Fracture and Structure of Highly Crosslinked Polymer Composites

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SYNOPSIS

The fracture toughness of silica filled dimethacrylate resins has been found to increase with the degree of cure of the network, and was previously attributed to increased crosslinking or the concomitant reduction in unreacted monomer (sol species). Studies of the dependence of the polymerization on the photoinitiator concentration and cure time of dimethacrylate resins illustrate the interrelation of the wt % sol and the degree of cure and reveal that a considerable amount of residual monomer remains in undercured networks, as predicted by simple gelation theory. In an attempt at separating the effects of residual monomer and crosslinking on the fracture behavior, several series of filled dimethacrylate and epoxy resins were studied in which the crosslink density and sol levels were independently varied without introducing significant changes in the chemical composition of the network. Although the fracture energy and toughness were raised by increasing the crosslink density in the epoxy resins, no significant variation was found for the dimethacrylates. Saturated analogues of dimethacrylates (used to represent residual monomer) significantly impaired the fracture resistance, suggesting that the reduction in residual monomer is responsible for the improved fracture toughness observed with postcured dimethacrylate networks.

INTRODUCTION

The isothermal polymerization of highly functionalized monomer systems commonly results in incomplete polymerization. This may be due to the location of some potentially reactive groups[1] in inaccessible regions (steric effects) or because vitrification occurs during the network formation when the curing temperature is less than the T_g of the fully cured system (the vitrification effect).[2] In either case the network will be imperfect, having a lower crosslink density, pendant reactive groups, and unreacted monomer or homologues (sol).

A number of studies[3–5] have interpreted the dependence of the fracture properties on curing time or temperature in terms of the variation in crosslink density or sol content. The role of crosslink density on the fracture process has been investigated[3,6–10] by varying the structural elements in the network, often with conflicting results. In part these discrep-

ancies may be due to dissimilar variation in the chemical composition of the networks as the crosslink density is altered. It is well known that, with other polymer properties such as the glass transition temperature,[11] the compositional variation must be minimized if the effect of crosslinking is to be established.

The dependence of fracture properties on curing temperature has relevance to the dimethacrylate composites used in dentistry for tooth fillings. These materials consist of a mixture of dimethacrylates (such as triethylene glycol dimethacrylate and bis-phenol-A diglycidylmethacrylate, bisGMA) and reinforcing filler (commonly 70–80 wt % silica). Polymerization is accomplished by free radical initiation via a chemical redox couple (e.g., benzoyl peroxide and dimethyl toluidine) or photochemically (using camphorquinone and an amine photoreducer).[12] Because the polymerization temperature (oral temperature, around 37°C) is well below the T_g of the fully cured resin, the degree of cure in these dental composite resins lies between 40 and 75%[12] and so suboptimum properties are to be expected.

In previous studies, we have investigated the influence of postcuring temperature[5] and chemical structure of the dimethacrylate monomer[13] on the fracture behavior of commercial and experimental dimethacrylate composite resins. In this paper, the dependence of the fracture properties on network structure is explored through systematic variations in the crosslink density and sol level which do not introduce significant compositional change. The two network classes studied are silica-filled dimethacrylate resins and silica-filled diamine-cured epoxy resins.

EXPERIMENTAL

The monomers and saturated analogues employed in the study are listed in Table I with their coding. BisGMA was obtained as a viscous resin from Freeman Chemicals Corp. (U.S.A.) and had a methacrylate concentration, which was 98% of theoretical. The TEGDMA dimethacrylate was a product of Es-

schem Co. (U.S.A.) and had a purity of 96%. The DGEBA epoxy (Epicote 828) was purchased from Shell Chemicals (Australia) and had an oxirane content of 5.4 mmol/g (cf. 5.88 mmol/g theoretical). All other commercially obtained reagents were of laboratory or analytical reagent quality.

Phenyl glycidyl methacrylate (PGEMA) was prepared by the condensation of phenyl glycidyl ether with a 10% molar excess of methacrylic acid at 100°C using 0.15 wt % triphenyl phosphine and 0.45 wt % triphenyl antimony as catalyst.[14] Completion of reaction was estimated by the disappearance of the 915 cm^{-1} IR peak of the oxirane ring. A chloroform solution of the reaction mixture was twice extracted with 10% sodium carbonate solution and with water before drying and vacuum stripping of the chloroform. Analysis of the final slightly viscous product using the morpholine method[15] gave a methacrylate content of 96% of theoretical. The refractive index at 23°C was 1.5225. Both IR and ^{1}H-NMR spectra were in accord with the expected structure.

Table I   Codes and Structures of the Monomers Used

Methyl methacrylate (MMA)
  $CH_2 = C(CH_3)COOCH_3$
Ethylene glycol dimethacrylate (EGDMA)
  $CH_2 = C(CH_3)COOCH_2CH_2OCOC(CH_3) = CH_2$
Ethylene glycol diisobutyrate (EGDBA)
  $CH_3CH(CH_3)COOCH_2CH_2OCOCH(CH_3)CH_3$
Triethylene glycol dimethacrylate (TEGDMA)
  $CH_2 = C(CH_3)COO(CH_2CH_2O)_3COC(CH_3) = CH_2$
Methoxyethyl methacrylate (MeOEtMA)
  $CH_2 = C(CH_3)COOCH_2CH_2OCH_3$
Triethylene glycol diisobutyrate (TEGDBA)
  $CH_3CH(CH_3)COO(CH_2CH_2O)_3COCH(CH_3)CH_3$
Phenyl glycidyl ether methacrylate (PGEMA)
  $CH_2 = C(CH_3)COOCH_2CH(OH)CH_2OC_6H_5$
Bis-phenol-A-diglycidylmethacrylate (bisGMA)
  $CH_2 = C(CH_3)COOCH_2CH(OH)CH_2OC_6H_4C(CH_3)_2C_6H_4OCH_2CH(OH)CH_2OCOC(CH_3) = CH_2$
Diglycidyl bis-phenol-A diisobutyrate (DGEBADBA)
  $CH_3CH(CH_3)COOCH_2CH(OH)CH_2OC_6H_4C(CH_3)_2C_6H_4OCH_2CH(OH)CH_2OCOCH(CH_3)CH_3$
n-Butylamine (BA)
  $CH_3(CH_2)_3NH_2$
Diamino-octane (DAO)
  $H_2N(CH_2)_8NH_2$
Aniline (An)
  $C_6H_5NH_2$
Benzidine (Bz)
  $H_2NC_6H_4C_6H_4NH_2$
Bis-phenol-A-diglycidyl ether (DGEBA)

