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Fracture toughness of tooth acrylics

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The hardness, fracture toughness, toughness, flexural strength and Young's moduli of three acrylic tooth polymers were investigated. The first polymer was based on a conventional homopolymer poly(methylmethacrylate). The second was based on cross-linked poly(methylmethacrylate) with an uncross-linked poly(methylmethacrylate) coating. The third material was based on an interpenetrating polymer network (IPN) of a cross-linked and uncross-linked poly(methylmethacrylate).

All three polymers had similar hardness values. The cross-linked and IPN polymers had higher fracture toughness (K_{IC}) and toughness (G_{IC}) values than the conventional homopolymer poly(methylmethacrylate) polymer and lower flexural strengths (σ_f). The toughness of the cross-linked and IPN polymers was higher due to crack deflection around the polymer bead structure and the polymer beads acting as crack pinning sites.

Introduction

Acrylic teeth used in the production of dentures are produced through a dough molding process. Poly(methylmethacrylate) (PMMA) suspension polymerized beads are mixed with methylmethacrylate monomer and a cross-linking agent, allowed to dough then compression molded into teeth. Ethylene glycol dimethacrylate (EGDM) is currently one of the cross-linking agents used in the production of acrylic teeth. The EGDM only produces a small increase in hardness, but is very important in improving the resistance of the material to crazing and environmental stress cracking. PMMA is used for acrylic teeth because of its good optical properties, excellent resistance to environmental degradation and because it is one of the hardest thermoplastic available. Acrylic teeth have excellent aesthetic properties and are compatible with the acrylic resins used for the denture base and bond well to the denture base by forming an interpenetrating polymer network. However acrylic teeth are prone to wear, delamination and chipping of the incisal edges. Abrasive wear is likely to be determined by a combination of hardness and fracture toughness. Khroshchov [1] related wear to indentation hardness. Ratner and Lancaster [2, 3] both related wear rate to the work of deformation, whilst Wilman [4, 5] found that wear was related to brittle fracture. In order to improve the wear resistance of acrylic teeth the hardness and fracture toughness must be improved. The related denture base polymers and bone cements have been studied extensively in the literature, however acrylic tooth polymers have not been studied at all.

In recent years, a number of new acrylic tooth polymers have been developed for the production of acrylic teeth. The objective of this study was to investigate the hardness, fracture toughness of two of these new acrylic tooth polymers and a conventional tooth acrylic.

The conventional tooth acrylic polymer is a suspension polymerized poly(methyl methacrylate). The cross-linked polymer bead is also suspension polymerized, but has a cross-linked center and an uncross-linked outer surface.

The third polymer is an interpenetrating polymer network of a cross-linked poly(methylmethacrylate) and a uncross-linked poly(methylmethacrylate). In this latter polymer, it is important to note that there are no covalent bonds between the two polymers.

Experimental

Materials

Three polymers were tested: a conventional tooth acrylic (D150FC) a tooth acrylic based on a cross-linked bead polymer (TS1352) and a tooth acrylic based on an interpenetrating polymer network (TS1554). The conventional tooth acrylic was obtained from Makevale Ltd Valley House, Marsh Lane, Ware, Herts SG12 9QP UK, whilst the cross-linked and IPN polymers were obtained from Bonar Polymers (Newton Aycliffe, Co. Durham, UK).

The methylmethacrylate monomer was obtained from ICI (Welwyn Garden City, Herts, UK) and the cross-

linking agent, ethylene glycol dimethacrylate (EGDM) from BDH (Poole, Dorset, UK).

Specimen fabrication

The methods used for fabrication of the test specimens closely simulated those used in commercial tooth production. The conditions used for the production of the test specimens were those specified by the manufacturers, including polymer powder to monomer ratio. The percentage of cross-linking agent EGDM in the methylmethacrylate was 5% v/v. The samples were compression molded and the standard cure cycle was 8 min at 130 °C under pressure followed by 8 min cooling under pressure. A final cure of 60 min at 90 °C in an oven was used to ensure a negligible residual monomer content in the samples.

The recommended cure cycle for the IPN material was slightly different from the standard cure cycle given above which recommended a cure for 4 min at 137 °C with no cooling cycle and no further heat treatment. In the case of the cross-linked bead polymer the manufacturer recommended that a 20 : 1 ratio of conventional beads to the cross-linked beads should be used. However, in this study the proportion of cross-linked beads used ranged from 0–40% by weight of the total. The 0% cross-linked bead polymer is also the conventional tooth acrylic material.

