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The mechanical properties of PMMA and its copolymers with ethyl methacrylate and butyl methacrylate

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The mechanical properties of polymethyl methacrylate and copolymers formed with both ethyl methacrylate and butyl methacrylate were investigated. Six polymers were produced by bulk polymerization, measured for molecular weight and glass transition temperature, T_g and assessed for modulus of elasticity and fracture toughness. Increasing the concentration of ethyl methacrylate or butyl methacrylate resulted in a linear decrease in the glass transition temperature, modulus of elasticity, and fracture toughness. A comparison of testing environments revealed that the modulus of elasticity was reduced when conditioned and tested in water at 37 °C compared to ambient laboratory conditions for all polymers. Similar comparisons of the fracture toughness showed an increase for testing in water at 37 °C; however, this was not significant for the lower T_g compositions. Both modulus of elasticity and fracture toughness were strongly correlated with the glass transition temperature and composition.

1. Introduction

The use of polymethyl methacrylate (PMMA) for various biomedical applications has been widespread. A number of different formulations of PMMA have been employed in dentistry as orthodontic and denture base materials, while the fixation of orthopaedic implants to bone was revolutionized by the introduction of PMMA bone cement as a fixation material [1]. For these applications, PMMA is formed from an initial mixture of the polymer powder and liquid monomer, resulting in a (two-phase) matrix–bead structure upon polymerization.

In view of these load-bearing applications, it is not surprising that a wide range of studies have been published on the mechanical properties of PMMA, addressing essentially all clinically relevant factors. Extensive reviews of this work have been published by Stafford *et al.* [2], Saha and Pal [3], and Krause and Mathis [4]. One dominant concern arising from both laboratory studies and clinical observations has been the "lack of toughness" of PMMA, as it exhibits brittle characteristics upon failure [3, 5].

While PMMA remains the dominant formulation for these applications, other compositions employing higher order methacrylate polymers, either as a copolymer with methylmethacrylate or as a component of the powder or liquid mixture [6, 7], have emerged. As bone cements, the chief attraction to these materials may be attributed to their lower modulus of elasticity, which would appear to offer the advantage of a "smoother" transmission of load across interfaces [8]. Furthermore, it is intuitively reasonable to suggest that such changes may produce a tougher or less brittle material. Despite the apparent advantages of employing these augmented formulations, there appear to be no studies addressing their basic mechanical properties.

The aim of this study was to determine the influence of chemical composition and structure of methacrylate polymers on the mechanical properties most relevant to these load-bearing applications. The materials investigated were polymethyl methacrylate, three methyl–ethyl methacrylate copolymers and two methyl–butyl methacrylate copolymers. To achieve a homogeneous single-phase material free of inclusions and voids, and to eliminate the variables associated with the polymer-bead and monomer-liquid preparations, bulk polymerization techniques were employed. The modulus of elasticity using the three-point bend test and fracture toughness using the compact specimen were examined, both in air at room temperature and, to simulate application conditions, in water at 37 °C.

2. Methods and materials

2.1. Polymer fabrication

Six polymer compositions using different ratios of the monomers methyl methacrylate (MM), ethyl methacrylate (EM), and butyl methacrylate (BM) were considered. Bulk polymerization was undertaken for initial monomer mixtures by volume of 100% MM

(100MM), 75% MM and 25% EM (75MM/25EM), 50% MM and 50% EM (50MM/50EM), 25% MM and 75% EM (25MM/75EM), 75% MM and 25% BM (75MM/25BM), and 50% MM and 50% BM (50MM/50BM).

The monomers with 0.10% benzoyl peroxide were placed into a beaker and heated to 75 °C for approximately 75 min until a pre-polymer syrup was produced. After cooling, the syrup was poured into a shallow metal pan, and a lid was placed (i.e. floated) on the surface of the syrup. This procedure aimed to isolate the mixture from oxygen, while allowing for contraction of the polymer during polymerization. The pan containing the pre-polymer syrup was placed in an oven at 55 °C for 24 h, followed by heating at 100 °C for 24 h. The resulting polymer slabs were removed from the pan after cooling to room temperature.