Methoxyethyl methacrylate (MeOEtMA) was synthesized by the dropwise addition of methacryloyl chloride to an equimolar amount of dried 2-methoxyethanol at 0°C. After 2 h, the reaction mixture was warmed to room temperature over 3 h, and then poured into ice water to hydrolyze any remaining acid chloride. A chloroform solution of the product was twice extracted with 10% sodium bicarbonate and with water prior to dying. After stripping off the chloroform, the crude MeOEtMA was distilled under vacuum at 55–57°C/7 mm Hg (cf. the literature value[16] of 65–67°C/10 mm Hg). The refractive index was 1.4289 at 23°C (cf. the literature value[16] of 1.4283 at 25°C).

The diisobutyrate of the diglycidyl ether of bis phenol-A (DGEBADBA) was prepared from isobutyric acid and DGEBA epoxy resin, in an analogous manner to PGEMA (see above). The acid value of the product was negligible. Saponification studies gave an ester concentration of 95% of theoretical. The refractive index of the final viscous product was 1.533 at 23°C.

Ethylene glycol diisobutyrate (EGDBA) and triethylene glycol diisobutyrate (TEGDBA) were synthesized by Dean and Stark condensation of ethylene glycol or triethylene glycol with isobutyric acid (10% in stoichiometric excess) in toluene using p-toluene sulfonic acid as catalyst. At the completion of the reaction as judged from the quantity of water collected, the product was extracted with 10% sodium carbonate and water and dried. After vacuum stripping of the toluene, the refractive indices of the liquid EGDBA and TEGDBA were 1.419 and 1.435, respectively, at 23°C. The acid values of the products was negligible. Saponification studies gave an ester concentration of 96 and 105% of theoretical, respectively, for EGDBA and TEGDBA.

The particulate SiO_2 filler (300 WQ; Commercial Minerals Ltd., Australia) had an average diameter of 17 μm. For the dimethacrylate resins, the filler was acid washed and silanized with 3-methacryloxy propoxy trimethoxy silane (A174, Union Carbide) as described elsewhere.[5] For the epoxy resins, 3-glycidoxy propoxy trimethoxy silane (A187, Union Carbide) was substituted as the silanizing agent.

Studies of the influence of postcuring on the fracture properties of partially cured dimethacrylate composites were performed with filled resins formulated from 21 wt % bisGMA, 9 wt % TEGDMA, 0.075 wt % camphorquinone (photo-initiator), 0.09 wt % N,N,3,5-tetramethyl aniline (photo-reducer), 0.015 wt % butylated-hydroxytoluene (inhibitor), and 70 wt % SiO_2 filler (treated and untreated). After photocuring at 23°C,[5] the samples were post-

treated at various temperatures for 24 h and were then slowly reequilibrated to room temperature, prior to test.

Other dimethacrylate composite resins were formulated by blending 75 parts of filler with 25 parts of the appropriate dimethacrylate mixture containing 0.25 wt % camphorquinone and 0.30 wt % N,N,3,5-tetramethyl aniline. Photopolymerization was performed by irradiating the specimens with a 170 klux xenon source (Hanau Suntest, Original Hanau Quartzlampen GmbH, W. Germany) for 10 min at 60°C. The spectral irradiance on the specimen plane was 4.0×10^{-4} W/cm²/nm at 470 nm (the wavelength of maximum absorption for camphorquinone)—more information about the spectral distribution can be found elsewhere.[17] After photopolymerization, the dimethacrylate specimens were postcured at 100°C (for the series of specimens prepared with saturated analogues) or at 150°C for 2 h (all other filled dimethacrylates).

The butylamine/diaminooctane/epoxy resins were prepared by mixing stoichiometric equivalents of DGEBA and the appropriate amounts of butylamine and diaminooctane (premelted at 60°C and avoiding loss of the volatile butylamine). The composite epoxy resins were prepared by blending 30 parts of this resin mixture with 70 parts of pretreated silica at 60°C. Due to the higher melting temperature of benzidine, the aniline/benzidine/epoxy systems were prepared by premixing the required quantities of filler and DGEBA and blending this preheated material with the melted mixture of the amines. The epoxy composites were cured at 60°C/24 h and then postcured at 150°C for 2 h.

The degree of cure (or conversion) of the dimethacrylate matrix was determined in duplicate by IR spectroscopy from the absorbance ratio of the C=C stretch of the methacrylate group (at 1636 cm^{-1}) to the reference aromatic ring peak (at 1607 cm^{-1}) in the cured and uncured materials, using standard baseline techniques. In specimens postcured above 100°C the degree of conversion was greater than 90%. The experimental error in the degree of conversion was estimated to be ±5% (relative). Full cure of the epoxy specimens was confirmed by the absence of the 915 cm^{-1} epoxy peak.

