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Extent of conversion and its effect on the mechanical performance of Bis-GMA/PEGDMA-based resins and their composites with continuous glass fibres

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The reaction mechanism of bisphenol A bis(2-hydroxy propyl) methacrylate (Bis-GMA) and polyethylene glycol dimethacrylate (PEGDMA) was characterized by differential scanning calorimetry (DSC) and infrared (IR) spectroscopy. Composites of S2-glass fibres with different formulations of Bis-GMA/PEGDMA were fabricated by filament winding. The mechanical properties of neat resins and composites were investigated by dynamic mechanical thermal analysis (DMTA) and a three-point-bending flexural test.

1. Introduction

Bisphenol A bis(2-hydroxy propyl) methacrylate (Bis-GMA) has been widely used as the main monomeric ingredient of the matrix resin for restorative dental materials. The aromatic rings in the main chain of each monomer unit contribute to the rigidity of the Bis-GMA resin, which is one of the main reasons for its wide use in dental applications. The main difficulty in using Bis-GMA alone, however, is its molasses-like viscosity, which makes it difficult to process. To overcome this problem, different methacrylate-based monomers of lower viscosity are usually added as diluents, which copolymerize with the Bis-GMA. To maintain the rigidity of such a copolymer, the concentration of Bis-GMA needs to be kept as high as possible. However, the use of high concentrations of Bis-GMA results in reduction of the extent of conversion of carbon–carbon double bond (C=C) of the methacrylate group [1, 2]. The unreacted residuals remain as pendant methacrylate groups (PMG) that have been found to be the main cause of chemical degradation of the Bis-GMA-based copolymer [3]. The extent of conversion was found to vary between 52 and 85% depending on the type and content of diluent [4, 5]. The diluent monomers vary in chain length, viscosity, surface tension, and compatibility with Bis-GMA [6], and ultimately affect the physical properties of the cured resin.

The most common monomer used as diluent is triethylene glycol dimethacrylate (TEGDMA). Many reports are available about the effect of TEGDMA concentration on the extent of conversion and the ultimate mechanical performance of Bis-GMA-TEGDMA copolymers [4, 7]. The cured TEGDMA is a very brittle material, and the combination of TEGDMA and Bis-GMA results also in a copolymer with low strain-to-failure. The strain-to-failure of a copolymer of 70% Bis-GMA and 30% TEGDMA was found to be less than 2%. Bis-GMA/TEGDMA copolymer has been successfully used for many years, and its low strain-to-failure has not been seen as an obstacle in most dental applications. However, in previous reports [8, 9], we have shown that the low strain-to-failure of the Bis-GMA/TEGDMA copolymer was the main reason for premature failure of uniaxially oriented continuous S2-glass fibre reinforced composites (FRC). FRC have been suggested for various dental applications [10–13]. In order to utilize the maximum stress–strain potential of S2-glass fibre in a composite, the matrix needs to have a strain-to-failure at least that of the fibre.

In this study, a polethylene glycol dimethacrylate (PEGDMA) was used as diluent to improve the strain-to-failure of the Bis-GMA-based copolymer. The purpose of this study was to investigate the effect of PEGDMA concentration on the extent of conversion and the mechanical properties of Bis-GMA/PEGDMA copolymer. The effect of different matrix formulations on the mechanical properties of S2-glass reinforced composites was also investigated.

2. Materials and formulations

Bis-GMA (MW = 512) and S2-glass fibres with an epoxy compatible sizing were provided by Esschem Co. and Owens-Corning, respectively. Polyethylene glycol dimethacrylate 400 (PEGDMA; MW = 536) and benzoyl peroxide (BPO) were purchased from Scientific Polymer Products Inc. and Aldrich Chemical Inc., respectively.

