin and the short glass fiber–epoxy composite: (a) good bonding; (b) poor bonding; (O) composite; (- -●- -) resin; (—) calculated value.

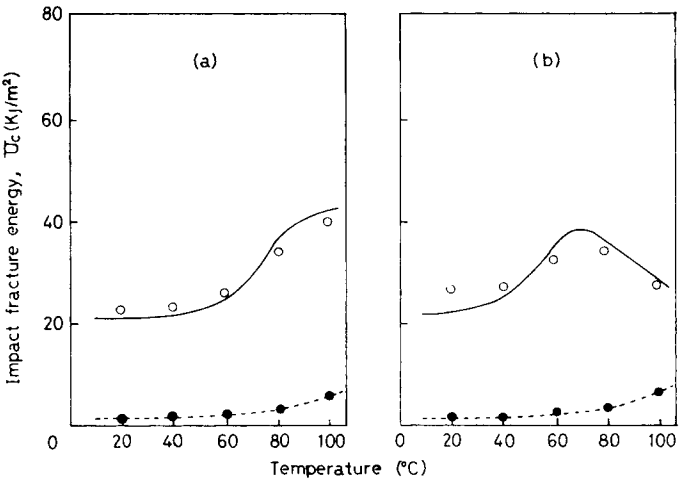

Fig. 5. Relation between temperature and impact fracture energy for the unsaturated polyester resin and the short glass fiber–unsaturated polyester composite: (a) good bonding; (b) poor bonding; (O) composite; (- -●- -) resin; (—) calculated value.

tically free from the resin phase in the specimen treated with the release agent, Figure 7(b). However, the fiber length protruding from the fracture surfaces is very long, which indicates that at a higher temperature the composites are mainly fractured by the pulling-out process. The resin phase shows cohesive failure or debonding at the fiber–matrix interface. These photographs only deal with the epoxy resin composites; however, similar tendencies occur in unsaturated polyester resin composites.

The solid lines in Figures 4 and 5 indicate theoretical values calculated by introducing into eq. (21) the critical fiber length l_c, the apparent shear strength τ at the interface,[8] and other parameters. The experimental values are in good agreement with the theoretical ones for each system and temperature level tested. This indicates that the theoretical eq. (21) derived from the temperature dependence of the critical fiber length and the breaking or pulling-out probability of the fibers is adequate.

The relationship between calculated impact fracture energies corresponding to different fracture mechanisms in the theoretical eq. (21) and temperature are shown in Figures 8 and 9 respectively for epoxy and unsaturated polyester resin systems. The impact fracture energy u_m of the matrix in the epoxy system shows little change below 80°C and tends to increase rapidly, up to threefold, when the temperature exceeds 80°C. The elastic deformation energy u_{fi} contributed by the fibers before crack initiation at the notch tip shows a similar value at temperature lower than 80°C, namely, $L \geqq (2/\pi)l_c$, and tends to decrease rapidly at $L < (2/\pi)l_c$ with increasing temperature. Furthermore, the energy u_{fb} necessary to break the fibers found in the crack surfaces during the crack propagation is very low for all temperature levels tested, and its contribution is slight. On the other hand, the energy u_{po} necessary to pull out the fibers tends to increase with increasing temperature. This trend is due to the increase in the pulling-out probability with increasing temperature.

Contrary to this, regardless of the nature of interfacial treatment, the unsaturated polyester systems have energies u_{fi}, u_{fb}, and u_{po} similar to those of the