Sol–gel studies were performed on four series of partially photocured, unfilled dimethacrylate resins. Two series of samples, I and II, were prepared from a bisGMA (90 wt %)/ethyl acetate (10 wt %) mixture and contained two levels of camphorquinone (0.3 and 0.03 wt %) and tetramethyl aniline (0.25 and 0.025 wt %), respectively. Series III and IV were prepared from a bisGMA (70 wt %)/TEGDMA (30

wt %) blend and contained two levels of camphorquinone (0.3 and 0.03 wt %) and tetramethyl aniline (0.25 and 0.025 wt %), respectively. An inhibitor level of 0.05 wt % butylated hydroxytoluene was used in all four series. The 1 mm thick sheet samples were photocured at 23°C/23 klux (5.0 × 10⁻⁵ W/cm²/nm at 470 nm) with the xenon source, for various periods and were then postcured at 45°C for 24 h. Some specimens were also postcured at 100°C. Finely ground samples of the network were extracted with refluxing $CHCl_3$ (containing benzoquinone as inhibitor) for 24 h. Extended extraction periods up to 48 h yielded identical results. The wt % sol was determined from the mass of residual material after rotary evaporation of the solvent extract. The experimental error in the wt % sol was less than 1% (absolute).

The double-torsion specimens used to determine the fracture toughness (K_c) were prepared in the form of plates 30 × 15 × 2 mm containing a 0.5 mm deep groove as a crack guide running down the center of one major face. As described elsewhere,[5] the use of a double torsion test rig with a universal testing machine allowed the measurement of the torsional force ($F/2$) on each side of the specimen groove required to produce controled crack growth along the groove, under a constant crosshead speed (0.05 mm/min). The fracture toughness (K_c) at 23°C was calculated from the torsional force according to the expression[18]

$$K_c = FW_m[(1 + \nu)/Wt^3 t_n K]^{1/2} \qquad (1)$$

where W_m is the length of the moment arm (5.7 mm), W is the width of the specimen (15 mm), t is the plate thickness (ca. 2 mm), t_n is the thickness of the plate in the plane of the crack (ca 1.5 mm), and K is a specimen dimension correction factor[18] (0.277). Poisson's ratio (ν) was approximated as 0.3. For most of the composite materials, stick-slip crack propagation was observed in the force–displacement trace. However, the difference between the arrest and propagation values was less than 10%. Therefore, the average value of the force in each force–displacement trace was used to compute K_c from a minimum of three specimens. The error in K_c was approximately ±0.1 MN/m³/².

Flexural strength specimens were prepared as 25 × 2 × 2 mm bars. The specimens were fractured under three point loading at 23°C using a crosshead speed of 1 mm/min. The flexural strength (σ) was calculated from a minimum of six specimens, using the equation[19]

$$\sigma = 3Fl/2bd^2 \qquad (2)$$

where F is the breaking force, l is the span (20 mm) between loading points, and b and d are the specimen width and depth, respectively. The flexural modulus (E) was calculated from the force–deformation trace[19]

$$E = Fl^3/4bd^3x \qquad (3)$$

where x is the deflection of the beam at F in the linear region of the force–deformation curve. Stress–relaxation experiments were also performed in flexure using 30 × 7 × 2 mm bars. The specimens were rapidly deformed in flexure by ca. 0.12 mm and the stress–relaxation modulus [$E(t)$] determined from the force required to maintain the deformation.

The fracture energy (G_c) was calculated from the expression[20a]

$$G_c = (1 - \nu^2)K_c^2/E \qquad (4)$$

RESULTS AND DISCUSSION

Effect of Postcuring

In accord with previously published results,[5] Figure 1 shows that postcuring raises the fracture toughness of dimethacrylates reinforced with a silanized filler. Although lower K_c values are found for the composites containing unsilanized silica filler (see Fig. 1), a similar trend is also found. As discussed above, this behavior could result from an increase in the level of crosslinking or be due to a reduction in the amount of unconnected dimethacrylate molecules (sol) in the network.

Crosslink Density and Fracture

The effect of crosslinking on fracture can be isolated by studying "fully" polymerized materials in which a certain number of the network strands are visualized as having been cleaved down the center.[11] For example, poly(methyl methacrylate) has virtually the same chemical composition as has the network formed from ethylene glycol dimethacrylate and can be considered to be derived from the network by cutting the ethane section in half.[11] PGEMA and MeOEtMA are monomethacrylate analogues of bisGMA and TEGDMA (see Table I). Similarly, the polymers formed from butylamine or aniline with DGEBA are the linear analogues of the diaminooctane/DGEBA or benzidine/DGEBA network.[21]
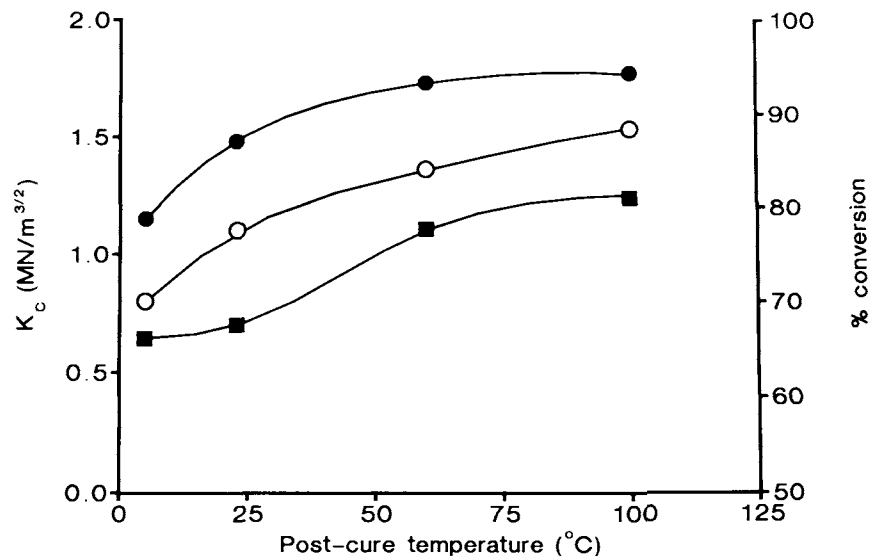
Figure 1 Influence of postcure temperature (for 24 h postcure) on K_c (circles) and degree of conversion (squares) for a bisGMA/TEGDMA resin filled with 70 wt % treated (closed circles) and untreated (open circles) silica.[5]

