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Formation and growth of crazes in multiphase acrylic systems

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The appearance of visible crazes and the growth of crazes during creep in tension for multiphase acrylic systems have been studied. The polymeric materials, commonly applied in bioengineering, were processed by polymerization of a mixture of liquid methacrylate monomers and poly(methyl methacrylate) (PMMA) powder. The specimens were made with various ratios of methyl methacrylate (MMA) and the crosslinking agent ethyleneglycol dimethacrylate (EGDMA) in the monomer liquid. Two different processing conditions were used, i.e. heat-polymerization at 100° C and auto-polymerization at 45° C. The critical strain value ε_c for the appearance of visible crazes under the influence of a constant tensile stress increased with increasing quantity of EGDMA in the heat-polymerized materials, and the crazes were equally distributed at the surface of the materials observed. In the cross-linked auto-polymerized materials, crazing started in the spherical polymer beads from the PMMA prepolymer powder, and ε_c was independent of the quantity of EGDMA. In the auto-polymerized materials crazes in a necked region opened up to form diamond-shaped cavities. Fracture started with a cavity that expanded through both matrix and polymer beads. The heat-polymerized materials failed in a brittle manner, whereas the auto-polymerized materials failed in a ductile manner.

1. Introduction

The failure mechanism of glassy polymers is very often related to the associated plastic deformation that occurs prior to the loss of mechanical integrity. The two principal modes of mechanical failure are shear yielding and brittle fracture, both involving localized plastic deformation [1]. In brittle crack propagation, localized plastic deformation takes place inside crazes. In many polymers crazing and shear yielding may be observed simultaneously and interactions occur between them [2].

Crazes are usually initiated under tensile stress either at surface imperfections such as flaws, cracks or scratches, and also at internal defects such as air bubbles, dust particles or molecular inhomogeneities [3]. Under tensile creep conditions in air, the critical strain for crazing decreases, and the induction period before crazing increases with decreasing levels of applied stress [4–6]. Brüller [7] demonstrated that a large number of small crazes become visible after a relatively short time at high stresses, whereas at low stresses a small number of large crazes becomes visible after a very long loading time.

The role of crazes in the fracture processes has been investigated in different polymeric materials. Lednicky and Pelzbauer [8] reported that fractures were initiated in the crazes of cavities produced by a mutual joining of small holes present in some polymeric materials, leading to brittle fracture. In polymers which undergo large deformations, i.e. necking before fracture during tensile testing, another fracture mechanism has been reported by Haward and co-workers [9, 10]. In these materials crazes are formed which survive the necking process almost unchanged. At a later stage of the process some of the crazes may open up to form diamond-shaped cavities. The diamond-shaped cavities grow to a size many times that of the craze until one cavity reaches a critical size and initiates a rapid failure [9].

The use of multiphase acrylic polymers for load-bearing devices in prosthetic dentistry and orthopaedic surgery has initiated research on the basic deformation and fracture behaviour of such materials. By fractography and mechanical testing, Kusy and Turner [11, 12] showed that two-phase acrylic polymers had a lower tensile strength than single-phase cast or moulded poly(methyl methacrylate) (PMMA), and that the strength of the materials varied with their microstructure [11, 12]. The reduced tensile strength has been explained by lower surface free-energy and higher inherent flaw size [13]. However, investigation of fatigue crack growth demonstrates that two-phase acrylic polymers exhibit enhanced fatigue crack growth resistance as compared to single-phase PMMA [14]. Fracture toughness measurements of denture base acrylics show a high degree of elastic behaviour compared to homogeneous bulk polymerized PMMA [15].

From recent work on multiphase acrylic polymers it may be concluded that the fracture properties depend on craze deformation prior to and during fracture [16]. However, little has been reported on craze formation and the growth of crazes in such materials. The purpose of this study was to investigate the formation and

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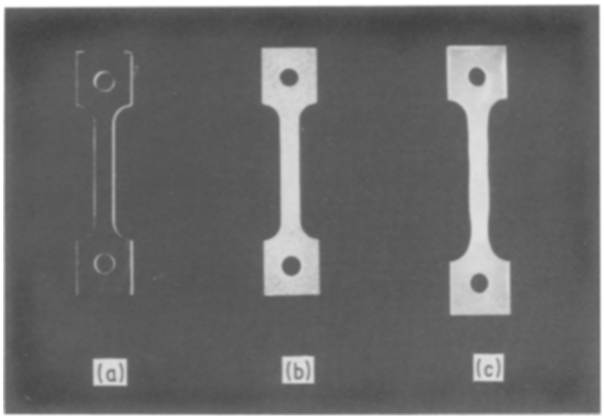

Figure 1 Unloaded (a) heat-polymerized and (b) auto-polymerized test specimens together with (c) a necked auto-polymerized specimen with 20% EGDMA.

growth of craze in multiphase acrylic polymers used for denture bases as a function of composition and processing conditions for these materials.