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Four different resin formulations of Bis-GMA/PEGDMA, with Bis-GMA concentrations of 100, 75, 50 and 0 wt%, were prepared. For each formulation, the BPO catalyst was mixed with the diluent (PEGDMA) using a magnetic stirrer. Then to the PEGDMA/BPO mixture the appropriate amount of Bis-GMA was added, and again mixed by magnetic stirring. The BPO content was 0.75 wt % based on the weight of resin formulation. In the case of neat Bis-GMA, the BPO was first dissolved in methylene chloride (CH_2Cl_2). Then Bis-GMA was mixed with the BPO/CH_2Cl_2 mixture, and after the mixing process was completed, CH_2Cl_2 was removed under vacuum (− 100 kPa) for 24 h.

2. Experimental procedures

2.1. Differential scanning calorimetry

A Perkin-Elmer DSC-7 differential scanning calorimeter was used to determine the heat of reaction of each resin formulation. Samples of 10–12 mg were placed in the DSC aluminum pans, hermetically sealed, and transferred to the sample holder of the instrument. The curing experiments were conducted under nitrogen at heating rates ranging from 20 to 50 °C/min. The heat of free radical polymerization of the methacrylate monomers was determined by dividing the area under the heat flow versus temperature curve by the mass of the sample [14].

2.2. Infrared spectroscopy

A Nicolet 60-SX IR-spectroscometer was used to investigate the extent of conversion of each resin formulation. A small drop of each resin formulation was placed on one surface of a NaCl disc with a diameter of 25 mm. The resin drop was squeezed between two matching discs to form a thin film. Each monomer sample was subjected to the incident beam of IR radiation before curing, and then cured in an oven at 100 °C for 2 h. After cooling to room temperature they were again subjected to the incident beam of IR radiation. The extent of conversion was measured by monitoring the decrease in the carbon–carbon double bond ($C=C$) absorbance at 1637 cm^{-1} of the methacrylate monomer. To compensate for the change of thickness due to thermal shrinkage during curing, the carbon–carbon double bond ($C=C$) absorbance of the benzene ring at 1608 cm^{-1} was used as a reference. Extent of conversion (EC) was calculated using the following equation:

$$EC = 1 - [(I/I_{\mathrm{Ref}})_{\mathrm{cured}}/(I/I_{\mathrm{Ref}})_{\mathrm{uncured}}] \qquad (1)$$

where I is the absorbance intensity of $C=C$ of methacrylate monomer, and I_{Ref} is the absorbance intensity of $C=C$ of the benzene ring. The reference absorbance of the benzene ring was used only for the formulation where Bis-GMA was present.

2.3. Dynamic mechanical thermal analysis

Dynamic mechanical thermal analysis was conducted using a DMTA-MKII system (Polymer Laboratories, Inc.). Samples of rectangular cross-section were prepared by casting in silicone rubber moulds. Each sample was 40 mm long. The width and thickness of the samples were about 10 and 0.5 mm, respectively. Experiments were conducted in a double cantilever bending mode with a frequency of 10 Hz. The experimental temperature ranged from − 50 to 250 °C. The temperature at which the tan delta (δ) curve exhibited its maximum was recorded as the glass transition temperature (T_g).

2.4. Flexural test

Specimens of rectangular bars for three-point flexural tests were prepared from different neat resins and composites. Neat resins or composite prepregs were inserted in appropriate teflon molds, and cured in an oven at 100 °C for 2 h. The dimensions of each specimen (2 × 2 × 25 mm) were chosen in accordance with specification no. 27 of the American Dental Association (ADA). The prepregs were prepared by a filament winding technique under optimized conditions. A detail description of the processing technique has been reported elsewhere [9]. Experiments were coducted on an Instron (Model 10II) at a crosshead speed of 3 mm/min. The span length, given by the ADA-specification, was 20 mm which resulted in a span-to-thickness ratio of 10. The flexural strength, strain and modulus were calculated from the load versus deflection curve, obtained by chart recorder, according to ASTM D790-90 [15].