LeMay and Kelley[9] have proposed that the Lake–Thomas theory[22] for the tear energy of elastomers could be applicable to the dependence of fracture energy on crosslinking in glassy networks if the chains in the crack tip zone were in a state of increased mobility similar to that in an elastomer. In the Lake–Thomas theory,[22] it is assumed that crack propagation occurs via the rupture of network strands (chains between crosslink points or permanent entanglements) crossing the tear path and that for a strand to break, all of the bonds in the strand are subjected to the same breaking force. Thus the energy expended in breaking the strand is not the bond energy U, but the total energy stored in the strand just prior to failure, nU, where n is the number of bonds in the strand. Since the tear (or fracture) energy T_0 is the energy dissipated during the formation of unit area of crack, T_0 is given by the product of the energy required to rupture a network strand (nU) multiplied by the number of strands per unit area of crack path. The latter term is $L\rho/2$,[22] where L is the average end-to-end distance of the strands and ρ is the concentration of strands per unit volume. Thus the general expression for the tear energy associated with primary bond rupture (T_0) is[22]

$$T_0 = (nU) \cdot (L\rho/2) \qquad (5)$$

For elastomers with a Gaussian distribution of end-to-end distances, L is proportional to $n^{1/2}$. Since the number of strands per unit volume (ρ) is recip-

rocally related to n, Lake and Thomas[22] showed that T_0 was proportional to the square root of the number of bonds per strand ($n^{1/2}$). Thus T_0 should increase as the crosslink density is lowered and then approach a plateau when the concentration of entanglements exceeds the concentration of chemical crosslinks. However, for short network strands, L may be better approximated by the number of bonds in the strand. In this case, eq. (5) would predict an initially linear dependence of tear energy on n.

For reinforced, viscoelastic materials, energy expenditure during crack growth may also occur due to viscous deformation mechanisms at the crack tip and by the influence of a rigid dispersed phase on the crack path. It is generally considered[20b,23] that these effects are multiplicative so that the total fracture energy (G_c) of a viscoelastic, reinforced solid may be expressed as

$$G_c = G_0 \cdot f_1(t, T) \cdot f_2(\phi) \qquad (6)$$

where G_0 is an intrinsic fracture energy of the matrix which neglects viscous energy dissipation, $f_1(t, T)$ is a function of time and temperature representing the energy absorbed in viscous deformation, and $f_2(\phi)$ is the contribution to the fracture energy associated with the fraction ϕ of reinforcing filler.

In the study by LeMay and Kelley[9] of the unreinforced [$f_2(\phi) = 1$] networks formed from a series of oligomers of DGEBA and diaminodiphenylsulfone, the viscous energy dissipation term [$f_1(t, T)$] may be considered to be constant. If T_0 can be
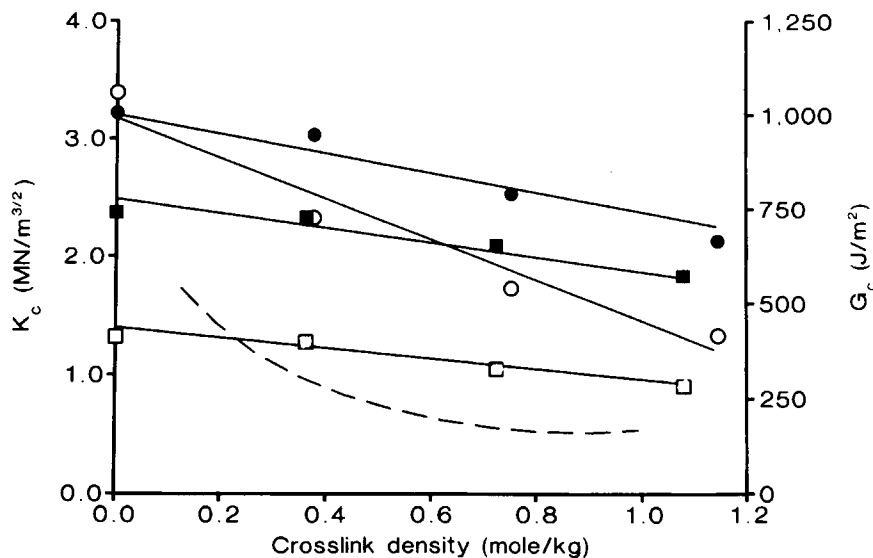
Figure 2 Dependence of fracture toughness K_c (closed symbols) and fracture energy G_c (open symbols) on crosslink density for 70 wt % filled BA/DAO/DGEBA (circles) and An/Bz/DGEBA (squares). The cross link density (expressed as mol diamine/g resin) was varied by altering the ratio of monoamine to diamine. The dashed line represents the G_c data of LeMay and Kelley.[9]

equated to G_0 (on the assumption that the chains in the crack tip zone are in a rubber-like state[9]), and if L is proportional to $n^{1/2}$, eqs. (5) and (6) predict a square root relationship between G_c and n. Such a relationship was observed by LeMay and Kelley.[9]

Figure 2 illustrates the variation of fracture toughness and energy on crosslinking for the aliphatic diamine-cured epoxy model networks. Although the data are not sufficient to test eqs. (5) and (6), the overall variation in G_c and K_c is similar to that found by LeMay and Kelley.[9] In contrast, the aromatic diamine system (Fig. 2) shows a much smaller dependence on crosslinking.

