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Mechanical properties of the glass fibre–polyester interphase

Part III *Effect of water on interface pressure and friction*

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Single-fibre pull-out experiments were carried out on samples which had been immersed in water at 22 °C, 60 °C and 75 °C for periods of up to 13 000 h. A curve-fitting technique was used to estimate the pressure and coefficient of friction during sliding, as the fibre was pulled out of the polymer. The immersion reduced the pressure from about 16 MPa to about 6 MPa for immersion at 75 °C. The effect was much smaller at 60 °C and still less at 22 °C. The results indicated that, except at 75 °C, the pressures were governed by the thermal and chemical shrinkages, water dilation of the polymer, and the change in Young's modulus of the polymer caused by the water. At 75 °C the apparent thermal shrinkage stress was anomalously low, taking into account the dilatation and plasticization of the resin. This could have been due to some slight dissolution of the glass by the water. The coefficient of friction was reduced, possibly by softening of the interphasial material when silanes were present. When the silane coating was removed the friction did not appear to obey Amontons law and it was concluded that a water film was probably present at the interface.

1. Introduction

In a reinforced polymer the shrinkage of the polymer during cure is important for providing a means for the polymer to grip the fibres, because standard theories of reinforcement require frictional stress transfer near the fibre ends [1]. Too great a shrinkage is undesirable, because it can cause the polymer to crack [2]. Such cracking appears to be particularly troublesome with Kevlar-reinforced epoxies. The shrinkage pressure also controls the across-the-grain fracture toughness [3, 4] and reducing it can enhance toughness [5].

With epoxies and polyesters, the pressure has two components: chemical and thermal. In the case of resins cured at relatively low temperatures where the thermal component is small, it was shown that chemical shrinkages could give pressures as high as 23 MPa with epoxies [6]. Coefficients of friction, μ, have been found to range from 0.18 for silicone-coated glass to 6.4 for carbon in an epoxy copolymer [6].

The effect of water on the pressure and coefficient of friction has not yet apparently been examined directly. It is known that water plasticizes and swells the resin so that we could well expect the interface pressure to be reduced. In addition, water sometimes aggregates at the interface, so μ could also be reduced. In this paper these effects are examined, using fibres embedded in polymers, and immersing the specimens in water for periods up to 13 000 h.

2. Experimental procedure

The materials used and experiments carried out have been described in Parts I and II [7, 8]. Isophthalic polyester resin was used as matrix, and E-glass fibres with various surface treatments were embedded in them. The specimens were immersed in water for various lengths of time at 22, 60 and 75 °C, and then the fibres were pulled out. This paper describes the post-debonding frictional pull-out process.

Fig. 4 in Part I [7] shows a typical pull-out curve. After debonding at a pull-out force, F_A, the force falls sharply, and is then re-established as frictional stresses are developed at the interface. It will be noted that after a few oscillations indicating stick-up behaviour, the frictional shear stress, given by the slope of the curve, increases as more fibre is pulled out. This is because the pressure at the interface is affected by Poisson's shrinkage of the fibre. This results in a pressure, P_f, which is given approximately by

$$P_f = P_0 - \nu_f E_m \sigma_f/(1 + \nu_m)E_f \qquad (1)$$

where P_0 is the pressure exerted by the polymer on an unstressed fibre, and arises from shrinkage of the polymer during cure. ν_f and ν_m are fibre and matrix Poisson's ratio, and E_f and E_m are the corresponding Young's moduli. σ_f is the stress in the fibre. If we write ν_s for $(\nu_f E_m/(1 + \nu_m)E_f)$, the frictional pull-out force,

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F_s, is a function of pulled out distance, approximately given by [3]

$$F_s = (\pi d^2 P_0/4\nu_s)(1 - e^{-4\nu_s\mu(L-x)/d}) \quad (2)$$

where μ is the coefficient of sliding friction at the interface.

For a nearly pulled out fibre, $x \simeq L$, and Equation 2 reduces to

$$F_s = \pi d \mu P_0(L - x) \quad (3)$$

So from the slope of the curve at the point the fibre emerges from the polymer, F'_s, estimate μP_0

$$\mu P = F'_s/\pi d \quad (4)$$

Next, assume a value for P_0, say 20 MPa, estimate μ using Equation 4 and then estimate a new value of P_0 using Equation 2 with $x = L/10$ or $L/5$. This new value of P_0 is used to repeat the process. Three or four iterations usually suffice.