3. Results

3.1. DSC results

Fig. 1 shows representative heat flow versus temperature curves for different Bis-GMA/PEGDMA formulations, obtained by DSC experiment at a heating rate of 20 °C/min. The overall reactions of all formulations were similar with only one exothermic reaction peak. The similarity in curing process was also found at higher heating rates. However, the peak temperature values (T_p) for different resin formulations were slightly different. The peak temperature was found to decrease slightly with the increase of PEGDMA. For the same resin formulation T_p increased with the increase of heating rate (Table I and Fig. 2) which is a very common phenomenon also found in other thermosets [16]. The activation energy (AE) was determined from the following relation given in [17, 18]:

$$AE = -0.951 \times R[(\Delta \ln r)/\Delta(1/T_p)] \qquad (2)$$

where R, r and T_p represent the gas constant, the heating rate, and the peak temperature, respectively. The activation energy value obtained by the above relation lies within 3% of that obtained by the isothermal method [19] under the condition that the conversion at the peak temperature is constant [18–20]. Because of the fact the conversion at peak temperature of each resin formulation investigated in this study was about constant (Fig. 2 and Table I), the activation energy was determined from the relation given in Equation 2. Plotting the values of In (rate) over ($1/T_c$)

resulted in a straight line for each resin formulation (Fig. 3). The apparent activation energy was determined by multiplying the slope of each straight line by (0.951R). The results are given in Table II, which revealed that the higher the Bis-GMA concentration, the higher the activation energy.

3.2. IR results

Figs 4 and 5 show the IR spectra of neat PEGDMA and Bis-GMA, respectively. In each figure the upper curve was obtained before curing, whereas the lower curve was obtained after curing. In Fig. 4, the absorbance peak of C=C of the methacrylate group observed at 1637 cm^{-1} was found to disappear after the sample was cured, indicating full curing of the PEGDMA sample. But in the case of neat Bis-GMA, the absorbance peak at 1637 cm^{-1} was still present after curing (Fig. 5). The presence of C=C peak at 1637 cm^{-1} indicated that there was a fraction of uncured Bis-GMA. Similar peaks at 1637 cm^{-1} were

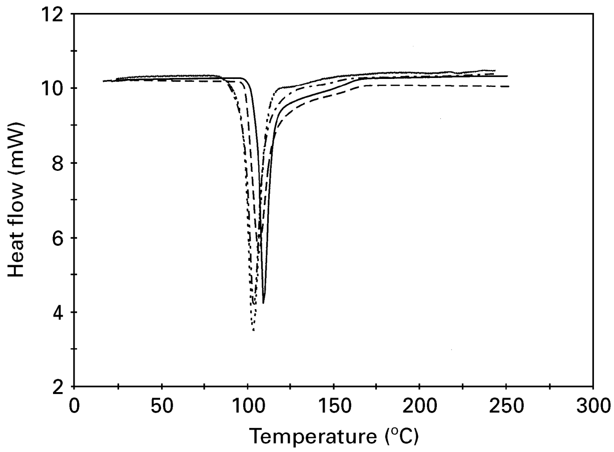

Figure 1 Heat flow versus temperature curve for different resin formulations, obtained from DSC at a heating rate 20 °C/min. Bis-GMA/PEGDMA ratio — 100/0; – – – 70/30; - - - - 50/50; ····· 0/100.

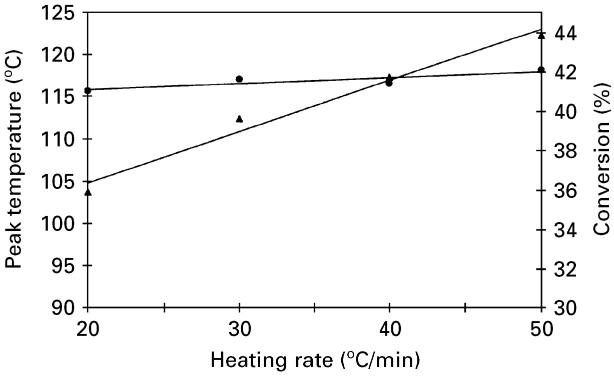

Figure 2 Influence of heating rate on peak temperature (▲) and conversion (●) at peak temperature, for Bis-GMA/PEGDMA (50/50).