Surprisingly the dimethacrylate networks show no significant dependence on crosslink density (Fig. 3) except for the lowest crosslink densities. Thus we find that the dependency of fracture resistance on crosslinking $(-dG_c/d\rho)$ increases according to the trend:

dimethacrylates

< aromatic diamine epoxy networks

< aliphatic diamine epoxy networks

It might be argued that the different trends in fracture behavior observed for the epoxy resins and dimethacrylates are related to the proximity of the glass transition temperatures to the testing tem-

perature through the term $f_1(t, T)$ in eq. (6). If it is assumed that the viscous energy dissipation has the dominant influence on G_c, then the closer the T_g is to room temperature, the larger will be the fracture energy. The butylamine/diaminooctane systems have T_g's ranging from 55 to 109°C,[21] so that the extent of energy dissipation may be expected to increase as the crosslink density is lowered, thus increasing fracture toughness. The aromatic diamine cured epoxies have higher T_g's (94–227°C[21]) and so would show a lesser dependence on crosslinking. Similarly, since the dimethacrylates have high glass transition temperatures,[24] the variation in viscous dissipation should be small and so little dependence on crosslinking should be found.

However, stress–relaxation studies, which provide a measure of viscoelastic energy dissipation, do not support this argument. According to the Schwarzl–Staverman approximation,[25] the logarithmic rate of stress relaxation is given by

$$d \log E(t)/d \log t = -\pi \tan \delta/2 \qquad (6)$$

where $\tan \delta$ is a measure of viscoelastic energy absorption. Table II shows that neither the BA/DAO/DGEBA networks nor the bisGMA/PGEMA/EGDMA/MMA dimethacrylate networks exhibit any systematic variation in $d \log E(t)/d \log t$, indicating that the proximity of the network T_g to
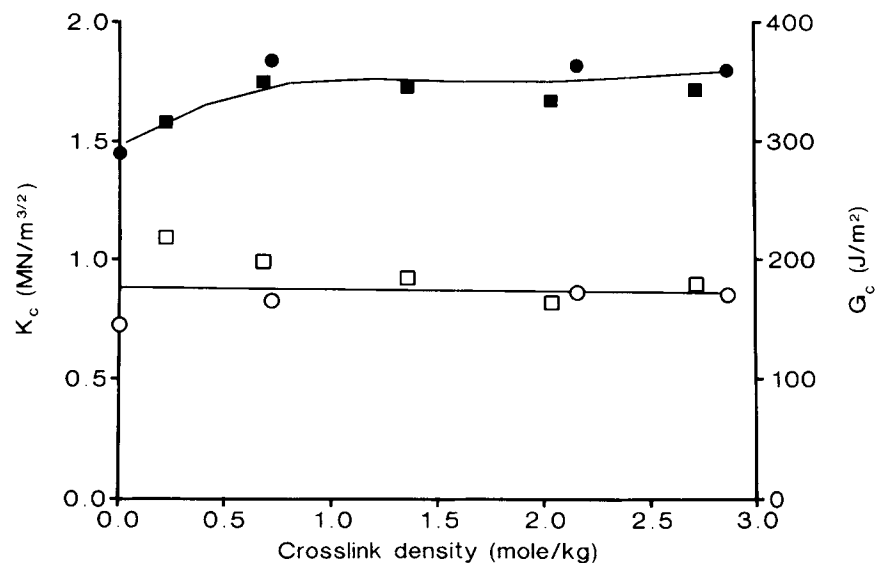
Figure 3   Dependence of fracture toughness K_c (closed symbols) and fracture energy G_c (open symbols) on crosslink density for 75 wt % filled MMA/EGDMA/PGEMA/bisGMA (70 wt % resin was PGEMA and bisGMA) (circles) and MeOEtMA/TEGDMA/PGEMA/ bisGMA (50 wt % resin was PGEMA and bisGMA) (squares). The crosslink density (expressed as mol dimethacrylates/g resin) was varied by altering the ratio of dimethacrylates to monomethacrylates.

room temperature does not explain the different trends in fracture resistance. Thus the variation of fracture resistance on cure (Fig. 1) does not appear to be controled by crosslink density alone.

Sol Species and Cure

As shown by the IR spectra in Figure 4, the extracted sol of partially cured dimethacrylates has a similar

Table II   Logarithmic Rate of Stress–Relaxation

System	$-d \log E(t)/d \log t$ [a]
BA/DAO cured epoxies, varying crosslink density, BA/DAO weight ratio	
1.0 : 0	0.012
0.33 : 0.66	0.011
0.66 : 0.33	0.012
0 : 1.0	0.015
Dimethacrylates, varying crosslink density, bisGMA/PGEMA/EGDMA/MMA weight ratio	
0.17 : 0.53 : 0.07 : 0.23	0.020
0.53 : 0.17 : 0.23 : 0.07	0.015
0.7 : 0 : 0.3 : 0	0.016
Dimethacrylates, varying sol level, Wt % sol [b]	
0	0.023
12.5	0.022
37.5	0.081
50.0	0.091
67.0	0.081

[a] Correlation coefficients were greater than 0.98 for stress–relaxation data collected over the range 1 and 7000 s.
[b] DGEBADBA (70 wt %)/TEGDBA (30 wt %).