The dilatation of the polyester by the water was also measured. For this, a strain gauge was attached to a sheet of the polymer before immersion using the polyester matrix material as adhesive, and protecting the strain gauge with more polyester. The strain was monitored using a model VE (Intertechnology Ltd.) strain indicator.

3. Results

Interface pressures were reduced by the water immersion, and the effect was greater at higher temperatures, Fig. 1. The surface treatment had no effect on the pressure, but when the pull-out tests were carried out with the specimens still hot as well as wet, the pressures were much lower. (Note: all the specimens which had been immersed in water were tested while wet; the specimen was surrounded by distilled water during the pull out.)

The pressure was much reduced when the polymer had 30% and 60% γ-methacryloxypropyltrimethyl siloxane (MPS) added to it, Fig. 2, though the percentage loss due to the water was about the same as with the neat polyester (i.e. about 30% at 100 h).

The coefficient of friction was not very sensitive to water. Fig. 3 shows the results for the MPS-coated fibres at 22, 60 and 75 °C: the losses were greater at higher temperatures. Fibres with different surface treatments all lost about the same relative amounts of friction, Fig. 4, but when the polymer contained MPS there was less loss in friction, Fig. 5.

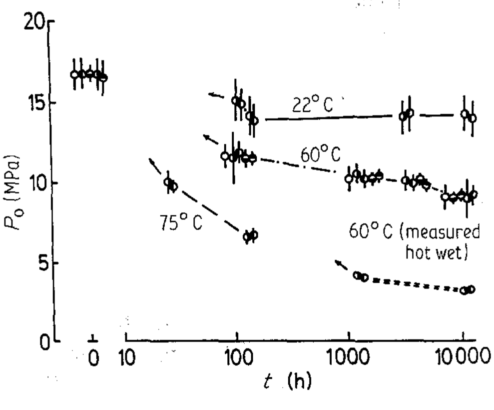

Figure 1 Effect of water immersion at 22, 60 and 75 °C on the pressure at the interface. (◒) Intact, (◓) THF-extracted, (○) pyrolysed, (◑) MPS-coated, (◐) MPS-coated then extracted.

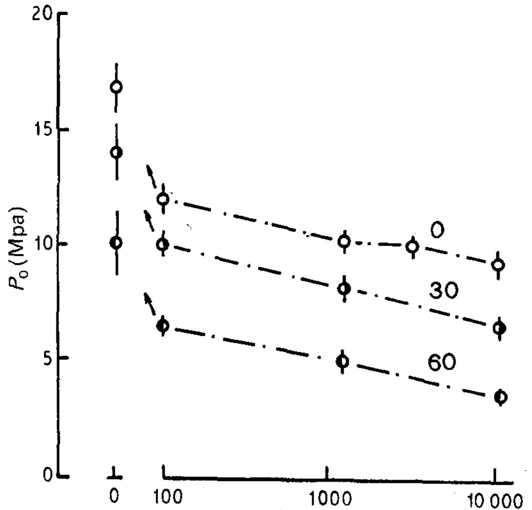

Figure 2 Interface pressure versus time of water immersion at 60 °C for fibres in polyester containing 0%, 30% and 60% MPS.

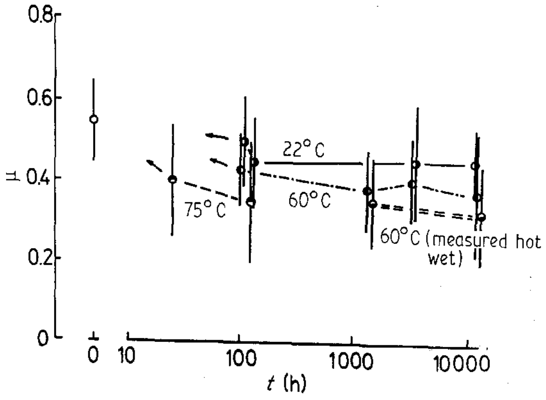

Figure 3 Interface friction coefficient versus time of water immersion at 22, 60 and 75 °C for MPS-coated fibres.

