Temperature Dependence of the Tensile Strength of Glass Fiber–Epoxy and Glass Fiber–Unsaturated Polyester Composites

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Synopsis

Epoxy and unsaturated polyester resins reinforced with random-planar orientation of short glass fibers were prepared and the temperature dependence of their tensile strength was studied. The tensile strength decreases as the temperature increases, and this tendency can be expressed in terms of critical fiber length l_c and apparent interfacial shear strength τ:

$$\sigma_{cs} \fallingdotseq \frac{2\tau}{\pi}\left[2 + \ln \frac{(1 - l_c/2L)\sigma_f \sigma_m v_f + \sigma_m \sigma'_m v_m}{\tau^2}\right], \qquad L \geqq l_c$$

$$\sigma_{cs} \fallingdotseq \frac{2\tau}{\pi}\left[2 + \ln \frac{\tau (L/d)\sigma_m v_f + \sigma_m{}^2 v_m}{\tau^2}\right], \qquad L < l_c$$

where σ_{cs} is the tensile strength of composite reinforced with random-planar orientation of short fibers, L is the fiber length, d is the fiber diameter, σ_f is the tensile strength of fiber, σ_m is the tensile strength of matrix, v_f is the volume fraction of fiber, v_m is the volume fraction of matrix, and σ'_m is the stress of the matrix at fracture strain of the composite. The experimental strength values at room temperature are considerably smaller than the theoretical values, and this difference can be explained by the thermal stress produced during molding due to the large difference in the thermal expansion coefficient between glass fiber and matrix resin.

INTRODUCTION

The temperature dependence of the tensile strength of fiber-reinforced resins based on the strength of the resins serving as matrix has been reported.[1,2] The strength of composites reinforced by short fibers is strongly governed by the critical aspect ratio and the interfacial shear strength. It therefore appears appropriate to study the temperature dependence of the strength of the composites in conjunction with the temperature dependence of the critical aspect ratio and the interfacial shear strength.

In this paper resins reinforced with random-planar orientation of short fibers were prepared from glass fiber and epoxy resin or glass fiber and unsaturated polyester resin[3] and the temperature dependence of the tensile strength of these composite materials was investigated. Furthermore, the temperature dependence of the critical aspect ratio and the apparent interfacial shear strength previously encountered[3] was applied to the composite systems.

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EXPERIMENTAL

The glass fibers and resins used in preparation of the specimens are the same as those previously described.[3] In the preparation of the resins reinforced with random-planar orientation of short fibers, special care was exercised to make the length of fibers uniform, to disperse each fiber into the matrix uniformly while random-planar oriented and to produce void free composites.

The specimen was prepared as follows: Glass fibers (R2220 MA 859X 16, Asahi Fiber Glass, 11.67 μm in diameter) in roving were bundled with the use of a 5% aqueous solution of PVA, dried, and cut into short fibers of a given length. The short fibers were suspended in a large quantity of water and then allowed to settle gently on a filter paper placed at the bottom of the vessel. The water was removed by pressing. Thereafter, the fibers were dried at 80°C for 24 hr. In this manner it was possible to obtain a mat in which the short fibers are oriented random-planarly and yet dispersed uniformly.

To prepare specimens differing in the bonding strength at the interface, random mats were immersed for 48 hr in a 3% toluene solution of a silane coupling agent (KBM 403, Shin-etsu Chemical) or in a 6% toluene solution of a releasing agent (KS 707, Shin-etsu Chemical) and dried first in air and then at 70°C for 8 hr.[3]

The distribution of fiber length in glass fibers randomly extracted from a mat which has received several treatments after cutting is shown in Figure 1. The glass fibers have been cut sufficiently uniformly and suffered virtually no damages in the subsequent treatments. The mean fiber length $\bar{L}$ is 3.29 mm. The following experiments were all carried out on fibers of this length.