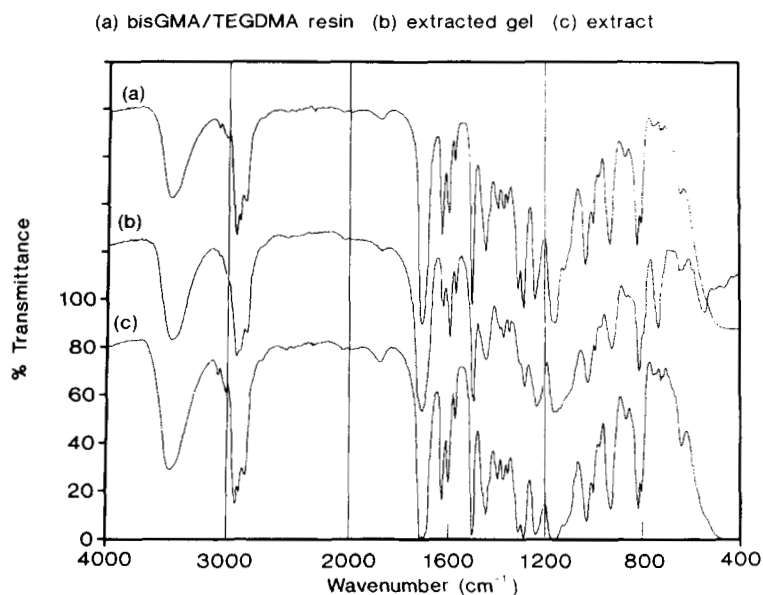(a) bisGMA/TEGDMA resin (b) extracted gel (c) extract

Figure 4 IR spectra of (a) uncured bisGMA/TEGDMA resin IV, and after cure (36% conversion) (b) the gel after extraction with CHCl₃ and (c) the extracted sol.

composition to the original uncured resin. The relative ratios of the aromatic (at 1607 cm⁻¹ from bisGMA) to unsaturation (at 1636 cm⁻¹ from bisGMA and TEGDMA) absorbance suggest that the fraction of TEGDMA in the extract is lower than in the virgin resin, presumably because TEGDMA has greater chain flexibility and hence higher pendant group reactivity than bisGMA. The

gel in partially cured samples also contains a number of pendant methacrylate groups (see Fig. 4) which remain unreacted.

The dependence of the extent of conversion and the sol fraction in dimethacrylate networks on the initiator concentration and the irradiation time is illustrated in Figure 5. According to simple free-radical polymerization kinetic theory,[26] the rate of po-
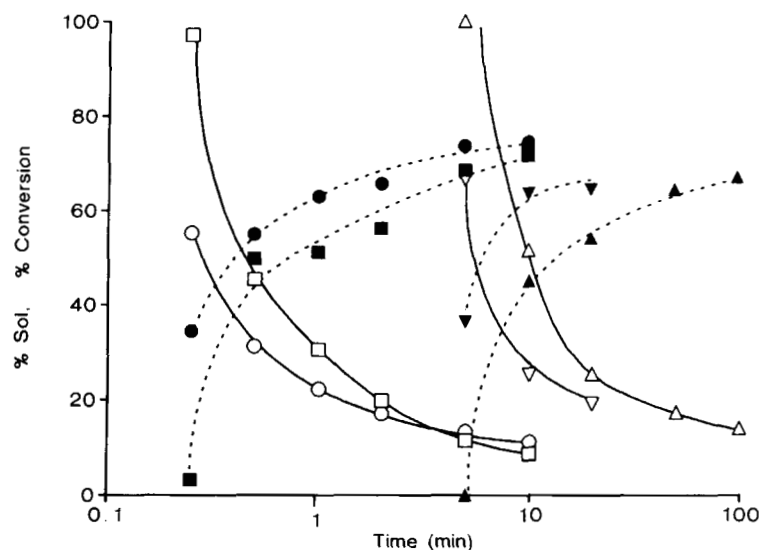

Figure 5 Curing time dependence of the wt % sol (unfilled symbols) and degree of conversion (filled symbols) in unfilled dimethacrylate networks prepared at 23°C (postcured at 45°C) from resins I (□), II (△), III (○), and IV (▽). The initiator concentration in resins II and IV was one-tenth that of resins I and III.
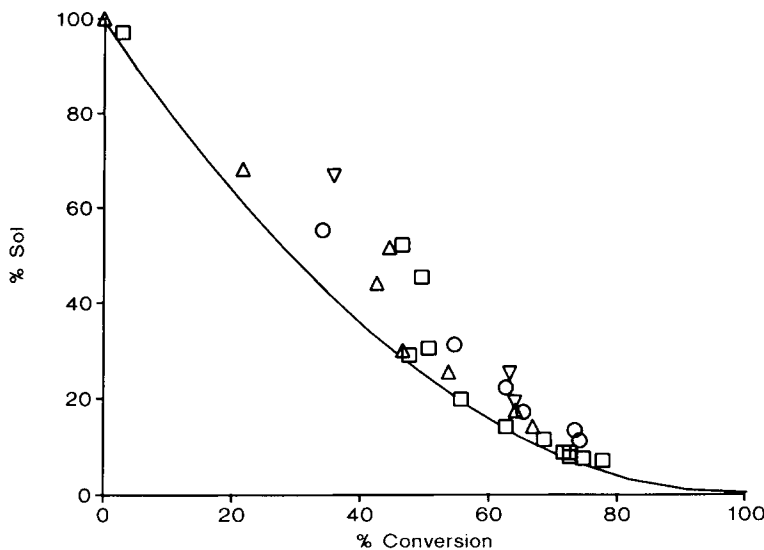
Figure 6   Dependence of wt % sol on the degree of conversion in networks prepared from resins I (□), II (△), III (○), and IV (▽). The prediction of the simple gelation model (see text) is shown by the solid curve.

