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Fibre–reinforced glasses: influence of thermal expansion of the glass matrix on strength and fracture toughness of the composites

H. HEGELER, R. BRÜCKNER
Institut für Nichtmetallische Werkstoffe, Anorganische Werkstoffe, Technische Universität Berlin, Englische Str. 20, 1000 Berlin 12

The reinforcement of glasses by incorporation of fibres was considered to depend on the force transfer from the matrix on the fibres in order to obtain optimum strength and fracture toughness. This may occur by thermal shrinking of the matrix on the fibres after the hot-pressing procedure. It is shown that an optimum exists for strain and stress transfer from the matrix to the fibres if this shrinkage process is neither so strong that no pull-out and no bend-over effect is produced nor so weak that no stress transfer is possible. Therefore, experiments were performed with Nicalon–SiC fibres and with selected glasses which show different thermal expansion coefficients. In this way it was possible to produce fibre-reinforced glass composites with well-tailored special properties. Estimations of tensile stresses within the glass matrix led to values which are partly above those of the bulk glass. Because no cracks occurred during cooling and during heat shock treatment from T_g, it was concluded that the strength of the thin glass layers between the very smooth surfaces of the Nicalon–SiC fibres cannot be compared with that of bulk glass but with that of protected (coated) glass fibres or thin sheet glass.

1. Introduction

The principle of reinforced matrices is the transfer of stress and strain from the matrix to a much stronger component. In order to produce fibre-reinforced glasses the high strength of glass fibres cannot be utilized, but that of ceramic fibres in the form of carbon and silicon carbide fibres can be. In order to realize optimum stress transfer, the fibres have to be incorporated into the glass matrix in such a way that the best possible adhesion is obtained. The effect of reinforcement and toughness is related to the consumption of fracture energy by tearing the fibres consecutively, and by partly pulling out the fibres from the matrix. The adhesion may be performed in two ways: by a chemical reaction of the two materials or by an interfacial component and by pure shrinking of the matrix on the fibres during preparation and cooling of the composites. In the case of chemical reaction, the bonding can be so strong that no pull-out effect exists and with that a brittle behaviour is obtained and/or the fibres are damaged, which leads to low reinforcement. In the case of pure mechanical adhesion by shrinking, the best conditions will be obtained with a larger thermal expansion of the glass matrix than that of the fibres with an optimum at a specific value of thermal expansion difference, α, because if shrinking is too low, adhesion and friction will be low and if shrinking is too high, adhesion and friction will be so high that no consecutive fibre fracture and no pull-out will take place. If the differences in thermal expansion between fibres and matrix are too large, the matrix will show tensile stress cracks.

The importance of these differences and the influence on strength were recognized by Aveston and co-workers [1, 2] as early as 1965, who developed a relation for an isotropic fibre to calculate the stress within the matrix due to the different thermal expansion coefficients. Sambell and co-workers [3, 4] calculated the stresses within the matrix for the combination Pyrex glass/anisotropic carbon fibre with the same equation, although the assumptions are not fulfilled. An astonishing point of the relation of Aveston *et al.* is that only the radial stresses are calculated.

In contrast to that, earlier calculations were made with respect to all three dimensions of the stress for a composite with different thermal expansions of their components by Poritzky [5] and Hull and Burger [6].

The objective of the present work was the systematic investigation of the influence of thermal expansion of fibre and glass matrix on the bending strength and fracture toughness of the composites with respect to the estimated stresses within the glass matrix from the mentioned theoretical relations and experimental data. For this reason composites with Nicalon–SiC fibres and glasses with various thermal expansion coefficients within the range 0.7 to $4.6 \times 10^{-6}\,\mathrm{K}^{-1}$ (20 to 300° C) were used.

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TABLE I Properties of the applied glasses (V_a = working temperature)

Glass	Youngs's modulus (GPa)	Density (g cm^{-3})	α (10^{-6} K^{-1})	T_g (°C)	V_a (°C) (log η = 4)
Duran	63	2.23	3.25	530	1260
Supremax	90	2.56	4.10	730	1230
A	73	2.44	2.09	624	1324
H	81	2.63	4.60	720	1254
SiO$_2$ +3% Duran	72	2.20	0.70	1220	> 1700
B	85	2.75	6.60	620	1095
D	85	2.54	4.10	643	1180

2. Materials

The properties of the applied glasses are listed in Table I. These glasses were made available by Schott Glaswerke, Mainz. The glasses Duran, Supremax, B, D and H are commercial products, glass A is a laboratory one (Table I). In order to reduce somewhat the viscosity of the SiO$_2$ glass, it was mixed with 3 wt % Duran glass and homogenized in a mixing mill.

The Nicalon–SiC fibre is a commercial fibre from Nippon Carbon, Tokyo; type NLM 202 was used in the experiments. The thermal expansion coefficient is given by Nippon Carbon to be 1 to 2 × 10^{-6} K^{-1}. Our own measurements with Nicalon fibre bundles using a method described by Stockhorst [7], resulted in 2.70 × 10^{-6} K^{-1} (20 to 300° C). Youngs modulus is given by Nippon Carbon to be 180 to 200 GPa. Scanning electron micrographs of the Nicalon fibres (Fig. 1) show smooth surfaces, thus adhesion by interlocking is not possible but only by pressing, shrinkage of the matrix, or chemical reaction.

3. Preparation, testing of the composite and results

The composites were prepared by a method described previously [8], in which the fibres were drawn continuously through a swirl bath where the fibres are loaded with glass powder and Si-alkoxide. After drying, the prepregs were hot-pressed. The preparation procedure was performed in such a way that a concentration range of 10 to 55 vol % for the fibres was covered.

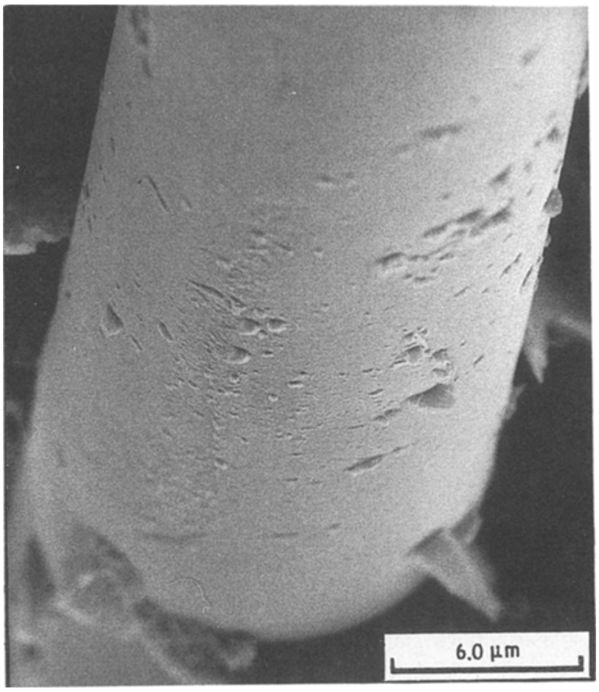


Figure 1 Scanning electron micrograph of a Nicalon–SiC fibre after isolation from a composite.

