CHAPTER 4: MATERIALS TESTED

4.1 DENTURE BASE POLYMERS

The denture base polymers chosen for this section of the investigation are listed in Table 4.1. The linear PMMA and the rubber-methacrylate graft copolymers were commercially available materials supplied in the form of powder and liquid, and were processed following normal dental methods. The polysulphone was supplied in the form of oversized blanks, injection moulded by the Japanese supplier; although commercially available in Japan, it is not at present on the Australian market.

4.2 EXPERIMENTAL CROSS-LINKED POLY(METHYL METHACRYLATE)

A selection of cross-linking agents with chains of various lengths and various flexibilities was chosen for this section of the investigation; they are listed in Table 4.2 with their structural formulae.

DVB was chosen to provide an extreme case, as the \( m \)-phenylene group would provide a short and very stiff cross-link. The hydrocarbon adducts 1,6-hexamethylene glycol dimethacrylate (1,6-HMGDMA) and 1,10-DMGDMA provide cross-linking chains with backbones made up essentially of a series of carbon atoms, apart from the two oxygen atoms near each end. The chains are 10 and 14 atoms long respectively.
<table>
<thead>
<tr>
<th>Product</th>
<th>Batch Number</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear Poly(methyl methacrylate)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Durodent</td>
<td></td>
<td>Dental Products, Victoria, Australia.</td>
</tr>
<tr>
<td>Rubber-Methacrylate Graft Copolymers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. Hircoe</td>
<td>(P)(^1) 090275*</td>
<td>Coe Laboratories, Inc., Chicago, U.S.A.</td>
</tr>
<tr>
<td></td>
<td>(P)(^2) 010176</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(L) 100175</td>
<td></td>
</tr>
<tr>
<td>3. Impact 76</td>
<td>(P) 01072</td>
<td>Sybron-Kerr, Michigan, U.S.A.</td>
</tr>
<tr>
<td></td>
<td>(L) 91347</td>
<td></td>
</tr>
<tr>
<td>4. Lucitone 199</td>
<td>(P) 013181</td>
<td>L.D. Caulk Co., Delaware, U.S.A.</td>
</tr>
<tr>
<td></td>
<td>(L) 011981</td>
<td></td>
</tr>
<tr>
<td>5. GC Luxon</td>
<td>(P) 251211</td>
<td>G-C Dental Industrial Corp., Japan.</td>
</tr>
<tr>
<td></td>
<td>(L) 101011</td>
<td></td>
</tr>
<tr>
<td>Polysulphone</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Two samples of powder were used.
<table>
<thead>
<tr>
<th>Cross-linking Monomer</th>
<th>Abbreviation</th>
<th>Chemical Structure</th>
<th>Batch Number</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Divinylbenzene</td>
<td>DVB</td>
<td><img src="image1" alt="Chemical Structure" /></td>
<td>00807</td>
<td>1</td>
</tr>
<tr>
<td>2. 1,6-Hexamethylene Glycol</td>
<td>1,6-HMOSMA</td>
<td><img src="image2" alt="Chemical Structure" /></td>
<td>GNA 009</td>
<td>2</td>
</tr>
<tr>
<td>Dimethacrylate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. 1,10-Decamethylene Glycol</td>
<td>1,10-DMSMA</td>
<td><img src="image3" alt="Chemical Structure" /></td>
<td>276-34</td>
<td>2</td>
</tr>
<tr>
<td>Dimethacrylate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4. Ethylene Glycol</td>
<td>EGMA</td>
<td><img src="image4" alt="Chemical Structure" /></td>
<td>GRE 298</td>
<td>2</td>
</tr>
<tr>
<td>Dimethacrylate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5. Tetraethylene Glycol</td>
<td>TEGMA</td>
<td><img src="image5" alt="Chemical Structure" /></td>
<td>GNF 390</td>
<td>2</td>
</tr>
<tr>
<td>Dimethacrylate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6. Polyethylene Glycol 600</td>
<td>PEG 600 DMA</td>
<td><img src="image6" alt="Chemical Structure" /></td>
<td>GRG 398</td>
<td>2</td>
</tr>
<tr>
<td>Dimethacrylate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7. Ethoxylated Bisphenol A</td>
<td>EBADMA</td>
<td><img src="image7" alt="Chemical Structure" /></td>
<td>GNG 443</td>
<td>2</td>
</tr>
<tr>
<td>Dimethacrylate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8. Trimethylolpropane</td>
<td>TMPTMA</td>
<td><img src="image8" alt="Chemical Structure" /></td>
<td>GNM 501</td>
<td>2</td>
</tr>
<tr>
<td>Trimethacrylate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1 Polysciences Inc., Warrington, U.S.A.
2 Sartomer Co., West Chester, U.S.A.
The ethylene oxide adducts EGDMA, TEGDMA and PEG 600 DMA form a series in which the cross-link contains one, four and an average of 13 -C-C-O- units respectively. A specific composition cannot be given for PEG 600 DMA as it is a mixture of monomers of various molecular weights, with an average of 754 (Dulik et al., 1981). The presence of an oxygen atom at every third site in the cross-linking chain would increase its flexibility.

EBADMA is based on the bisphenol A structure, and so is related to Bis-GMA (Cowperthwaite et al., 1980). It was included in this study because the presence of two p-phenylene groups in the cross-linking chain would stiffen it considerably.

Finally, TMPTMA was chosen because, as it is a trifunctional monomer, it would contribute to the formation of a close three-dimensional network structure.
CHAPTER 5: EXPERIMENTAL METHODS

5.1 SPECIMEN PREPARATION

5.1.1 Denture Base Polymers

Specimens of the four rubber-methacrylate graft copolymers and the linear PMMA denture base polymer were made following normal dental methods. Oversized patterns (square section prisms 10 mm x 10 mm x 60 mm) were made by casting molten wax into silicone rubber moulds, and these were invested in dental flasks in groups of three, using cast gypsum as a mould material. A new set of plaster moulds was made for each set of specimens.

All specimens were prepared from a dough mixed in the proportion 2.4 powder:1 liquid by mass. Durodent specimens were processed in a water bath at 70 ± 2°C for 18 hours, before slow cooling to room temperature. The four rubber-methacrylate graft copolymers were heat-cured in the manner specified by the manufacturers. In all cases this required heating in a water bath from room temperature to 74 ± 2°C, holding at that temperature for 1.5 hours, and further heating at 100°C for 0.5 hours, followed by slow bench cooling.

The polysulphone was supplied in the form of injection-moulded oversize blanks by the Japanese supplier. Injection moulding involved melt temperatures in the range 335-400°C and injection by hydraulic pressure, using a
computer-controlled injection moulding machine developed by the supplier of the polysulphone.

With all materials, the blanks were machined to correct specimen size, square section prisms 8 mm x 8 mm x 55 mm, following the recommendations in ISO 2818 (International Standards Organisation, 1980). A hand-operated machine was supplied with the Hounsfield Plastics Impact Tester, for cutting notches in the 5/16 in. specimens the machine was intended to test. This cut a V-notch, depth 1/8 in., radius of notch 0.010 in., included angle 45°, across the midpoint of one face. This machine was modified to fit the 8 mm square specimens produced for this section of the experiments, but this notch did not comply with the notches specified in ISO 179 (International Standards Organisation, 1982). Because the cutter followed a circular path relative to the specimen, the notch was not of uniform depth along its length, reaching its normal 1/8 in. only at the midpoint. Therefore specimens were notched in a milling machine using a flycutter ground to the correct profile to comply with the dimensions for a type B Charpy notch given in ISO 179: depth 2 mm, radius of tip 0.25 mm, included angle 45°. (Fig. 5.1)

Machined specimens were rubbed down on successively finer grades of wet silicon carbide paper to 1200A, before light surface polishing with pumice slurry on a cloth wheel. This polishing removed surface irregularities from specimen machining which in early experiments were found to act as stress-raisers during fracture. (Fig. 5.2)
Dimensions are in millimetres unless otherwise stated.

**FIG. 5.1** DIMENSIONS OF A TYPE B CHARPY NOTCH AS GIVEN IN INTERNATIONAL STANDARD ISO 179.
FIG. 5.2  IRREGULARITIES ON THE SURFACES OF SPECIMENS BEFORE POLISHING, WHICH IN EARLY EXPERIMENTS WERE FOUND TO ACT AS STRESS-RAISERS DURING FRACTURE.
Specimens were then conditioned to constant mass in distilled water at 37 ± 1°C before testing. At least 10 specimens were tested at that time, and at least 10 more after storage under the same conditions for a further 12 months.

5.1.2 Experimental Cross-linked Poly(methyl methacrylate)

In early experiments in this section of the research, the wax patterns were invested in a thin layer of silicone rubber 1 to 1.5 mm thick, with the remainder of the flask filled with plaster, so that the moulds could be reused. However, difficulties were encountered at the packing stage, as the rubber prevented development of an adequate packing pressure. When specimens from these moulds were deflasked, they had a dry powdery surface, and appeared to be incompletely polymerised. It seemed possible that the rubber moulds allowed evaporation of free monomer from the dough while packed in the moulds, but before placement in the water bath.

