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Temperature and wavelength dependent transmission of optically transparent glass fibre poly(methyl methacrylate) composites

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The temperature and wavelength dependent transmission was measured for glass fibre reinforced transparent composites prepared by sheet lamination and pressure curing processes. A mathematical model using fibre volume content, glass fibre diameter, refractive index of the fibre and matrix, non-wet fibre content and thickness of the composites was used to predict the transmission of the composite as a function of temperature and wavelength. The transmission calculated from the model for 20–70 °C and between 500 to 800 nm agreed well with the measured optical transmission for a thin composite containing < 10 vol % of 17 μm glass fibres. A small amount of non-wet fibre (e.g. 2.0% of total fibre) was predicted to reduce the maximum transmission by up to 17% for a composite containing 7.2 vol % fibres and a thickness of 0.5 mm.

1. Introduction

Composite materials are widely used as structural materials because of their light weight and high specific strength. However, a composite consisting of a transparent matrix, such as poly(methyl methacrylate) (PMMA), usually becomes translucent or opaque when a transparent reinforcement (glass fibre) is introduced because of light scattering which occurs at the interface of the two materials [1]. By carefully matching the refractive index of the glass fibres with that of PMMA, highly transparent PMMA composites have been prepared [2–4].

Compared to glass fibres, the optical properties of PMMA are highly temperature dependent [5, 6]. The refractive index of PMMA decreases with increasing temperature at a rate (dn/dT) of -1.1×10^{-4} or $-1.3 \times 10^{-4}\,°C^{-1}$ [6, 7] below T_g ($\approx 100\,°C$) of PMMA. In comparison, the temperature dependent change in refractive index for BK-10 glass ($dn/dT = +3.5 \times 10^{-6}\,°C^{-1}$) [8] below the T_g of PMMA is so small it can be ignored. Thus, the refractive index of these two materials can be equal (matched) only at one temperature (T_{max}). At T_{max} the light scattering will be minimum and the optical transmission maximum. The light transmission of composites made from these two materials is expected to be temperature dependent because of the difference in the temperature coefficients of the refractive index (dn/dT) for the PMMA matrix and the glass fibre reinforcement. The difference between dn/dT of the PMMA and glass fibre determines the rate of change in the mismatch in refractive index of the PMMA and glass fibre as the temperature deviates from T_{max} and controls the temperature dependent transmission of a composite.

The change in refractive index with wavelength (dispersion) for glass and PMMA are also quite different [8, 9]. In general, the slope ($dn/d\lambda$) of the dispersion curve for PMMA is much larger than that of the glass, especially near 400 nm. Since the mismatch in the refractive index will also change with wavelength, the transmission of a glass fibre/PMMA composite is expected to be wavelength dependent.

The purpose of the present study was to mathematically model the temperature and wavelength dependent optical transmission of a composite in terms of the differences in the refractive index between PMMA and the glass fibre caused by changes in temperature and wavelength. The model has been verified by comparison with the experimentally measured transmission, but limitations of the model are discussed.

2. Mathematical model

The scattering of an electromagnetic wave by any material is related to the optical heterogeneity of that material [10, 11]. In addition to the reirradiance (scattering) of electromagnetic energy, absorption may also occur. Both scattering and absorption remove energy from a beam of light traversing the material so that the beam is attenuated. This attenuation (extinction) is defined as

$$\text{extinction} = \text{scattering} + \text{absorption}$$

When an incident beam of intensity I_0 traverses a slab of particles over an optical path of length h, assuming multiple scattering can be neglected and no change in phase and wavelength of the light after scattering, the