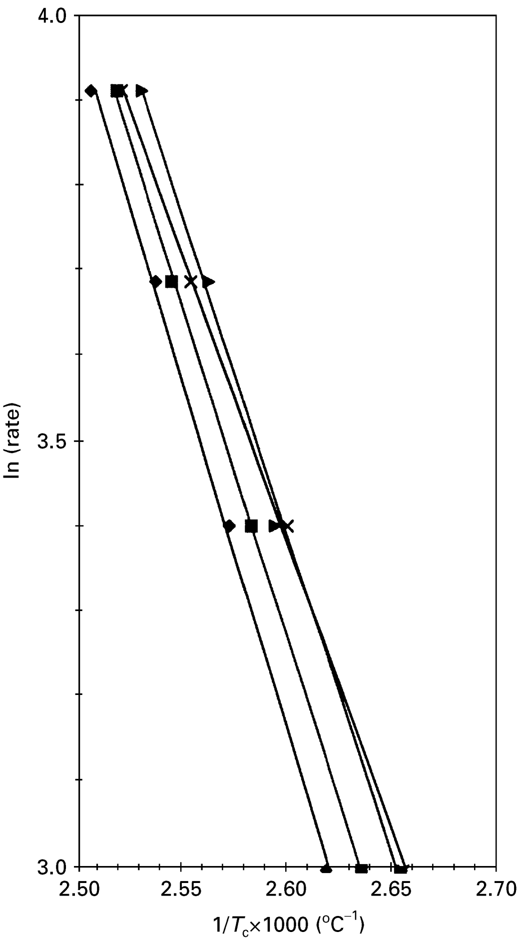

Figure 3 Arrhenius plot for activation energy of different resin formulations. Bis-GMA/PEGDMA ratio ◆ 100/0; ■ 70/30; ▲ 50/50; × 0/100.

TABLE I Peak temperatures and conversions of different resin formulations

Rate (°C/min)	Peak temperature (°C)				Conversion (%)			
	B/P (100/0)	B/P (70/30)	B/P (50/50)	B/P (0/100)	B/P (100/0)	B/P (70/30)	B/P (50/50)	B/P (0/100)
20	108.8 [0.4]	106.4 [0.1]	103.7 [0.4]	103.5 [0.1]	32.3 [0.6]	30.2 [0.9]	41 [0.3]	43.6 [0.8]
30	115.7 [0.5]	114.1 [0.14]	112.4 [0.6]	111.5 [0.5]	31.2 [0.7]	34.2 [0.2]	41.6 [0.3]	44.2 [0.4]
40	121.2 [0.9]	120 [0.6]	117.3 [0.9]	118.6 [0.2]	31.1 [0.5]	33.1 [2.1]	41.4 [0.2]	44.6 [0.9]
50	126.1 [0.8]	124.1 [1.6]	122.3 [0.3]	123.8 [0.4]	32.8 [0.4]	32.6 [1.3]	42.1 [0.6]	43.3 [0.2]

Each value is an average of five replications, and the values in the parenthesis are standard deviations.
B and P refer to Bis-GMA and PEGDMA, respectively.

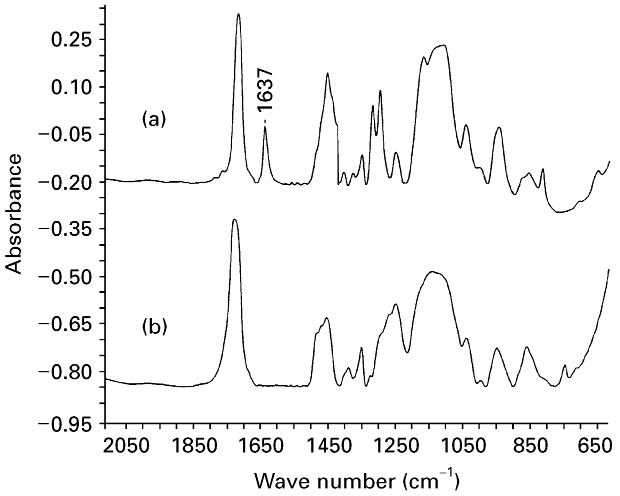

Figure 4 Infrared spectrum of neat PEGDMA before (a) and after (b) curing.