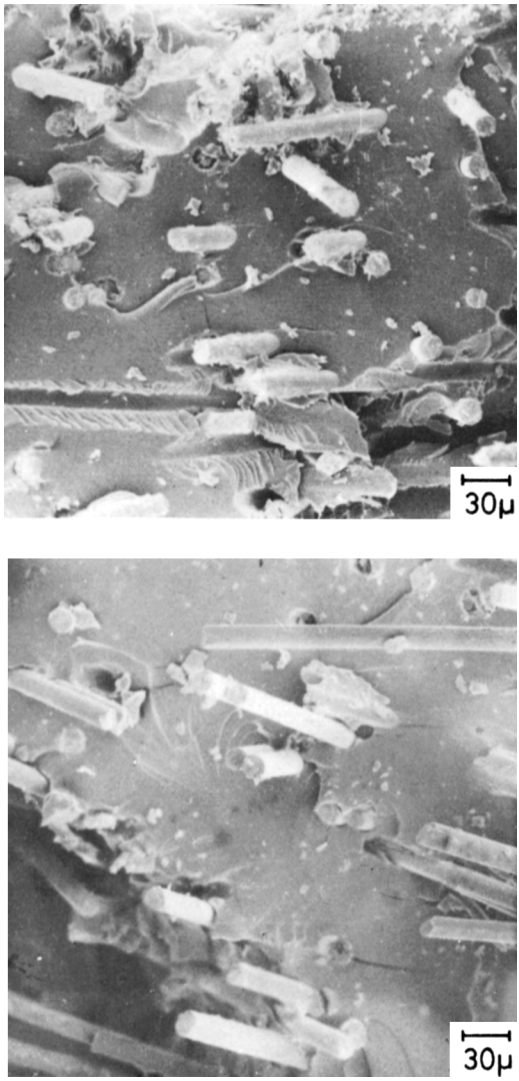

Fig. 6. Scanning electron photomicrographs of the fracture surface of the short glass fiber–epoxy resin composite by Izod impact test at 20°C: (a) good bonding; (b) poor bonding.

epoxy resin systems, but the fracture energy u_m of the matrix is very low for all temperature levels tested, and its contribution is minute.

CONCLUSIONS

The temperature dependence of the impact fracture energies of composites reinforced with random-planar orientation of short fibers were theoretically and experimentally studied.

The theoretical values of the impact fracture energies of these composites can be expressed as the sum of the fracture energy of the matrix and the fibers and the energy necessary to pull the fibers out of the crack surface. The temperature dependence of the critical fiber length l_c, the apparent interfacial shear strength

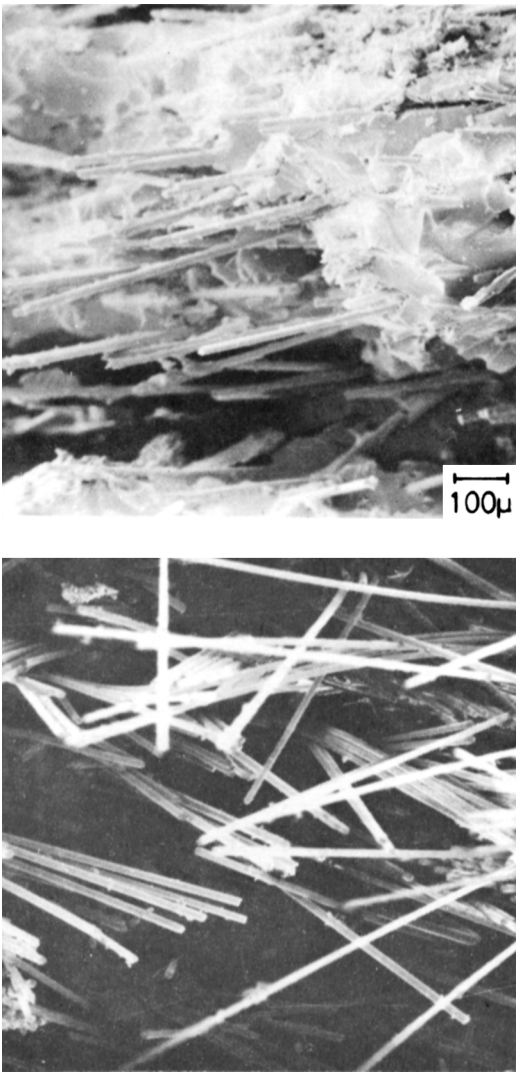

Fig. 7. Scanning electron photomicrographs of the fracture surface of the short glass fiber–epoxy resin composite by Izod impact test at 100°C: (a) good bonding; (b) poor bonding.