2.2. Test specimen fabrication and conditioning

Flexural test specimens were produced by cutting the slabs into beams using a band saw, followed by grinding and polishing to final dimensions on a grinding wheel (320 grit paper) under water irrigation. The depth of the specimen was selected based on the criteria of ASTM Standard D790-90 [9]. The depth (2.91 ± 0.20 mm) and width (6.15 ± 0.020 mm) of all specimens were measured at centre span with a micrometer.

The compact specimens used in the determination of fracture toughness were cut from the slabs using a band saw, and ground and polished as above. Holes were drilled to accommodate the loading pins, and a slot was cut with the band saw to form the initial crack. This test specimen, which conformed to ASTM Standard E399-90 [10], is illustrated in Fig. 1. In order to enhance the initiation of a pre-crack, a notch was produced along the slot with a scalpel blade using a constant force of approximately 80 N for 5 s. Fatigue precracking of the specimen was conducted under cyclic loading at a stress intensity factor of 0.5–1.0 MPa m$^{1/2}$ at 3.0 Hz on an Instron 1350 servohydraulic testing machine. Following growth of the pre-crack to a length of 2–3 mm, loading was terminated and the full crack measured with a vernier caliper under (× 10) magnification.

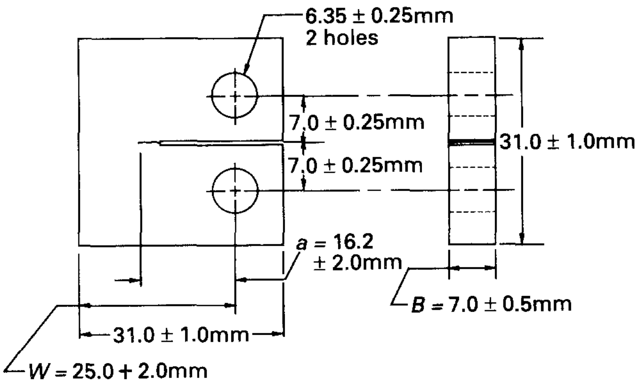

Figure 1 Geometry of the compact specimen used to measure fracture toughness.

All test specimens were conditioned in their testing environments of either room conditions (23 °C) or distilled water (37 °C) for a period of at least 3 weeks prior to the date of testing. For storage and testing in air, the temperature range was 23 ± 2 °C while in water the temperature range was 37 ± 0.5 °C.

2.3. Chemical and physical properties

During the machining of the compact test specimens, shavings of the polymers were isolated for determination of residual monomer and chemical composition. Specimens were analysed for residual monomer using quantification by bromination and iodometric titration with sodium thiosulphate, and the compositions of three samples of each copolymers were determined by pyrolysis and gas chromatography [11]. The glass transition temperatures for each polymer were measured using a thermo-mechanical analyser (Perkin–Elmer TMA7). For molecular weight determinations, one sample of each polymer was dissolved in tetrahydrofuran at 0.1% (wt/vol), and was subject to size exclusion gel permeation chromatography. For detection, a diode array ultraviolet/visible detector (Perkin–Elmer, Model LC35) was used. The molecular weight was determined from the retention time using a calibration curve with a PMMA standard [11].

2.4. Mechanical testing

All mechanical tests were performed on the Instron machine for both conditions, with load and deflection signal output monitored on a strip chart recorder. The specimens tested in water at 37 °C were transferred from the storage container to the testing bath, and allowed to equilibrate at these conditions for a minimum of 5 min.

2.4.1. Measurement of the modulus of elasticity

A three-point load test apparatus with loading and support pins of 7.9 mm diameter, and a span length of 50 mm was used. This apparatus met the specifications of ASTM D790-90 [9]. Loading was imposed at a constant displacement rate of 1.4 mm min^{-1}, corresponding to an outer fibre strain rate of 0.01 min^{-1}. Testing was conducted to a mid-span deflection of 6.25 mm, corresponding to a maximum outer fibre strain of 4.5%. The resulting load–deflection tracing was used to determine the modulus of elasticity. Extraneous deflections as a consequence of machine deflections for this loading configuration (i.e. machine stiffness) were measured independently and determined to be negligible relative to the accuracies of these measurements.