2. Experimental procedure

2.1. Materials

The materials were processed by polymerization of a mixture of 30 wt % methacrylate monomers and 70 wt % PMMA powder. The specimens were made with various ratios of methyl methacrylate (MMA) and the crosslinking agent ethyleneglycol dimethacrylate (EGDMA) in the monomer liquid. Two different processing conditions were used, heat-polymerization and auto-polymerization.

When heat-polymerized the PMMA powder containing 0.5 wt % benzoyl peroxide (BPO) was mixed with the monomer liquid. After 30 min at 22° C the resulting dough was pressed into a gypsum mould, submerged in water at 73 ± 1° C for 90 min and then immersed in boiling water for 30 min.

When auto-polymerized the PMMA powder containing 0.5 wt % BPO and the monomer liquid with 0.75 wt % N,N-dimethyl-*p*-toluidine (DMPT) were mixed for 20 sec. After 2 min the mixture was placed in a gypsum mould and kept at 45° C for 30 min at a pressure of 220 kPa.

2.2. Creep measurements

Dumb-bell specimens with a parallel gauge portion 16 mm long, 3 mm wide and 2 mm thick (Fig. 1) were cut from the polymerized specimens and polished with Al_2O_3 paste (Buehler Ltd., Greenwood, Illinois, USA). Two pastes with grain sizes 0.3 and 0.05 μm were used.

The creep test was performed at a constant stress in an Andrade–Chalmers type lever arm tension rig [17]. The force exerted on the specimen was calibrated. The strain was measured using a linear variable differential transformer (Hewlett, Packard, Palo Alto, California, USA). Creep behaviour was determined at 37 ± 0.2° C and 50 ± 5% relative humidity with a constant stress of 30.5 MPa. Three or more specimens were tested for each variation in specimen composition and processing condition.

2.3. Microscopic studies

The formation of the first visible craze in the test pieces (Fig. 1) under constant tensile load, and the growth of the crazes, was studied in an optical microscope using transmitted light (Leitz Orthoplan, Ernst Leitz GmbH, Wetzlar, Germany). The crazed materials were also analysed by scanning electron microscopy (SEM) (Jeol Model 50 A, Japan Electron Optics Laboratory, Nakagami, Japan).

2.4. Determination of insoluble polymer (gel)

Pieces of the test specimens were immersed in tetrahydrofuran (THF) at room temperature for 24 h. A Soxhlet extraction procedure [18] was carried out for 24 h to remove all solubles (sol) from the insoluble part of the materials. The insoluble part of the materials was dried to a constant weight under vacuum at 80° C in a drying tube. This weighed mass was considered to be the gel part.

3. Results and discussion

The mechanical strength of multiphase acrylic systems is generally regarded as being less than that of single-phase cast or moulded materials [12]. Furthermore, auto-polymerized materials are weaker than heat-polymerized materials [19]. The present investigation

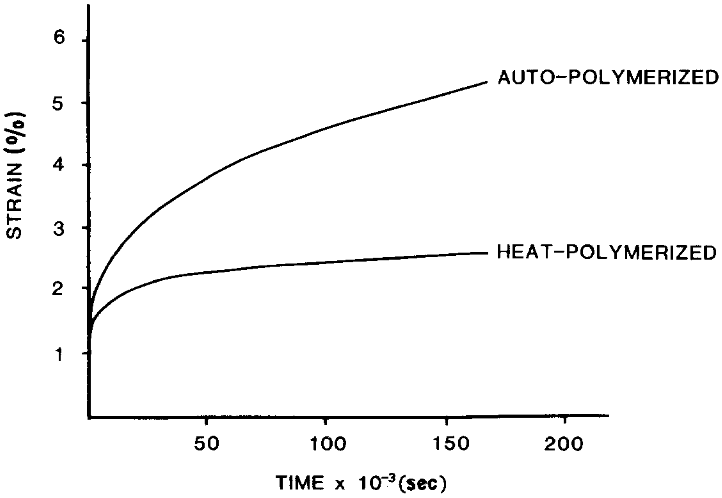

Figure 2 Strain as a function of time in heat-polymerized and auto-polymerized materials without crosslinking at 30.5MPa and 37° C.

