Compressive creep of denture base polymers

IVAR EYSTEIN RUYTER & SVEIN ESPEVIK

NIOM, Scandinavian Institute of Dental Materials, Oslo, Norway

Ruyter, I.E. & Espevik, S. Compressive creep of denture base polymers. *Acta Odontol. Scand.* 1980, 38, 169 – 177

The creep characteristics of heat-polymerized and auto-polymerized dough and pour type denture base materials were measured at 23, 37, and 50°C with emphasis on secondary steady state creep rates. The creep rates were correlated to the processing conditions and material composition. Two different creep mechanisms were evident, depending on the stress levels. Below 20 – 40 MNm $^{-2}$ at 37°C, the creep was due to a homogeneous deformation. At higher stress levels the creep was ascribed to an inhomogeneous deformation mechanism.

The lowest creep rates were found for the heat-polymerized materials. Variations in the creep rates for the other materials could generally be related to composition differences.

Key-words: Dental materials; mechanical properties; prosthetics; polymethacrylates

I. Eystein Ruyter, NIOM, Scandinavian Institute of Dental Materials, Forskningsveien 1, Blindern, Oslo 3, Norway

The use of polymeric methacrylate materials for load bearing devices has initiated research on the basic deformation behavior of different types of denture base polymers. Creep behavior in cantilever bending (4–6), three-point bending (14) and by indentation tests (8, 14) has been reported. Heat-polymerized materials have smaller initial deformation, less creep and quicker recovery than autopolymerized materials (4, 5).

In dilational stress processes, e.g. tension and flexure, crazing plays an important role with respect to deformation properties. Tensile creep experiments have given a critical strain for crazing as low as $8 \cdot 10^{-3}$ in air for poly(methylmethacrylate) (PMMA) (9). By using uniaxial compression tests the tendency to brittle fracture and crazing of amorphous glassy polymers may to some extent be suppressed. A recent investigation has, however, shown that crazes may originate from flaws in the PMMA with a non-dilational applied stress (1). In uniaxial compression such crazes are formed at strains of between $6 \cdot 10^{-2}$ and $8 \cdot 10^{-2}$ at a strain rate of $4.2 \cdot 10^{-4} s^{-1}$ (10).

The method of uniaxial compression was chosen to elucidate the «bulk» deformation properties of denture base polymers. Creep behavior at various stress levels applied at 23, 37 and 50°C was studied. The influence of composition and processing conditions was assessed.

Received for publication, December 7, 1979

MATERIALS AND METHODS

The materials listed in Table 1 were investigated. They comprised heat-polymerized and auto-polymerized dough and pour type resins of different composition. The powder/liquid ratios used were according to the manufacturer's instructions. The heat-polymerized resin specimens were processed according to the International Organization for Standardization Recommendation 1567 (ISO R 1567), 1st Edition, June 1970. The auto-polymerized resins were processed according to manufacturer's instructions. Cylindrical test specimens with a diameter of 3.5 mm and a length of 7 mm were machined from the processed plates.

The creep test was conducted at a constant load on a creep apparatus. A lever arm was used, and the force exerted on the specimen was calibrated. The strain was measured using a linear variabel differential transformer (Hewlett Packard, Palo Alto, CA). Special care was taken to ascertain a parallel positioning of the compression plates. Creep behavior was determined at 23 ± 1, 37 ± 0.2 and 50 ± 0.2°C in the compressive stress range of 5 to 75 MNm^{-2}. The test lasted from a few minutes to 50 h depending on the creep rate.

The data were calculated as secondary steady state creep rates determined at strains $< 6 \cdot 10^{-2}$. When the strain was $< 4 \cdot 10^{-2}$ after 48 h loading the creep rate was determined after shorter loading times (30–40 h). The stress dependence of the creep rate was expressed as σ^n, where σ is the nominal stress and n the stress exponent.