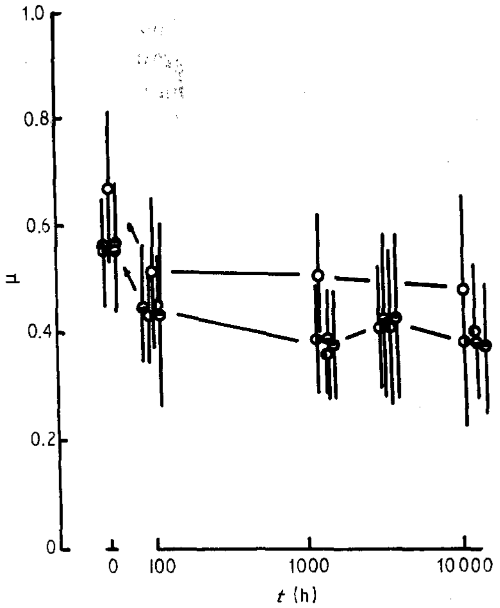

Figure 4 Effect of water immersion on interface friction for fibres with various surface treatments. (◒) Intact, (◓) THF-extracted, (○) pyrolysed, (◑) MPS-coated, (◐) MPS-coated then extracted.

The Young's modulus of the polymer was reduced by hot water, but not by water at 22 °C, Fig. 6. When hot (as well as wet) during the tensile test, the modulus was reduced by an additional 20–30%. The polymer expanded about 0.15% when saturated at 22 °C, Fig. 7. (At this point the water content was about 1.5%.) The presence of MPS increased the dilatation, more or less in proportion to the amount of water absorbed (i.e. about 0.15% and 0.17% for the 30% and 60% MPS additions respectively.)

4. Discussion

The interfacial pressure, P, arises from two processes: (i) the differential thermal shrinkage between polymer and fibre, and (ii) the chemical shrinkage that results from the bonding and cross-linking of the polymer during cure. The thermal shrinkage can be estimated theoretically when the expansion coefficients of polymer and fibre are known, see the Appendix.

The interfacial pressure before water immersion was independent of fibre surface treatment, and this was also true of the water-immersed samples; see Fig. 1. Thus the curing reaction does not appear to involve an interaction with the interphasial material such that preferential expansion or contraction takes place there, as might be expected with the physisorbed layer. Also it seems that water absorption into the interphase did not cause preferential expansion there.

Equation A16 (see Appendix) can be used for the samples before water immersion to estimate the pressure due to thermal effects. This comes to 8.2 MPa. The observed pressure (16.5 MPa) is about twice this. Hence it is deduced that the chemical and thermal shrinkages are about equal. This gives a chemical shrinkage stress of about 8 MPa, which is about the same as recently estimated for an epoxy [9]. The first column in Table I gives the estimated strains for thermal shrinkage, ε^T, and chemical shrinkage, there designated as residual shrinkage.

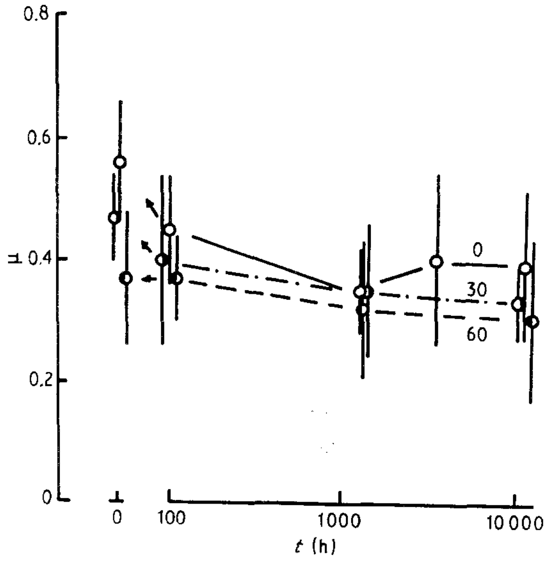

Figure 5 Interface friction versus time of water immersion at 60 °C for fibres in polyester containing 0%, 30% and 60% MPS.