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transmitted intensity, I_t, is given by [11]

$$I_t = I_0 \exp(-A_e h) \qquad (1)$$

where the attenuation coefficient, A_e, is

$$A_e = nC_e = nC_a + nC_s \qquad (2)$$

where n is the number of particles per unit volume, C_e is the extinction cross-section and C_a and C_s are the cross-section for absorption and scattering, respectively. For a mixture of different particles the attenuation coefficient is

$$A_e = \sum n_j C_{e,j} \qquad (3)$$

Since n_j is the particle number density, $1/n_j$ is the average volume allocated to a single particle of type j, the volume fraction, $V_{f,j}$, of the particles in the system is $n_j v_j$, where v_j is the volume of a single particle of type j. Thus, A_e can be written as $A_e = \sum (V_{f,j}/v_j) C_{e,j}$. For non-absorbing particles, A_e can be expressed as

$$A_e = \sum n_j C_{s,j} = \sum V_{f,j} C_{s,j}/v_j \qquad (4)$$

The scattering cross-section is related to the scattering efficiency, $Q = C_s/G$, where G is the geometrical cross-section which is $2R$ per unit length for an infinite cylinder of radius R. The attenuation coefficient of composites containing glass fibres with radius R_g becomes

$$A_e = 2V_{f,g} Q_g / \pi R_g \qquad (5)$$

where Q_g is the scattering efficiency of the glass fibres. For normally unpolarized incident light, Q_g in the forward direction can be expressed as [13]

$$Q_g = (1/x) \sum_{n=0}^{\infty} \varepsilon_n (\|An_{|}\|2 + \|an_{||}\|2) \qquad (6)$$

where

$$An_{|} = \frac{Jn(mx)Jn'(x) - mJn'(mx)Jn(x)}{Jn(mx)Hn'(x) - mJn'(mx)Hn(x)} \qquad (7)$$

$$\mathrm{An}_{||} = \frac{mJn'(x)n(mx) - Jn(x)Jn'(mx)}{mJn(mx)Hn(x) - Jn'(mx)Hn(x)} \qquad (8)$$

where $\varepsilon_n = 2$ when $n > 0$ and $\varepsilon_0 = 1$; $x = 2\pi R_g/\lambda$ and λ is the wavelength in the PMMA matrix; $m = n_{\text{glass}}/n_{\text{PMMA}}$ is the relative refractive index of the glass fibre (n_g) and PMMA (n_p); Jn is a Bessel function of the first kind; Hn is a Hankel function of the second kind; and the primes denote differentiation of the functions with respect to their arguments.

The refractive index of PMMA depends strongly on temperature ($dn/dT = -1.1 \times 10^{-4}\,°\text{C}^{-1}$). The refractive index of PMMA at any temperature T (in °C) above 25 °C and below T_g (100 °C) can be written as

$$n_{\text{PMMA}}(T) = 1.4925 - 1.1 \times 10^{-4}(T - 25) \qquad (9)$$

for PMMA with $dn/dT = -1.1 \times 10^{-4}\,°\text{C}^{-1}$ and refractive index (n_D) of 1.4925 at 25 °C. In comparison, the change in refractive index with temperature for the glass fibre was negligible ($dn/dT = +0.035 \times 10^{-4}\,°\text{C}^{-1}$) in this small temperature range. The relative refractive index (m) of the 17 μm glass fibre ($n_D = 1.4907$) and PMMA at any temperature below the T_g of the PMMA is

$$m(T) = 1.4907/[1.4925 - 1.1 \times 10^{-4}(T - 25)] \qquad (10)$$

For the wavelength (λ in nm) dependent refractive index at a constant temperature the refractive index of the 17 μm BK 10 fibre was $n_{\text{glass}}(\lambda) = 1.4794 + 3920\lambda^{-2} - 808\lambda^{-4} + 0.1\lambda^{-6}$. The equivalent equation for PMMA (L method, described later) was $n_{\text{PMMA}}(\lambda) = 1.4794 + 4557\lambda^{-2} + 903\lambda^{-4} + 0.1\lambda^{-6}$. The relative refractive index of the glass fibre and PMMA at 25 °C was $m(\lambda) = (1.4794 + 3920\lambda^{-2} - 808\lambda^{-4} + 0.1\lambda^{-6})/(1.4794 + 4557\lambda^{-2} + 903\lambda^{-4} + 0.1\lambda^{-6})$. (11)

The scattering efficiency of a composite, $Q_g = Q_g(T, \lambda)$, and the transmission were functions of temperature because of the temperature dependent relative refractive index. Equation 1 can be rewritten as

$$I_t(T, \lambda)/I_0 = \exp(-\sum 2V_{f,g} Q_g(T, \lambda) h / \pi R_g) \qquad (12)$$

According to Equation 12, the optical transmission for a PMMA composite containing glass fibres will vary exponentially with the volume fraction of fibres ($V_{f,g}$), the radius of the glass fibres (R_g), the optical path length (h, thickness of the composite) and the temperature of the composite.