The measurements of bending strength of the samples were done with the three-point method using a support length of 75 mm with a length/thickness ratio $l/d > 18$ in order to minimize shear stresses during the test. At least five measurements were done to obtain the mean value and its standard deviation.

As a first step towards optimization of the composite, the fibre content was varied by the concentration of glass powder in the slurry. The dependence of the strength on fibre content is shown in Fig. 2. Although the maximum strength is obtained at about 50 vol % the following experiments were carried out at a fibre content of 40 ± 2 vol % because the interval of the maximum is small and the strength decreases very abruptly above 50 vol %, and both the fibre content and the strength are better controlled at the lower values.

The optimization of the bending strength of Duran glass/SiC composites due to the processing parameters (temperature, high-temperature pressure and time) was described previously [8] and is shown in Fig. 3a,

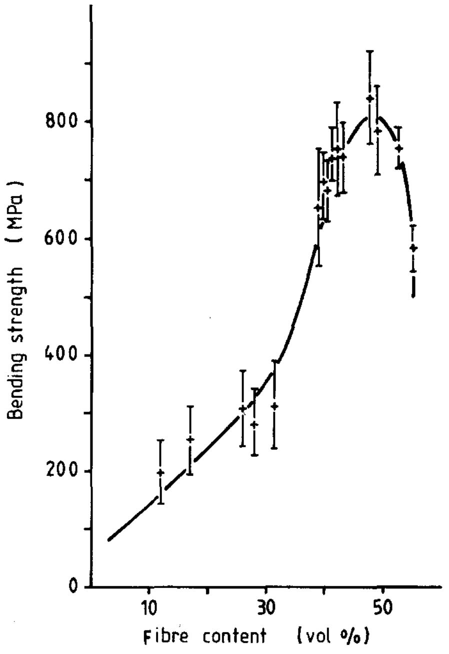


Figure 2 Variation of bending strength of SiC fibre-reinforced Duran glass with fibre content.

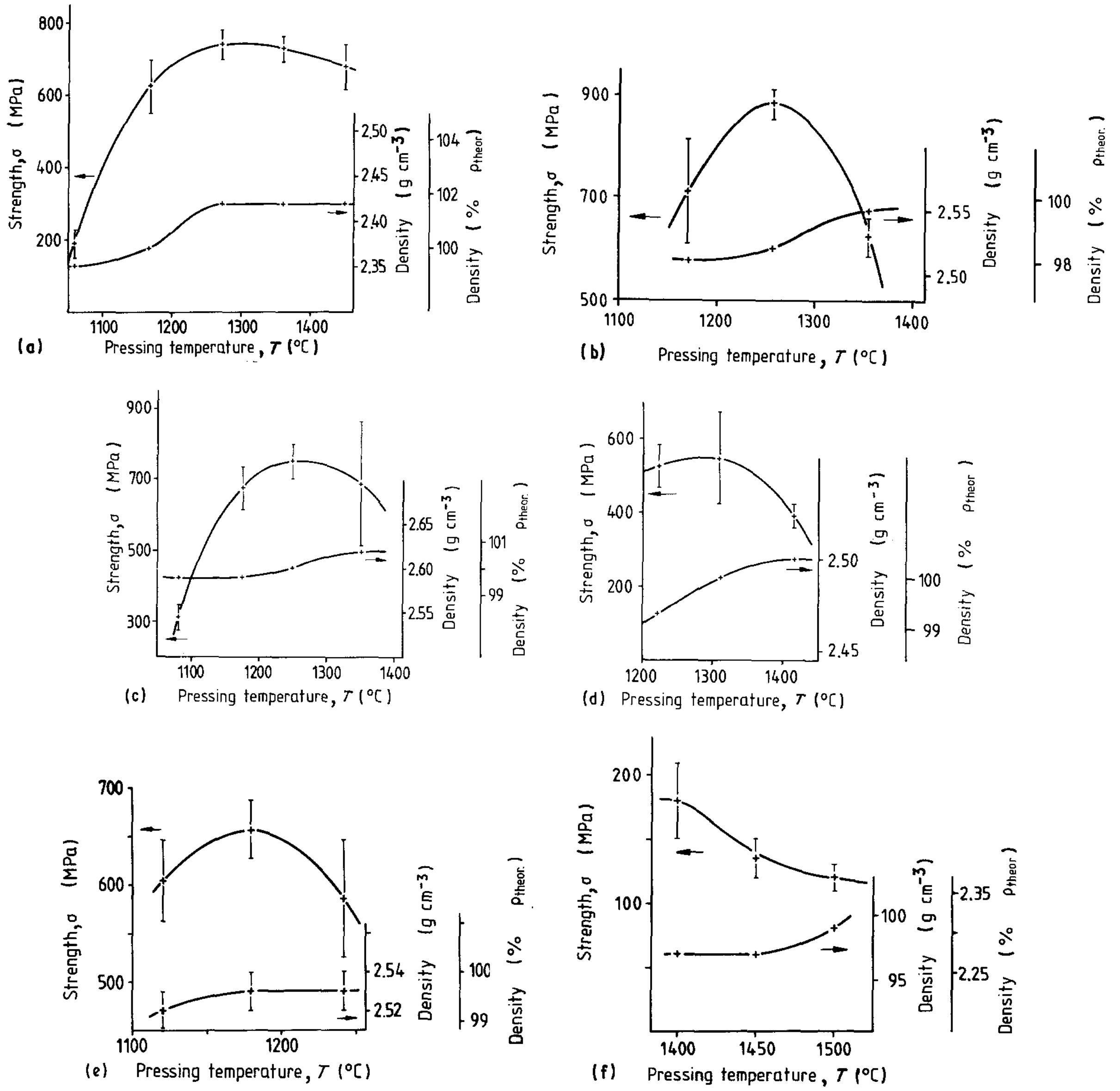


Figure 3 Bending strength and density as a function of pressing temperature. Compression stress 10 MPa, fibre content 40 ± 2 vol %. (a) Duran-glass/SiC composites, (b) Supremax glass/SiC composites, (c) glass H/SiC composites, (d) glass A/SiC composites, (e) glass D/SiC-composites, (f) SiO_2 + 3% Duran glass/SiC composites.

particularly the dependence of strength on pressing temperature at 10 MPa pressure and 5 min pressing time.

The results of the composites with the glasses Supremax, D, H and A are presented in Figs 3b to e. As in the case of Duran, the maximum strength of these composites was found at temperatures which were in the range of the working temperatures (at a viscosity about 10^4 dPa sec) of the particular glasses. The pressure stress was 10 MPa. It is remarkable that the densities of the composites, also shown in Figs 3b to e, do not show their maximum values at the maximum bending strength. The end values of densities are reached at higher temperatures than at the "optimum" pressing temperature.