Hardness

A Leco Vickers micro-indentation hardness tester, with a Beuhler imaging analysis computer interface was used for determination of hardness. The length of the diagonal indent was measured after applying a fixed load and the Vicker's hardness number calculated. Ten indentations were performed for each material.

Double torsion test

The double torsion (DT) test was selected because of its many advantages. For example the specimens are easy to manufacture and blunt cracks can readily be detected. The test is a linear compliance one and the crack length is not required for the calculation of the fracture toughness. In addition for stable crack propagation the crack propagates at constant load down the specimen. Finally, after fracturing, the large DT specimens can be cut down to make three-point bend specimens, making economical use of materials and resources.

The test method has been described previously [6]. DT specimens $50 \times 95 \times 3.0\,\text{mm}^3$, were produced in the form of rectangular plates. A sharp groove 0.5 mm deep was cut down the center of the specimen. A fine slot was cut at one end of the specimen, using a diamond wafer blade.

The DT test was performed using and Instron electromechanical testing machine (Instron, High Wycombe, Bucks, UK). During the test, the specimen was supported on two parallel rollers of 3 mm diameter and spaced 40 mm apart and load applied at a constant rate ($0.5\,\text{mm}\,\text{min}^{-1}$) to the slotted end via two 3 mm diameter ball bearings spaced 10 mm apart. The specimen was therefore subjected to four-point bend loading, during which the crack initiated and propagated, along the center of the specimen, within the groove. The test was carried out in air at 19 ± 2 °C. The groove depth was chosen to eliminate the need for crack shape corrections [7].

In a DT test the mode I stress intensity factor K_1 is independent of crack length and is given by [8]:

$$K_1 = P_c W_m \left(\frac{3(1+\nu)}{W t^3 t_n} \right)^{1/2}$$

where W_m is the moment arm, W the specimen width, t the specimen thickness, t_n is the thickness in the crack plate and ν Poisson's ratio (assumed to be 0.33). Values for K_1, the fracture toughness, were obtained by substituting the appropriate specimen dimensions along with the load at fracture P_c into the above equation. Three values were taken for each specimen and three specimens were tested.

The flexural test

Immediately after testing the DT specimens, the broken halves were cut up into three-point bend specimens, measuring $3.0 \times 3.5 \times 30\,\text{mm}^3$. The test and method are based on ASTMS D790-1 [9]. In a three-point bend specimen the relationship between the applied load (P) and the deflection at the center of the specimen (δ) for a specimen of rectangular cross-section is given by:

$$P = \frac{4\delta E b t^3}{s^3}$$

where t is the beam thickness, b the beam width and s the span. A span of 50 mm was used, with a crosshead displacement rate of $1.4\,\text{mm}\,\text{min}^{-1}$. This gives an almost identical strain rate to that used in the DT tests. All tests were carried out in tap water at 37 ± 2 °C. The Young's modulus was calculated from the initial slope of the load deflection plot. The un-notched fracture strength is defined by:

$$\sigma_f = \frac{3Ps}{2bt^2}$$

Six specimens were tested for each test condition. Any specimens that were not visually flaw free were discarded prior to testing.

Calculation of the strain energy release rate (G_1) from DT specimens

The strain energy release rate was calculated assuming that pure linear elastic fracture mechanics apply using the following expression

$$G_1 = \frac{K_1^2(1-\nu^2)}{E}$$

Calculation of the inherent Griffith flaw size

The inherent Griffith flaw size was calculated from:

$$a^* = [K_{IC}/1.93^* \sigma_f]^2$$

Y is a geometrical calibration factor equal to 1.93 for a single edge notched beam specimen in the absence of a

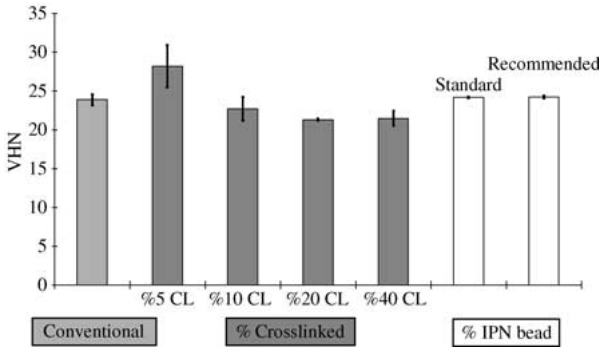

Figure 1 Hardness values for conventional, cross-linked and IPN acrylics.