Brass patterns were machined to the dimensions shown in Fig. 5.3. These had sufficient taper of their side faces to allow their removal from a gypsum mould. These patterns were invested in groups of three in dental flasks using high strength stone as a mould material. The processed specimens could also be easily removed, leaving an intact mould which could be reused repeatedly for the production of satisfactory specimens.
FIG. 5.3 DIMENSIONS OF THE BRASS PATTERN USED TO PRODUCE THE MOULDS FOR THE EXPERIMENTAL CROSS-LINKED POLY(METHYL METHACRYLATE) SPECIMENS.
All specimens were prepared from a dough mixed in the proportion 2.4 powder:1 liquid by mass. The liquid used for the control specimens (linear PMMA) was unmodified Durodent monomer. In the cross-linked specimens some of the monomer in the mix was replaced by the various cross-linking monomers in concentrations up to 50 or 60 per cent by mass. Twenty specimens were prepared from each mix of each concentration of cross-linking agent. Addition of the cross-linking monomers, particularly in higher concentrations, markedly extended the doughing times beyond what could be regarded as a practicable limit.

In the case of one monomer, EGDMA, the series was continued up to 100 per cent concentration; this was to allow a comparison of results obtained here with those published by Harrison et al. (1978), who also made impact tests on specimens containing EGDMA in concentrations up to 100 per cent. The use of 100 per cent EGDMA as a monomer increased the doughing time to 16 hours (Table 5.1).

All sets of specimens were subjected to the same curing cycle. The flasks were immersed in a water bath at 70 ± 2°C for 1.5 hours; then the temperature was raised to 100°C and maintained there for 18 hours, to ensure that as high a degree of polymerisation as possible was achieved. The moulds were then allowed to bench cool to room temperature before the specimens were deflasked.

All specimens were machined and notched following
TABLE 5.1

The doughing times of poly(methyl methacrylate) powder with the various monomers tested.

<table>
<thead>
<tr>
<th>Cross-linking Monomer</th>
<th>Percentage Concentration in Total Monomer</th>
<th>Doughing Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control (Linear PMMA)</td>
<td>0</td>
<td>1.5</td>
</tr>
<tr>
<td>Divinylbenzene</td>
<td>20</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>2.3</td>
</tr>
<tr>
<td>1,6-Hexanethylene Glycol Dimethacrylate</td>
<td>10</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>1.3</td>
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<tr>
<td></td>
<td>50</td>
<td>9.0</td>
</tr>
<tr>
<td>1,10-Decamethylene Glycol Dimethacrylate</td>
<td>10</td>
<td>1.3</td>
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<tr>
<td></td>
<td>25</td>
<td>3.5</td>
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<tr>
<td></td>
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<td>6.0</td>
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<tr>
<td></td>
<td>50</td>
<td>6.5</td>
</tr>
<tr>
<td>Ethylene Glycol Dimethacrylate</td>
<td>10</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>1.5</td>
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<td></td>
<td>50</td>
<td>4.2</td>
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<tr>
<td></td>
<td>75</td>
<td>6.5</td>
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<tr>
<td></td>
<td>100</td>
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<td>1.3</td>
</tr>
<tr>
<td></td>
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<td>1.5</td>
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<td>3.2</td>
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<td></td>
<td>60</td>
<td>6.0</td>
</tr>
<tr>
<td>Polyethylene Glycol 600 Dimethacrylate</td>
<td>10</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
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<td>2.0</td>
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<td></td>
<td>50</td>
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<td>Ethoxylated Bisphenol A Dimethacrylate</td>
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<td>1.7</td>
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<td></td>
<td>50</td>
<td>6.7</td>
</tr>
<tr>
<td>Trimethylolpropane Trimethacrylate</td>
<td>10</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>8.3</td>
</tr>
</tbody>
</table>
the method described in section 5.1.1, and smoothed with the same grades of wet silicon carbide paper, but no polishing with pumice slurry was performed, as this was found to round the edge of the notched surface and reduce the effective depth of the notch. All specimens were again water saturated to constant mass at 37 ± 1°C before testing.

5.2 MODIFICATION OF THE TESTING MACHINE

Impact tests were made in a Hounsfield Plastics Impact Tester*; this is basically a small Charpy-type machine, designed for testing polymers, in which the pendulum swings through a height of only 30 cm, and specimens have a loaded span of 40 mm. In order to match the available pendulum energy to the expected fracture energy of the specimen, seven interchangeable pendulums are provided, ranging in energy from 0.04 to 2.72 J in factors of two. In standard Charpy machines, the specimen is struck at the midpoint of the span opposite the notch, giving a system of symmetrical three-point loading; in the Hounsfield machine, however, the pendulum is provided with two striking edges 10 mm apart, equidistant from the midpoint of the span, giving a system of symmetrical four-point loading. (Fig. 5.4)

* Monsanto Ltd., Swindon, U.K.
FIG. 5.4 DIAGRAMMATIC REPRESENTATION OF THE HOUNSFIELD PLASTICS IMPACT TESTER SHOWING THE STRIKING EDGES OF THE PENDULUM, EQUIDISTANT FROM THE MIDPOINT OF THE SPAN, GIVING A SYSTEM OF SYMMETRICAL FOUR-POINT LOADING.
The machine was supplied with a metal bar for aligning the pendulum, and specimen supports for testing specimens of two configurations: one with a circular cross-section 5/16 in. in diameter, and the other with a square cross-section with 5/16 in. sides. The shape of these supports, however, did not conform to the shape as specified in the International standard ISO 179 (International Standards Organisation, 1982).

A set of supports for specimens 10 mm square had been constructed, conforming to the International standard specifications, for a previous study (Mori and Earnshaw, 1980). It was found that using these supports with the specimens from this investigation allowed the pendulum to contact the specimen before the pendulum had reached the lowest point of its swing, so that the pendulum had not attained its calibrated energy when specimen fracture was initiated.

For these present experiments, a set of specimen supports for 8 mm square specimens, also conforming to the International standard specifications, was constructed. Although the size of these specimens would have allowed use of the original specimen supports, the supports did not conform to the shape as specified in the International standard. A new metal bar for aligning the pendulum was also constructed.

The machine was modified to allow toss correction
to be made according to ASTM D256-78, Method C (American Society for Testing and Materials, 1980); this required the provision of a reproducible method of positioning the pendulum for its second (lower) swing. (Section 2.4.2.2) The original tester is shown in Fig. 5.5; the modified tester is shown in Fig. 5.6. A frame was attached, pivoted coaxially with the pendulum, and a second scale provided which allowed the setting of the pendulum at intermediate heights. The frame could be clamped at any required position, and carried an electromagnet which supported the pendulum. Pendulum release occurred when current flow to the electromagnet was interrupted.

A video tape of the action of the pendulum fracturing trial specimens, when viewed in slow motion, showed that one part of the fractured specimen was projected forwards, while the other part hit the supports of the machine and was projected backwards. When bearing blue was smeared lightly on the metal bar for aligning the pendulum, it was found that the pendulum was contacting the specimen with only one of its striking edges. (Fig. 5.7) Adjustment of the pendulum to contact the specimen with both striking edges resulted in the forwards projection of both parts of the fractured specimen.

Whenever pendulums were changed to match the expected fracture energy of the specimen, it was necessary to move the supports laterally to realign the midpoints of the specimen and the striking face of the new pendulum. This
FIG. 5.5 THE HOUNSFIELD PLASTICS IMPACT TESTER BEFORE MODIFICATION TO ALLOW TOSS CORRECTION ACCORDING TO ASTM STANDARD D256-78.
FIG. 5.6  THE HOUSFIELD PLASTICS IMPACT TESTER AFTER MODIFICATION ACCORDING TO ASTM STANDARD D256-78, SHOWING THE ATTACHED FRAME PIVOTED COAXIALLY WITH THE PENDULUM, THE POSITION OF THE ELECTROMAGNET AND THE SECOND SCALE FOR SETTING THE PENDULUM AT INTERMEDIATE HEIGHTS.
FIG. 5.7 BEARING BLUE SMEARED LIGHTLY ON THE METAL BAR USED FOR ALIGNING THE PENDULUM SHOWING THAT THE PENDULUM IS CONTACTING WITH ONLY ONE OF ITS STRIKING EDGES.
always resulted in loss of even contact of the two striking edges with the specimen; even contact could only be restored by bending and twisting the pendulum shaft by trial and error.