Fig. 3f shows the strength of the SiO_2 (with Duran addition)-SiC composites as a function of pressing temperature. However, the optimizing experiments had to be stopped at 1500° C because of the low-temperature resistance of the Nicalon fibre above 1450° C, due to recrystallization [9, 10]. Therefore, the strength is higher at a pressing temperature of 1400° C than that at 1500° C. This is only an apparent maximum value at 1400° C for this composite caused by recrystallization of the Nicalon fibre at higher temperatures and by the incomplete densification due to the very high viscosity and the modified SiO_2 glass melt at lower temperatures. The samples prepared at 1500° C show a typical brittle fracture behaviour like a glass without fibres. On the other hand, our own investigations on the strength of fibres, which were prepared from a hot-pressed composite, treated by the same procedure, do not show further degregation of the strength caused by the hot-pressing process: the fibres show the "normal" loss of strength by the heat-treatment. The same result was found by Prewo [11].

For reasons which will be discussed in Section 5, it was impossible to obtain composites with glass B.

With the possibility of varying the conditions of the preparation method described previously [8] it is possible to produce composites with a distinct chemical adhesion performed by chemical reaction. This was done as an example with the help of a titanium alkoxide solution instead of the silicon alkoxide solution which was normally used. Titanium reacts at

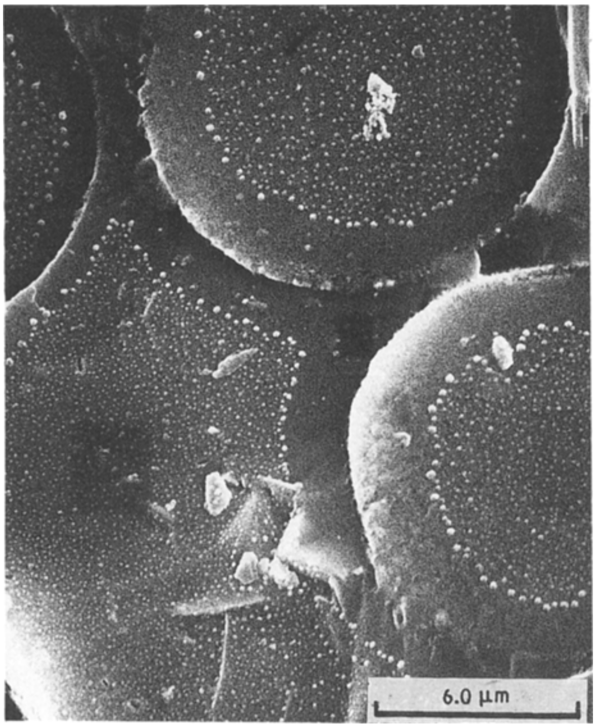


Figure 4 Scanning electron micrograph of a Duran glass/SiC composite produced with a titanium alkoxide solution.

elevated temperatures with the SiC fibre and forms TiC [12] and other reaction products easily. In contrast to the preparation with silicon alkoxide solutions, where supposedly only physical adhesion takes place, the reaction with titanium leads to a typical, very strong chemical bonding. The reaction zones in the matrix as well as in the fibres are clearly seen in Fig. 4. The samples show a pronounced brittle fracture behaviour and the strength decreases to 100 MPa, while those prepared with silicon alkoxide solution show strength values of about 800 MPa.

4. Calculations of stresses within the composites and results

As the SiC fibre shows isotropic thermal expansion [13] the equation of Aveston *et al.* [1] may be applied to calculate the stress within a composite with different expansion coefficients of its components. On the other hand, Sambell and co-workers [3, 4] have calculated the stress with the help of Aveston *et al.*'s equation in the composite Pyrex glass/carbon fibres in spite of the fact that the latter show anisotropic expansion behaviour [14]. Nevertheless they obtained plausible results.

The stress, σ_M, within the matrix may be calculated according to [1]

$$\sigma_M = \frac{(\alpha_M - \alpha_F)\, E_F V_F\, \Delta T}{1 + V_F\,(E_F/E_M - 1)} \tag{1}$$

where α_M, α_F are thermal expansion coefficients of matrix and fibre, E_M, E_F the Youngs moduli of matrix and fibre, V_F the volume of fibres (%), ΔT the temperature difference between room temperature (T_R) and that temperature at which no further relaxation is possible (T_X). At T_X stress in the matrix is introduced and below T_X the stresses in the glass matrix increase with decreasing temperature because the glass matrix no longer flows and becomes a solid. It contracts, but it is handicapped, if the fibre has a smaller thermal expansion coefficient than the glass and compressive stress will be introduced. If, on the other hand, the thermal expansion coefficient of the fibres is larger than that of the glass, the fibre will shrink away from the glass matrix and finally no mechanical adhesion will be maintained.

In order to calculate the stress using Equation 1 as a first approximation the glass transition temperature T_g will be taken for T_X in spite of the fact that stresses can build up within the glass melt above T_g, depending on the cooling rate (see, for example, the case of enamels [15]). Thus, the mean thermal expansion coefficients of the Nicalon fibre and the distinct glasses within the range T_R and T_g will be applied. The corresponding values are summarized in Table II, in which those for the glasses Duran, Supremax, A, B, D and H were made available to us by Schott Glaswerke, those for the Nicalon fibre were measured by us and those for SiO_2 + 3% Duran were calculated using the mixing rule. The calculated stresses within the glass matrix according to Equation 1 and the measured bending strengths of the composites are listed in Table III (the compressive stresses in the matrix are negative, the tensile stresses are positive) together with the differences of the thermal expansion coefficients between fibre and glass matrices.

The radial stresses in the matrix were also calculated for a higher temperature T_x, the dilatometric softening temperature of the glasses T_{ds} (for data see Table IV).

Figs 5a and b show the calculated stresses and the measured bending strengths as a function of the differences in thermal expansion coefficients with respect to Equation 1: Fig. 5a,. $T_x = T_{T_g}$; Fig. 5b, $T_x = T_{ds}$.

As mentioned in Section 1, Aveston *et al.*'s Equation 1 [1] is only a first approximation, because the stress–strain problem is regarded only in one dimension, thus the influences of Poisson ratio, fibre diameter and mean distance between the fibres are neglected and no stress distribution can be obtained.