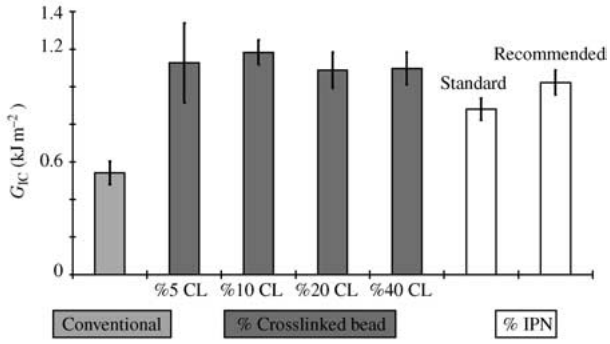

Figure 3 Critical strain energy release rate values for conventional, cross-linked and IPN acrylics.

crack. The a^* value is a measure of the size of the largest flaw present which causes failure

Scanning electron microscopy

Scanning electron microscopy was carried out on the fracture surfaces from DT specimens in order to identify the fracture path and the fracture mechanisms. The fracture surfaces were sputter coated with gold prior to examination and viewed using secondary electrons using a JEOL JSM 840 Scanning Electron Microscope with an accelerating voltage of 15 kV and a working distance of 20–25 mm.

Results and discussion

The results of the hardness tests are shown in Fig. 1. The hardness values vary between 23 and 25 VHN. The error bars shown are equal to twice the standard deviation. The results show no significant increase in hardness for either the cross-linked bead polymers, or the interpenetrating polymer network polymers compared to the conventional tooth acrylic. This is probably a result of a low level of cross-linking in the cross-linked bead and IPN materials.

The fracture toughness results are shown in Fig. 2. The fracture toughness results for the conventional poly (methylmethacrylate) homopolymer are comparable to conventional heat cured denture base polymers [6] measured using the double torsion test. For example Hill *et al*. [6] obtained fracture toughness values in the range 1.29–1.51 MPa $\sqrt{m}$. The cross-linked bead polymers and the interpenetrating polymer network polymer all have significantly higher fracture toughness values than the conventional bead polymer. The values range from 1.7 to 1.9 MPa $\sqrt{m}$.

Incorporating 5% of the cross-linked bead polymer increased the fracture toughness from 1.28 MPa $\sqrt{m}$ to 1.8 MPa $\sqrt{m}$. On raising the proportion of cross-linked bead polymer to 10% the fracture toughness increased to about 1.9 MPa $\sqrt{m}$. Increasing the proportion of cross-linked bead polymer above 10% did not result in any further increase in fracture toughness. The recommended cure cycle for the IPN material resulted in a slight higher fracture toughness values compared to the standard cure.

The critical strain energy release rate or toughness values for the three materials are given in Fig. 3. The conventional bead polymer had a toughness of about 500 Jm^{-2} comparable to that of homogenous cast sheet acrylic. The strain energy release rate, or toughness of the cross-linked bead polymers and IPN bead polymer materials were all about twice those of the conventional bead polymer.

The Young's moduli values are given in Table I. The Young's moduli of all three materials are approximately 2.5–3.0 GPa. The Young's moduli are all comparable to

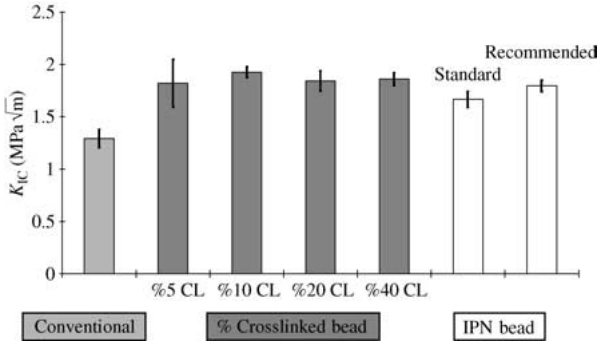

Figure 2 Fracture toughness values for conventional, cross-linked and IPN acrylics.