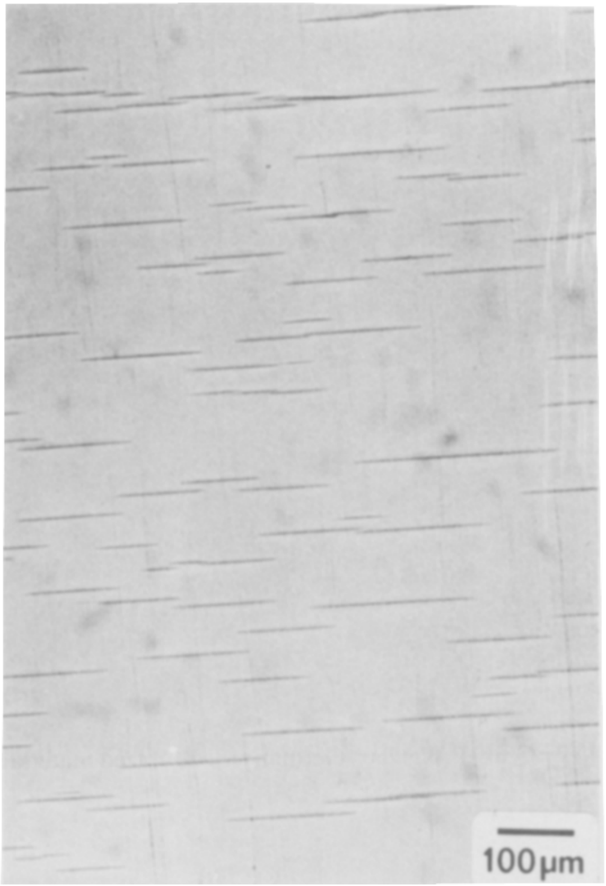

Figure 3 Crazes in heat-polymerized materials (light microscopy).

showed higher creep values for the auto-polymerized than for the heat-polymerized materials (Fig. 2). In heat-polymerized materials, variations in EGDMA resulted in no or only minor differences in creep values when measured at a constant stress of 30.5 MPa. The auto-polymerized materials showed greater variation in creep values, probably due to the inhomogeneous structure of these materials [20].

The average critical strain values ε_c for initial craze formation are presented in Table I. Gotham [21] found that the craze sensitivity correlated with the nature of ultimate failure, i.e materials that failed in a ductile manner had more resistance to crazing than those that failed in a brittle manner.

3.1. Heat-polymerized materials

Unstressed heat-polymerized materials were transparent (Fig. 1A), and the crazes wre equally distributed throughout the stressed materials (Fig. 3). The critical strain value (ε_c) increased with increasing quantity of EGDMA (Table I). This is in agreement with earlier investigations reported by Kambour [2] and Kramer [3] who concluded that the ability of glassy polymers to undergo craze formation decreased gradually with increasing crosslinking density. A doughing time of 30 min before polymerization ensured an effective penetration of monomers into the PMMA powder, and the increase of insoluble polymer with increasing quantity of crosslinking agents (Table II) indicated a special case of IPN (interpenetrating polymer network) formation [18].

TABLE I Average critical strain values ε_c for initial craze formation

Concentration of EGDMA (%)	ε_c (%)	
	Heat-polymerized	Auto-polymerized
0	1.6	1.8
2.5	1.7	2.4*
10	1.8	2.4*
20	2.0	2.4*

*Crazes observed only in the spherical polymer beads.

TABLE II Ratio between quantity of gel and initial quantity of monomer liquid

Concentration of EGDMA (%)	Gel/monomer liquid (wt/wt)	
	Heat-polymerized	Auto-polymerized
0	0	0
2.5	1.7	1.3
10	2.0	1.3
20	2.7	1.3

The introduction of chemical crosslinks into a polymer may improve many of the physical properties, such as modulus of elasticity, heat distortion temperature, solvent resistance, and glass transition temperature [22], but reduces the tensile strength due to embrittlement [23]. In the investigated systems with polymerized MMA and EGDMA the addition of PMMA beads may serve to increase localized plastic deformations [24]. In addition the small quantities of unreacted monomers (0.5 to 1.0%) may act as plasticizers [18]. Although the heat-polymerized materials were regarded as being semi-ductile, crazing rather than yielding played the dominant role in mechanical failure.