RESULTS

The data from the creep experiments presented as a strain/time function are shown in Fig. 1. Three steps can be distinguished: An initial rapid, nearly instantaneous, deformation, a primary creep stage with decelerated creep and a secondary, almost steady state, creep stage; the latter stage being used for calculation of creep rates. The data may also be presented as a log strain/log time function with linear relationships (Figs. 2, 3). At strains below $4–5 \cdot 10^{-3}$ the curves are parallel. At higher strain/stresses, the

Table 1. *Materials used in the investigation*

Material	Batch no.			Manufacturer
	Code	Powder	Liquid	
Paladon 65	PD	5062900	5061472	Kulzer & Co. GmbH, Germany
Palacast	PC	6100080	610349	
Palapress	PP	6030545	6110357	
Swe Base	SB	603	602	Svedia Dental-Industri AB, Sweden
Swe Flow	SF	514	612	
Swebond Compact	SC	602	610	
SR 3/60	SR	20784	1904 IV 5611	Ivoclar AG, Liechtenstein
Ivocast	IC	19821 19593	2109 IZ 4841	
Quick 10	Q10	22279	0904 IR 6485	

PD, SB, and SR are heat-polymerized materials
PC, SF, and IC are auto-polymerized pour type materials
PP, SC, and Q10 are auto-polymerized dough type materials

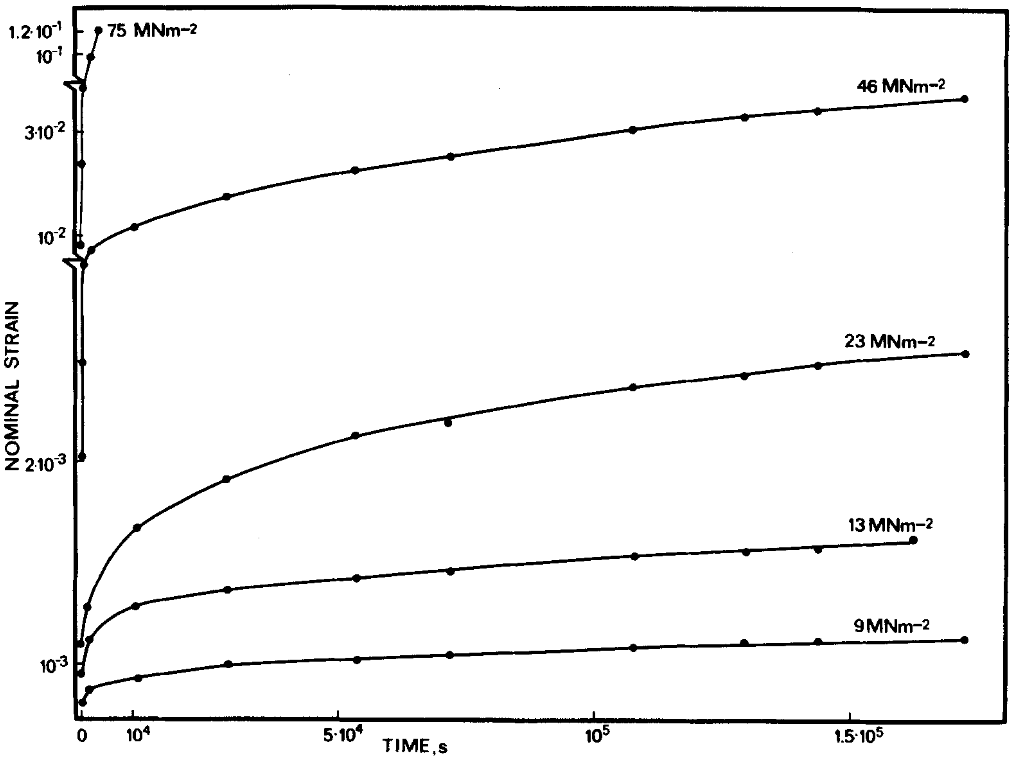

Fig. 1. Strain as function of time (creep) at 23°C for an auto-polymerized dough type material, Q10. After an initial rapid deformation a primary stage with creep rates decreasing with time is found, followed by an almost steady state secondary creep.

curves deviate, showing an increased slope with increasing stress levels. The strain values are higher for the pour type material (Fig. 3) than for the heat-polymerized one (Fig. 2). The pour type material has higher creep rates since the deviation from the parallelism of the curves occurs at lower stress values. At high strain with high stress a distinct deformation occurred. This deformation was practically fully recovered when the specimen was heated to 120°C for 30 min (Fig. 4).