If the pressure is well behaved, we should expect it to be reduced by the dilatation induced by the water absorption. The second column shows that this is so: the residual shrinkage plus the dilatation ($\varepsilon^c + \Delta = 0.35\%$) is not very different from the chemical shrinkage in Column 1, i.e. 0.32%. The same is true for the 60 °C water immersion (Column 3), but the deviation was greater (12%) when the testing temperature was 60 °C (Column 4). For the 75 °C immersion, $\varepsilon^c + \Delta$ was very low (0.19%). This perhaps indicates that the water had attacked the glass and removed a significant amount. Examination of the fibres in the microscope after hot-water treatment did show some loss of material; the surface had become rough.

Adding MPS to the polymer reduced the pressure for the non-immersed samples, but the pressure was well behaved in these cases also; Columns 6–9 in Table I. (Note that for this reasoning we used $\alpha_m = 70\ \mathrm{MK}^{-1}$, which is about the geometric mean of the limiting values for polyester resin, which are 50 and $100\ \mathrm{MK}^{-1}$ [10]. Using a higher value of α_m would increase all ε^T values and decrease all ε^c values, but would not have a very big effect on the comparison on the bottom line of Table I. Likewise, while a lower

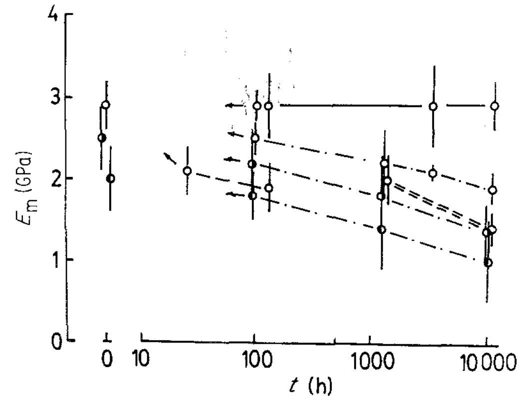

Figure 6 Effect of water immersion at (——) 22, (—·—) 60 and (– – –) 75 °C on Young's modulus of polyesters containing (○) 0%, ◑ 30% and ◐ 60% MPS. (= = =) 60 °C HW test carried out with specimen immersed in water at 60 °C.

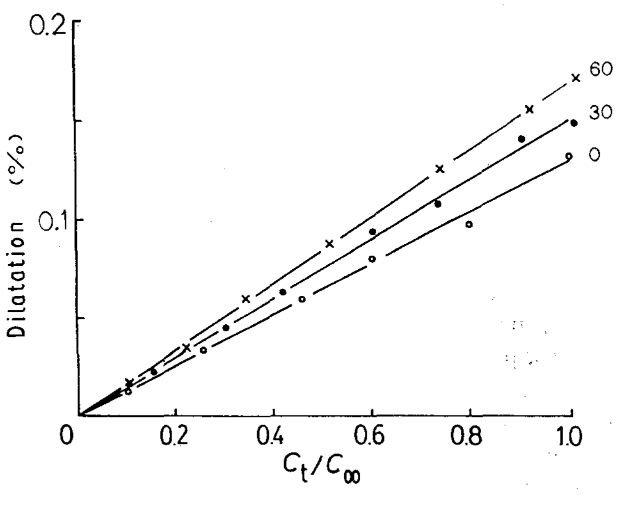

Figure 7 Dilatation of resins as a function of degree of saturation for polyesters containing 0%, 30% and 60% MPS.

TABLE I Estimated shrinkage strains

Immersion temperature (°C)	Testing temperature (°C)	Pressure, P (MPa)	Modulus, E_m (GPa)	Total shrinkage (%)	Thermal shrinkage[a], ε^T (%)	Residual shrinkage, ε^c (%)	Dilatation[b], Δ (%)	$\varepsilon^c + \Delta$ (%)
–[c]	22	16.5	2.9	0.64	0.32	0.32	0.00	0.32
22	22	14.1	2.9	0.54	0.32	0.22	0.13	0.35
60	22	9.1	1.9	0.53	0.32	0.21	0.13	0.34
60	60	3.2	1.4	0.26	0.11	0.15	0.13	0.28
75	22	6.5	1.9	0.38	0.32	0.06	0.13	0.19
–[c, d]	22	13.8	2.5	0.62	0.32	0.30	0.00	0.30
60[d]	22	6.5	1.4	0.52	0.32	0.20	0.15	0.35
–[c, e]	22	10.0	2.0	0.5	0.32	0.24	0.00	0.24
60[e]	22	3.5	1.0	0.39	0.32	0.07	0.17	0.24

[a] $\varepsilon^T = \varepsilon_f^T - \varepsilon_m^T$; estimated using Equation A10.