2.4.2. Measurement of fracture toughness

In order to produce tensile loading on the compact specimen, a specialized jig was constructed which

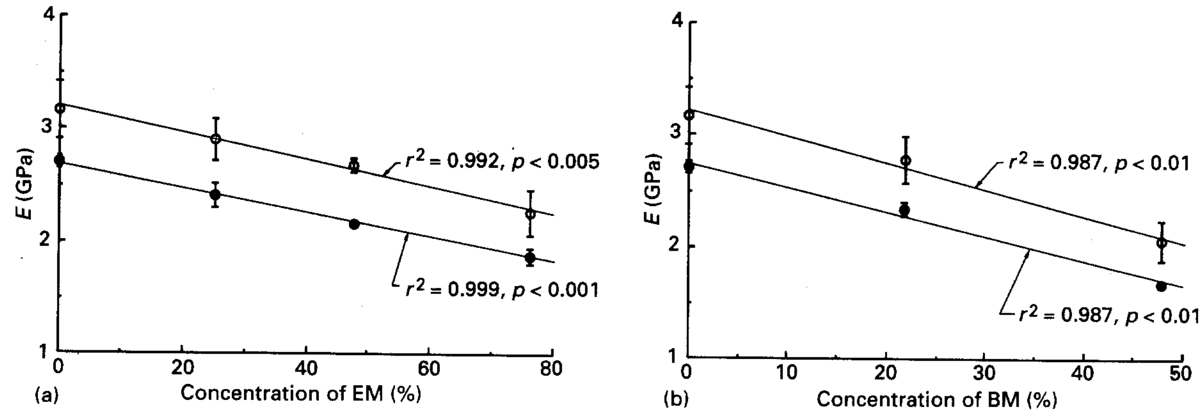

Figure 2 A plot of the modulus of elasticity, E (mean ± 1 standard deviation), versus composition of polymethyl methacrylate (100 MM) and copolymers formed with (a) ethyl methacrylate (EM) and (b) butyl methacrylate (BM) in (○) air at 23 °C, and (●) water at 37 °C. (Standard deviations of E less than 0.05 MPa are not shown.)

TABLE I The composition, molecular weight, MW, and glass transition temperature, T_g, (mean and standard deviation in parentheses, $n = 3$) of the six polymers fabricated

Polymer	Composition (%)			MW($\times 10^6$)	T_g(°C)
	MM	EM	BM		
100MM	100.0	–	–	1.62	114.3 (0.9)
75MM/25EM	75.0	25.0	–	1.69	101.0 (0.7)
50MM/50EM	52.2	47.8	–	2.04	91.3 (1.2)
25MM/75EM	23.9	76.1	–	2.07	79.4 (4.9)
75MM/25BM	78.3	–	21.7	1.59	89.0 (1.5)
50MM/50BM	52.3	–	47.7	2.21	64.8 (0.4)

TABLE II The modulus of elasticity, E, and fracture toughness, K_{IC}, of the six polymers fabricated for conditioning and testing in air at 23 °C and water at 37 °C. The data are given as mean and standard deviation (in parentheses). (E, $n = 5$; K_{IC} in air/23 °C, $n = 3$ except 75MM/25BM where $n = 2$; K_{IC} in water/37 °C, $n = 5$)

Polymer	E (GPa)		K_{IC} (MPa m$^{1/2}$)	
	23 °C/air	37 °C/water	23 °C/air	37 °C/water
100MM	3.18 (0.26)	2.70 (0.05)	1.21 (0.08)	1.76 (0.17)
75MM/25EM	2.91 (0.19)	2.42 (0.11)	1.03 (0.06)	1.45 (0.09)
50MM/50EM	2.68 (0.06)	2.17 (0.04)	0.98 (0.05)	1.24 (0.11)
25MM/75EM	2.27 (0.20)	1.89 (0.07)	0.85 (0.01)	0.98 (0.14)
75MM/25BM	2.79 (0.21)	2.34 (0.06)	0.99 (0.00)	1.10 (0.10)
50MM/50BM	2.08 (0.18)	1.68 (0.05)	0.73 (0.07)	0.75 (0.05)

produced tensile loading via compression of the testing machine. Using this device, alignment of the specimen was less difficult to achieve than when employing a tension loading system, and testing in water was much simplified.

As the fracture toughness is unknown prior to testing, an estimate was made to select appropriate specimen dimensions. Using a yield strength of 37.0 MPa and fracture toughness of 1.50 MPa m$^{1/2}$ for PMMA [12], a minimum specimen width of 4.1 mm was computed, which was thus satisfied by the dimensions of the specimens ($B = 7.0$ mm) used in this study.