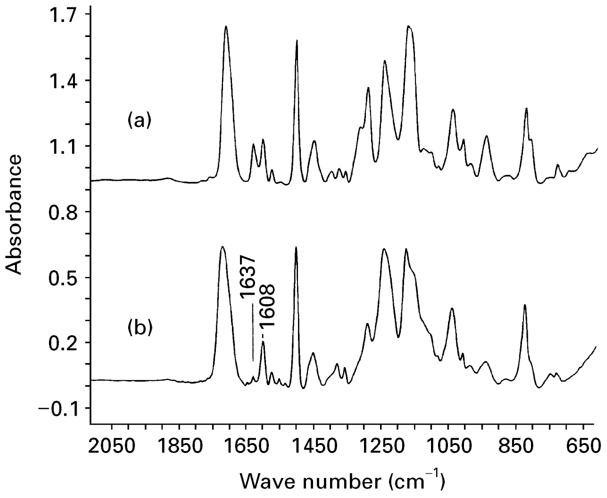

Figure 5 Infrared spectrum of neat Bis-GMA before (a) and after (b) curing.

also found in the resin formulations containing Bis-GMA in concentrations of 70 and 50 wt %. Values of extent of conversion of all resin formulations determined by Equation 1 are given in Table II. The results indicate that the extent of conversion decreases with the increase of Bis-GMA concentration. The formulation with neat Bis-GMA was found to have the lowest extent of conversion, 83%.

3.3. DMTA results

Tan δ versus temperature curves for different resin formulations obtained by DMTA at a frequency of 10 Hz are shown in Fig. 6, and the glass transition temperatures are listed in Table II. The T_g of neat Bis-GMA and PEGDMA are 13 and 148 °C, respectively. In the case of other two resin formulations, T_g is found to increase with the increase of Bis-GMA concentration. The tan δ curve for neat Bis-GMA is broader than those of other resin formulations, probably due to the presence of unreacted carbon–carbon double bonds (C = C) of methacrylate groups.

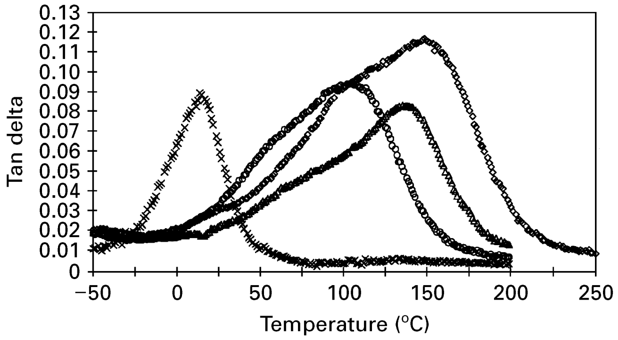

Figure 6 Tan δ versus temperature curves of different resin formulations. Bis-GMA/PEGDMA ratio: ◇ 100/0; △ 70/30 ○ 50/50; × 0/100.