3. Experimental

The glass fibre used for reinforcing the PMMA matrix was produced from an optical glass whose refractive index at 25 °C in bulk form was $n_D = 1.49776 \pm 0.00001$. The glass was re-melted and fined in a resistance heated Pt/Rh ten-hole bushing at 1250 °C for 45 min to remove bubbles. When fibres were drawn at 1204 °C at a speed of 4.0 or 8.0 m s^{-1}, the average diameters were 17 and 13 μm, respectively, with a standard deviation of 2.3 μm. Because of rapid cooling, these fibres had a lower refractive index ($n_D = 1.4907$ for 17 μm and 1.4901 for 13 μm) with a standard deviation of 0.0002. Strips of fibres were prepared by moving a rotating collection drum at a controlled speed in a horizontal direction normal to the pulling direction for the fibres. No coating was applied to the fibres.

Composite specimens with unidirectionally aligned glass fibres were prepared by either a sheet lamination (method L) or by polymerization of MMA (methyl methacrylate) in a pressure vessel (method P). The composite made by method L contained 7.2 vol % of 17 μm fibres, while the composite made by method P contained 10.2 vol % of 13 μm fibres.

For method L a strip of fibres was rinsed with MMA and placed between two PMMA sheets (75 μm in thickness) to form a sandwich prepreg. Several layers of prepreg were stacked vertically, with the fibre aligned unidirectionally, and then hot-pressed at 140 °C for 180 min. For method P a dip-coating procedure was used to apply a silane coupling agent [3-(trimethoxysilyl)propyl methacrylate] to the fibre strip which had been cut to size and bound at one end. This procedure consisted of immersing the bound fibres in a 3 vol % silane in MMA solution at 23 °C for 2 min followed by rinsing in pure MMA. The dip coating and rinsing were done in an ultrasonic bath to get better wetting of the fibres and rinsing action. Surface water on the fibre hydrolysed the silane coupling agent from the methoxy to the hydroxy species which could condense and bond to the glass surface. This dip coating procedure is known to deposit 3–8 monolayers (< 10 nm) of the trifunctional coupling agent onto the fibre surface [12].

From the rinse bath, the coated fibres were put into a mould consisting of two $10.2 \times 15.2 \times 0.6\ cm^3$ glass plates separated by a tube gasket and held together by binder clips. The two piece poly(ethylene) lid of the mould, which was machined to fit over the glass plates, also served to bind the fibres and suspend them unidirectionally (vertically) in the mould during polymerization. The mould was filled with the monomer mixture (99.3 vol % MMA, 0.5 vol % tetraethyleneglycol dimethacrylate, 0.1 vol % USP-245 and 0.1 vol % methyl ethyl ketone peroxide) and then degassed. The assembly was placed in a stainless steel pressure vessel and heated to 65 °C by external heating elements. The pressure vessel, 61.0 cm deep and 15.2 cm in diameter, was pressurized to 6.9 MPa with nitrogen. After 18 h at 65 °C the vessel was depressurized, opened and the composite removed from the mould while still warm.

The volume fraction of fibre in the composites was determined by a burn-out method. The composite was weighed and then put into a Pt crucible which was placed in a furnace at 600 °C for 4 h to burn off the PMMA. The glass fibre residue was weighed after the PMMA had burned off. The density of the PMMA ($1.19\ g\,cm^{-3}$) and bulk glass ($2.39\ g\,cm^{-3}$) were used for calculating the fibre volume content.