This problem arose because location of the specimen supports in the frame of the machine was only by grub screws bearing on flats machined on the supports, and this was not positive enough to give reproducible positioning of the supports after adjustment. More accurate location of the supports was achieved by attaching locating plates to the frame, dowelled and screwed into position, bearing on the flats on the supports. (Fig. 5.8) These provided positive location of the supports so that the latter could be adjusted laterally without losing their alignment relative to the pendulum. After this modification had been made no further bending of pendulums was necessary. After each pendulum change, alignment was checked with bearing blue, as already described, but it was always found to be accurate. (Fig. 5.9)

5.3 IMPACT TESTING

In order to calculate impact resistance, it was necessary to determine the nominal fractured area (i.e. the cross-sectional area at the base of the notch) of each specimen. Therefore measurements were made of specimen width, and specimen depth at the base of the notch. Each of these measurements was made in three places, and averaged
FIG. 5.8 LOCATING PLATES, DOWELLED AND SCREWED INTO POSITION, BEARING ON THE FLATS ON THE SPECIMEN SUPPORTS AND PROVIDING MORE ACCURATE LOCATION OF THE SUPPORTS DURING CHANGES OF PENDULUM SIZE.
FIG. 5.9 BEARING BLUE SMEARED LIGHTLY ON THE METAL BAR
USED FOR ALIGNING THE PENDULUM SHOWING THAT
THE PENDULUM IS CONTACTING WITH BOTH ITS
STRIKING EDGES.
to give a single value for specimen width and for effective depth, from which the nominal fractured area could be calculated.

Initially, both a dial gauge comparator and a micrometer screw gauge were used for these measurements. The dial gauge comparator gave consistently higher and less reproducible measurements in comparison with the micrometer; therefore the latter was used for all specimen measurements in the experiments quoted in this work. The moving anvil of the micrometer was reground to allow penetration to the root of the notch. (Fig. 5.10)

Specimens were stored in water at 37 ± 1°C, and tested within 10 sec of their removal. In the initial test, the intact specimen was positioned on the machine with its notch at the centre of the loaded span, using the notch register attached to the machine underneath the specimen supports. (Fig. 5.11) At this position, the notch is opposite the points of pendulum impact, and thus at the line of maximum tensile stress.

Each specimen was fractured by releasing the pendulum from its highest position (Fig. 5.6); it was then reassembled and repaired by flowing a fillet of inlay wax 1 to 1.5 mm thick into the notch, and replaced on the supports of the machine. Mori and Earnshaw (1980) showed that adding a small amount of brittle wax produces a negligible effect on toss energy measurements. The rotating
FIG. 5.10  THE MICROMETER USED FOR SPECIMEN MEASUREMENTS SHOWING THE MOVING ANVIL THAT WAS REGROUND TO PERMIT PENETRATION TO THE ROOT OF THE NOTCH.
FIG. 5.11 USE OF THE NOTCH REGISTER FOR POSITIONING THE SPECIMEN WITH ITS NOTCH AT THE CENTRE OF THE LOADED SPAN, AND OPPOSITE THE POINTS OF IMPACT OF THE PENDULUM.
frame was adjusted so that the pendulum was supported at
the same height to which it rose after initial fracture
(Fig. 5.12); then it was released, to throw the two pieces
of the specimen a second time. The new height to which it
rose was recorded; toss energy was calculated as the
difference between that reading and the reading given by a
free swing from the same starting point. The toss energy
determined in this way was subtracted from the reading
obtained during the initial fracture of the specimen to
give a corrected value for fracture energy. The impact
resistance of each specimen was calculated as the corrected
fracture energy divided by the cross-sectional area at the
base of the notch, and expressed in J m\(^{-2}\).

During the testing of the specimens of the experi-
mental cross-linked PMMA, half the specimens of each batch
of each concentration of cross-linking agent were tested
according to the method described above. The remainder of
each batch was tested under reverse notch conditions in
order to obtain a measure of the effect of the various
cross-linking agents on notch sensitivity under impact
loading. (Section 2.3.4).

Both Izod and Charpy methods were originally
developed for impact testing of metallic materials, and an
important application there is to study the tough-brittle
transition. Metallic specimens are always notched, to
ensure that ductile or tough specimens do fracture during
the test (Hulse, 1965). The notch acts to concentrate
FIG. 5.12  THE HOUNSFIELD PLASTICS IMPACT TESTER WITH THE ROTATING FRAME ADJUSTED TO SUPPORT THE PENDULUM AT THE HEIGHT TO WHICH IT ROSE AFTER INITIAL FRACTURE, IN PREPARATION FOR ITS RELEASE TO THROW THE SPECIMEN PIECES A SECOND TIME.
stresses at the line of maximum tensile stress, and more importantly it sets up a system of triaxial tensile stresses at its base (Parker, 1957; Vincent, 1962c; Hulse, 1965; Bucknall, 1977). This prevents plastic deformation of the specimen, and ensures that it does fracture during the course of one blow.

Since under impact conditions glassy polymers would show negligible plastic deformation, notching is not necessary to ensure fracture, and current practice allows the use of both notched and unnotched specimens (Haward, 1949b; Vincent, 1962c; Nielsen, 1974b; Brown, 1981). Comparison of the results would give an indication of the relative susceptibility of a polymer to the effect of stress raisers on its behaviour under impact loading. It has been suggested that the ratio of the impact resistances unnotched:notched can be used as a measure of the notch sensitivity of the material (notch sensitivity ratio) (Acquaviva, 1971; Brown, 1981).

Instead of using unnotched specimens, ASTM D256-78 (American Society for Testing and Materials, 1980) recommends testing notched specimens in reverse, so that the notch is in a region of maximum compressive stress and has minimal effect on specimen fracture. This has the advantage that notched and 'unnotched' specimens have the same mass and the same cross-sectional area at the base of the notch. Mori and Earnshaw (1980) found that in the case of Charpy impact tests on cast gypsum, reverse notch
specimens gave slightly lower but more reproducible values for impact resistance, than true unnotched specimens; the improved reproducibility with reverse notch specimens probably resulted from the fact that the fracture path was much more constant, always terminating at the notch.

An advantage of the Hounsfield Impact Tester over other Charpy-type machines, is that in reverse notch testing the double loading noses on each pendulum straddle the central notch. (Fig. 5.4)

5.4 NMR SPECTROSCOPY

Loshaek and Fox (1953) found that the number of cross-linkages produced in a polymer is not equal to the number of bifunctional cross-linking molecules used, i.e. that the cross-linking efficiency is always less than one. This is due to the limitation of movement imposed on one end of a bifunctional molecule when the other end is incorporated into a polymer chain. Therefore a mobile monomer molecule polymerises more quickly than the now pendant bifunctional molecule. Loshaek and Fox suggest that restrictions on diffusibility of pendant vinyl groups may be severe enough not only to lower the reactivity ratio, but to prevent completely their further reaction, so removing their ability to form a cross-link. Unpolymerised vinyl groups on the other end of these pendant chains would add to the plasticising effect of any residual monomer remaining after the curing cycle.
Loshaek and Fox also predicted that high efficiency in a cross-linking reaction may be obtained by employing a divinyl molecule with a very long flexible chain between vinyl end groups, and found as practical confirmation that DMGDMA gave a higher degree of cross-linking than EGDMA. Both of these cross-linking monomers were included in the present study. (Section 4.2) Also included in this study were a series of cross-linking monomers whose chains were made more flexible by the presence of in-chain oxygen atoms (Section 4.2). In particular, following Loshaek and Fox's prediction, a very high level of cross-linking should occur with PEG 600 DMA, which has an average cross-linking chain length of 40 atoms, every third one of which is an oxygen atom.

Measurements were therefore made to determine the degree of cross-linking by estimating the concentration of residual double bonds in polymerised specimens from the investigation. Dr R. Gilbert of the Department of Chemistry, University of Sydney, suggested that NMR Spectroscopy could detect the residual double bonds. Preliminary studies by Dr B. Cornell at the CSIRO Division of Food Research, North Ryde, Sydney, on control specimens of linear PMMA and cold-cured PMMA gave equivocal results. Measurements by Dr J. O'Donnell, Department of Chemistry, University of Queensland, of solid-state $^{13}$C NMR spectra obtained with a Bruker CXP300 spectrometer, allowed the quantitative determination of the concentration of unreacted double bonds.
CHAPTER 6. RESULTS

6.1 DENTURE BASE POLYMERS

The results for these tests are shown in Table 6.1 and Fig. 6.1. In Fig. 6.1 the values for impact resistance are plotted on the vertical axis in thousands of joules per square metre; the height of each bar represents the mean value of at least nine specimens, and the small superimposed bar shows the standard deviation. In this figure the mean values for initial impact resistance (left hand bars) are compared with the impact resistance after 12 months' water saturation (right hand bars) for all six denture base polymers tested.

6.2 EXPERIMENTAL CROSS-LINKED POLY(METHYL METHACRYLATE)

The results for these tests are shown in Table 6.2 and Figs. 6.2 to 6.25. The effects of the cross-linking agents on the notch sensitivity ratios are shown in Table 6.3 and Figs. 6.26 to 6.33.