[b] For dilatations, see Fig. 7.

[c] Before water immersion; all others immersed 13 000 h, except 75 °C immersed 300 h.

[d] Polymer contained 30% MPS.

[e] Polymer contained 60% MPS.

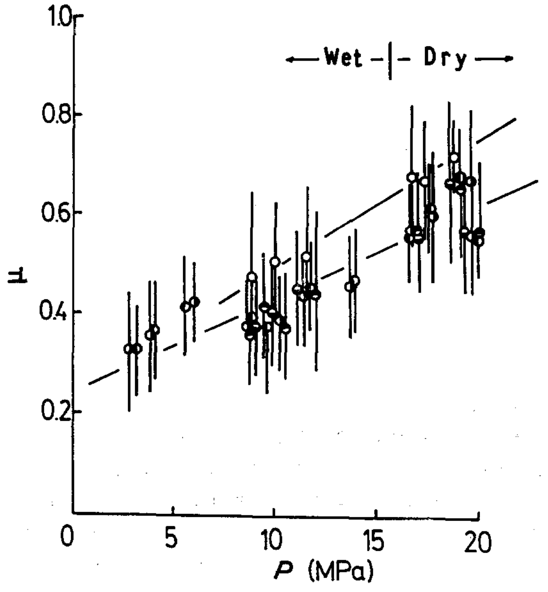

Figure 8 Correlation between friction coefficient and interface pressure for fibres with different surface treatments.

value of α_m would decrease ε^T and increase ε^c, it would also affect the bottom line comparison very little.)

The as-received and coated and the THF-extracted fibres all gave about the same coefficient of friction, Fig. 4. The pyrolysed fibres had a somewhat higher value. Water immersion always decreased μ, Figs 3–5, presumably due to water softening the interphasial material. The friction coefficient and pressure did show some slight correlation, Fig. 8, with the results for the pyrolysed fibres fitting the upper line, and the otherwise treated fibres giving a better fit to the lower line, which indicated almost no correlation at all. Because μ and P have quite different origins, we do not expect any correlation. The slight correlation in the case of the pyrolysed fibre, therefore, suggests that the sliding is not perfectly governed by Amonton's law. This could be an indication of a water film at the sliding surface. Higher pressure could then increase μ by decreasing the film thickness.

5. Conclusion

The pressure at the sliding interface between the polymer and the glass appeared to be well behaved, so long as the water in which the fibre is immersed was not too hot (≤ 60 °C). The water causes a change in pressure due to the reduction in the Young's modulus of the polymer as it is plasticized by the water, and due to the dilatation of the polymer. The pressure, due to differential thermal shrinkage between fibres and polymer, is only about half the total pressure in the case of the unwetted interphase. It appears to be reversible, because testing when hot reduced the pressure by the expected amount.

The coefficient of friction was affected by the immersion, probably due to the softening of the interphasial material. However, in the case of the pyrolysed fibre, which had no coating on it, there was some indication the Amonton's laws were not obeyed, suggesting that a water film may have been present.

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Appendix. Thermal stresses

First consider expansions (and contractions) in the direction of the fibre axis, z. Let the fibre thermal expansion strain be ε_{fz}^T and the polymer be ε_{mz}^T, in the absence of each other. When the fibre is embedded in the polymer, the expansion of both is the same, i.e. ε_{cz} (see Fig. A1) so both fibre and polymer suffer elastic strains, ε_{fz} and ε_{mz}, and

$$\varepsilon_{cz} = \varepsilon_{fz}^T + \varepsilon_{fz} = \varepsilon_{mz}^T + \varepsilon_{mz} \qquad \text{(A1)}$$

In the radial direction, the corresponding displacements are similarly related

$$u_{cr} = r\varepsilon_{fr}^T + r\varepsilon_{fr} = r\varepsilon_{mr}^T + u_{mr} \qquad \text{(A2)}$$

where $2r$ is the fibre diameter, and the elastic displacement in the polymer, u^1_{mr}, is given in standard texts [11] as

$$u^1_{mr} = P_T r[\nu_m + (1 + V_f)/V_m]/E_m \quad (A3)$$

where P_T is the pressure exerted on the polymer by the fibre expanding relative to the polymer. The polymer is a thick-walled tube, outer diameter $2R$, so that $V_f = (r/R)^2$ and $V_m = 1 - V_f$. However, in this case, because there is an axial stress in the polymer, we must superimpose the strain due to this. Thus the total elastic displacement of the polymer, u_{mr}, is given by

$$u_{mr} = r(P_T[\nu_m + (1 + V_f)/V_m] - \nu_m \sigma_{mz})/E_m \quad (A4)$$

where σ_{mz} is the axial stress in the polymer.