The creep rates at 37°C and 50°C as a function of stress are shown in Figs. 5–9. A general feature in these curves is the transition from a fairly small stress dependence at low stress levels to high stress dependence at high stress levels. The stress exponent n at low stresses (<23 MNm^{-2}) was 1.4 to 1.5 at 37°C and it showed little variation for the nine materials. At higher stress levels ($>$ 46 MNm^{-2}) n was found to be 10 to 11, and again about the same value for all materials. The transition occurred at stresses in the range of 20 to 40 MNm^{-2} at 37°C. The strain where the deformation mode with the high stress dependence became dominant was between $5 \cdot 10^{-3}$ and $3 \cdot 10^{-2}$.

A comparison between the creep rates of the materials with 46 MNm^{-2} nominal stress at 23, 37 and 50°C is shown in Fig. 10. At 23°C the heat-polymerized materials had low creep rates, whereas higher rates were found for the auto-polymerized materials. At 37°C the creep rates increased for all materials. The differences in creep rates seen at 23°C between heat- and auto-polymerized materials were amplified. One material (PP) occu-

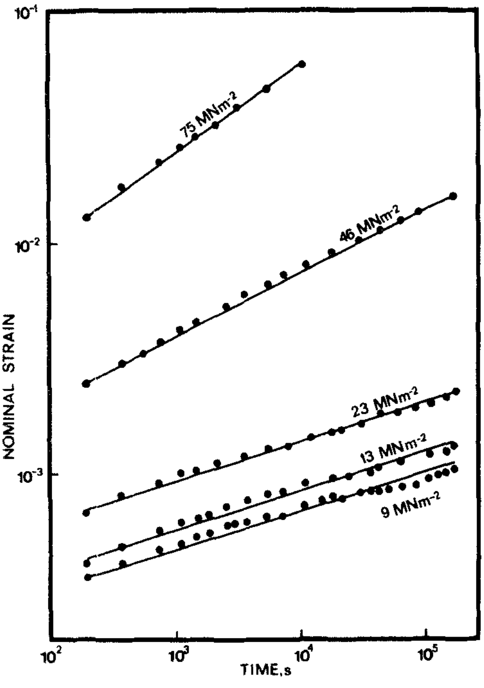

Fig. 2. Creep curves at 23°C of a heat-polymerized material. SR. Log strain vs. log time at different stress levels.

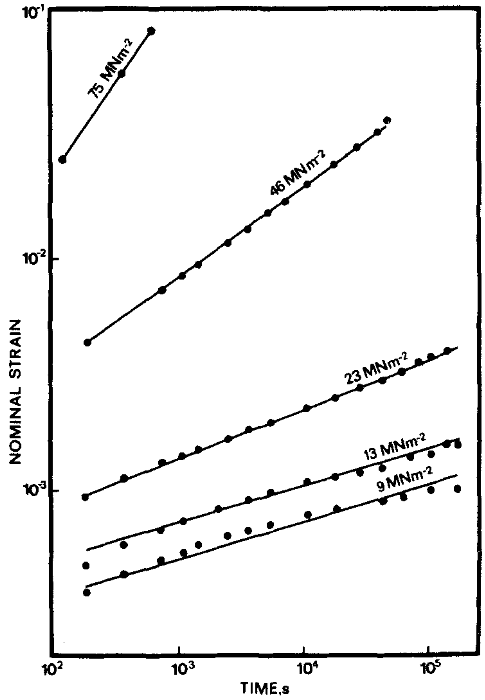

Fig. 3. Creep curves at 23°C of an auto-polymerized pour type material. IC. log strain vs. log time at different stress levels.

pied an intermediate position. At 50°C the materials can be divided into two groups: The heat-polymerized and the auto-polymerized materials.