3.4. Results of flexural tests

The results of flexural tests of neat Bis-GMA and the two copolymers are listed in Table III. The values in parentheses are the standard deviations. Flexural testing of the neat PEGDMA was inconclusive, since the samples were too soft, and the instrumental arrangement was not suitable for measuring the strength of the samples. The 50/50 formulation of Bis-GMA/PEGDMA gave the highest average flexural strength and strain, but the lowest stiffness (modulus). The highest stiffness was found in the 70/30 formulation of Bis-GMA/PEGDMA. Fig. 7 shows the stress–strain behaviour of samples of a 70/30 and a 50/50 formulation under flexural loading, indicating that the 50/50 formulation experiences earlier yielding than the 70/30 formulation. The flexural strengths of composites based on S2-glass fibre and the three different resin formulations are listed in Table IV. Normalized strengths lead to the conclusion that the composite system with 70/30 formulation as matrix provides the highest flexural strength.

4. Discussion

The extent of conversion of Bis-GMA/PEGDMA formulation was found to be dependent on the mixture ratio of the two components. The exothermic heat of reaction liberated from the free radical polymerization of the methacrylate monomers was assumed to be directly proportional to the number of carbon–carbon double bonds (C = C) undergoing reaction. By the IR method, the conversion was determined by monitoring the carbon–carbon double bond (C = C) absorbance of the methacrylate group. An attempt was made to correlate the heat of reaction obtained from DSC to the extent of conversion obtained from IR spectroscopy, by using the following equation:

$$\Delta H = (\Delta H_B \times W_B)/\eta_B + (\Delta H_P \times W_P)/\eta_P \qquad (3)$$

where ΔH and W refer to the heat of reaction and the weight fraction of a resin constituent, respectively. η represents the extent of conversion monitored by IR, and was used to normalize the heat of reaction to 100% conversion of C = C. The subscripts B and P refer to Bis-GMA and PEGDMA, respectively.

The average experimental values of ΔH and η of neat Bis-GMA and PEGDMA were used to calculate

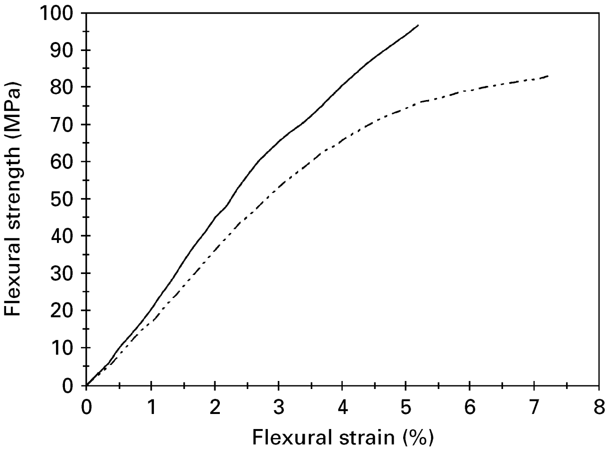

Figure 7 Flexural strength–strain curves of different resin formulations: Bis-GMA/PEGDMA ratio — 70/30; –··– 50/50.

the heat of reaction of Bis-GMA/PEGDMA formulation at different mixture ratios. A polynomial fitting of the calculated values is presented by the solid line in Fig. 3. The experimental values of 70/30 and 50/50 formulations were less than the calculated values. The differences are assumed to be due to the fraction of carbon–carbon double bonds that did not participate in the reaction process.

Experimental results show that the heat of reaction decreases nonlinearly with increase of Bis-GMA concentration (Fig. 8). The reason for the nonlinear behaviour can be traced to the increasing residual of unreacted carbon–carbon double bonds. This can be demonstrated by the results of the DMTA experiment. The glass transition temperature (T_g) increases with the increase of Bis-GMA concentration (Fig. 9). The higher residue of unreacted carbon–carbon double bonds might have acted as plasticizer which could be the main reason for the lower value of T_g and the broadness of tan δ versus temperature curve.

The plasticizing effect is also evident from the flexural strengths of the resins. The flexural strength of a Bis-GMA/PEGDMA copolymer is expected to be controlled by two factors: the mixing ratio of the components and the extent of conversion. Accordingly, with the extent of conversion of 0.96 (Table II) and 50 wt% Bis-GMA concentration, the 50/50 formulation shows the highest flexural strength (Table III). Further increase of Bis-GMA concentration (70 and 100%) does not increase the flexural strengths, indicating that flexural strengths in those formulations are reduced by the unreacted carbon–carbon double bonds.