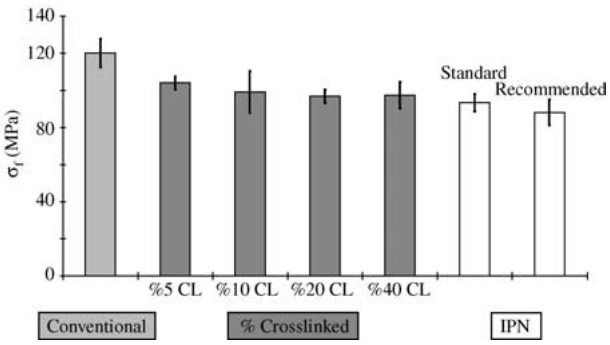

Figure 4 Un-notched fracture strength values for conventional, cross-linked and IPN acrylics.

TABLE I Young's moduli values

Polymer	E (MPa)	SD ($n = 6$)
Conventional (D150FC)	2970	265
5% cross-linked	2501	258
10% cross-linked	2942	203
20% cross-linked	2922	397
40% cross-linked	2850	306
IPN standard cure	2904	188
IPN recommended cure	2854	201

the moduli found for heat cured denture base acrylics tested under identical conditions [6] The un-notched fracture/flexural strength values are shown in Fig. 4. The strength of the conventional poly(methylmethacrylate) polymer is approximately 120 MPa significantly higher than the cross-linked or IPN polymers which have strengths in the range 90–105 MPa.

Fractography

Scanning electron micrographs of the fracture surfaces of the double torsion specimens are shown in Figs. 5 and 6. The fracture surfaces are markedly different. In the case of the conventional bead polymer the fracture surface is relatively smooth (Fig. 5) and there is no obvious bead structure present. The fracture surface is very similar to those found for heat cured denture base and to homogenous cast sheet acrylic. Fracture appears to have taken place both through the matrix and bead phases. This suggests that the conventional acrylic is fairly homogenous and that the original polymer beads have dissolved almost completely into the monomer prior to polymerization. In contrast in the cross-linked (Fig. 6) and the IPN materials (Fig. 7) the original polymer beads are clearly exposed on the fracture surface. Crack propagation has taken place through the matrix and in many cases through the bead–matrix interface of the larger beads, rather than through the bead phase. Beaumont and Young [12, 13] also found evidence of exposed beads on the fracture surface of Simplex bone cement. There is also some evidence of the bead phase acting as crack pinning points, causing the crack front to bow out between the beads, resulting in steps on the fracture surface. This is most obvious where debonding between the matrix and the bead phase has occurred and this is expected as a requirement for the crack pinning mechanism of toughening is a poor particle–matrix bond strength [10, 11]. The fracture toughness and toughness are greatest for the IPN and cross-linked bead polymers. Much of the increased toughness, probably arises from the crack pinning process and the fact that much more fracture surface being produced as a result of cracks being deviated around the bead structure.

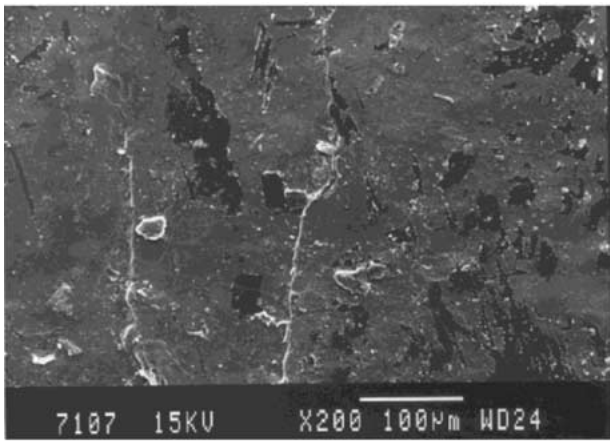

Figure 5 Fracture surface of the conventional tooth acrylic. Note the relatively smooth fracture surface and the absence of any exposed beads.