The resin mixtures were prepared as follows: A mixture of 100 parts of the epoxy resin (Epikote 828, Mitsubishi Yuka) and 10 parts of the amine-type curing agent (S-cure 661, Nihon Kayaku), or a mixture of 100 parts of the unsaturated polyester resin (Rigolac 2004 WM-2, Showa Kobunshi) and 2 parts of a curing catalyst MEKPO (Parmek N, Nihon Yushi) was agitated thoroughly and then defoamed under vacuum for about 20 min.

Next, a random mat was introduced into an impregnating apparatus. A vacuum was used to remove the air entrapped in the fiber mat. The resin mix-

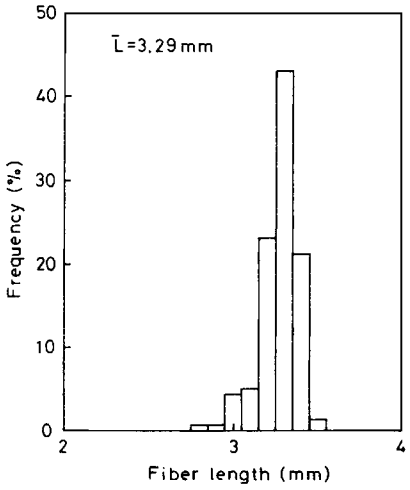


Fig. 1. Frequency distribution of short glass fiber.

ture was poured into the apparatus until the mat was completely impregnated. Thereafter, atmospheric pressure was gradually applied to expedite impregnation of the resin mixture. Following this, the mixture was cured at 65°C for 17 hr and then postcured at 140°C for 5 hr. The composite was then allowed to cool to room temperature at a cooling rate of about 0.5°C/min. This procedure yielded bubble-free resins reinforced with random-planar orientation of short fibers. The volume fraction of glass fiber can be determined by the extent of pressing of the mat before impregnation, and it was set at 15.5% for the epoxy resin composite and 21.0% for the unsaturated polyester resin composite.

Test specimens were cut from these composites in accordance with JIS 7113 and subjected to the tensile test at a test speed of 1 mm/min with the aid of a Shimadzu Autograph IS 5000. Measurements were made at intervals of 20°C from 20 to 120°C. All the test specimens were subjected to the tensile test 10–14 days after molding.

RESULTS AND DISCUSSION

The relationship between tensile strength and temperature for the epoxy-short glass fiber composite is shown in Figure 2 while that for the unsaturated polyester-short glass fiber composite is shown in Figure 3. For comparison, the tensile strength of the matrix is also plotted. With these composites, regardless of the nature of interfacial treatment, the strength reaches a peak near 40°C and thereafter decreases with increasing temperature.

Examples of the fracture surfaces of these composites are shown in Figures 4 and 5. In the specimens treated with a coupling agent, the resin phase adheres to the surface of fibers; the resin phase fails cohesively; consequently, the fibers are pulled out and the composite fails. On the other hand, in the specimens treated with a releasing agent, the surface of fibers are practically free from the resin phase, debonding occurs at the fiber–matrix interface, the fibers are pulled out, and the composite fails. These phenomena were observed to occur at any of the temperatures examined.