Testing of these specimens were conducted at a rate of 2.5 mm min^{-1} until failure occurred. Following testing, all specimens were examined under a ×10 power light microscope to assess the morphology of fracture.

2.5. Statistical methods

Statistical analysis of the six polymer formulations employed the multiple comparison Student–Newman Kuels rank order test. A two-tailed student t-test was also used to compare data between the two testing conditions. Least-square linear regression analyses were performed for the various graphical correlations considered.

3. Results

With the exception of porosity on the surface of the polymer slabs (probably arising due to polymerization contraction), there were no aberrations or defects observed. All test specimens produced subsequent to machining were porosity-free transparent polymers, similar to those produced commercially.

3.1. Chemical and physical properties

The residual monomer of the six polymers were determined to be less than 1.0%. The chemical composition and molecular weights for the various polymers synthesized are given in Table I. The data on composition of the copolymers showed that the original ratios of the monomers used were essentially maintained. The molecular weight values, representing the peak of the distribution of retention times through the column of the chromatograph, demonstrated no clear relationship to composition.

Table I also gives the glass transition temperature, T_g, of the polymers assessed. Increasing the concentration of the ethly methacrylate or butyl methacrylate component in the copolymer resulted in a progressive reduction in T_g ($p < 0.01$).

3.2. Modulus of elasticity

The load–deflection curve of all specimens exhibited an initially linear region (with no discernible toe-in region), followed by yielding. The data for modulus of elasticity, E, determined from this linear portion of the curve are listed in Table II. A plot of composition versus E for both ethyl and butyl series is given in Fig. 2a and b, respectively, for both testing conditions. Statistical comparisons conducted on all data demonstrated a significant difference between PMMA (100MM) and the copolymers ($p < 0.01$). A plot of E versus T_g for both test conditions is given in Fig. 3.

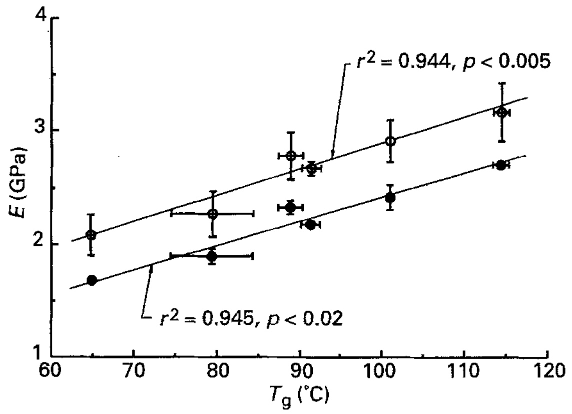

Figure 3 A plot of modulus of elasticity, E, versus glass transition temperature, T_g (mean ± 1 standard deviation) for the six compositions in (○) air at 23 °C, and (●) water at 37 °C. (Standard deviations of E less than 0.05 MPa and of T_g less than 1.0 °C are not shown.)

For all polymers the magnitude of E when stored and tested in water at 37 °C was significantly lower than the value measured in air at 23 °C ($p > 0.01$). Significant differences were also noted in the degree of scatter between the two test conditions. The mean coefficient of variation (standard deviation/mean × 100) was 59.0% less for specimens tested in water at 37 °C ($p > 0.005$).

3.3. Fracture toughness

The load–deflection curve consisted of an initial toe-in region due to settling and tightening of the fixture and grips, followed by a linear curve until fracture. The maximum load was used to determine fracture toughness in accordance with ASTM E399-90 [10]. Examination of the failure sites on the specimens revealed a transverse fracture surface consisting of distinct regions of fatigue pre-cracking and fast fracture. The formation of shear lips was not evident on any specimens.

The data for fracture toughness, K_{IC}, of the various polymers and the two test conditions is given in Table II, and a plot of composition versus fracture toughness for both ethyl and butyl series is given in Fig. 4a and b, respectively. Multiple comparisons conducted on all data demonstrated a significant difference between PMMA (100MM) and all copolymers for both test conditions ($p < 0.01$). A plot of K_{IC} versus T_g is given in Fig. 5.

Storage and testing in water at 37 °C resulted in significant increases in K_{IC} for the PMMA homopolymer ($p < 0.01$) and for two of the methyl–ethyl copolymers (75MM/25EM, $p < 0.01$; 50MM/50EM, $p < 0.01$). This was not, however, significant for the other compositions.