3.2. Auto-polymerized materials

Probably because of their inhomogeneous structure, the auto-polymerized materials appeared less translucent than the heat-polymerized materials (Fig. 1b). Optical micrographs of the materials showed a multiphase system consisting of a dispersed phase formed from the polymer beads originally present in the PMMA powder and a matrix formed from the monomer liquid. The short period between mixing and polymerization prevented an efficient penetration of monomers into the PMMA powder, resulting in less IPN formation [18]. This is illustrated by the relatively small and constant gel portion, irrespective of EGDMA concentration (Table II).

The initial appearance of visible crazes in the material without EGDMA was localized to the matrix (Fig. 4). This indicated that the matrix was the most brittle phase. This is in agreement with the results from crack propagation studies in corresponding systems [25].

In the crosslinked auto-polymerized materials crazing started in the polymer beads. After 48 h at a constant stress of 30.5 MPa, crazing was still limited to the polymer beads (Fig. 5). This may be due to the craze resistance in the matrix and an inefficient penetration of monomers into the PMMA beads. The results further demonstrated an increased ε_c by incorporation of 2.5%

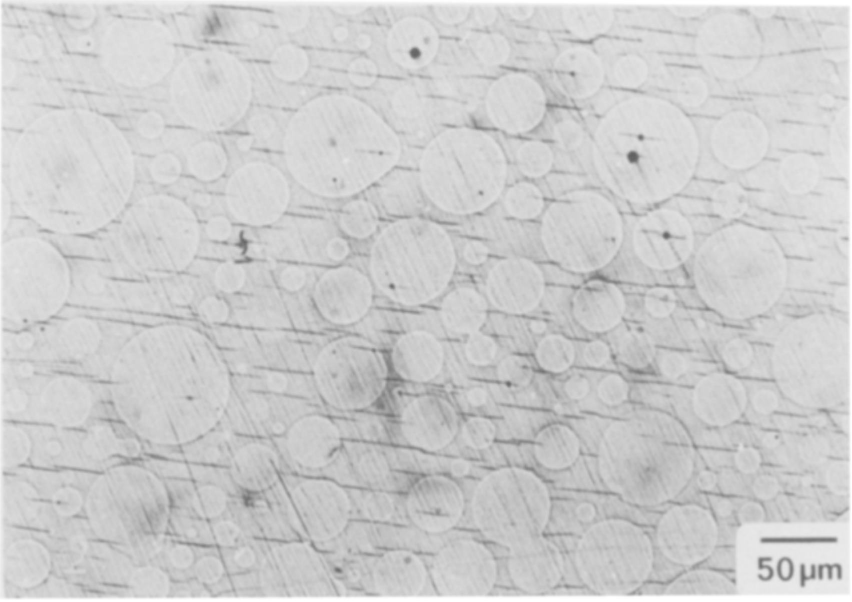

Figure 4 Crazes localized in the matrix of auto-polymerized materials without EGDMA (light microscopy).

EGDMA in the monomer liquid, but no further increase was observed with increasing quantity of EGDMA (Table I). In crosslinked materials the growth of crazes seemed to be limited by the size of the polymer beads (Fig. 5). The craze plane was oriented normal to the stress direction, and a characteristic fibrillar structure appeared in the crazes of the PMMA beads (Fig. 6).

A previous investigation [18] indicated a relatively high degree of unreacted monomer in the auto-polymerized materials. Values as high as 15% unreacted MMA of the initial monomer quantity were observed. In addition, about 40% of the reacted EGDMA was registered with a pendant methacrylate group (PMG). Both residual MMA and PMG may influence the mechanical properties by acting as plasticizers [18, 25]. The PMMA beads may also act as rigid fillers and induce enhanced shear yielding of the matrix, especially at the poles of the spherical beads, SEM micrographs of the surface in the crosslinked materials after 48 h at 30.5 MPa illustrated this effect