Only minor differences were seen in creep rate among the heat-polymerized materials at the same temperature. However, the creep rates were 20 times higher at 50°C than at 37°C. Relatively large differences in creep rate existed between the different auto-polymerized materials. For the whole group of materials when tested at 50°C the highest creep rate was about 10^3 times larger than the lowest. This factor was about $3 \cdot 10^2$ at 37°C and about 15 at 23°C.

DISCUSSION

Denture base polymers represent a complex group of materials. They are made from polymer beads and monomer liquids of many formulations (11–13). A

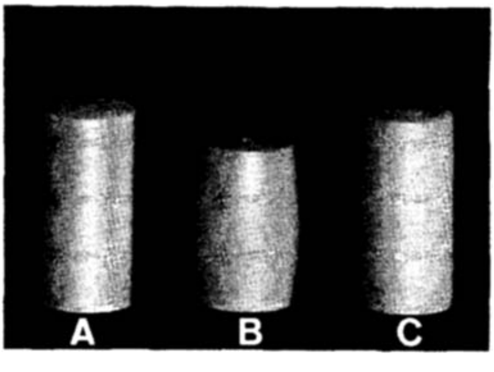

Fig. 4. Thermal recovery of a deformed denture base material. PP. A: Specimen before deformation. B: specimen deformed by compression, and stored for six months at 23°C, i.e. an apparent permanent deformation. C: After heating at 120°C for 30 min the original form and size of the specimen was recovered.

polymerized denture base material is assumed to be a multiphase system with three main phases, i.e. the part of the polymer beads which has not been pene-

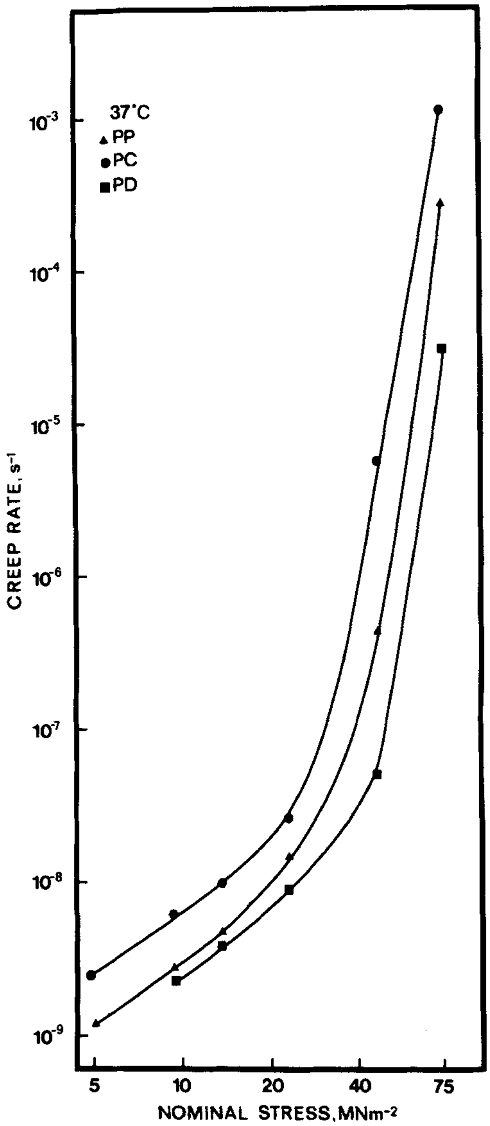

Fig. 5. Secondary creep rates at 37°C as a function of stress for an auto-polymerized pour type material, PC; an auto-polymerized dough type material, PP; and a heat-polymerized material, PD. All materials contained 1,4-BDMA as cross-linking agent.