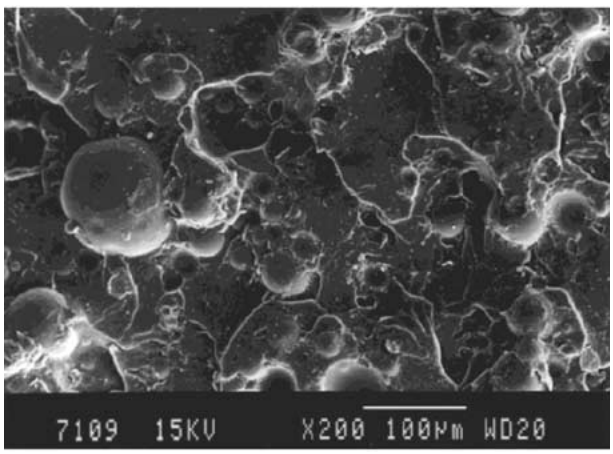

Figure 6 Fracture surface of the cross-linked bead polymer containing 40% of the cross-linked bead polymer. Note the exposed beads in the fracture surface.

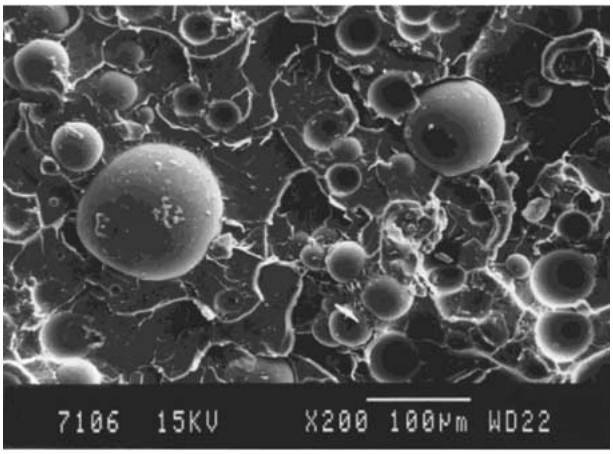

Figure 7 Fracture surface of the IPN polymer. Note the exposed beads in the fracture surface.

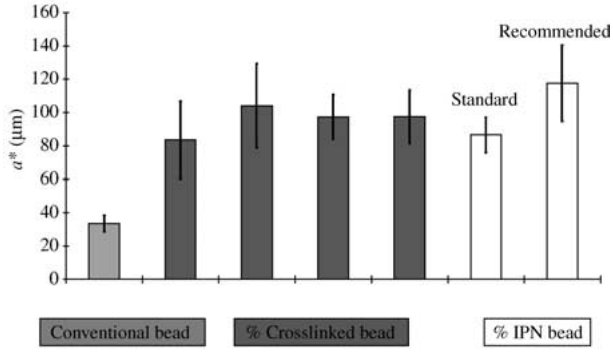

Figure 8 Calculated inherent Griffith flaw sizes.

The calculated inherent Griffith flaw sizes (Fig. 8) are largest for the IPN and cross-linked bead polymers and are approximately 100 µm, comparable to the size of the largest beads observed on the fracture surface of both materials. This suggests that the weak bead–matrix interface may result in the beads acting as Griffith Flaws and acting to reduce the flexural strength. However, at the same time the weak bead–matrix interface serves to increase the toughness.

Beaumont and Young [12, 13] proposed that the higher fracture toughness they obtained for Simplex acrylic bone cement compared to homogenous cast sheet acrylic was a result of the two phase nature of the bone cement

and the crack deflection processes that occurred as a result of a weak bead–matrix interface. Hill *et al*. [4] observed exposed beads only on the fracture toughness of cold cured denture base acrylics and not on the fracture surfaces of heat cured acrylics. This observation was attributed to the limited time available to form a homogenous interpenetrating polymer network, between the bead and the matrix with the cold cured acrylics. The fact that crack propagation takes place preferentially at the bead matrix interface in the cross-linked and IPN polymers may be a result of the failure of the bead phase to dissolve in these materials, as a result of being cross-linked, resulting a much more heterogenous microstructure. The Simplex bone cement studied by Beaumont and Young consists of a mixture of two bead polymers one of which is a homopolymer poly(methylmethacrylate) the other is a copolymer of methylmethacrylate and styrene. The styrene present will cause the copolymer beads to become partially cross-linked on gamma irradiation during sterilization. It is possible the beads exposed on the fracture surface of Simplex are the cross-linked methylmethacrylate–styrene copolymer, which have failed to dissolve.

Conclusions

The cross-linked bead polymer and the IPN polymer both have increased fracture toughness and toughness compared to the conventional bead polymer. The increased fracture toughness and toughness would be expected to give these materials increased resistance to edge chipping and improved wear resistance, compared to conventional tooth acrylics.

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