Figs. 6.2 to 6.9 show the effect of the cross-linking agents on the impact resistance of the cured materials. Percentage cross-linking agent (m/m) in the monomer component is shown on the horizontal axis plotted against the impact resistance on the vertical axis in thousands of joules per square metre. All values are the mean of at least nine tests and the superimposed
vertical bars show the standard deviations. Figs. 6.10 to 6.17 show the effect of the cross-linking agents on the impact resistance of the cured materials when tested with the notch in the reverse position on the testing machine.

Figs. 6.18 to 6.25 show the percentage change in impact resistance for each concentration of each cross-linking agent when compared with the control (linear PMMA).

The equilibrium water content of saturated linear and cross-linked PMMA specimens, shown by the weight loss on drying specimens previously saturated at 37°C, is shown in Table 6.4.

The solvent uptake of linear and cross-linked PMMA specimens, after immersion of dried specimens in dibutyl phthalate until constant mass was achieved at 21°C, is shown in Table 6.5.

The results of the NMR spectroscopy of the cross-linked materials is shown in Table 6.6 and Figs. 6.34 and 6.35.

6.3 STATISTICAL ANALYSIS

Results for both the denture base polymer and the experimental cross-linked PMMA specimens were analysed using the student t test, and the level of significance taken at both 5 per cent ($p \leq 0.05$) and 1 per cent ($p \leq 0.01$).
6.3.1 Denture Base Polymers

Analysis of results of specimens tested immediately on saturation at 37°C showed significant differences between all specimens except Hircoe and GC Luxon, at both the 5 and 1 per cent levels. Analysis of results of specimens aged in water for 12 months showed significant differences between all specimens except Durodent and Impact 76, and between Lucitone 199 and GC Luxon, at the 5 and 1 per cent levels. Analysis of results of specimens tested immediately on saturation at 37°C, compared with those tested after ageing for 12 months, showed significant differences between all specimens except Lucitone 199 and Hircoe, at both the 5 and 1 per cent levels.

6.3.2 Experimental Cross-linked Poly(methyl methacrylate)

Results for both notched and reverse notch specimens were tested for significant differences at concentrations of 50 per cent cross-linking agent in the monomer component (m/m).

Analysis of results for notched specimens showed that all results showed significant differences between specimens except for PMMA and EBADMA, DVB and EGDMA, HMGDMA and DMGDMA, and TEGDMA and PEG 600 DMA, at both the 5 and 1 per cent levels, and between DVB and TMPTMA at the 5 per cent level only.
Analysis of results for reverse notch specimens showed that all results showed significant differences between specimens except for DVB and EGDMA, DVB and TMPTMA, HMGDMA and DMGDMA, HMGDMA and EBADMA, DMGDMA and TEGDMA, DMGDMA and EBADMA, and EGDMA and TMPTMA, at the 5 and 1 per cent levels, and between PMMA and HMGDMA, and HMGDMA and TEGDMA, at the 5 per cent level only.
TABLE 6.1

Corrected impact resistance of the six denture base polymers studied. Specimens were saturated at 37°C before testing. All values are the mean of at least 10 tests, and the standard deviations are also given.

<table>
<thead>
<tr>
<th>Material</th>
<th>Impact Resistance ((10^3 \text{ J m}^{-2}))</th>
<th>Change on Aarging (per cent)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>On Reaching Saturation</td>
<td>Aged One Year in Water at 37°C</td>
</tr>
<tr>
<td>Durodent</td>
<td>1.28 ± 0.08</td>
<td>1.13 ± 0.06</td>
</tr>
<tr>
<td>Hircoe</td>
<td>2.48 ± 0.09</td>
<td>2.48 ± 0.23</td>
</tr>
<tr>
<td>Impact 76</td>
<td>1.46 ± 0.18</td>
<td>1.10 ± 0.09</td>
</tr>
<tr>
<td>Lucitone 199</td>
<td>1.95 ± 0.11</td>
<td>1.95 ± 0.10</td>
</tr>
<tr>
<td>GC Luxon</td>
<td>2.39 ± 0.15</td>
<td>1.91 ± 0.18</td>
</tr>
<tr>
<td>Reigning Resin</td>
<td>4.63 ± 0.19</td>
<td>5.27 ± 0.17</td>
</tr>
</tbody>
</table>
FIG. 6.1 THE EFFECT OF 12 MONTHS' WATER SATURATION ON THE IMPACT RESISTANCE OF THE DENTURE BASE POLYMERS TESTED. D: DURODENT; I: IMPACT 76; LC: LUCITONE 199; LX: LUXON; H: HIRCOE; R: REIGNING RESIN.

THE HATCHED BARS REPRESENT THE IMPACT RESISTANCE OF THE MATERIALS IMMEDIATELY FOLLOWING THEIR WATER SATURATION TO CONSTANT MASS AND THE UNHATCHED BARS REPRESENT THE IMPACT RESISTANCE AFTER WATER SATURATION FOR 12 MONTHS.
<table>
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<tr>
<th>Cross-Linking Monomer</th>
<th>Percentage of Total Monomer</th>
<th>Notched Specimens (J·m$^{-2}$ x 10$^3$)</th>
<th>Reverse Notch Specimens (J·m$^{-2}$ x 10$^3$)</th>
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</thead>
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<td>13.24 ± 1.08</td>
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<td>0.96 ± 0.08</td>
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<td>40</td>
<td>0.43 ± 0.10</td>
<td>10.51 ± 1.77</td>
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<td>8.57 ± 2.56</td>
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<td>1.42 ± 0.09</td>
<td>15.89 ± 1.72</td>
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<tr>
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<td>25</td>
<td>1.32 ± 0.08</td>
<td>15.69 ± 1.90</td>
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<tr>
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<td>50</td>
<td>1.04 ± 0.16</td>
<td>15.68 ± 2.98</td>
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<td>1,10-Decanethylene Glycol Dimethacrylate</td>
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<td>15.62 ± 1.76</td>
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<td>1.40 ± 0.14</td>
<td>14.69 ± 2.20</td>
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<td>1.22 ± 0.08</td>
<td>17.33 ± 2.83</td>
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<td>1.12 ± 0.09</td>
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<td>40</td>
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<td>17.31 ± 2.96</td>
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<td>18.14 ± 1.94</td>
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<td>16.06 ± 1.61</td>
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<td>1.33 ± 0.11</td>
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<td>14.69 ± 1.62</td>
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<td>25</td>
<td>1.16 ± 0.12</td>
<td>15.64 ± 1.85</td>
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<tr>
<td></td>
<td>50</td>
<td>0.64 ± 0.09</td>
<td>7.55 ± 1.56</td>
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FIG. 6.3 THE EFFECT OF ETHYLENE GLYCOL DIMETHACRYLATE ON THE IMPACT RESISTANCE OF NOTCHED SPECIMENS.
FIG. 6.4 THE EFFECT OF TETRAETHYLENE GLYCOL DIMETHACRYLATE ON THE IMPACT RESISTANCE OF NOTCHED SPECIMENS.
FIG. 6.5  THE EFFECT OF POLYETHYLENE GLYCOL 600 DIMETHACRYLATE ON THE IMPACT RESISTANCE OF NOTCHED SPECIMENS.
FIG. 6.6
THE EFFECT OF 1,6-HEXAMETHYLENE GLYCOL DIMETHACRYLATE ON THE IMPACT RESISTANCE OF NOTCHED SPECIMENS.
FIG. 6.7 THE EFFECT OF 1,10-DECAMETHYLENE GLYCOL DIMETHACRYLATE ON THE IMPACT RESISTANCE OF NOTCHED SPECIMENS.
FIG. 6.8 THE EFFECT OF ETHOXYLATED BISPHENOL A DIMETHACRYLATE ON THE IMPACT RESISTANCE OF NOTCHED SPECIMENS.
Resistance of Notched Specimens.