For this reason an estimation of stress calculation with the help of equations developed first by Poritzky [5] will be applied. Poritzky has given the mathematical basis for a three-dimensional calculation of stresses for the example of a coated cylinder. The assumption for this theory is an infinitely extended

TABLE II Thermal expansion coefficients of Nicalon fibres and of the applied glasses and their differences

	$\alpha_{20/300}$ (10^{-6} K^{-1})	T_g (°C)	α_{20/T_g} (10^{-6} K^{-1})		Difference in α (10^{-6} K^{-1})
			Glass	Nicalon	
Nicalon	2.70				
SiO_2 + 3% Duran	0.7	1220	0.8	4.0	−3.2
A	2.09	624	2.30	3.09	−0.79
Duran	3.25	530	3.37	2.94	0.434
Supremax	4.10	730	4.60	3.26	1.344
D	4.10	643	4.82	3.15	1.67
H	4.60	720	5.10	3.25	1.85
B	6.60	620	7.50	3.09	4.41

TABLE III Stresses calculated using Equation 1 and measured bending strength of the glass/SiC composites and their bendover stresses

Composites with matrix	Difference in α ($10^{-6}\,K^{-1}$)	Stress within the glass matrix (MPa)		Bending strength (MPa)	Bendover stress	
		$T_x = T_{T_g}$	$T_x = T_{ds}$		(MPa)	(%)
SiO$_2$ + 3% Duran	−3.2	+181	151	179 ± 27	–	–
A	−0.79	+ 23	− 21	547 ± 135	547	100
Duran	0.43	− 9	− 26	743 ± 42	698	94
Supremax	1.34	− 51	− 82	879 ± 38	369	42
D	1.67	− 54	− 89	657 ± 31	501	80
H	1.85	− 65	− 98	752 ± 50	662	88
B	4.41	−137	−175	378 ± 42	111	29

cylinder, thus the influence of the ends is neglected. Further neglected is the viscous flow of the coating glass. If a uniaxially reinforced composite is considered as an aggregate of glass-coated fibres, it should be possible to apply the equations for a three-dimensional stress calculation at the fibre–glass matrix interface and the spacial course of the stress within the matrix. Wedge stuffings between the cylinders are not considered. Hull and Burger applied the results of Poritzky [5] to calculate the stresses in glass-coated metal wires and compared them with experimental values [6]. They obtained good agreement. Redston and Stanworth [16] found some discrepancies in the theoretical treatment and simplifications, but the final results did not lead to relevant errors and agree well with their experiments.

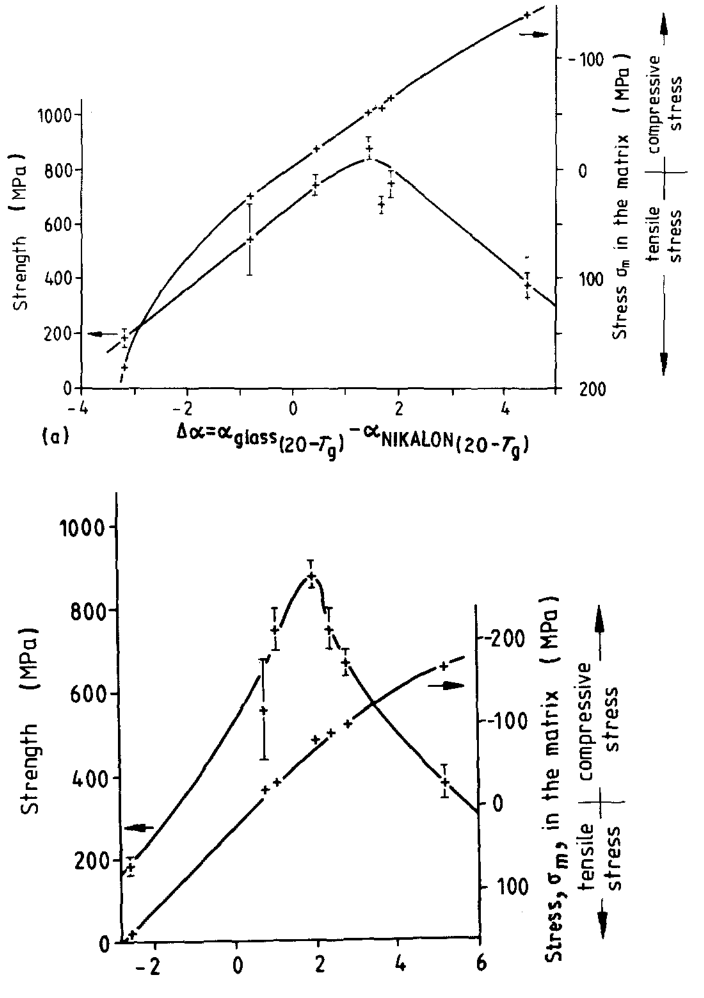
The applied simplified equations for the three stress components neglecting viscous flow are

Radial stress, p_r

$$p_r = -\frac{E_2\delta}{1 + k + k\beta R}\left(\frac{a^2}{b^2} - \frac{a^2}{r^2}\right) \tag{2a}$$

Axial stress, p_z

$$p_z = -\frac{E_2\delta}{1 + k + k\beta R}\left(2\mu\frac{a^2}{b^2} + \frac{1 + k + k\beta R}{1 + \beta R}\right) \tag{2b}$$



(b) $\Delta\alpha = \alpha_{glass(20\,-\,T_{ds})} - \alpha_{Nicalon(20\,-\,T_{ds}glass)}$

Figure 5 Bending strength and radial stresses calculated from Equation 1 within the glass matrix of the glass/SiC composites as a function of the difference in the thermal expansion coefficients of glass and fibre. Fibre content 40 ± 2 vol %. (a) $\alpha = \alpha_{glass(T_{20} - T_g)} - \alpha_{Nicalon(T_{20} - T_g)}$ and stresses built up from $T_x = T_g$; (b) $\alpha = \alpha_{glass(T_{20} - T_{ds})} - \alpha_{Nicalon(T_{20} - T_{ds})}$ and stresses built up from $T_x = T_{ds}$.

Circumferencial stress, p_0

$$p_0 = -\frac{E_2\delta}{1 + k + k\beta R}\left(\frac{a^2}{b^2} + \frac{a^2}{r^2}\right) \qquad (2c)$$

where E_1 is the Youngs's modulus of the fibre of wire, E_2 the Young's modulus of the glass, μ Poisson's ratio, a, b the radii of fibre and coating glass, respectively, $R = E_2/E_1$, $k = (a^2/b^2)\ (1 - 2\mu)$, $\beta = b^2/a^2 - 1$, $\delta = (\alpha_{\text{glass}} - \alpha_{\text{fibre}})(T_R - T_x)$ and α is the mean thermal expansion coefficients of glass and fibre between room temperature, T_R, and that temperature, T_x, from which the stresses are created on cooling (setting temperature).