The optical transmission of each composite was measured from 20 to 70 °C at 589 nm using a spectrophotometer (acceptance angle $\sim 0.2°$) equipped with a cell that was heated at $0.5\ °C\,min^{-1}$. In order to eliminate surface reflections, the composite was placed (normal to the beam with the fibre oriented vertically) in an optical cell which was filled with a laser liquid whose refractive index ($n_D = 1.4920 \pm 0.0002$ at 25 °C) was close to that of the composite. The transmission versus temperature curve was recorded with an x–y recorder. The temperature of the cell was measured by a J-type thermocouple which was calibrated to ± 0.1 °C.

4. Results and discussion

The transparency and clarity of the composites prepared by methods L and P are clearly illustrated in Fig. 1. Both composites were highly transparent at 22 °C, as indicated by the ease with which the word beneath each sample is read. Fig. 2 shows the typical temperature dependent transmission of PMMA composites containing 7.2 and 10.2 vol % 17 μm glass fibres. With increasing temperature, the transmission of both composites initially increased to a maximum and then decreased. For the composite containing 7.2 (method L) and 10.2 vol % (method P) glass fibres, the maximum transmission of 96.1 and 87.3% occurred at 49 and 28 °C, respectively, because of the small difference in the refractive index of PMMA in each composite.

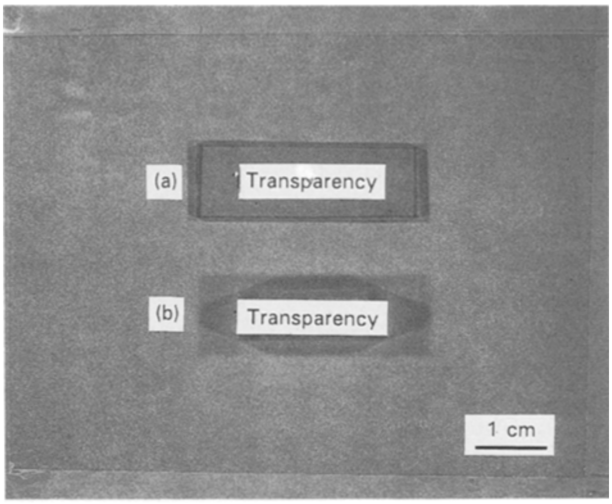

Figure 1 Optical transparency and clarity of glass fibre reinforced PMMA composites prepared by (a) method L (0.50 mm thick and 7.2 vol % of 17 μm fibre) and (b) method P (6.80 mm thick and 10.2 vol % of 13 μm fibre). The word "Transparency" beneath each sample is easily read.

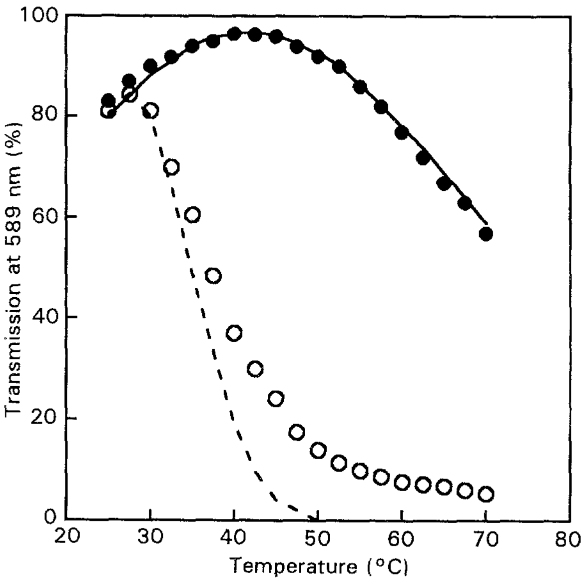

Figure 2 Temperature dependent transmission of composites prepared by method L (●) and method P (○). Solid (7.2 vol %) and dashed (10.2 vol %) lines were calculated from Equation 12.