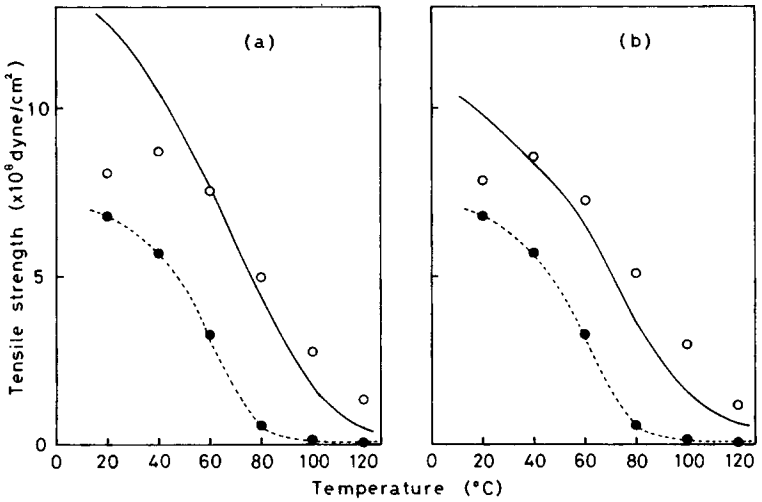


Fig. 2. Relationship between temperature and tensile strength for epoxy resin and epoxy–short glass fiber composite: (a) good bonding; (b) poor bonding; (O) composite; (· · · ● · · ·) resin; (—) calculated value.

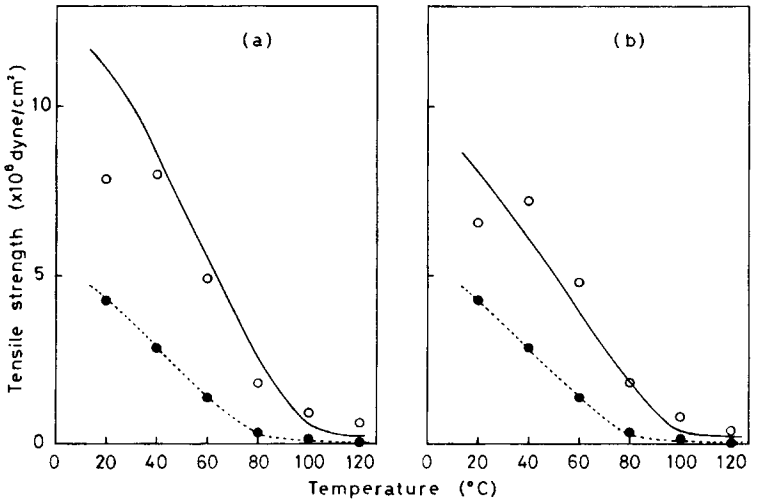


Fig. 3. Relationship between temperature and tensile strength for unsaturated polyester resin and unsaturated polyester–short glass fiber composite: (a) good bonding; (b) poor bonding; (O) composite; (··· ● ···) resin; (—) calculated value.

Stowell et al.[4] studied the fracture of composites reinforced with unidirectionally oriented continuous fibers and proposed that there exist three modes of breakdown depending upon the magnitude of angle θ between tensile direction and fiber. The strength σ_θ for each mode can be expressed as follows:

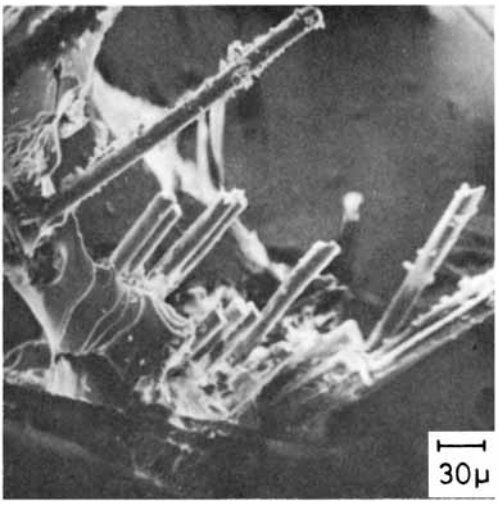
$$\begin{aligned} \sigma_\theta &= \frac{\sigma_\parallel}{\cos^2\theta} && 0 \leqq \theta \leqq \theta_1 \\ \sigma_\theta &= \frac{\tau}{\sin\theta\cos\theta} && \theta_1 \leqq \theta \leqq \theta_2 \\ \sigma_\theta &= \frac{\sigma_{mp}}{\sin^2\theta} && \theta_2 \leqq \theta \leqq \frac{\pi}{2} \end{aligned} \tag{1}$$

where $\sigma_\parallel$ is the tensile strength of the composite when stressed in the direction of the fiber, τ is the shear strength at the fiber–matrix interface, and σ_{mp} is the tensile strength of matrix under plane strain. Moreover, $\theta_1 = \tan^{-1}(\tau/\sigma_\parallel)$ and $\theta_2 = \tan^{-1}(\sigma_{mp}/\tau)$.