4. Discussion

Almost all biomedical applications of these polymers employ the two-phase system which results from an

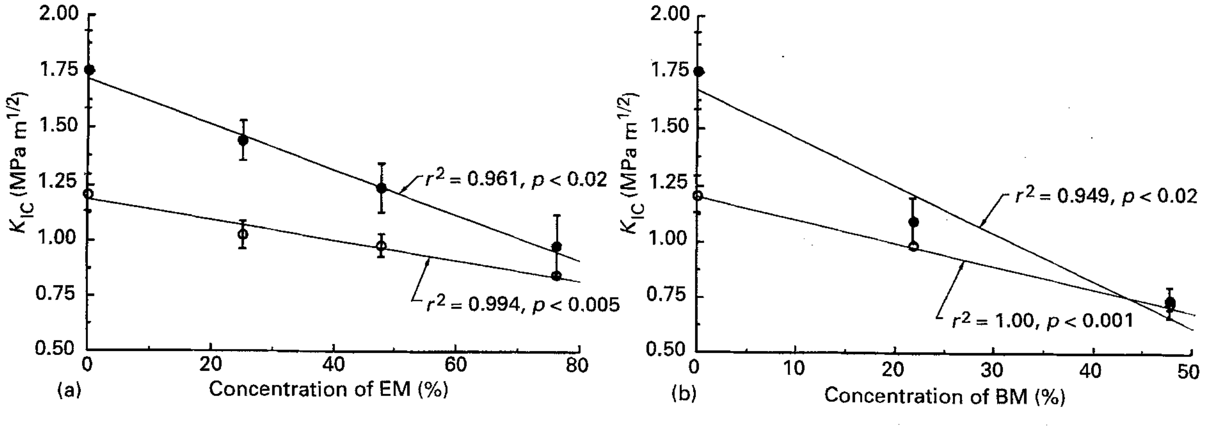

Figure 4 A plot of the fracture toughness, K_{IC} (mean ± 1 standard deviation), versus composition of polymethylmethacrylate (100 MM) and copolymers formed with (a) ethyl methacrylate (EM) and (b) butyl methacrylate (BM) in (○) air at 23 °C, and (●) water at 37 °C. (Standard deviations of K_{IC} less than 0.02 MPa $m^{1/2}$ are not shown.)

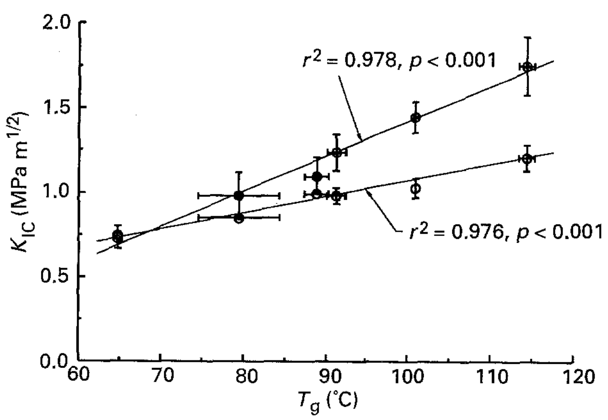

Figure 5 A plot of the fracture toughness, K_{IC}, versus glass transition temperature, T_g (mean ± 1 standard deviation), for the six compositions in (○) air at 23 °C, and (●) water at 37 °C. (Standard deviations of K_{IC} less than 0.02 MPa m$^{1/2}$ and of T_g less than 1.0 °C are not shown.)

initial polymer bead and monomer liquid mixture. However, some problems are associated with the test ing of commercial bone cements and dental polymers. These materials are inhomogeneous, and the structure and degree of porosity may vary depending on the technique employed to form the monomer–polymer bead composition. A further complication is that dental and orthopaedic polymers are not transparent, and thus crack lengths are difficult to measure in any fracture analysis. It would seem important then, from the viewpoint of understanding the relative effect of molecular composition on mechanical properties, to study single-phase polymers or copolymers produced by bulk polymerization. By employing this controlled chemistry, these polymers are free from interference of porosity and other inhomogeneities, variable molecular weight, and polymer bead–matrix interface complications.