See Fig. 6.9: The Effect of Trimethylolpropane Trihydroxylate on the Impact.
FIG. 6.11 THE EFFECT OF ETHYLENE GLYCOL DIMETHACRYLATE ON THE IMPACT RESISTANCE OF REVERSE NOTCH SPECIMENS.
FIG. 6.12 THE EFFECT OF TETRAETHYLENE GLYCOL DIMETHACRYLATE ON THE IMPACT RESISTANCE OF REVERSE NOTCH SPECIMENS.
FIG. 6.13 THE EFFECT OF POLYETHYLENE GLYCOL 600 DIMETHACRYLATE ON THE IMPACT RESISTANCE OF REVERSE NOTCH SPECIMENS.
FIG. 6.14 THE EFFECT OF 1,6-HEXAMETHYLENE GLYCOL DIMETHACRYLATE ON THE IMPACT RESISTANCE OF REVERSE NOTCH SPECIMENS.
FIG. 6.15 THE EFFECT OF 1,10-DECAMETHYLENE GLYCOL DIMETHACRYLATE ON THE IMPACT RESISTANCE OF REVERSE NOTCH SPECIMENS.
FIG. 6.16  THE EFFECT OF ETHOXYLATED BISPENOL A DIMETHACRYLATE ON THE IMPACT RESISTANCE OF REVERSE NOTCH SPECIMENS.
FIG. 6.17  THE EFFECT OF TRIMETHYLOLPROPANE TRIMETHACRYLATE ON THE IMPACT RESISTANCE OF REVERSE NOTCH SPECIMENS.
FIG. 6.18 THE PERCENTAGE CHANGE IN IMPACT RESISTANCE WITH THE ADDITION OF DIVINYLBENZENE. THE SOLID LINE REPRESENTS THE CHANGE IN IMPACT RESISTANCE OF NOTCHED SPECIMENS, AND THE BROKEN LINE REPRESENTS THAT OF REVERSE NOTCH SPECIMENS.
FIG. 6.19 THE PERCENTAGE CHANGE IN IMPACT RESISTANCE WITH THE ADDITION OF ETHYLENE GLYCOL DIMETHACRYLATE. THE SOLID LINE REPRESENTS THE CHANGE IN IMPACT RESISTANCE OF NOTCHED SPECIMENS AND THE BROKEN LINE REPRESENTS THAT OF REVERSE NOTCH SPECIMENS.
FIG. 6.20  THE PERCENTAGE CHANGE IN IMPACT RESISTANCE WITH THE ADDITION OF TETRAETHYLENE GLYCOL DIMETHACRYLATE. THE SOLID LINE REPRESENTS THE CHANGE IN IMPACT RESISTANCE OF NOTCHED SPECIMENS AND THE BROKEN LINE THAT OF REVERSE NOTCH SPECIMENS.
FIG. 6.21  THE PERCENTAGE CHANGE IN IMPACT RESISTANCE WITH THE ADDITION OF POLYETHYLENE GLYCOL 600 DIMETHACRYLATE. THE SOLID LINE REPRESENTS THE CHANGE IN IMPACT RESISTANCE OF NOTCHED SPECIMENS AND THE BROKEN LINE THAT OF REVERSE NOTCH SPECIMENS.
FIG. 6.22  THE PERCENTAGE CHANGE IN IMPACT RESISTANCE WITH THE ADDITION OF 1,6-HEXAMETHYLENE GLYCOL DIMETHACRYLATE. THE SOLID LINE REPRESENTS THE CHANGE IN IMPACT RESISTANCE OF NOTCHED SPECIMENS AND THE BROKEN LINE THAT OF REVERSE NOTCH SPECIMENS.
FIG. 6.23  THE PERCENTAGE CHANGE IN IMPACT RESISTANCE WITH THE ADDITION OF 1,10-DECAMETHYLENE GLYCOL DIMETHACRYLATE. THE SOLID LINE REPRESENTS THE CHANGE IN IMPACT RESISTANCE OF NOTCHED SPECIMENS AND THE BROKEN LINE THAT OF REVERSE NOTCH SPECIMENS.
FIG. 6.24 THE PERCENTAGE CHANGE IN IMPACT RESISTANCE WITH THE ADDITION OF ETHOXYLATED BISPHENOL A DIMETHACRYLATE. THE SOLID LINE REPRESENTS THE CHANGE IN IMPACT RESISTANCE OF NOTCHED SPECIMENS AND THE BROKEN LINE THAT OF REVERSE NOTCH SPECIMENS.
FIG. 6.25 THE PERCENTAGE CHANGE IN IMPACT RESISTANCE WITH THE ADDITION OF TRIMETHYLOLPROPANE TRIMETHACRYLATE. THE SOLID LINE REPRESENTS THE CHANGE IN IMPACT RESISTANCE OF NOTCHED SPECIMENS AND THE BROKEN LINE THAT OF REVERSE NOTCH SPECIMENS.
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<th>Percentage Concentration in Total Monomer</th>
<th>Ratio</th>
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FIG. 6.27  THE EFFECT OF ETHYLENE GLYCOL DIMETHACRYLATE ON THE NOTCH SENSITIVITY RATIO OF THE SPECIMENS.
FIG. 6.28  THE EFFECT OF TETRAETHYLENE GLYCOL DIMETHACRYLATE ON THE NOTCH SENSITIVITY RATIO OF THE SPECIMENS.
FIG. 6.29 THE EFFECT OF POLYETHYLENE GLYCOL 600 DIMETHACRYLATE ON THE NOTCH SENSITIVITY RATIO OF THE SPECIMENS.
NOTCH SENSITIVITY RATIO

% POLYETHYLENE GLYCOL 600 DIMETHACRYLATE
FIG. 6.30  THE EFFECT OF 1,6-HEXAMETHYLENE GLYCOL DIMETHACRYLATE ON THE NOTCH SENSITIVITY RATIO OF THE SPECIMENS.
FIG. 6.31  THE EFFECT OF 1,10-DECAMETHYLENE GLYCOL DIMETHACRYLATE ON THE NOTCH SENSITIVITY RATIO OF THE SPECIMENS.
FIG. 6.32  THE EFFECT OF ETHOXYLATED BISPHENOL A DIMETHACRYLATE ON THE NOTCH SENSITIVITY RATIO OF THE SPECIMENS.
FIG. 6.33  THE EFFECT OF TRIMETHYLOLPROPANE TRIMETHACRYLATE ON THE NOTCH SENSITIVITY RATIO OF THE SPECIMENS.
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<tr>
<td></td>
<td>25</td>
<td>- 2.07</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>- 2.06</td>
</tr>
</tbody>
</table>
TABLE 6.5
Solvent uptake of linear and cross-linked poly(methyl methacrylate) specimens. Specimens were immersed in dibutyl phthalate at 21°C until constant mass was achieved.

<table>
<thead>
<tr>
<th>Cross-Linking Monomer</th>
<th>Percentage Concentration in Total Monomer</th>
<th>Percentage Weight Change on Solvent Uptake</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control (Linear PMMA)</td>
<td>0</td>
<td>+ 0.89</td>
</tr>
<tr>
<td>Diallylbenzene</td>
<td>20</td>
<td>+ 1.10</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>+ 1.00</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>+ 1.10</td>
</tr>
<tr>
<td>1,6-Hexamethylene Glycol Dimethacrylate</td>
<td>10</td>
<td>+ 1.00</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>+ 1.05</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>+ 0.93</td>
</tr>
<tr>
<td>1,10-Decamethylene Glycol Dimethacrylate</td>
<td>10</td>
<td>+ 0.96</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>+ 0.87</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>+ 0.90</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>+ 1.15</td>
</tr>
<tr>
<td>Ethylene Glycol Dimethacrylate</td>
<td>10</td>
<td>+ 1.01</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>+ 1.13</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>+ 0.41</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>+ 1.53</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>+ 1.23</td>
</tr>
<tr>
<td>Tetraethylene Glycol Dimethacrylate</td>
<td>10</td>
<td>+ 0.99</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>+ 1.06</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>+ 1.14</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>+ 1.00</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>+ 1.63</td>
</tr>
<tr>
<td>Polyethylene Glycol 600 Dimethacrylate</td>
<td>10</td>
<td>+ 0.98</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>+ 1.06</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>+ 1.15</td>
</tr>
<tr>
<td>Ethoxylated Bisphenol A Dimethacrylate</td>
<td>10</td>
<td>+ 0.92</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>+ 0.96</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>+ 1.16</td>
</tr>
<tr>
<td>Trimethylolpropane Trimethacrylate</td>
<td>10</td>
<td>+ 1.03</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>+ 1.13</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>+ 1.20</td>
</tr>
</tbody>
</table>
### TABLE 6.6

Compositions of copolymers analysed in this study, and the proportions of unreacted C=C double bonds determined by solid-state $^{13}$C NMR.