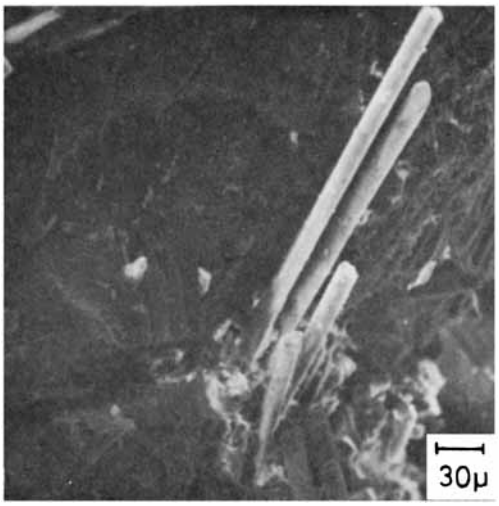
In continuous fibers oriented random-planarly, the three above-mentioned modes of breakdown are contained and the tensile strength σ_c of the composite can be expressed according to the method of Lee[5]:

$$\begin{aligned} \sigma_c &= \frac{\int_0^{\pi/2} \sigma_\theta d\theta}{\int_0^{\pi/2} d\theta} \\ &= \frac{2}{\pi}\left[\int_0^{\theta_1} \frac{\sigma_\parallel}{\cos^2\theta}\,d\theta + \int_{\theta_1}^{\theta_2} \frac{\tau}{\sin\theta\cos\theta}\,d\theta + \int_{\theta_2}^{\pi/2} \frac{\sigma_{mp}}{\sin^2\theta}\,d\theta\right] \\ &\fallingdotseq \frac{2\tau}{\pi}\left[2 + \ln\frac{\sigma_\parallel\sigma_m}{\tau^2}\right] \end{aligned} \tag{2}$$

where the relation $\sigma_{mp} \fallingdotseq \sigma_m$ is assumed.



(a)



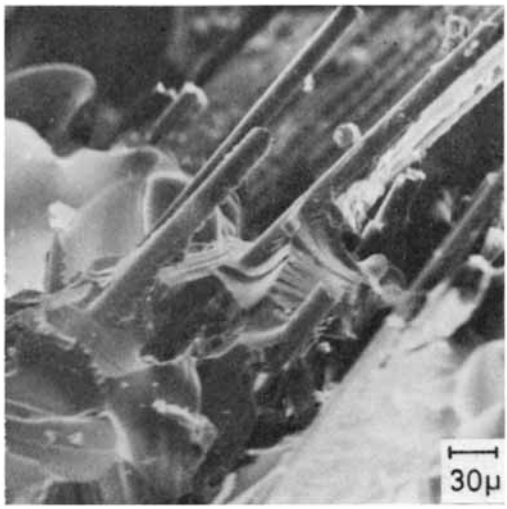
(b)

Fig. 4. Electron scanning photomicrographs of fracture surface of epoxy–short glass fiber composite: (a) good bonding at 20°C; (b) poor bonding at 80°C.