Flaws of various types, such as voids, any small distribution (non-uniformity) in the refractive index of the fibres and non-wet fibres (fibres not completely immersed in the PMMA matrix but surrounded by an air pocket), in a composite would scatter light and reduce the optical transmission if they produced a mismatch in the refractive index with the matrix. For a perfect composite, i.e. without flaws, the maximum transmission should be 100% (disregarding surface reflection loss) at the temperature where the refractive index of the glass fibres exactly matches that of PMMA. The distribution (standard deviation, σ) in the refractive index for the 17 μm glass fibre, $\sigma = 0.0002$, was considered of minor importance since the reduction in transmission caused by such a distribution was predicted to be only 0.5% for a composite 0.68 mm thick and containing 10 vol % of 17 μm fibre [13].

A small amount of non-wet fibre was found to be the predominant flaw in the composite prepared by method P, as revealed by the white lines in Fig. 3. Very few voids or gas bubbles were observed in the composites used in the present work and whose cross-sections were examined with a scanning electron microscope, see Fig. 4. Because of the surrounding air gap (refractive index of air is ≈ 1.0), the effective refractive index of the non-wet fibre was assumed to be 1.0 when the transmission of a composite was calculated from Equation 12. The effect of non-wet fibre on the maximum transmission of a composite with a thickness of 0.50 mm and containing 7.2 vol % of 17 μm fibres ($\sigma = 0.0002$) was calculated from Equation 12 for various amounts of non-wet fibres. A maximum transmission 99.5% was calculated for a composite with no non-wet fibres. However, when only 0.5% of the total fibres present were non-wetted, then the maximum transmission decreased to 97.3%. For a composite assumed to contain 1.0% non-wet fibres, the maximum transmission was 93.4%. Table I summarizes the calculated and measured maximum transmission for a composite containing 7.2 vol % of 17 μm fibre. The transmission calculated for a composite containing 0.7% non-wet fibres agreed best with the measured maximum transmission (96.1%) of the composite fabricated by method L. It is important to note that as little as 2.0% of non-wet fibres in a composite caused a loss of $\approx 17\%$ in the optical transmission and, thereby, severely lowered the optical transparency of the composite.

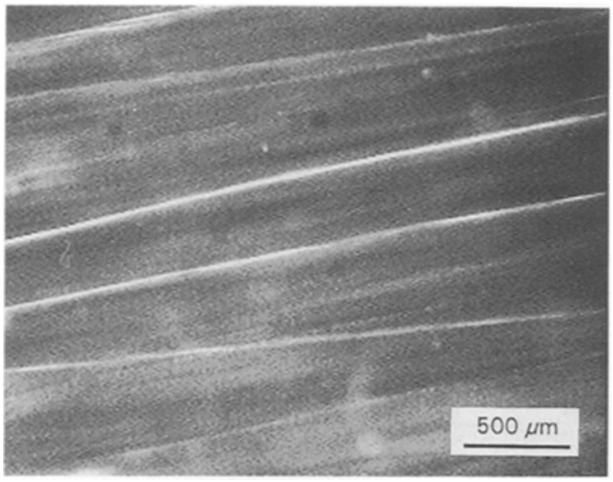
Figure 3 Dark field optical micrograph of glass fibres in a composite made by pressure curing (method P) which shows the presence of non-wet fibres (white lines).

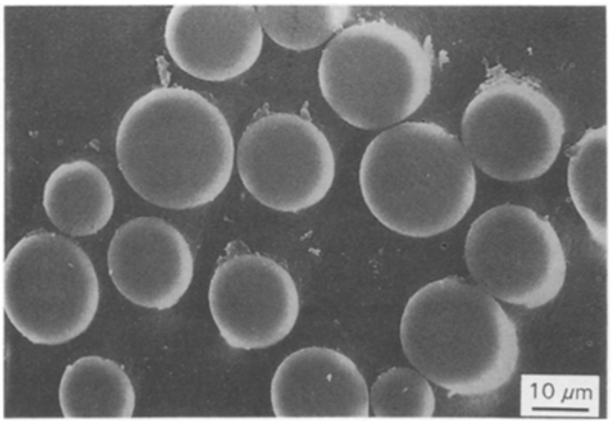
Figure 4 SEM micrograph of polished cross-section showing no voids in the PMMA matrix of the composites prepared by method P.