The assumption that the Poisson ratios, μ, of the two components are equal can also be considered approximately for the fibre-reinforced glasses. Most of the technical glasses have values between 0.19 and 0.24 [17]. Bulk SiC shows values between 0.16 and 0.19 [18]. The influence of different values of the Poisson ratio is small. Thus, a variation of $\mu = 0.25$ to 0.30 results in a difference of 2% for the stress. The temperature dependence of the Young's moduli is neglected, too. Important are the setting temperature, T_x, which depends on cooling rate from above T_g (transformation temperature), and the thermal expansion coefficients. For a rough approximation it seems reasonable to apply T_g ($\log \eta = 13$) for T_x at low cooling rates and the dilatometric softening temperature T_{ds} ($\log \eta \approx 11$) for T_x at high cooling rates. At extreme cooling rates, still higher or lower temperatures may be applied with the extreme values being either T_L (Littleton temperature; $\log \eta = 7.65$) or T_{sp} (strain point; $\log \eta = 14.5$, η in dPa sec).

In Equations 2a to c viscous flow and relaxation processes are neglected. With respect to the difficulty to determine T_x, these effects seem to be of second order and they would greatly complicate the calculations [19]. In addition, these effects are very difficult to determine experimentally for the composites. Another handicap of the simple model might be that no interaction between the stresses among the fibres and their glass matrix is considered. However, this approximation may be still valuable enough for an estimation of the three stress components in various composites used in the present paper.

The results of the calculations with the help of Equations 2a to c and with the assumptions for $T_x = T_g$ and $T_x = T_{ds}$ are illustrated in Figs 6a and b, respectively. The mean thermal expansion coefficients used are those from room temperature to T_g or T_{ds}, respectively, which are given in Table IV. The calculated stresses are listed in Table V. It may be seen that the radial and circumferencial stresses are maximal at the fibre/glass matrix interface and the axial stress is constant within the matrix. The radial stresses are smaller compared with those calculated from Aveston *et al.*'s Equation 1. The circumferential and axial stresses reach values which are partly higher than the tensile strengths of the glasses. But no cracks in the matrix could be observed and the stress–strain curve is strictly linear and without hysteresis in the range below the bendover stress (compare Figs 8a to e). This is of special interest in so far as obviously not the usual strength of the bulk glass ($\approx$ 50 to 100 MPa) has to be considered here but much higher strength values which tend to values of glass fibres or thin films (about 1000 MPa) or at least those of bulk glass with excellent (heat-polished) surfaces. This, again leads to the conclusion that the glass matrix/SiC fibre interface must be excellent and totally free from interfacial cracks and micro cracks. The frequently observed thin carbon layer [20, 21] obviously acts as a protection layer in addition to its purpose to act as an adhesive or even gliding interlayer in order to give rise to the pull-out effect and its accompanying improved fracture toughness. A remarkable effect is also the difference between the results for the two temperatures $T_x = T_g$ and $T_x = T_{ds}$ is the shift of the radial stress for glass A from the tensile stress range ($T_x = T_g$) to the compressive stress range ($T_x = T_{ds}$). Thus the matrix of glass A can also shrink on the SiC fibres according to the cooling rate of the sample, which might explain the relatively large bending strength of 500 MPa of the SiC fibres/glass A composite.

5. Discussion

Fig. 7 summarizes the three calculated stress components and the measured bending strengths of all the composites investigated here as a function of the difference of the thermal expansion coefficients of the applied glasses and those of the SiC fibres.

In both Figs 5 and 7, the stress increases with increasing difference of thermal expansion. With respect to this, a shrinking-on effect (shrinking of the matrix on the fibres) takes place with positive expansion differences which is the case for Duran, Supremax, D, H and B glass. A shrinking-off takes place for the other glasses with negative expansion differences.

TABLE IV Mean thermal expansion coefficients of glasses and SiC fibre (Nicalon) and the differences in the thermal expansion coefficients according to $T_x = T_g$ (transformation temperature) and $T_x = T_{ds}$ (dilatometric softening temperature)

Glass	T_g (°C)	Glass			Fibre		Difference Glass-fibre	
		α_{T_g} (10^{-6} K^{-1})	T_{ds} (°C)	α_{ds} (10^{-6} K^{-1})	α_{T_g} (10^{-6} K^{-1})	α_{ds} (10^{-6} K^{-1})	α_{T_g} (10^{-6} K^{-1})	α_{ds} (10^{-6} K^{-1})
SiO_2 + Duran	1220	0.60	1290	0.90	3.10	3.15	−2.5	−2.25
A	624	1.87	705	2.85	2.72	2.77	−0.85	0.13
Duran	530	3.16	630	3.52	2.64	2.72	0.52	0.80
Supremax	730	3.82	780	4.17	2.80	2.83	1.02	1.34
D	643	3.79	720	4.38	2.75	2.80	1.04	1.58
H	720	4.45	770	4.70	2.80	2.83	1.65	1.87
B	620	6.35	670	6.89	2.70	2.75	3.65	4.14