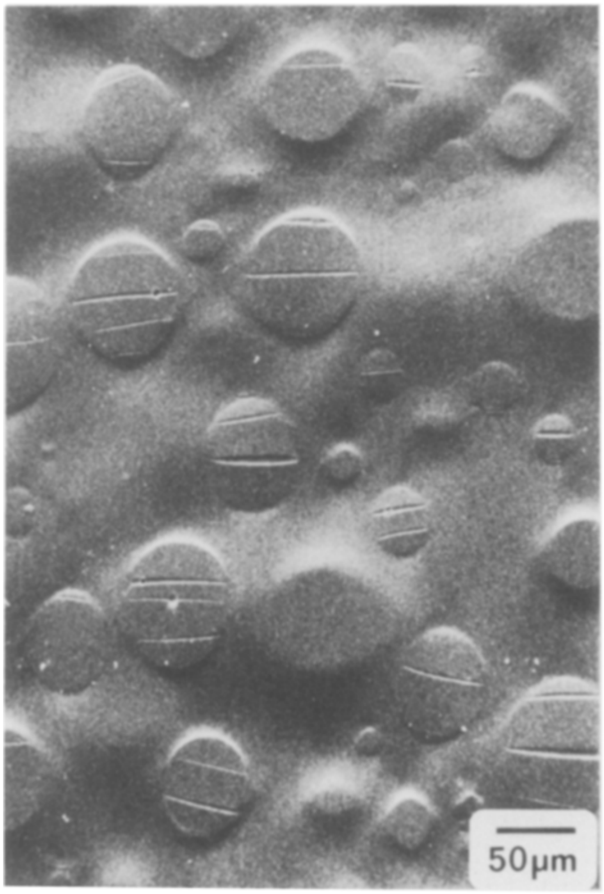

Figure 5 Crazes limited to the polymer beads in auto-polymerized materials with 20% EGDMA after 48 h at 30.5 MPa (SEM).

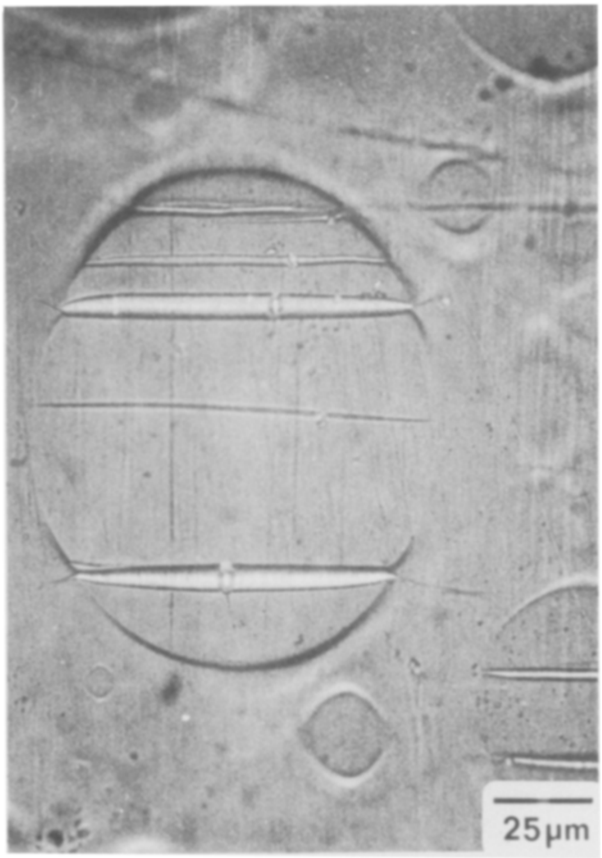

Figure 6 Fibrillar structure in the crazes in auto-polymerized materials with 10% EGDMA (light microscopy).

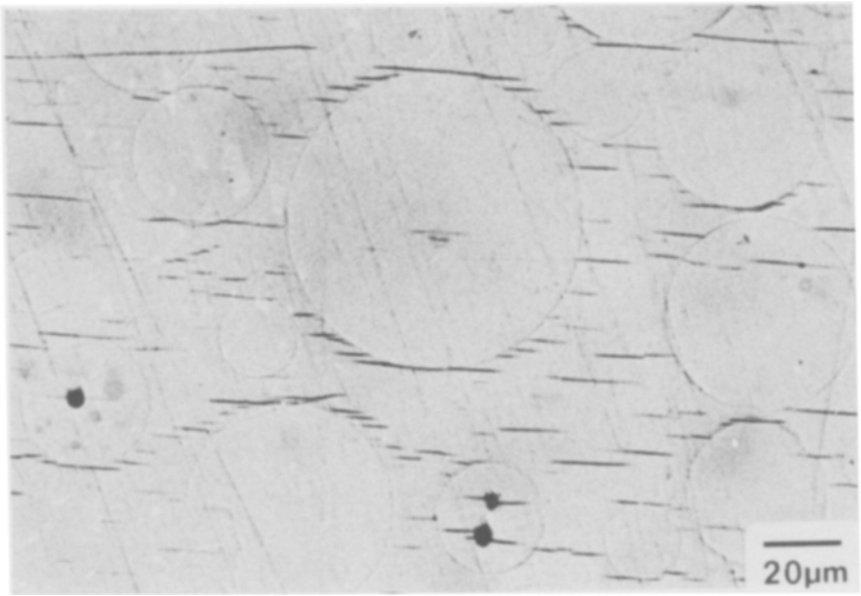

Figure 7 Crazes at the interface between matrix and polymer beads in auto-polymerized materials without EGDMA (light microscopy).