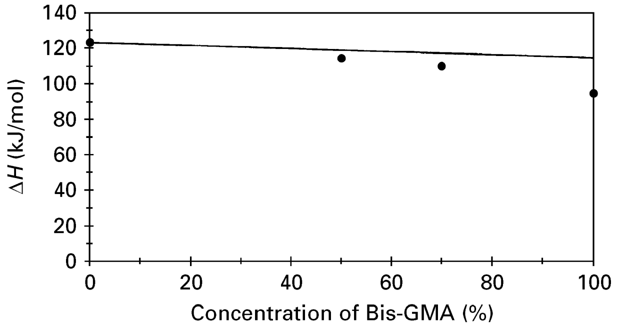

Figure 8 Effect of Bis-GMA concentrations on the heat of reaction (— Equation 3).

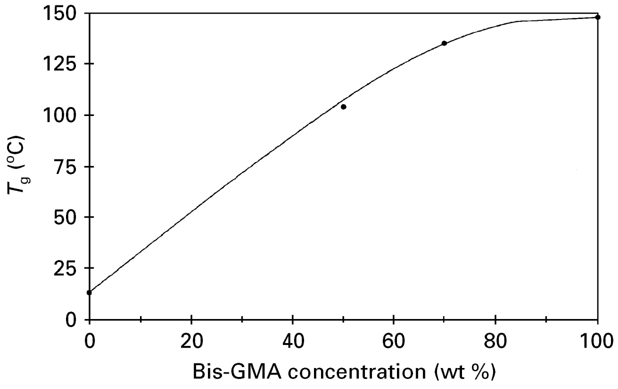

Figure 9 Effect of Bis-GMA concentrations on the glass transition temperature.

TABLE II Results of activation energy (*AE*), extent of conversion (*EC*) and glass transition temperature of different resin formulation

Resin formulation	*AE* (kJ/mol)	*EC*	T_g(°C)
Bis-GMA/PEGDMA (100/0)	62	0.83	148
Bis-GMA/PEGDMA (70/30)	61	0.87	135
Bis-GMA/PEGDMA (50/50)	59	0.96	104
Bis-GMA/PEGDMA (0/100)	53	1	13

TABLE III Flexural properties of neat resins.

Matrix formulation	Strength (MPa)	Strain (%)	Modulus (GPa)
Bis-GMA/PEGDMA (100/0)	71.7 (7.2)	4.9 (0.3)	2.3 (0.2)
Bis-GMA/PEGDMA (70/30)	81.9 (12.1)	3.8 (0.9)	2.6 (0.1)
Bis-GMA/PEGDMA (50/50)	83.5 (1.4)	7.7 (1.1)	2.1 (0.1)

Each value is an average of five replications, and the values in the parenthesis are standard deviations

When all of the three resins listed in Table III were reinforced with S2-glass fibres, the average flexural strengths of the composite with 70/30 formulation was the highest (Table IV). When a composite sample is subjected to flexural load, the span length-to-thickness ratio (*l*/*d*) must be greater than a critical value in order to utilize the maximum reinforcing efficiency of the fibres. For uniaxially glass fibre reinforced composite the critical value for *l*/*d* ratio was found to be 50 [21], while the ADA-specification, which was followed in this study, specifies an *l*/*d* ratio of only 10. With such a low *l*/*d* ratio, the uniaxially composite samples experience more of an interlaminar shear stress than a pure flexural stress [9]. Therefore, the higher stiffness of the 70/30 resin formulation (Table III) could contribute to the higher flexural strength of its composite. Consequently, the lowest stiffness of the 50/50 formulation was the main reason for the lowest flexural strength of its composite. Fig. 7 shows that the 50/50 formulation experiences earlier yielding than the 70/30 formulation. The scanning electron microscopy (SEM) photograph of the compressive surface of the