<table>
<thead>
<tr>
<th>Cross-Linking Monomer</th>
<th>Molecular Weight</th>
<th>Composition (moles %)</th>
<th>Mole % MA groups from crosslinker</th>
<th>% unreacted groups in polymer (a)</th>
<th>% co-monomer with an unreacted C=C bond (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Divinylbenzene</td>
<td>130</td>
<td>12.0</td>
<td>21.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1,6-Hexanethylene Glycol Dimethacrylate</td>
<td>254</td>
<td>6.6</td>
<td>12.2</td>
<td>0.9 ± 0.5</td>
<td>14.6</td>
</tr>
<tr>
<td>1,10-Decamethylene Glycol Dimethacrylate</td>
<td>282</td>
<td>5.9</td>
<td>11.1</td>
<td>0.8 ± 0.5</td>
<td>14.4</td>
</tr>
<tr>
<td>Ethylene Glycol Dimethacrylate</td>
<td>198</td>
<td>8.2</td>
<td>15.1</td>
<td>4.3 ± 0.5</td>
<td>58</td>
</tr>
<tr>
<td>Tetrethylene Glycol Diisethacrylate</td>
<td>330</td>
<td>5.1</td>
<td>9.7</td>
<td>&lt; 0.5</td>
<td>-</td>
</tr>
<tr>
<td>Polyethylene Glycol 600 Dimethacrylate</td>
<td>754</td>
<td>2.3</td>
<td>4.5</td>
<td>&lt; 0.5</td>
<td>-</td>
</tr>
<tr>
<td>Ethoxylated Bisphenol A Dimethacrylate</td>
<td>452</td>
<td>3.8</td>
<td>7.3</td>
<td>&lt; 0.5</td>
<td>-</td>
</tr>
<tr>
<td>Trimethylolpropane Triethacrylate</td>
<td>339</td>
<td>4.9</td>
<td>13.4</td>
<td>3.2 ± 0.5</td>
<td>72</td>
</tr>
</tbody>
</table>

(a) Per cent of unreacted methacrylate groups (i.e. C=C) obtained from the area of the peak at 167 ppm, due to C=O adjacent to C=C, compared with the total area due to C=O (167 and 172 ppm).

(b) Per cent of multi-functional monomers that have only one reacted methacrylate group, assuming that the multi-functional monomers have reacted at one position only.
FIG. 6.34  SOLID STATE $^{13}$C NMR SPECTRA OF

(A) POLY(METHYL METHACRYLATE) POLYMERISED
WITH MONOMER CONTAINING 50 PER CENT METHYL,
METHACRYLATE AND 50 PER CENT ETHYLENE GLYCOL
DIMETHACRYLATE BY MASS;

(B) POLY(METHYL METHACRYLATE) POLYMERISED
WITH MONOMER CONTAINING 50 PER CENT METHYL
METHACRYLATE AND 50 PER CENT DECAMETHYLENE
GLYCOL DIMETHACRYLATE BY MASS;

(C) POLY(METHYL METHACRYLATE) POLYMERISED
WITH MONOMER CONTAINING 50 PER CENT METHYL
METHACRYLATE AND 50 PER CENT TETRAETHYLENE
GLYCOL DIMETHACRYLATE BY MASS.
FIG. 6.35  SOLID STATE $^{13}$C SPECTRA OF

(A) POLY(METHYL METHACRYLATE) POLYMERISED
WITH MONOMER CONTAINING 50 PER CENT METHYL
METHACRYLATE AND 50 PER CENT TRIMETHYLOL-
PROPANE TRIMETHACRYLATE BY MASS;
(B) POLY(METHYL METHACRYLATE) POLYMERISED
WITH MONOMER CONTAINING 50 PER CENT METHYL
METHACRYLATE AND 50 PER CENT DIVINYLBENZENE
BY MASS.
CHAPTER 7: DISCUSSION

7.1 DENTURE BASE POLYMERS

Under the experimental conditions outlined in Section 5.1.1, when specimens which had just reached equilibrium under oral conditions were tested, the impact resistance of the linear PMMA, Durodent, was $1.25 \times 10^3$ J m$^{-2}$. The impact resistance of the four rubber-modified methacrylates varied from $1.46 \times 10^3$ J m$^{-2}$ for Impact 76 (little better than Durodent) to $2.48 \times 10^3$ J m$^{-2}$ for Hircoe. The polysulphone, Reigning Resin, though clearly not unbreakable, had a significantly higher impact resistance of $4.63 \times 10^3$ J m$^{-2}$, about twice as strong as the best rubber-modified methacrylate, and about four times as strong as ordinary PMMA.

Ageing for 12 months under oral conditions affected the various materials differently. Hircoe and Lucitone 199 were unaffected, while Durodent, Impact 76 and Luxon all showed a marked decrease in impact resistance. This decrease may have resulted from slow continued leaching of residual monomer. Smith (1959) showed that when polymerised denture base resin is first immersed in water there is rapid initial extraction of residual monomer from a thin surface layer, which soon becomes depleted. The subsequent extraction rate depends on slow diffusion of monomer from the interior of the polymer, and in impact specimens the relatively low surface area:volume ratio,
compared with a denture or a flat plate, would slow the rate of long-term monomer loss. As residual monomer functions as a plasticiser, its continued loss would make the aged specimens more brittle.

The increase in impact resistance found in the injection moulded polysulphone, on ageing under oral conditions, is of interest, since this polymer does not contain any residual monomer. The increase is paralleled by a similar observation made by Stafford and Smith (1968b) on an injection moulded polycarbonate denture base resin. Also using a Hounsfield Impact Tester, they found an increase of 16 per cent in fracture energy, when specimens aged in water for 12 months at 37°C were compared with others aged for only three months.

Polycarbonates and polysulphones have similar properties (Brydson, 1982c); in both cases the specimens were fabricated by injection moulding, and in neither specimen could residual monomer exist. Stafford and Smith suggested that the increase in impact resistance of polycarbonate occurring on extended ageing in water may have been the result of the plasticising effect of sorbed water. This would imply that water sorption continued, probably at a very slow rate, for periods of up to 12 months. If this were so, it might equally be likely in the case of the polysulphone studied here.

Stafford and Smith also reported that the polycarbonate they studied, Andoran, had an impact resistance...
over eight times as high as a linear PMMA, Kallo dent 333, which is very similar to Durodent. Other authors claim that the impact resistance of polycarbonate is between 10 and 20 times higher than that of PMMA (Smith, 1962; Stafford and Smith, 1967; Combe and Grant, 1973; McCabe and Wilson, 1974; Williams and Cunningham, 1979b). The polysulphone studied in this investigation had an impact resistance only four times as high as Durodent, which confirms the general observation (Brydson, 1982c) that the impact resistance of polysulphones is inferior to that of polycarbonates.

It is not possible to compare directly the present results with those obtained by earlier workers, as they used specimens of different sizes and reported their results in terms of fracture energy only. It is interesting, though, to compare the ranking obtained in these experiments on the rubber-modified methacrylates with those found in results published by other workers. Stafford et al. (1980) used a Hounsfield Impact Tester and included Hircoe, Impact, Lucitone 199 and an unmodified PMMA denture base material (Trevalon) in their study. They obtained relative values for fracture energy of Trevalon, 1; Hircoe, 1.2; Lucitone 199, 2.3; Impact, 2.7. In the present investigation the relative values for impact resistance were: unmodified PMMA (Durodent), 1; Impact 76, 1.2; Lucitone 199, 1.6; Hircoe, 2.0. Stafford and his co-workers may have obtained a better performance from Impact because they used the material as
originally introduced, while in these experiments a later version, Impact 76, was tested. Impact 76 has improved doughing and packing characteristics, but these may have been developed at the expense of its impact resistance. It is difficult to explain, however, the discrepancy in the ranking of Hircoe in these two studies.

Stafford and Smith (1968b) used a Hounsfield Impact Tester to compare the impact resistance of an unmodified PMMA (Kallodent) and Impact, under wet and dry conditions. They found Impact to be about three times as strong as Kallodent, both when specimens were tested dry and saturated. Again, Impact used in the latter experiments was the original material; the results are consistent with those of Stafford et al. (1980).

Schreiber (1974) used a Hounsfield Impact Tester to compare the impact resistance of Lucitone 199 and Impact with an unmodified PMMA (Lumacryl); conditions of testing were not stated. Lucitone 199 was twice as strong as Lumacryl, and Impact was nearly three times as strong. Braden and Causton (1979), quoting results obtained with a Hounsfield Impact Tester, predicted that a high-impact acrylic resin should be over 2.5 times as strong as heat-cured PMMA, but again testing conditions were not stated. Hirabayashi et al. (1984b) compared Luxon with various unmodified PMMA materials and found that Luxon had a slightly higher impact resistance than the other materials (ranging from 1.4 times to 1.1 times as
strong as PMMA). Results in the present investigation give Luxon a slightly higher impact resistance than this when compared with PMMA; here Luxon had an impact resistance value about twice as high as that of Durodent. The various unmodified PMMA denture base materials referred to above (Trevalon, Durodent, Kalldent and Lumar) could each be expected to have similar compositions and comparable mechanical properties.

All these results confirm that the addition of rubber to methacrylate denture base polymers increases the impact resistance of the materials under wet conditions. However some materials have their impact resistance increased to a greater extent than others; possibly due to differences in quantity of rubber added, or in method of manufacture. Of the materials studied in the present investigation, Impact 76, Lucitone 199 and Luxon showed similar doughing characteristics to those of Durodent. Hircoe formed a dough which was slightly drier and more granular than the others, but showed a higher impact resistance than the other materials; its impact resistance was unaffected by water saturation for 12 months. Although Reigning Resin showed an outstanding resistance to impact forces, and a subsequent improvement in this value after water saturation for 12 months, the cost and inherent difficulties concerned with injection moulding, including the differential thermal shrinkage of polymer and gypsum mould inducing a high level of residual tensile stresses in the case of complex mouldings such as dentures,
make its popularity as a denture base polymer unlikely.