(Fig. 5). In the specimens without EGDMA, crazes were initiated at the interface between the beads and the matrix (Fig. 7). The craze density was highest near the poles. Maximum stress concentrations at the poles of the spherical beads in multiphase systems have been demonstrated in the presence of perfect bonding between matrix and fillers [26].

In addition to the inhomogeneous deformation of the crosslinked matrix, stresses were transmitted to the beads resulting in craze formation in the polymer beads. The simultaneous crazing and localized shear yielding were even more pronounced at higher stresses. Owing to the inhomogeneous composition of the materials, localized stress concentration may result in neck formation of the specimens. At a constant stress of 36.6 MPa all specimens of the auto-polymerized materials showed neck formation before fracture (Fig. 1c). The time prior to fracture increased with increasing quantity of EGDMA [20]. Necking appeared as a rapid increase in creep rate owing to plastic yielding. The materials with the highest crosslinking density in the matrix showed a decelerated creep rate before

Figure 8 Opening up of a craze in the necking region in auto-polymerized materials with 20% EGDMA (light microscopy).

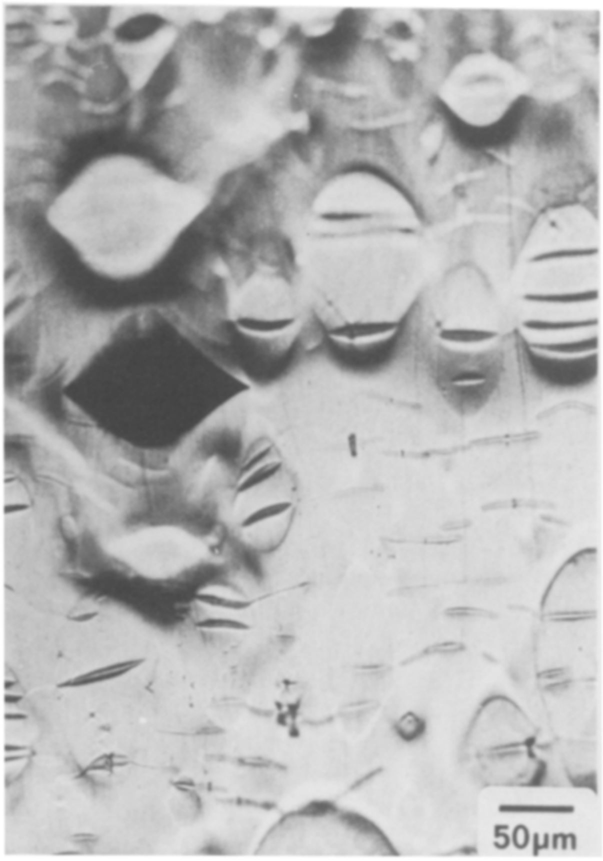

Figure 9 Formation of a diamond-shaped cavity in auto-polymerized materials with 20% EGDMA (light microscopy).

Figure 10 Growth of a diamond-shaped cavity through both matrix and polymer beads in auto-polymerized materials with 20% EGDMA (light microscopy).

fracture. In the necked region the PMMA beads were extensively deformed. The crosslinked matrix seemed to inhibit a growth of the crazes from the beads into the matrix. Instead, the crazes in the polymer beads seemed to open up (Fig. 8) and form diamond-shaped cavities (Fig. 9). The cavities were only seen within the necked region, which is in agreement with previously presented requirements for the formation of diamond-shaped cavities [27]. The size of the cavities increased until one reached a critical size and expanded with crack formation through both matrix and polymer beads (Fig. 10).

4. Conclusions

Depending on the processing conditions and monomer composition, three types of craze formation were observed:

(i) Heat-polymerized PMMA–MMA/EGDMA systems showed evenly distributed crazes throughout the material and had an increasing ε_c value with increasing quantity of EGDMA.

(ii) In auto-polymerized materials without crosslinking agent the initial craze formation appeared in the matrix.

(iii) In auto-polymerized materials with crosslinking agent the initial craze formation appeared in the spherical PMMA beads. The ε_c values were independent of EGDMA concentration.

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