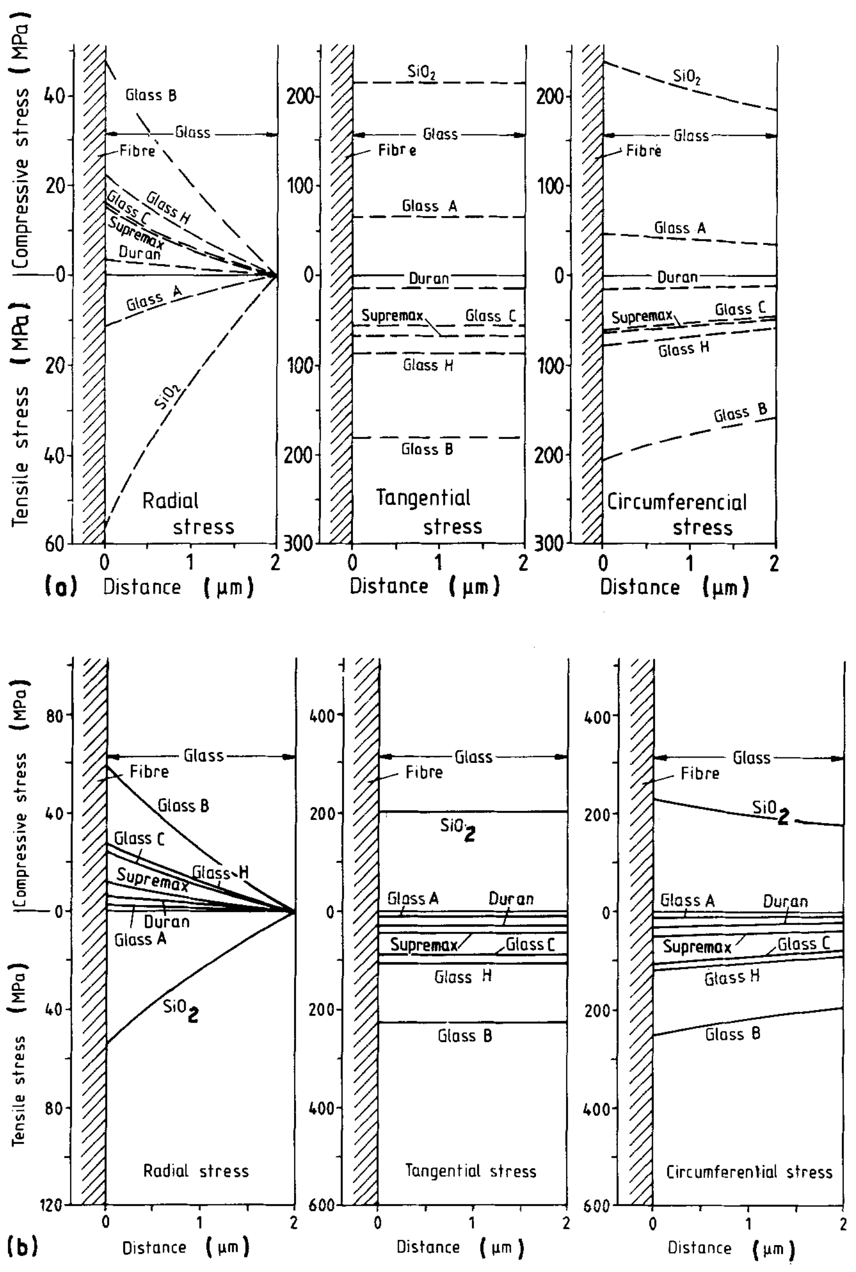


Figure 6 Distribution of the three stress components within the glass matrix of coated fibres, calculated from Equations 2a to c. (a) Stresses built up from $T_x = T_g$, (b) stresses built up from $T_x = T_{ds}$.

For that reason the calculated stresses in the matrix change their sign from positive to negative values at $\Delta\alpha = 0$, assuming that the fibres have a good contact with the matrix. However, this contact will decrease with increasing negative values. Thus, the bending strength will be reduced more and more due to the decreasing contact. On the other hand, the bending strength increases with increasing shrinking-on; however, only up to a certain degree which is obtained with the Supremax glass. The strength of the composite with the H glass is lower because the shrinking-on effect is too strong and produces too large tensile stresses in the matrix at and near the fibre/glass interface. The tensile stresses in the composite glass H/SiC are in a range of maximum possible stresses. Samples with a fibre content of 30 vol % show cracks perpendicular to the fibres after preparation. For this fibre content the glass thickness between the fibres is larger than that for a fibre content of 40 vol %, thus, the tensile strength of the matrix is shifted back towards

TABLE V Stresses in composites calculated from Equations 2a to c for $T_x = T_g$ and $T_x = T_{ds}$ (compressive stresses in the matrix are negative, tensile stresses are positive)

Glass	Radial stress (MPa)		Axial stress (MPa)		Circumferencial stress (MPa)	
	$T_x = T_g$	$T_x = T_{ds}$	$T_x = T_g$	$T_0 = T_{ds}$	$T_x = T_g$	$T_x = T_{ds}$
SiO_2 + Duran	56	53	−214	−204	−241	−230
A	11	− 3	− 42	11	− 48	12
Duran	− 4	− 7	14	27	15	30
Supremax	−14	−12	66	45	63	51
D	−15	−24	53	89	61	102
H	−23	−28	86	105	78	120
B	−47	−59	178	221	204	253

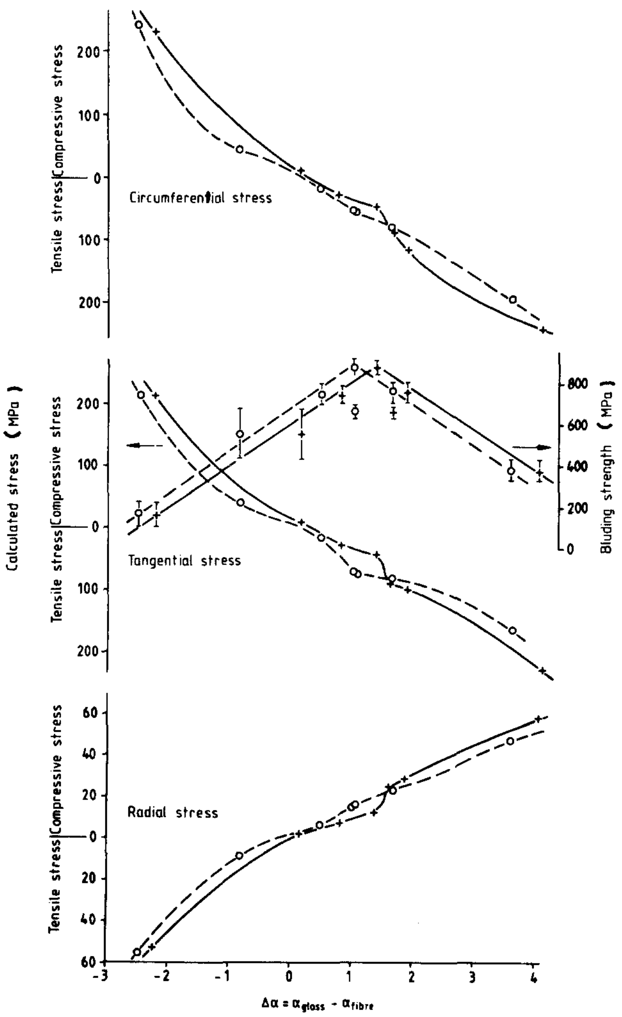


Figure 7 Bending strength of the composites investigated and the maximum stress components in the glass matrix at the fibre glass interface of the various composites plotted against the difference in thermal expansion coefficients, calculated from Equations 2a to c for stresses built up from (- - -) $T_x = T_g$ and (——) $T_x = T_{ds}$.

the tensile strength of the bulk glass and therefore the tensile strength is exceeded by the axial stresses.

The stresses in the composite glass B/SiC are so high that even for a fibre content of 40 vol % no suitable samples could be prepared at all. As a consequence, flexural strength of the glass B/SiC composites is relatively low (378 ± 42 MPa) and the stress–strain diagram (Fig. 8a) shows a low stress at which the curve deviates from linearity. This means that the bending behaviour is no longer reversible and that the sample has altered its Young's modulus. The stress at this point is called the bendover stress at which micro-cracks are formed in the matrix, the lower bendover stress indicating the pre-damage of the glass matrix by the too large mismatch of thermal expansion. Thus, an optimum in bending strength at an expansion difference of $1.3 \times 10^{-6} \mathrm{K}^{-1}$ is the result. An increase in the expansion difference up to 1.85 (glass H/SiC composite) corresponds to an increase of radial stress and leads to a decrease in bending strength of about 100 MPa (Figs 5a and b calculated with Equation 1). The detailed stress components with respect to Equations 2a to c may be seen from Figs 6 and 7 which show that they are of the same order of magnitude. Here, the above-mentioned case is obtained: the mechanical adhesion between fibres and matrix is too strong. This condition is produced by the high tensile stress in the matrix and the result is two-fold; first, the strength is lowered and, second, the pull-out effect is reduced; the latter effect leading to lower values for work of fracture, meaning lower fracture toughness.