Owing to differences in the polymerization processes and microstructures which exist between the two-phase polymer and monomer mixtures to those of the single-phase bulk polymerized material, differences in mechanical properties would not be unexpected. Based on observations of the microstructure of fracture surfaces, Kusy and Turner [13] have reported that two-phase acrylic materials have inferior mechanical properties to the single-phase cast or moulded PMMA. The reduced strength of such systems may also be attributed to the presence of porosity [14]. However, it is not apparent that obvious differences exist between the data of this study and the range of published values for both modulus of elasticity and fracture toughness of the two-phase materials [3].

When methacrylate polymers are formed using a bulk polymerization technique, molecular weights in the range of 10^6 are typically measured [15], consistent with values found in the present investigation. It has been shown that variations in the fracture surface energy due to molecular weight occur at molecular weight values below 10^5, with no apparent effect on properties above this range [16]. It is thus highly unlikely that the differences in physical and mechanical properties observed amongst the various polymers in the present study can be attributed to the marginal differences in this range of molecular weights. Furthermore, there was no apparent relationship between molecular weight and composition.

Glass transition temperature provides basic information which is characteristic of the polymer microstructure, in particular the degree of bonding and the relative mobility between the polymer chains. As expected, strong correlations were found between the glass transition temperature and the fraction of ethylmethacrylate and butylmethacrylate in the copolymers. Increasing the concentrations of these components results in an increase in the number of bulky side groups on the molecular chains, and thus the physical separation (free volume) between adjacent chains is increased, producing a corresponding increase in the mobility between adjacent chains. This can be likened to plasticization, which results in a lowering of the glass transition temperature.

The modulus of elasticity is highly dependent on the degree of molecular mobility at a given stress level. It is reasonable to postulate, therefore, that the relationship observed between modulus of elasticity and composition can be attributed to the increase in free volume which occurs with the number and size of these side groups. The correlations observed between glass transition temperature and the modulus of elasticity would tend to corroborate this theory.

The reduction in modulus when tested in water at 37 °C compared to testing in air at 23 °C was consistent for all polymers examined. At an elevated temperature, the stiffness of the molecular structure would be reduced due to an increase in molecular mobility, while the presence of water acting as a plasticizer may also produce an increase in the mobility of the molecules. The reduction in modulus of elasticity when tested under conditions associated with the physiological environment have been observed in studies on PMMA bone cements [17]. With regard to the impressively low coefficient of variation for specimens tested in water at 37 °C, this may be due to the reduction in the variability of friction between adjacent molecules due to the presence of water molecules which act as a plasticizer.

The lack of published standards for the measurement of fracture toughness of polymers makes it difficult to select a priori the width of the test specimen to ensure plain strain conditions. The specimen width was based upon preliminary calculations using values from the literature for fracture toughness and yield strength in accordance with ASTM E399-90 [10]. Because slanted fracture surfaces or "shear lips" were not observed on the periphery of the fracture surface, it would appear that plane strain conditions were dominant. The crack to width ratio, a/W, of the majority of specimens were within the range 0.45–0.55, as recommended in ASTM E399-90 [10]. With respect to specimens with dimensions falling outside this tolerance, it is anticipated that inaccurate results would not have resulted [12, 18].

Owing to the complexities of the deformation and fracture processes in polymers, it is difficult to ascribe to one mechanism the reduction in fracture toughness which occurred progressively with increasing concentrations of ethyl methacrylate or butyl methacrylate, and it is possible that a number of mechanisms may be synergistically operating. On the molecular basis, the strength and fracture of polymers are influenced not only by the chemical structure of the chain, but also by the characteristics of the supramolecular structure, as fracture is a complex combination of chemical and inter-molecular bond failure. Assuming that the strength of the polymer is proportional to the number of covalent bonds broken per unit cross-section multiplied by the maximum value of the "quasi-elastic" force of the chemical bond, molecules with large effective cross-sectional areas would tend to exhibit a lower strength than those with smaller cross-sectional areas. This is consistent with the data of this study, because the effective cross-sectional areas of the copolymers would increase with the increase in fraction of ethyl methacrylate or butyl methacrylate.