7.2 EXPERIMENTAL CROSS-LINKED POLY(METHYL METHACRYLATE)

The effect of chain structure on the properties of polymers has been described by several authors (Anderson et al., 1974; McCabe and Wilson, 1974; Ruyter and Svendsen, 1978). Ruyter and Svendsen found that increasing the distance and number of ether bridge linkages between methacrylate groups increases both the flexibility of the monomers and the mobility of the elements containing the unreacted methacrylate groups, and that the degree of conversion can be correlated with the quantity of the relatively heavy and rigid aromatic monomers. McCabe and Wilson (1974) discussed the ease with which chain conformation can be altered by rotations about the bonds making up the backbone of the chain. They stated that a chain can be made more flexible by incorporating oxygen-carbon links into a chain composed entirely of carbon atoms, and that stiffness can be increased by the addition of phenyl groups. They classified ease of bond rotation in the order:

-\text{O-} > -\text{CH}_2- > \text{O-}

They also added that increasing the stiffness of the chain usually leads to an increase in $T_g$ and elastic modulus of the material. They pointed out that side groups can affect the chain packing of polymers. If the
pendant group was stiff and its bulk close to the backbone chain, they predicted an increase in $T_g$, but if the groups were flexible, the effect of increasing the intermolecular distance, and therefore the free volume, would predominate and $T_g$ would be reduced.

Anderson et al. (1974) predicted that projecting side groups would not only inhibit bond rotation, but would also inhibit the free sliding of chain over chain. This would affect the flexibility of the material. Flexibility could therefore be increased by separating the bulky side groups by the inclusion of extra atoms in the backbone of the chain. Suitable units for this purpose are oxygen or sulphur atoms.

7.2.1 Tests on Standard Notched Specimens

Under the experimental conditions outlined in Section 5.1.2, when specimens which had just reached equilibrium under oral conditions were tested, the impact resistance of notched specimens generally decreased with increasing concentration of cross-linking agent. The impact resistance of reverse notch specimens generally increased with low concentrations of cross-linking agent; with higher concentrations of the cross-linking agents, the impact resistance continued to increase with four of the cross-linking agents: TEGDMA, PEG 600 DMA, 1,10-DMGDMA and EBADMA; the impact resistance decreased with three of the agents: EGDMA, DVB and TMPTMA; it remained
constant with the remaining cross-linking agent: 1,6-HMGDMA.

The results for DVB and EGDMA confirm the findings of Goggin and Boyer (1946), Amos et al. (1952) and Wollff (1962) that cross-linking with short or relatively short cross-linking chains decreases the impact resistance of the polymer. The extreme brittleness of specimens with high concentrations of DVB made it difficult to machine the specimens to correct size for the present investigation without fracturing their edges. Amos et al. (1952) also observed that styrene-divinylbenzene copolymers with high concentrations of DVB were very brittle. Their limiting concentration of 5 per cent cross-linking agent in the specimens produced by bulk polymerisation of monomer gives good agreement with the specimens used by Wollff (1962) for his tensile testing of cross-linked specimens, where the limiting concentration of 25 per cent cross-linking agent in the monomer corresponded to a content of 8 per cent in the final polymerised specimens. Amos et al. and Wollff found a decrease in tensile strength of specimens where the cross-linking agent exceeded this concentration.

EBADMA, 1,6-HMGDMA and 1,10-DMGDMA with their long, but relatively inflexible chains had little effect on impact resistance at low concentrations, but gradually decreased it at higher concentrations.
Comparison of the results of the addition of the ethylene oxide adducts to the monomer component is shown in Fig. 7.1. From the short chain of EGDMA, the chains of TEGDMA and PEG 600 DMA are longer and more flexible, and the results for PEG 600 DMA show a dramatic improvement over those for EGDMA. Comparison of these results with those for the addition of the hydrocarbon adducts (Fig. 7.2) shows that increasing the chain length from 1,6-HMGDMA to 1,10-DMGDMA led to a slight improvement in impact resistance, but this is less pronounced than with increases in both the length and flexibility of the chain.

This agrees with the work of Satoh (1977), who found that the use of longer chain dimethacrylates as comonomers improved the impact resistance of cross-linked specimens produced by the 'fluid resin' technique.

Comparison of the effect of the addition of DVB, EBADMA and TMPTMA to the monomer component is shown in Fig. 7.3. DVB with its rigid cross-link severely reduces the impact resistance of the polymer. This effect is similar to that with TMPTMA, where formation of a network polymer reduces the impact resistance. EBADMA with its long but relatively inflexible chain has little overall effect on the impact resistance. The results with TMPTMA confirm the statements of Young (1979) and Atkinson and Brinson (1984) that three-dimensional network polymers are extremely brittle.
FIG. 7.1 THE EFFECT OF THE ETHYLENE OXIDE ADDUCTS: ETHYLENE GLYCOL DIMETHACRYLATE, TETRAETHYLENE GLYCOL DIMETHACRYLATE AND POLYETHYLENE GLYCOL 600 DIMETHACRYLATE ON THE IMPACT RESISTANCE OF NOTCHED SPECIMENS.
FIG. 7.2 THE EFFECT OF THE HYDROCARBON ADDUCTS: 1,6-HEXAMETHYLENE GLYCOL DIMETHACRYLATE AND 1,10-DECAMETHYLENE GLYCOL DIMETHACRYLATE ON THE IMPACT RESISTANCE OF NOTCHED SPECIMENS.
FIG. 7.3 THE EFFECT OF DIVINYLBENZENE, ETHOXYLATED BISPHENOL A DIMETHACRYLATE AND TRIMETHYLOLPROPANE TRIMETHACRYLATE ON THE IMPACT RESISTANCE OF NOTCHED SPECIMENS.
7.2.2 Tests on Reverse Notch Specimens

Comparison of the effect of the addition of the ethylene oxide adducts to the monomer component of reverse notch specimens is shown in Fig. 7.4. Again, there is a drastic decrease in the impact resistance with EGDMA, and a progressive improvement in the impact resistance with the longer and more flexible chains of TEGDMA and PEG 600 DMA.

Comparison of the effect of the addition of the hydrocarbon adducts is shown in Fig. 7.5. Both materials show a slight increase in impact resistance at high concentrations of cross-linking agent.

Comparison of the effect of the addition of the remaining agents is shown in Fig. 7.6. DVB and TMPTMA again show a drastic reduction in the impact resistance, and EBADMA has little overall effect.

7.2.3 Notch Sensitivity Ratio

The effect of the cross-linking agents on the notch sensitivity ratio of the cured polymers is shown in Fig. 7.7. With all the cross-linking agents, increasing their concentration in the monomer increased the notch sensitivity of the cured polymer, as shown by the increase in the notch sensitivity ratios. This effect was most marked in the case of DVB and least marked in the case of TEGDMA.
FIG. 7.5  THE EFFECT OF THE HYDROCARBON ADDUCTS: 1,6-HEXAMETHYLENE GLYCOL DIMETHACRYLATE AND 1,10-DECAMETHYLENE GLYCOL DIMETHACRYLATE ON THE IMPACT RESISTANCE OF REVERSE NOTCH SPECIMENS.
FIG. 7.6 THE EFFECT OF DIVINYLBENZENE, TRIMETHYLOLPROPANE TRIMETHACRYLATE AND ETHOXYLATED BISPHENOL A DIMETHACRYLATE ON THE IMPACT RESISTANCE OF REVERSE NOTCH SPECIMENS.
The increase in notch sensitivity ratio indicates an increase in the susceptibility of the polymer to the effect of stress raisers on its behaviour under impact loading. The increase in notch sensitivity ratio was less marked where the cross-linking agent had a longer and more flexible cross-linking chain.

7.2.4 NMR Spectroscopy

To confirm that any improvement in impact resistance resulted from cross-linking rather than from other effects, the degree of cross-linking was determined by estimating the concentration of residual double bonds in samples cut from the polymerised specimens used for the impact resistance tests. This was done by solid state $^{13}$C NMR spectroscopy (Section 5.4). This technique was chosen because the pigment content of the polymers, and their consequent opacity, combined with the insolubility of the polymer matrix caused by the high level of cross-linking, precludes solution methods and normal spectroscopic techniques for this investigation.

It was expected that increasing the chain length from EGDMA to 1,6-HMGDMA and 1,10-DMGDMA would result in a decrease in the residual double bond concentration. This result is observed in Table 6.6, with the reduction in the proportion of unreacted double bonds in the specimens from 28.5 per cent to 7.2 per cent.
The effect of increasing chain flexibility as well as chain length is shown by the ethylene oxide adduct results in Table 6.6. There is no peak measurable by this technique for TEGDMA and PEG 600 DMA, therefore the concentration of C=C bonds must be very small.