The high bending strength in the case of the Supremax glass/SiC composite suggests that an optimum is reached between adhesion and pull-out effect. A lower shrinkage or even a shrinking away from the matrix from the fibres produces indeed a larger pull-out effect, and in this connection a larger fracture toughness, but a lower adhesion and lower strength of the composite. At too low a shrinkage, finally, the pull-out effect does not contribute to the work of fracture.

The behaviour described becomes evident also from the stress–strain diagrams. Fig. 8b shows the stress–strain diagram of the glass A/SiC composite. The stress increases linearly with strain up to the maximum value at which the matrix breaks and the weakly embedded fibres are pulled out leading to a large strain after the strain of maximum stress. The composite shows a very controlled breaking behaviour.

Fig. 8c shows the stress–strain diagram of a Duran glass/SiC composite for which the bendover stress is at 94% of the maximum stress. In contrast to the preceding example, the fibre is able to take over the acting stress because of the better adhesion and incorporation of the fibres in the matrix. The calculated shrinking stresses are higher than for glass A/SiC composites. Therefore, the fibres are not so easily pulled out from the matrix as in the case of Fig. 8b; the stress can be increased further up to the maximum values after which a relatively good fracture toughness behaviour is observed.

In the case of the composite Supremax glass/SiC (Fig. 8d) the bendover stress is only 42% of the maximum stress. As in the case of the composite Duran glass/SiC the maximum strain of the matrix is exceeded at a stress of about 600 MPa. Because the fibres are embedded strongly in the matrix and the tensile stress of the glass matrix is not yet too high, the fibres are able to bridge the micro-cracks and the composite shows a high strength of about 1250 MPa with a relatively good toughness behaviour.

The situation is altered with the composite glass H/SiC (Fig. 8e) for which the bendover stress is increased to about 88% of the maximum stress and the strength is reduced to about 810 MPa due to the high shrinking stress of 65 MPa (Equation 1). Because of the strong adhesion between fibre and matrix, the bending stress can be transfered well to the fibres. However, the high tensile stress in the matrix acts against this advantage and the whole bending strength is lowered compared to the Supremax glass/SiC composite. After exceeding the bendover stress, a short range of micro-cracks appears and the composite breaks abruptly with a bad toughness behaviour, because the fibre pull-out is low.

Although the Supremax glass and glass D have the same thermal expansion coefficient ($\alpha = 4.10 \times 10^{-6} \mathrm{K}^{-1}$ for 20 to 300° C) the temperature dependence

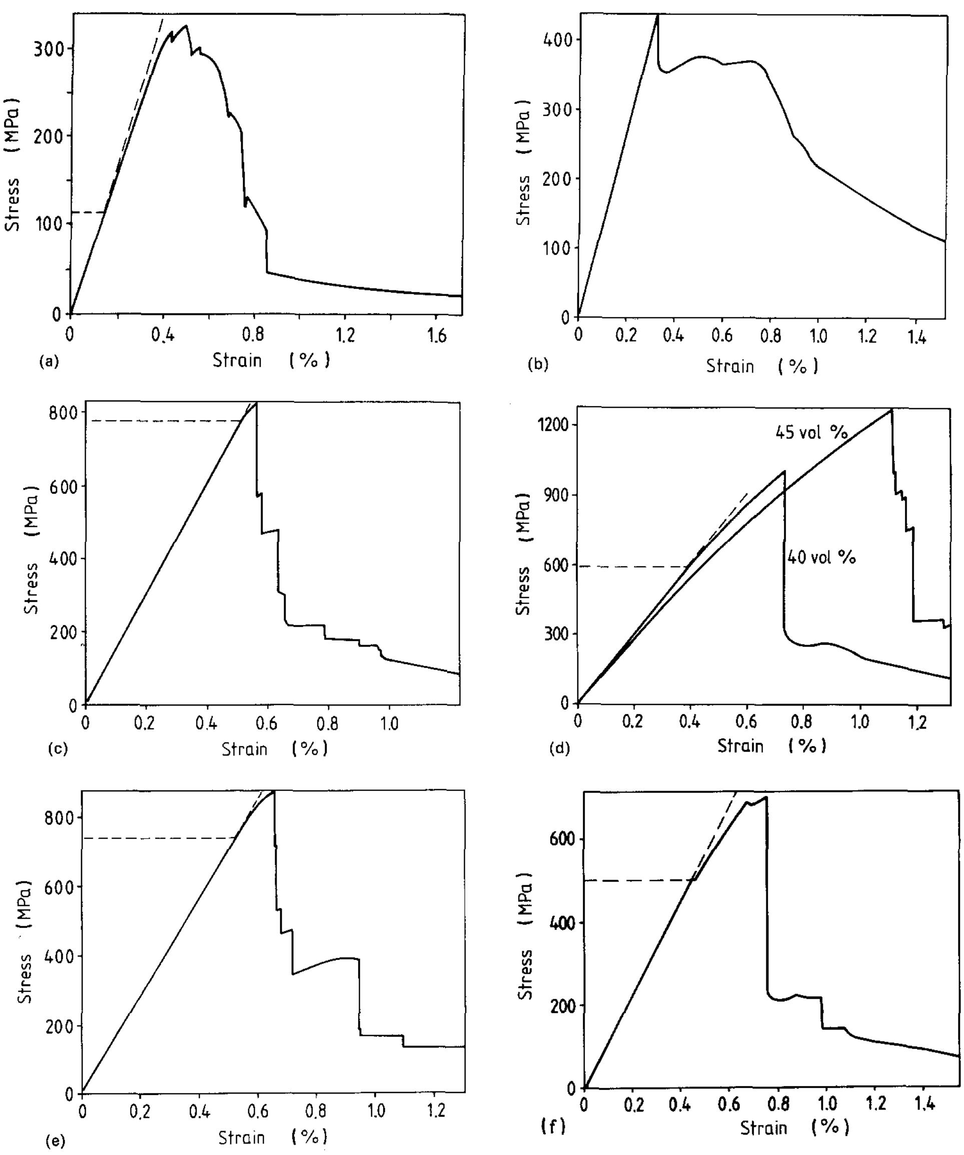


Figure 8 Stress–strain diagrams of glass/SiC composites. (a) Glass B/SiC composites, (b) glass A/SiC composites, (c) Duran glass/SiC composites, (d) Supremax glass/SiC fibres, (e) glass H/SiC composites, (f) glass D/SiC composites.

of α is different at higher temperature. The stresses of the glass D/SiC composite are close to, but somewhat lower than, those of the composite Supremax glass/SiC composites for $T_x = T_{ds}$ (Table V).