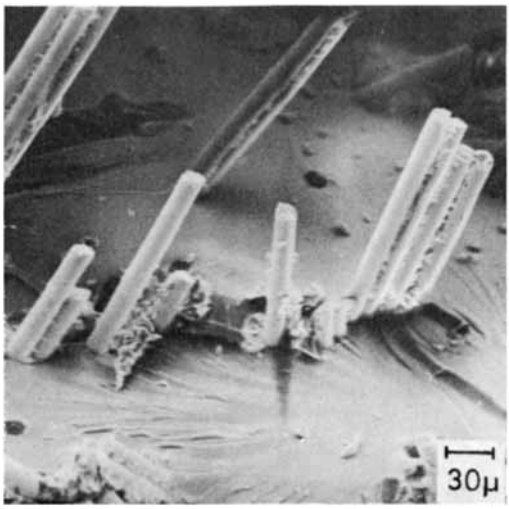
On the other hand, Kelly et al.[6] express the tensile strength $\sigma_{\parallel s}$ of a composite in which short fibers are oriented unidirectionally as follows while taking into account the critical fiber length:

$$\sigma_{\parallel s} = \left(1 - \frac{l_c}{2L}\right) \sigma_f v_f + \sigma_m' v_m \qquad L \geq l_c$$
$$\sigma_{\parallel s} = \frac{\tau L}{d} v_f + \sigma_m v_m \qquad L < l_c \tag{3}$$

where l_c is the critical fiber length, L is the fiber length, d is the fiber diameter, τ is the shear strength at the fiber–matrix interface, σ_f is the tensile strength of the fiber, σ_m is the tensile strength of the matrix, v_f is the volume fraction of the



(a)



(b)

Fig. 5. Electron scanning photomicrographs of fracture surface of unsaturated polyester–short glass fiber composite: (a) good bonding at 100°C; (b) poor bonding at 20°C.

fiber, v_m is the volume fraction of the matrix, and σ'_m is the stress of the matrix at fracture strain of the composite.

Therefore, the tensile strength σ_{cs} of a composite in which short fibers are oriented random-planarly can be given as follows from eqs. (2) and (3):

$$\sigma_{cs} \fallingdotseq \frac{2\tau}{\pi}\left[2 + \ln\frac{(1 - l_c/2L)\sigma_f\sigma_m v_f + \sigma_m\sigma'_m v_m}{\tau^2}\right] \quad L \geqq l_c$$

$$\sigma_{cs} \fallingdotseq \frac{2\tau}{\pi}\left[2 + \ln\frac{\tau(L/d)\sigma_m v_f + \sigma_m{}^2 v_m}{\tau^2}\right] \quad L < l_c \tag{4}$$

The above equations show that the strength of a composite in which short fibers are oriented random-planarly depends in a large measure upon the interfacial shear strength.

When the bonding strength at the fiber–matrix interface is extremely small, the fibers act merely as voids and the strength of the composite may be expressed as $\sigma_{cs} = \sigma_m v_m$. Therefore, eq. (4) is applicable only in a range of τ where the calculated value of σ_{cs} is sufficiently larger than $\sigma_m v_m$.

The solid lines in Figures 2 and 3 represent theoretical values obtained by substituting the critical fiber length l_c and the apparent interfacial shear strength τ. The experimental values roughly agree with the theoretical values at all temperatures except room temperature. The tensile strength of the composite at room temperature is considerably smaller than the theoretical value. A possible cause for this is a thermal stress produced by the difference in thermal expansion coefficient between glass fiber and matrix during molding of the composite.

When a large number of cylindrical fibers are placed in close proximity as shown in Figure 6, the tensile stress σ_r in the matrix at a distance r from the center of fiber can be expressed as follows according to McGarry et al.[7]:

$$\sigma_r = P\left[\left(\frac{d}{2r}\right)^2 + \left(\frac{d}{2(s-r)}\right)^2\right] \tag{5}$$

where d is the fiber diameter and s is the fiber center-to-center distance as shown in Figure 6. In this equation, P is the pressure at the fiber–matrix interface produced by the difference in thermal expansion coefficient[8] and is given as follows[3]:

$$P \fallingdotseq \frac{\alpha_m E_m}{1 + \nu_m} \Delta T \tag{6}$$

where α_m is the thermal expansion coefficient of the matrix, E_m is Young's modulus of the matrix, ΔT is the difference in temperature from the molding temperature, and ν_m is Poisson ratio of the matrix.