With respect to the critical stresses generated in the zone of the crack tip, the characteristics of these polymers would tend to produce an opposite effect. With the increasing fraction of ethylmethacrylate or butylmethacrylate incorporated into the copolymer, yielding occurs at a lower stress resulting in an increase in the size of the plastic zone at the crack tip. Therefore similar far-field stress levels (i.e. similar magnitudes of load on the specimen), the increased size of the plastic zone would produce a lowering of the effective stress intensity factor. This "blunting" at the crack tip with reduced yield strength is desirable, and tends to improve the toughness of the material. The results of these experiments, however, suggest that an increase in toughness due to this process was not apparent for these polymers, and that failure was dominated by the reduction in strength.

Testing in water at 37 °C resulted in an increase in the fracture toughness in some compositions; however, this was not observed on the copolymers with higher fractions of ethylmethacrylate or butylmethacrylate. With respect to the influence of water, one possible explanation of this relationship is that the presence of water molecules in the inter-molecular spaces reduces frictional and inter-molecular forces between adjacent chains, resulting in an increase in the degree of yielding and thus an increase in the radius of the plastic zone at the crack tip. This increases the absorbed energy, effectively increasing the fracture toughness. In a related fashion, elevated temperatures will result in an increase in mobility amongst the molecular chains (as described previously), resulting in a higher degree of plasticity at the crack tip. However, as the distance between the molecular chains is increased with higher concentrations of ethyl methacrylate or butyl methacrylate, the influence of these environmental variables would become less pronounced. It is possible that the degree of water sorption differed amongst these polymers, and this alone may have produced the results observed. The increase in fracture toughness when tested and stored at physiological conditions has been observed in other studies on PMMA bone cements [19].

The selection of materials in this study was aimed to examine the properties of hard polymers, or strictly speaking, polymers in the glassy state. It is clear that polymers above their glass transition temperature behave very differently mechanically, and the traditional fracture toughness test is probably invalid. In order to maintain all polymers in the sufficiently glassy regime, no attempt was made to fabricate copolymers with higher concentrations of ethyl methacrylate or butyl methacrylate. However, if the range of ethyl methacrylate copolymers assessed had been extended beyond 75% ethyl methacrylate –25% methylmethacrylate, it is anticipated that measurements of the modulus of elasticity very similar to those obtained by extrapolation of the data would have been obtained. This was substantiated to some extent by extrapolating the correlation line of modulus of elasticity versus composition for methyl/ethyl methacrylate compositions (Fig. 2a) for the tests in air at 23 °C. The modulus of elasticity predicted for (100%) polyethyl methacrylate using this method was determined to be 2.02 GPa, which is in exact agreement with published data generated from uniaxial tests on the same composition [20]. However, a similar extrapolation of the methyl/butyl methacrylate data (Fig. 2a) yielded a modulus of elasticity of 0.68 GPa for polybutylmethacrylate, which compares less favourably with the published value of 0.57 GPa [20]. This discrepancy is, in all likelihood, due to the proximity of the glass transition temperature of these materials to the testing temperature. With respect to testing at 37 °C, it is highly likely that this method of extrapolation would be invalid for butyl methacrylate, because this material has a glass transition temperature of approximately 33 °C [21]. This would imply that an inflection in the relationship between modulus of elasticity and composition would occur at the composition associated with a glass transition temperature in the range of 37 °C.

Cement systems formed from the monomer and polymer powder with different compositions are composite bead–matrix systems, and thus differ structurally from the materials investigated in this study. Strictly speaking, the results of this study apply only to the monophasic structures and it may be unreasonable to speculate on the properties of these biphasic cement systems. It would appear, however, that employment of these higher order methacrylates (i.e. ethyl methacrylate and butyl methacrylate) as either the bead or matrix component of the structure would not produce a tougher material as assessed by the testing protocol of this study.

With respect to the design of polymer systems for biomedical applications, it is apparent that incorporation of these higher order components into the methacrylate structure will produce a material with a lower modulus of elasticity and fracture toughness. Considering the reduction in modulus of elasticity alone, it is perhaps reasonable to conclude that the use of these materials would be beneficial as they tend to reduce the magnitudes of peak stresses in, for example, the cement layer of the femoral hip replacement structure [8]. It would not appear, however, that these materials are efficacious from the viewpoint of mechanical strength as measured by fracture toughness. It should also be noted that other factors such as creep and fatigue crack propogation rates would also seem relevant with regard to these applications, and a full assessment would likely employ a suitable laboratory model.

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