It is expected from the $\Delta\alpha$ values and from the stresses that the two composites, glass D/SiC and Supremax glass/SiC, should have a similar fracture behaviour. The stress–strain diagram (Fig. 8f), however, shows a behaviour similar to the composites Duran glass/SiC and glass H/SiC (Figs 8c and e). The difference in the fracture behaviour of the glass D/SiC and Supremax glass/SiC composites, and the large stress increase above the bendover stress, may have its origin in the already mentioned ductile layer on the SiC fibres. Indeed, a thin carbon layer was observed on the SiC fibres but in the case of the Supremax glass it might be possible that additionally a P_2O_5 layer is formed, because this glass is the only one of the glasses used with P_2O_5 (7.90 wt %) and this tends to vaporize at pressing temperatures causing visible smoke in the furnace. The different values of flexural strength of the two composites Supremax glass/SiC and glass D/SiC show that at least at high stress levels not only mechanical but also chemical properties and thin layers at the fibre/glass boundary play an important role.

The variation of bendover stresses with the differences of the thermal expansion coefficients in Fig. 9 demonstrate the described behaviour once more, and show the reverse course compared with the bending strength of the composites; thus when the strength increases the bendover stress decreases.

An additional indication for the improvements of the matrix properties may be seen from the strains at the bendover stresses. The first damage of the glass matrix does not take place at a strain of 0.1 to 0.2%, which is typical for bulk glasses, but at values above 0.4%, as is clearly seen from the stress–strain diagrams of Figs 8b to f.

The tough fracture behaviour of the glass/SiC composites described as is shown in the stress–strain diagrams was also measured directly as K_{IC} values in the usual manner for other materials in order to obtain a relative measure. A very similar trend for the K_{IC} values is observed (Fig. 10) as for the strength values. The fracture toughness shows an optimum with $26 \pm 4\,\mathrm{MPa\,m^{1/2}}$ for the Supremax glass/SiC composites for a fibre content of 40 ± 2 vol %. If the

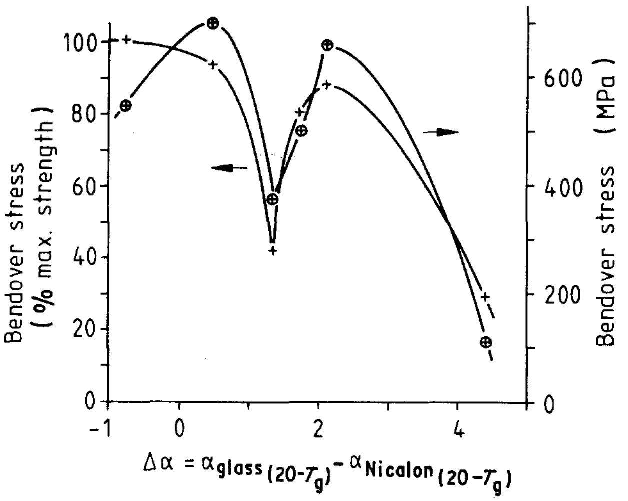


Figure 9 Bendover stresses of the glass/SiC composites as a function of the difference in the thermal expansion coefficients of glass and fibre. Fibre content 40 ± 2 vol %.

fibre content is increased, K_{IC} values up to 36 ± 7 MPa m$^{1/2}$ for 50 vol % fibre content are observed.

The influence of different thermal expansion coefficients of fibre and glass on the fibre/glass contact was investigated experimentally by Bender *et al.* [22] with relatively thick single fibres (140 μm) incorporated into glass and glass ceramic matrices with larger and smaller expansion coefficients than the SiC fibre. In order to measure the adhesion between fibre and matrix, the fibres were pressed in the axial direction by a Vickers diamond along a definite thickness of the matrix, a method which was developed by Marshall [23]. The interfacial shear strength measured in this way is regarded as a measure of the adhesion of the fibres within the matrix. If the thermal expansion coefficient of the fibre is larger than that of the matrix, no force was measured to push the fibres into the matrix. In the reverse cases, the force increased with the difference of the thermal expansion coefficients.

Brun and Singh [24] determined the stress which is necessary to pull out SiC fibres coated with a layer of BN from a mullite matrix. The difference of thermal expansion coefficients was $0.8 \times 10^{-6}\,{}^{\circ}C^{-1}$ and is between that of the composites Duran glass/SiC and Supremax/SiC (Table II). The authors measured a stress of 25 to 30 MPa which is related to the surface of the cylinder. This value is between the stresses calculated using Equation 1 for the Duran/SiC and Supremax/SiC composites (Table III).

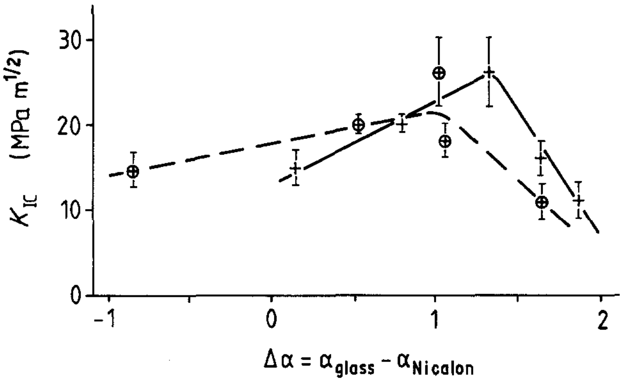


Figure 10 Fracture toughness (K_{IC}) plotted against differences in the mean thermal expansion coefficients as in Figs. 5 and 7. (– – –) $\Delta\alpha_{T_R - T_g}$, (——) $\Delta\alpha_{T_R - T_{ds}}$.

6. Conclusions

The results show that a direct correlation exists between the difference in the thermal expansion coefficients of fibre and glass, on the one hand, and the strength and bendover stress of the composites, on the other. This opens the possibility to produce well-tailored or even "tailor-made" composites with special properties. This is important for technical applications because the linearity of the stress increases and the range of fracture safety after the bendover effect (formation of micro-cracks in the matrix) can be accommodated in different ways. For technological purposes a composite can be prepared with low strength and linear stress increase but with high toughness (e.g. glass A), or a high strength with a lower toughness (e.g. Duran and H glasses). The relevant points for that well-defined force transfer from the matrix to the fibres and vice versa are

1. the friction coefficient between fibre and matrix which depends on mechanical adhesion, interface roughness and/or chemical bonding,
2. the pressure which was used for hot pressing the composite,
3. the interfacial area of cohesion or bonding, depending on viscosity, pressure and time of preparation,
4. the stresses which occur by thermal expansion mismatch,
5. the stress components within the glass matrix and their distribution,
6. interface layers which influence the friction coefficient,
7. chemical and thermal stability of fibres, matrix and their interface during preparation and application.

In particular, with Supremax glass and SiC fibres it is possible to prepare composites with high strength and with a large range of fracture safety, because the stress increase continues up to high values, thus the design engineer can calculate using a high strength and a high fracture safety factor. The different properties especially those of the composites Supremax and glass D/SiC, indicate the significance and the influence of the interfacial properties. In this direction a great field may be expected for possible improvements for fibre-reinforced composites.

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