lymerization is proportional to the square root of the initiator concentration. The data in Figure 5 suggest that the rate has a greater dependency on initiator concentration than that predicted. This is probably due to the presence of the inhibitor in the dimethacrylate matrix: This inhibitor will cause an induction period in the polymerization process, which is inversely proportional to the initiator concentration[26] rather than its square root. Both the degree of cure and the fraction of sol approach a plateau at long exposure times, presumably due to the vitrification effect.[2]

The correlation of the wt % extractable material on the % conversion of the methacrylate groups is shown in Figure 6. It is interesting to note that the experimental data for networks with conversions greater than 50% lie close to that predicted by simple gelation theory[26]: If the probability for the reaction of methacrylate unit is p, then the probability of two unsaturated groups residing on the same molecule is $(1 - p)^2$. The data deviate from this theoretical curve at lower conversions, implying non-random polymerization. This could be caused by the formation of regions of highly crosslinked network in a matrix of less highly polymerized material, or could result if the pendant methacrylate groups were less reactive than those groups on unreacted molecules. Figure 6 thus shows that incompletely cured dimethacrylate resins contain considerable levels of sol which may act as diluents and reduce the fracture properties.

Sol Species and Fracture

The role of monomeric sol species (the most common sol species in chain growth polymerization[26]— see Fig. 4) on the fracture properties can be ascertained by substituting an unreactive analog for a portion of the monomer prior to full cure. Examples of the unreactive analogues of the monomer are EGDBA (cf. EGDMA), TEGDBA (cf. TEGDMA), and DGEBADBA (cf. bisGMA)—see Table I.

Figures 7 and 8 show the influence of substituting the saturated analogues DGEBADBA, EGDBA and TEGDBA for the respective dimethacrylates in the network. These sol analogs exert a significant effect on the fracture toughness and energy and on the flexural strength. Reference to Figures 1 and 6 suggests that the reduction in unreacted dimethacrylate sol is responsible for the improvement in fracture resistance with increasing cure.

Assuming that the sol acts only as a diluent of the network strands and does not influence the mode of formation of the network itself, eqs. (5) and (6) predict that G_c should be proportional to ρ and thus increase linearly with the wt % of network strands (or decrease linearly with the wt % sol) because the terms U, n, and L in eq. (5) are constant. While G_c decreases with increasing sol level (Figs. 7 and 8), a linear relationship is not observed. In fact G_c shows little variation for sol levels less than 25 wt %.

In addition, the data in Figures 7 and 8 cannot be explained in terms of linear viscoelastic energy
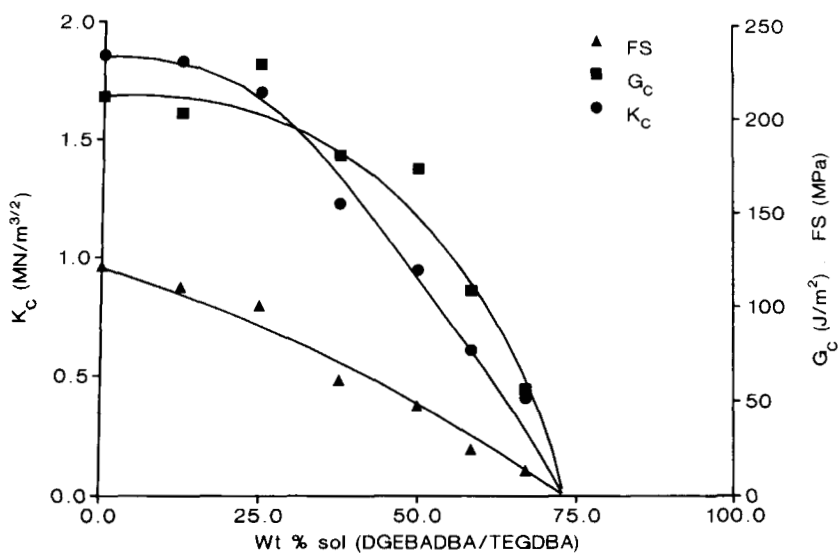
Figure 7   Dependence of fracture toughness K_c (circles), fracture energy G_c (squares) and flexural strength FS (triangles) on wt % sol (the ratio of DGEBADBA : TEGDBA in the sol was 7 : 3) in TEGDMA/TEGDBA/bisGMA/DGEBADBA networks (the ratio of bisGMA : TEGDMA was 7 : 3). The filler level was 75 wt %.

dissipation. In fact, Table II shows that for the diluent series, the rate of stress–relaxation increases rapidly between 12.5 and 37.5 wt % sol, whereas the fracture parameters decrease during and after this region.