In cases where the fiber volume fraction is 15% or more and the fibers are oriented randomly as in the present experiment, the fibers would come into contact with each other at a fairly high frequency. When the fibers are in contact, $s = d$. The thermal stress becomes maximal very near the fiber–matrix interface

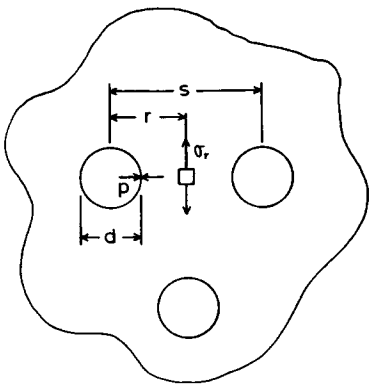


Fig. 6. Schematic diagram of thermal stress produced in fiber resin composite.

or $r = d/2$, and it is likely that the composite starts to fail at this point. The tensile stress produced in the matrix is expressed as follows:

$$\sigma_r = 2P \fallingdotseq \frac{2\alpha_m E_m \Delta T}{1 + \nu_m} \tag{7}$$

If a thermal stress of this magnitude is present in advance in a material, the material should fail at the stress which is smaller than the true strength by σ_r.

The values of σ_r were calculated by substituting the values of E_m and α_m at each temperature[3] for those in eq. (7). It is seen in Table I that a fairly large tensile stress is potentially present below 40°C. If this potential thermal stress were absent in the composite, a tensile strength larger than the experimental value by σ_r (Table I) would be expected at each temperature. Therefore, the values of σ_r were added to the experimental values plotted in Figures 2 and 3. As is apparent in Figures 7 and 8, the new values are closer to the theoretical values obtained earlier from eq. (4) over an entire range of experimental temperatures for any of the composites.

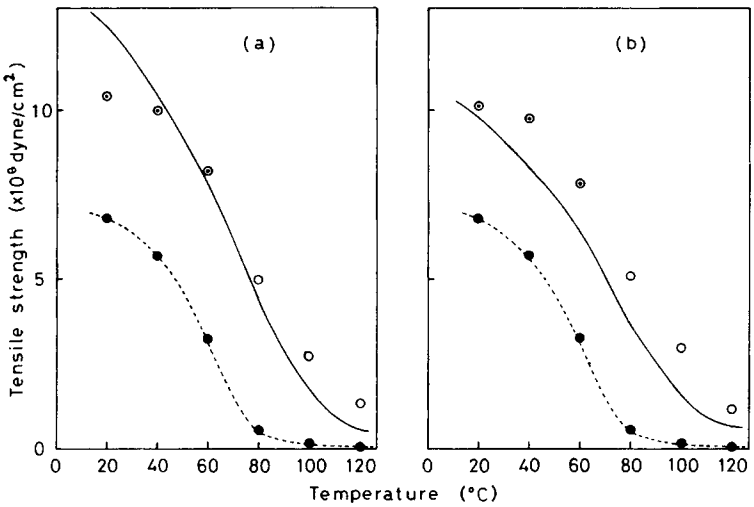


Fig. 7. Relationship between temperature and tensile strength for epoxy resin and epoxy–short glass fiber composite: (a) good bonding; (b) poor bonding; (○) composite; (· · · ● · · ·) resin; (⊙) modified value; (—) calculated value.