The trifunctional monomer TMPTMA has an unfavourable structure for the complete reaction of its C=C groups; 24 per cent of these bonds remain unreacted in the co-polymer. DVB shows a high level of conversion of its double bonds, with the proportion of unreacted groups less than 0.5 per cent.

Loshaek and Fox (1953) predicted that use of a divinyl molecule with a very long and flexible chain between vinyl groups would increase the cross-linking efficiency. NMR results for the present study have confirmed that prediction. Cowperthwaite et al. (1980) also found that long, straight chain diols were more efficient cross-linking agents than short chain EGDMA or highly branched monomers in highly cross-linked networks. Cook et al. (1985) quote the work of Ruyter and Svendsen (1978) who found that increasing the distance and number of ether bridge linkages between the methacrylate groups increased the monomer flexibility and the mobility of the elements containing the unreacted methacrylate groups in the polymer matrix. This reduced the concentration of residual monomer groups in the matrix.
It seems likely that a cross-linking agent with a long and flexible chain could be used at a higher concentration in the monomer component of the dough, with a subsequent improvement in the solvent resistance of the cured polymer without reducing its impact resistance. As was seen in the results for PEG 600 DMA, use of this cross-linking agent led to an increase in the impact resistance at all concentrations up to 50 per cent in the monomer (20 per cent of final polymerised material).

7.2.5 Water Sorption

The total water content of specimens was measured to investigate whether increasing amounts of cross-linking changed the water uptake. Results from this section of the investigation confirm the results of Rose et al. (1955) that cross-linking does not significantly affect the water sorption of acrylic resin (Table 6.4).

7.2.6 Solvent Uptake

The absorption of dibutyl phthalate by previously dehydrated specimens was measured, to investigate whether increasing amounts of cross-linking had any effect on solvent absorption. Results of this section of the investigation show that there is no correlation between solvent uptake and amount of cross-linking (Table 6.5).
CHAPTER 8: CONCLUSION

8.1 SUMMARY OF THE PRESENT WORK

8.1.1 Impact Testing of Denture Base Polymers

In an initial study, measurements were made of the impact resistance of some commercially available denture base polymers claimed to be of high impact strength; in several cases the materials were claimed by their manufacturers to be 'unbreakable'. This group comprised four rubber-modified methacrylate graft copolymers, processed by normal dental dough moulding methods, and a polysulphone, processed by injection moulding. For comparison, a standard linear poly(methyl methacrylate) homopolymer, representative of presently available denture base acrylic resins, was also included in this study. All specimens were conditioned in water at 37°C until they attained constant mass.

When specimens were tested on reaching constant mass, the rubber-modified materials had mean impact resistances ranging from only 1.2 to 2.0 times better than that of the traditional linear PMMA. The polysulphone had an impact resistance more than four times as high as that of the linear PMMA, and about twice as high as that of the best graft copolymers. While this represents a worthwhile improvement, it hardly confirms the manufacturer's claim that this polysulphone denture base material is 'unbreakable'.

Ageing specimens for 12 months under oral conditions affected the impact resistances of the various materials differently. The linear PMMA, and two of the graft copolymers, suffered reductions in impact resistance ranging from 10 to 24 per cent. The other two graft copolymers were unaffected. One of these now had an impact resistance 2.2 times as high as that of the linear PMMA. In general, the results obtained for the graft copolymers did not support their manufacturers' rather extravagant claims for improved mechanical properties.

Ageing the polysulphone under oral conditions produced a 13 per cent increase in impact resistance, possibly caused by the plasticising effect of additional sorbed water. Despite this high impact resistance, it seems unlikely that polysulphone will gain general acceptance as a denture base polymer, because of the complexity of the associated processing technique.

8.1.2 The Effect of Cross-linking on Impact Resistance

As a result of experience gained in the preliminary study referred to in Section 8.1.1, structural modifications were made to the impact testing machine which improved its performance. It was then used in the main study, an investigation of the effect of cross-linking on the impact resistance of the same linear PMMA homopolymer that was used as a reference material in the preliminary study. A range of cross-linking agents was used, with various characteristics.
Most modern denture base polymers contain a cross-linking agent in the monomer, to improve the solvent resistance of the cured polymer and so reduce its susceptibility to crazing. The concentration of cross-linking agent used does not exceed 15 per cent by mass, because higher concentrations have been found to increase the brittleness of the cured polymer to an unacceptable extent. At this level of cross-linking in the polymer matrix, the susceptibility to solvent crazing is greatly reduced but not eliminated.

Cross-linking comonomers used in current denture base resins typically provide stiff short-chain cross-links, which would contribute to the brittleness of the cured polymer. This investigation was undertaken to explore the possibility that cross-linking with chains that were longer, or more flexible, or both, would allow a higher level of cross-linking to be introduced into cured PMMA denture base resin, with a further improvement in its solvent resistance, but without prejudicing its mechanical properties. Eight bifunctional vinyl comonomers were used, in concentrations of up to at least 50 per cent by mass in the monomer component of the dough. These were chosen to represent a wide range of cross-linking chain lengths and chain flexibilities.

All specimens were conditioned to constant mass in water at 37°C. Impact tests were made with the conventional Charpy specimen disposition (notch in tension). Tests were then repeated with a second series of specimens positioned in reverse (notch in compression). The latter tests gave
conditions approximating to tests on unnotched specimens, and so from the two sets of results notch sensitivity ratios were calculated.

The results confirmed that when conventional cross-linking agents such as EGDMA are used, monomer concentrations higher than 10 per cent produce a marked reduction in both notched and 'unnotched' impact resistance, and a considerable increase in notch sensitivity. The effect of the other comonomers varied, in general as could be predicted from their structures. Chain flexibility was found to be a more important factor than chain length, although the most effective cross-linking agent was found to be PEG 600 DMA, which has the longest chains as well as relatively flexible ones. At monomer concentrations up to 50 per cent by mass, this comonomer increased the impact resistance of the cured polymer both in notched and 'unnotched' tests. All the comonomers studied increased the notch sensitivity, though in this regard the effect of PEG 600 DMA was one of the least marked.

In general, these results suggest very strongly that by using a comonomer such as PEG 600 DMA, acrylic resin denture base materials could be formulated which had an improved solvent resistance, but which had an impact resistance no worse, and probably slightly better, than the conventional PMMA material.
8.2 INDICATIONS FOR FUTURE WORK

8.2.1 Ease of Repair

Although a solvent resistance is desirable which is high enough to prevent crazing of denture base polymers during service or during laboratory procedures, it should not be so high as to prejudice the ease of repair or addition which is one of the practical advantages of current acrylic resin materials. Craze testing therefore should be carried out on specimens made with various concentrations of the cross-linking agents which performed well in the current investigation, to see whether complete craze resistance can be obtained at a level of cross-linking which still allows satisfactory repairs to be made with current laboratory procedures. If limiting concentrations of suitable cross-linking agents could be established, this would be practical information of use in formulating improved denture base polymers.

8.2.2 Other Physical Properties

8.2.2.1 Creep

Linear polymers such as PMMA are visco-elastic materials, and so under service loading could be expected to show retarded elasticity, delayed recovery, and creep. Glantz and Stafford (1973) confirmed that this behaviour in denture base resins under repeated occlusal loading at mouth temperature is of clinical significance.

Creep in linear polymers would be the result of
chain sliding, and it may be possible to reduce this by cross-linking at a level higher than that currently employed in commercially available acrylic denture base resins. The possibility of a relationship between concentration of cross-linking agent and resistance to creep at mouth temperature is worthy of further study.

8.2.2.2 Heat Resistance

Currently available heat cured acrylic resin denture base materials warp severely if heated (perhaps inadvertently) to temperatures approaching 100°C (Woelfel, 1971), which is close to the \( T_g \) of linear PMMA (Anderson et al., 1974; McCabe and Wilson, 1974). This deformation is a manifestation of stress relief by delayed elastic recovery, whose rate is accelerated by heating to temperatures near \( T_g \). A high level of cross-linking raises \( T_g \) (Nielsen, 1974a), and it would be interesting to study the heat resistance of highly cross-linked PMMA, perhaps by the determination of Vicat softening temperatures at different concentrations of cross-linking agents.

8.2.2.3 Fracture Toughness

The fracture toughness of some commercially available acrylic resin denture base materials, including a rubber-modified methacrylate, has been studied by Hill et al. (1983, 1984). Essentially a measure of relative ease of crack propagation under brittle fracture conditions, fracture toughness is a property basic to the consideration of failure of glassy polymers under both impact and fatigue conditions. These are the two types of failure likely to
occur in an acrylic resin denture in service (Hargreaves, 1969).

It is felt, therefore, that determinations of fracture toughness should be included in future studies of the effect of high levels of cross-linking on the fracture behaviour of denture base polymers.
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