CONCLUSIONS

In this work, the effects of crosslinking and sol content on fracture behavior in filled networks have been separated by utilizing nonreactive and chain-
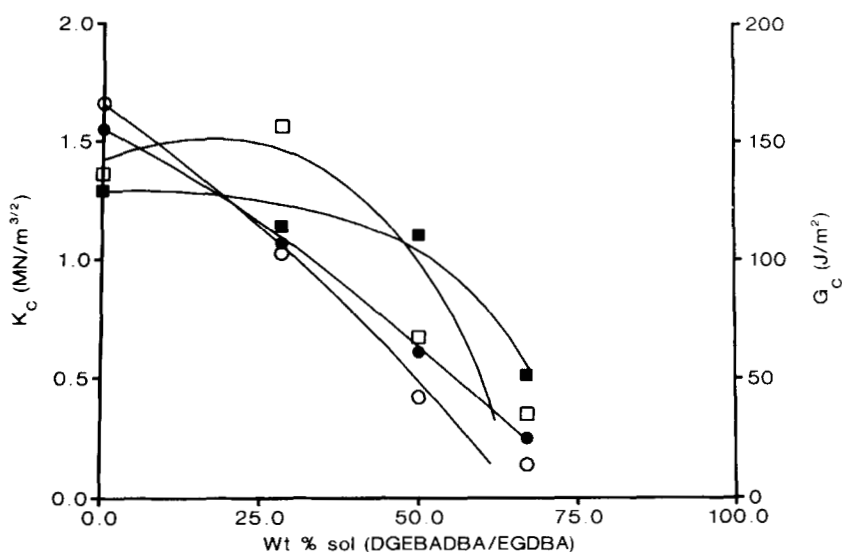

Figure 8   Dependence of fracture toughness K_c (circles) and fracture energy G_c (squares) on wt % sol (ratio of DGEBADBA : EGDBA was 7 : 3) in EGDMA/EGDBA/bisGMA/DGEBADBA (the ratio of bisGMA : EGDMA was 7 : 3) (closed symbols) and in EGDMA/MMA/EGDBA/bisGMA/PGEMA/DGEBADBA (the ratio of EGDMA : MMA : bisGMA: PGEMA was 3 : 3 : 7 : 7) (open symbols) networks. In both series, the filler level was 75 wt % of the total mass.

extending analogues of the network forming species so that variations in chemical composition are minimal. For the systems studied, no common dependency of the fracture properties on crosslink density was observed.

The improvement in fracture resistance obtained by postcuring partially cured networks could not be explained in terms of increased crosslink density or variations in the linear viscoelastic energy dissipation. In fact, for the epoxy resins studied here and by other workers,[9] the dependence of fracture energy on crosslinking is opposite to the influence of postcuring on epoxy resins[3,4] and dimethacrylate networks.

Partially cured dimethacrylate networks contain unreacted dimethacrylate monomer in considerable amounts which may be approximately estimated from simple gelation theory. These species appear to exert the dominant influence on the fracture properties of partially cured dimethacrylate networks.

REFERENCES

1. J. G. Kloosterboer, G. M. M. van de Hei, and H. M. J. Boots, *Polym. Commun.*, **25**, 354 (1984).
2. M. T. Aronhime and J. K. Gillham, *Adv. Polym. Sci.*, **78**, 83 (1986).
3. S. Yamini and R. J. Young, *J. Mater. Sci.*, **14**, 1609 (1979).
4. J. Mijovic and J. A. Koutsky, *Polymer*, **20**, 1095 (1979).
5. W. D. Cook and M. Johannson, *J. Biomed. Mater. Res.*, **21**, 979 (1987).
6. J. A. Manson, S. L. Kim, and L. H. Sperling, Technical Report AFML-TR-76-124, Materials Research Center, Lehigh University, PA, 1976.
7. K. Selby and L. E. Miller, *J. Mater. Sci.*, **10**, 12 (1975).
8. H. R. Brown and I. M. Ward, *J. Mater. Sci.*, **8**, 1365 (1973).
9. J. D. LeMay and F. N. Kelly, *Adv. Polym. Sci.*, **78**, 115 (1986).
10. D. C. Phillips, J. M. Scott, and M. Jones, *J. Mater. Sci.*, **13**, 311 (1978).
11. W. D. Cook, *Eur. Polym. J.*, **14**, 715 (1978).
12. W. D. Cook, D. R. Beech, and M. J. Tyas, *Biomaterials*, **6**, 362 (1985).
13. W. D. Cook and M. Moopnar, *Biomaterials*, **11**, 272 (1990).
14. T. E. Doyle, F. Fekete, P. J. Kernan, and W. J. Plant, U.S. Pat. 3,317,465 (1967).
15. F. E. Critchfield, G. L. Funke, and J. B. Johnson, *Anal. Chem.*, **28**, 76 (1956).
16. K. Yokota, M. Kani, and Y. Ishii, *J. Polym. Sci., A-1*, **6**, 1325 (1968).
17. W. D. Cook and M. P. Chong, *Biomaterials*, **6**, 257 (1985).
18. R. J. Young and P. W. R. Beaumont, *J. Mater. Sci.*, **12**, 684 (1977).
19. G. C. Ives, J. A. Mead, and M. M. Riley, *Handbook of Plastics Test Methods*, CRC Press, London, 1971, p. 147.
20. A. J. Kinloch and R. J. Young, *Fracture Behaviour of Polymers*, Applied Science, London, 1983: (a) p. 93; (b) p. 85, 445–448.
21. J. M. Charlesworth, *J. Macromol. Sci. B Phys.*, **26**, 105 (1987).
22. G. J. Lake and A. G. Thomas, *Proc. Roy. Soc. (Lond.)*, **A300**, 108 (1967).
23. A. G. Evans, S. Williams, and P. W. R. Beaumont, *J. Mater. Sci.*, **20**, 3668 (1985).
24. R. L. Clarke, *Biomaterials*, **10**, 549 (1989).
25. N. G. McCrum, B. E. Read, and G. Williams, *Anelastic and Dielectric effects in Polymeric Solids*, Wiley, New York, 1967.
26. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953.