TABLE I
Thermal Stress

Temperature °C	Epoxy–short glass fiber composite, $\times 10^8$ dyn/cm^2	Unsaturated polyester–short glass fiber composite, $\times 10^8$ dyn/cm^2
20	2.27	2.43
40	1.48	1.28
60	0.71	0.30
80	0.025	0.013
100	0.0046	0.0076
120	0.0022	0.0034

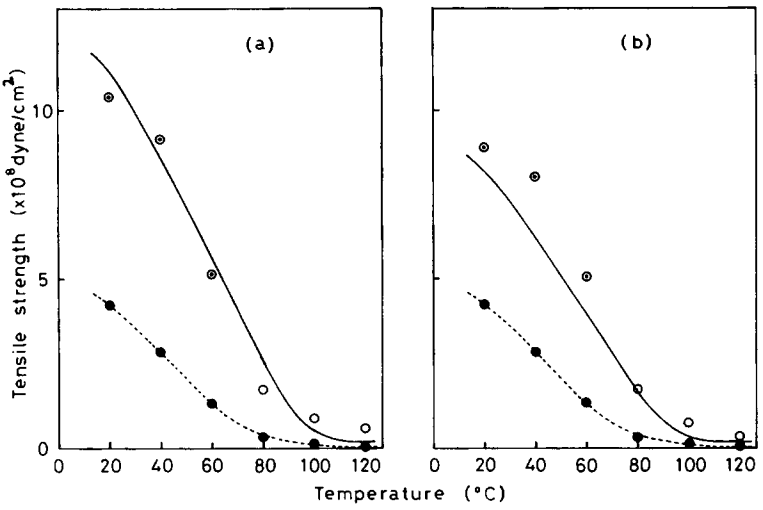


Fig. 8. Relationship between temperature and tensile strength for unsaturated polyester resin and unsaturated polyester–short glass fiber composite: (a) good bonding; (b) poor bonding; (○) composite; (· · · ● · · ·) resin; (◎) modified value; (—) calculated value.

The experimental values agree with the calculated values at 60°C or above where the thermal stress can virtually be ignored. The expected strength, allowing for the thermal stress, is closer to the calculated value obtained from eq. (4) at 40°C or below. It is therefore possible to estimate the tensile strength of composites reinforced with random-planar orientation of short fibers using eq. (4), which takes into account the interfacial shear strength. An agreement between the experimental value and the value calculated using eq. (4) at each temperature supports the reliability of the measured values of critical fiber length and apparent interfacial shear strength.[3]

The tensile strength of composites falls markedly at room temperature due to the residual stress. Hence, in order to produce a high reinforcing effect, it is clearly important not only to improve the interfacial shear strength but also to sufficiently relax the thermal stress produced during molding.

CONCLUSIONS

Epoxy resin or unsaturated polyester resin reinforced with random-planar orientation of short glass fibers were prepared and the temperature dependence of the tensile strength of such composites was examined. The tensile strength decreases with increasing temperature, and this tendency can be expressed as follows using the critical fiber length l_c and the apparent interfacial shear strength τ[3]:

$$\sigma_{cs} \fallingdotseq \frac{2\tau}{\pi}\left[2 + \ln\frac{(1 - l_c/2L)\sigma_f\sigma_m v_f + \sigma_m\sigma'_m v_m}{\tau^2}\right] \qquad L \geqq l_c$$

$$\sigma_{cs} \fallingdotseq \frac{2\tau}{\pi}\left[2 + \ln\frac{\tau(L/d)\sigma_m v_f + \sigma_m{}^2 v_m}{\tau^2}\right] \qquad L < l_c$$

where σ_{cs} is the tensile strength of the composite reinforced with random-planar orientation of short fibers, L is the fiber length, d is the fiber diameter, σ_f is the

tensile strength of the fiber, σ_m is the tensile strength of the matrix, v_f is the fiber volume fraction, v_m is the matrix volume fraction, and σ'_m is the matrix stress at fracture strain of the composite.

The experimental values for tensile strength at room temperature are considerably smaller than theoretical values. The difference at a given temperature roughly agrees with the thermal stress at the temperature estimated by McGarry et al.[7] It was speculated that the difference between experimental and theoretical values for tensile strength at room temperature is attributed to the thermal stress produced during molding due to a large difference in the thermal expansion coefficient between glass fiber and matrix resin.

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