Fig. 2 shows that the transmission calculated from Equation 12 (solid line) agreed well with the measured transmission for the thin composite (0.5 mm thick) containing 7.2 vol % of the 17 μm glass fibre when a $\mathrm{d}n/\mathrm{d}T$ of $-1.1 \times 10^{-4}\,^{\circ}\mathrm{C}^{-1}$ for the PMMA was assumed. The calculated transmission as a function of temperature for the thick composite (6.8 mm) containing 10.2 vol % of 13 μm fibres did not agree as well with the measured transmission when compared to the thinner composite containing less fibre. In the thicker composite the calculated transmission was more temperature dependent and decreased more rapidly on the higher temperature side of the transmission peak than the measured transmission, see Fig. 2.

Since the shapes of the dispersion curves for glass and PMMA are different, the match in refractive index could be at only one wavelength. Fig. 5 shows that the transmission at 25 °C decreased with decreasing wavelength in the visible region for composites containing either 7.2 or 10.2 vol % fibres because of the increasing mismatch in the refractive index of the glass fibre and PMMA which occurred at wavelengths below 500 nm. The rapid decrease in transmission below 450 nm for composite prepared by method L was due mainly to the larger mismatch in the refractive index between the fibre and matrix and a u.v. absorber present in the PMMA (which caused a large reduction in transmission below 400 nm). For the composite prepared by method P a small transmission maximum appeared near 550 nm, followed by a nearly constant transmission between 600 and 800 nm.

The refractive index as a function of wavelength for the glass fibre was estimated by shifting the dispersion

TABLE I Calculated and measured maximum transmission for a PMMA composite containing 7.2 vol % of 17 μm ($\sigma = 2.3$ μm) BK10 glass fibres with a mean refractive index of 1.4907 ($\sigma = 0.0002$). Composite thickness was 0.50 mm

Assumed percent of non-wet fiber	Calculated from Equation 12 maximum transmission (%)
0.0	99.5
0.5	97.3
0.7	95.7
1.0	93.4
2.0	82.9
Measured	96.1

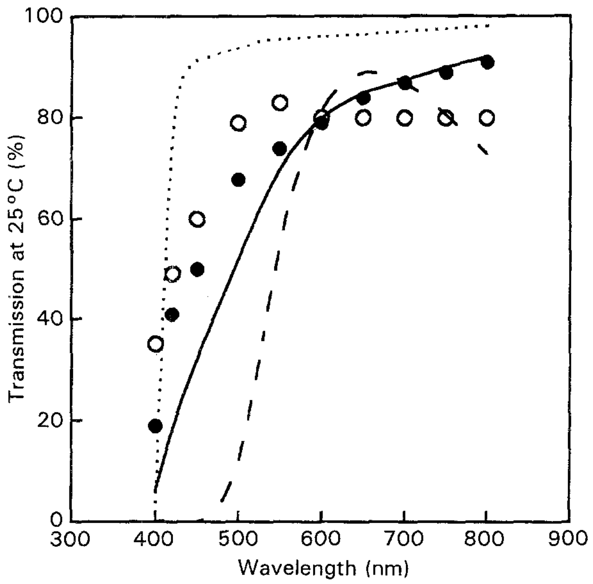

Figure 5 Wavelength dependent transmission of composites made by method L (●) 7.2 vol % fibre, and method P (○) 10.2 vol % fibre, and for PMMA used in method L (dotted line). Solid (method L) and dashed lines (method P) were calculated from Equation 12.