τ,[8] and the breaking or pulling-out probability of the fibers must be taken into consideration. The derived equations are as follows:

$$U_c = u'_m(1 - v_f) + \frac{\bar{\sigma}_f^2 D v_f}{18E_f} + \frac{\sigma_f^2 l_c v_f}{6E_f}\left(1 - \frac{2l_c}{\pi L}\right) + \frac{\tau l_c^2 v_f}{6d}\left(\frac{2l_c}{\pi L}\right) \qquad L \geqq \frac{2}{\pi} l_c$$

$$U_c = u'_m(1 - v_f) + \frac{\bar{\sigma}_f^2 D v_f}{18E_f} + \frac{\tau L^2 v_f}{6d} \qquad L < \frac{2}{\pi} l_c$$

$$\bar{\sigma}_f = \left(1 - \frac{l_c}{2L}\right)\sigma_f \qquad L \geqq l_c$$

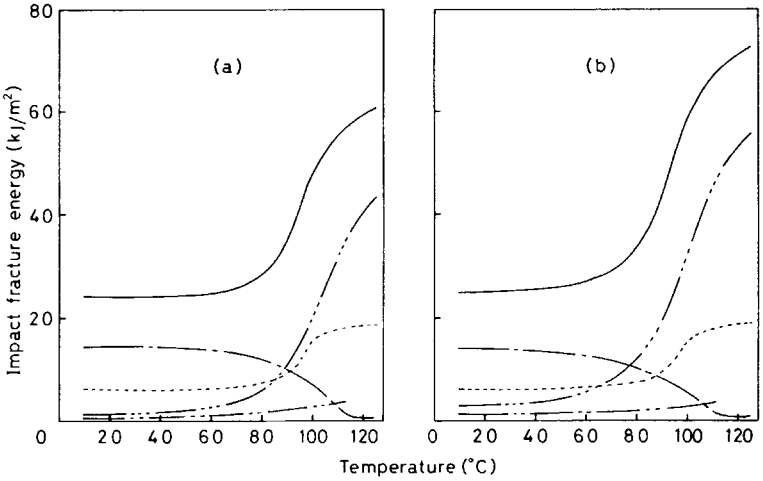

Fig. 8. Contribution of various factors on the impact fracture energy of the short glass fiber–epoxy composite: (a) good bonding; (b) poor bonding; (—) U_c with eq. (21); (- - -) u_m with eq. (2); (— - —) u_{fi} with eq. (6); (— - - —) u_{fb} with eq. (18); (— - - - —) u_{po} with eq. (20).

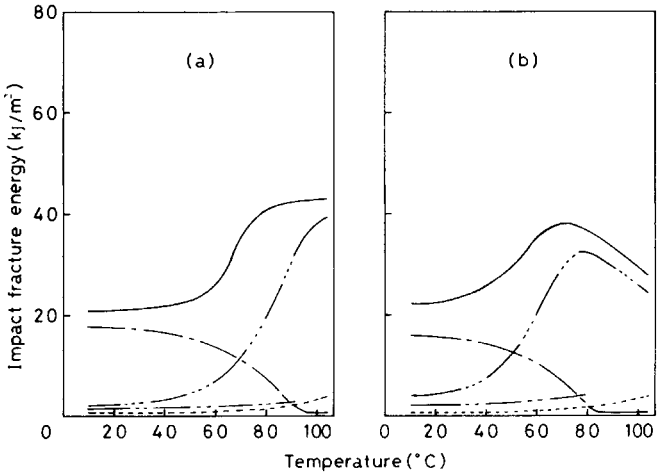

Fig. 9. Contribution of various factors on the impact fracture energy of the short glass fiber–unsaturated polyester composite: (a) good bonding; (b) poor bonding; (—) U_c with eq. (21); (- - -) u_m with eq. (2); (— - —) u_{fi} with eq. (6); (— - - —) u_{fb} with eq. (18); (— - - - —) u_{po} with eq. (20).

$$\bar{\sigma}_f = \left(\frac{L}{2l_c}\right)\sigma_f \qquad L < l_c$$

where u_m' is the fracture energy per unit area of matrix, σ_f is the tensile strength of the fibers, E_f is Young's modulus of the fibers, L is the fiber length, d is the fiber diameter, v_f is the volume fraction of the fibers, and D is the distance from the notch tip to the hammer impact point.

The impact fracture energies were studied experimentally to evaluate the adequacy of the above equations for epoxy and unsaturated polyester reinforced with random-planar orientation of short glass fibers. The theoretical values of the impact fracture energies were in good agreement with the experimental values.

The impact fracture energies of the composites were nearly the same in a temperature range from room temperature to 60°C; however, they increased with increasing temperatures above 60°C.

In general, the contribution of the fiber fracture energy is considerable in the room temperature range, while the fiber pull-out energy is more significant in the higher temperature range.

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Received December 2, 1977
Revised March 20, 1978