The stresses are

$$\sigma_{fr} = \sigma_{f\theta} = \sigma_{mr} = -P_T \quad (A5)$$

using polar co-ordinates r and θ. Also [11]

$$\sigma_{m\theta} = P_T(1 + V_f)/V_m \quad (A6)$$

Equilibrium of forces in the axial direction requires that

$$V_f \sigma_{fz} + V_m \sigma_{mz} = 0 \quad (A7)$$

and there are six stress–strain relations of the type

$$\varepsilon_i = \{\sigma_i - \nu(\sigma_j + \sigma_k)\}/E \quad (A8)$$

for fibre and polymer, where i, j and k represent r, θ and z, as appropriate, with additional subscripts f for the fibre and m for the polymer.

By successive substitutions of Equations A3–A8 in Equations A1 and A2 we obtain ε^T_{fr}

$$P_T = \frac{V_m E_m E_f\{T(\varepsilon^T_{fr} - \varepsilon^T_m) + U(\varepsilon_{fz} - \varepsilon^T_m)\}}{W V_f E_f^2 + X V_m E_m E_f + Y V_m^2 E_m^2} \quad (A9)$$

for anisotropic fibres in an isotropic matrix ($\varepsilon^T_m = \varepsilon^T_{mz} = \varepsilon^T_{mr}$) with

$$T = V_f E_f + V_m E_m \quad (A10)$$

$$U = \nu_m V_f E_f + \nu_f V_m E_m \quad (A11)$$

$$W = (1 + \nu_m)[V_m + 2V_f(1 - \nu_m)] \quad (A12)$$

$$X = V_f(3 - \nu_f - 4\nu_m \nu_f) + V_m(1 + \nu_m) \quad (A13)$$

$$Y = (1 + \nu_f)(1 - 2\nu_f) \quad (A14)$$

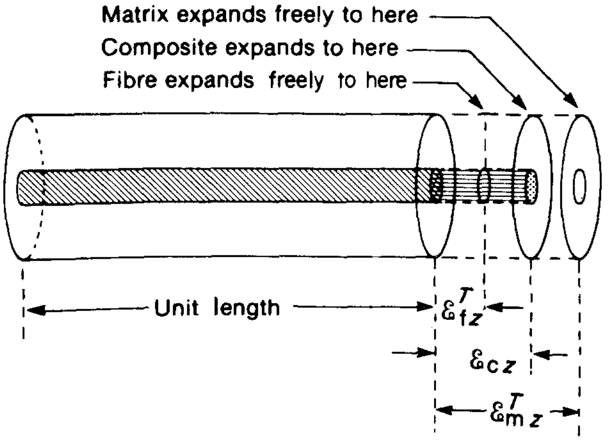

Figure A1 Fibre and matrix axial displacements.

In the case of glass fibres of 22 μm diameter, in a polyester bar of 22 mm diameter, $V_f = 10^{-6}$, and $E_f \gg E_m$, so that Equation A9 contains many terms which may be neglected. If we further assume the fibres are isotropic so that $\varepsilon^T_{fr} = \varepsilon^T_{fz} = \varepsilon^T_f$, then

$$P_T \simeq (\varepsilon^T_f - \varepsilon^T_m)E_m(1 + \nu_f)/(1 + \nu_m) \quad (A15)$$

For an 80 °C cure, $(\varepsilon^T_f - \varepsilon^T_m) = -58(15.5–70) \times 10^{-6}$ which comes to 3.16×10^{-3}. For polyester $\nu_m = 0.34$ and for glass $\nu_f = 0.20$, so that

$$P_T \simeq 2.83 E_m \quad (A16)$$

for P_T in MPa and E_m in GPa.

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