TABLE IV Flexural properties of S2-glass composites with different resin formulations

Matrix formulation	Fibre (vol %)	Strength (MPa)	Normalized strength (MPa) to 100% fibre content
Bis-GMA/PEGDMA (100/0)	36	567.2 (21.7)	1575.6
Bis-GMA/PEGDMA (70/30)	31.5	526.9 (31.3)	1672.6
Bis-GMA/PEGDMA (50/50)	30.5	356.7 (18.2)	1169.6

Each value is an average of five replications, and the values in the parenthesis are standard deviations

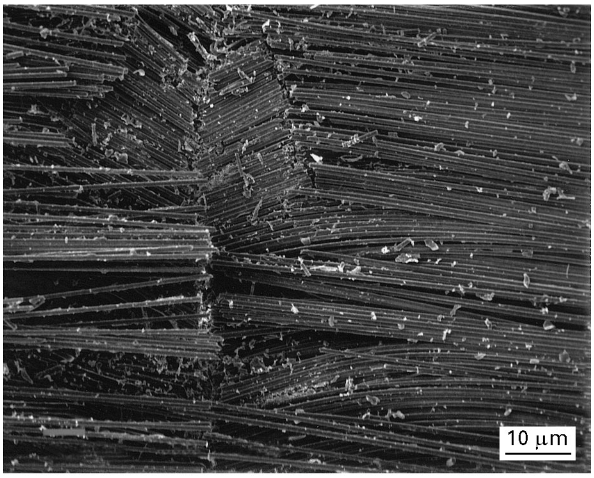

Figure 10 Scanning electron microscopy photograph of the compressive surface of the composite sample from S2-glass with Bis-GMA/PEGDMA (50/50), after flexural test.

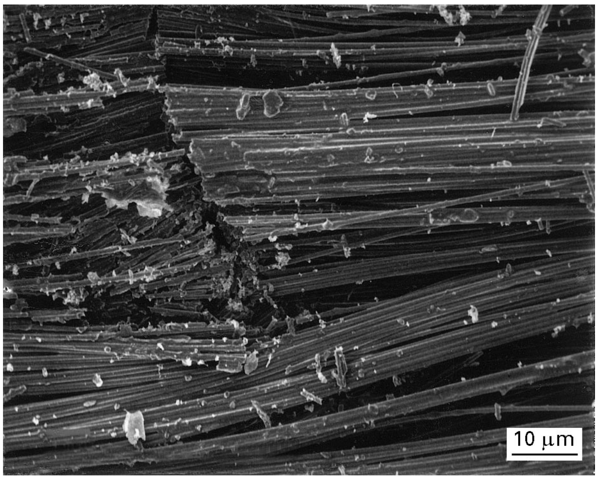

Figure 11 Scanning electron microscopy photograph of the compressive surface of the composite sample from S2-glass with Bis-GMA/PEGDMA (70/30), after flexural test.

composite sample with 50/50 formulation (Fig. 10) shows small broken pieces of fibres which could be the effect of earlier yielding of the matrix. On the other hand, the SEM photograph of the compressive surface of the composite sample with 70/30 formulation (Fig. 11) shows more of a brittle nature of failure, supposedly due to the brittleness of the matrix itself. The results of the flexural tests also support our previous findings [9] that while the higher strain of a matrix may be the main requirement for the higher strain of a composite in tensile loading, in flexural loading with small *l*/*d* ratio, it is the stiffness of a matrix that controls the flexural strength of the composite.

5. Conclusions

The extent of conversion of Bis-GMA/PEGDMA resin formulations increased with increasing concentration of PEGDMA. The glass transition temperature and flexural strengths of the neat resins were found to be influenced by the extent of conversion. However, the extent of conversion did not have any direct influence on flexural strengths of composites. The flexural strengths of composites were apparently controlled by the stiffness of the matrices.

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