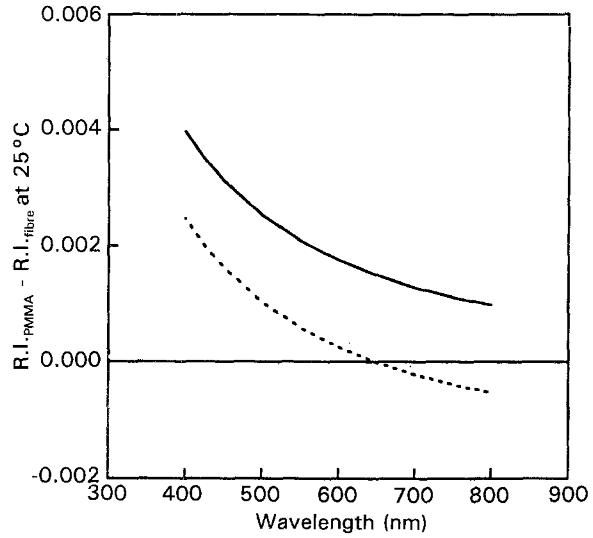

Figure 6 Difference in refractive index between BK-10 glass fibre and PMMA matrix 25 °C for composite made by method L, 17 μm fibres (solid line) and by method P, 13 μm fibres (dashed line) as a function of wavelength.

curve for the BK-10 glass [8] along the wavelength axis until the measured n_D value of the glass fibre laid on the dispersion curve, and then fitting the dispersion curve by a Cauchy equation. The Cauchy equation obtained by least squares fit was $n(\lambda) = 1.4794 + 3920\lambda^{-2} - 808\lambda^{-4} + 0.1\lambda^{-6}$ and $n(\lambda) = 1.4788 + 3920\lambda^{-2} - 808\lambda^{-4} + 0.1\lambda^{-6}$ for 17 and 13 μm glass fibres, respectively. The same method was applied to estimate the dispersion curve for PMMA based on the dispersion data from a commercial PMMA [9]. The least squares fitted Cauchy equation was $n(\lambda) = 1.4794 + 4557\lambda^{-2} + 903\lambda^{-4} + 0.1\lambda^{-6}$ and $n(\lambda) = 1.4773 + 4557\lambda^{-2} + 903\lambda^{-4} + 0.1\lambda^{-6}$ for PMMA prepared by methods L and P, respectively. The difference in refractive index between the fibre and PMMA matrix as a function of wavelength is shown in Fig. 6.

The wavelength dependent transmission at 25 °C for the composites was calculated between 400 and 800 nm using the parameters given in Table II. As seen in Fig. 5, the calculated transmission (solid line) agreed well with the measured transmission (●) above 500 nm at 25 °C for the composite prepared by method L. For the composite prepared by method P, the calculated transmission (dashed line) agreed less well with the measured transmission (○) except between 600 and 750 nm. According to Fig. 6, the predicted maximum transmission would be at 650 nm, but the measured transmission peak appeared at 550 nm. This disagreement may indicate that the dispersion data for PMMA from Ref. 9 may be slightly different from that for the pressure cured PMMA which may be responsible for the poorer agreement between the calculated and measured transmission.

5. Conclusions

The transmission of glass fibre reinforced PMMA composites was temperature and wavelength dependent because of the differences in the temperature coefficient for the refractive index (dn/dT) and the different shapes of the dispersion curves ($dn/d\lambda$) for the glass fibre and PMMA. The optical transmission of transparent composites was mathematically modelled in terms of the ratio of the refractive index of fibre and matrix, fibre diameter, fibre volume fraction, composite thickness and quantity of non-wet fibre. The calculated and measured temperature dependent transmissions were in good agreement for a thin composite (0.50 mm thick) containing 7.2 vol % of 17 μm fibres, but agreed less well for a thicker composite (6.8 mm thick) containing 10.2 vol % 13 μm fibres. Similar agreement was observed for the wavelength dependent transmission. The percentage of non-wet fibres in a composite was the single most important factor affecting its transmission when the refractive index of the fibre closely matched that of the matrix.

TABLE II Parameters used for calculating wavelength dependent transmission at 25 °C

Parameter		Cauchy equation				Thickness (mm)	Composite radius (μm)	Fibre content (vol %)
		n_0	n_1	n_2	n_3			
Method L	Fibre	1.4794	3920	− 808	0.1	0.5	8.5	7.2
	PMMA	1.4794	4557	903	0.1			
Method P	Fibre	1.4788	3920	− 808	0.1	6.8	6.5	10.2
	PMMA	1.4773	4557	903	0.1			

The amount of non-wet fibre had to be minimized to achieve a highly transparent composite, since as little as 2.0% non-wet fibre could reduce the transmission by up to 17%.

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