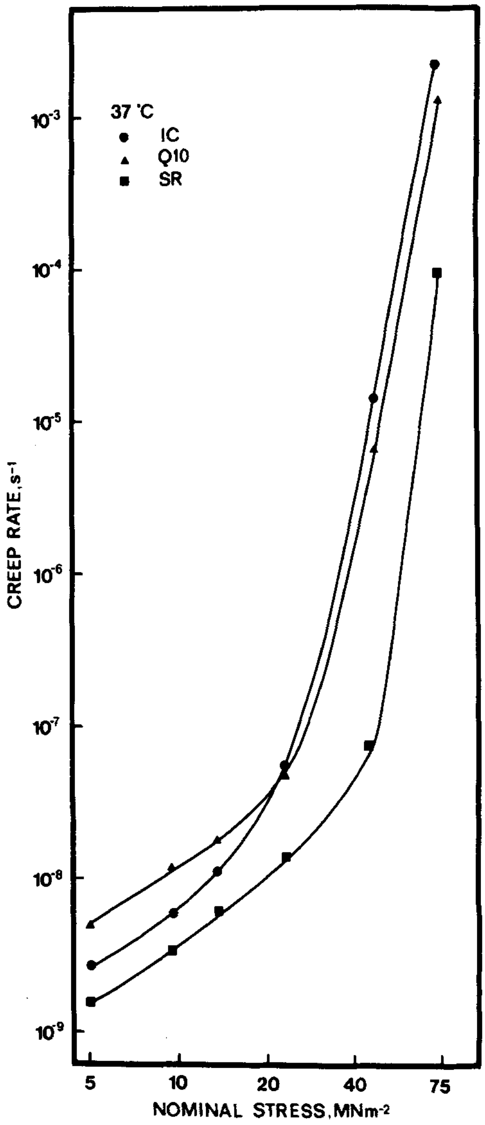

Fig. 6. Secondary creep rates at 37°C as a function of stress for an auto-polymerized pour type material, IC, an auto-polymerized dough type material, Q10, and a heat-polymerized material, SR. All materials had 8 to 9% of the cross-linking agent EGDMA.

trated by the monomers, the part of the polymer beads penetrated by the monomers forming a final interpenetrating network (IPN) (2) and a matrix from the monomer liquid. The ratio of the phases in a given material depends on the type of material, processing conditions, and powder/liquid ratios.

Several creep equations have been proposed for PMMA, but they are all more cumbersome to use than graphical presentation (16). For polymers, in general, it has been established that the resistance to creep in a uniaxial compression is superior to the resistance to creep in tension (16).

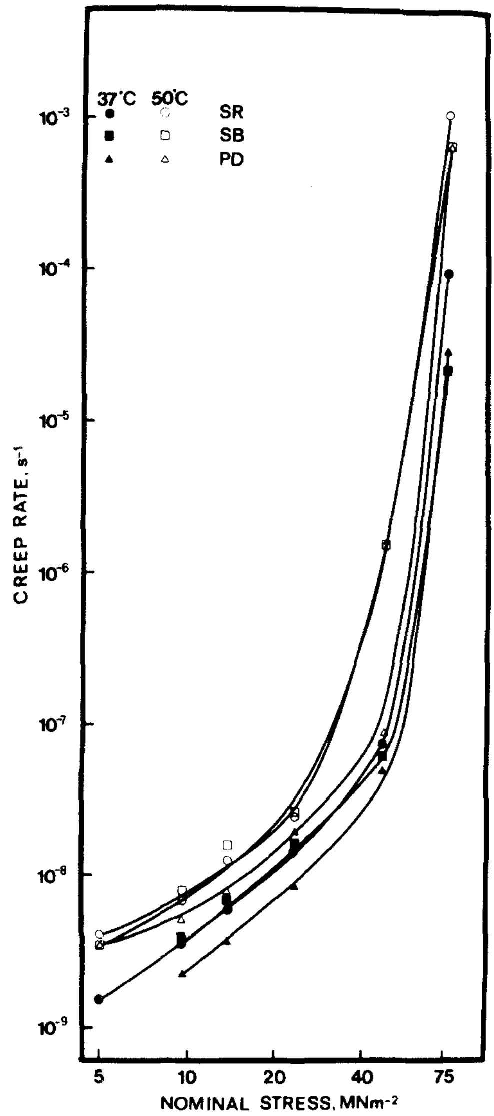

Fig. 7. Secondary creep rates for heat-polymerized materials as a function of stress at 37 and 50°C with 9% EGDMA, SR; 3% EGDMA, SB; and 3.3% 1,4-BDMA, PD, in their monomer liquids.

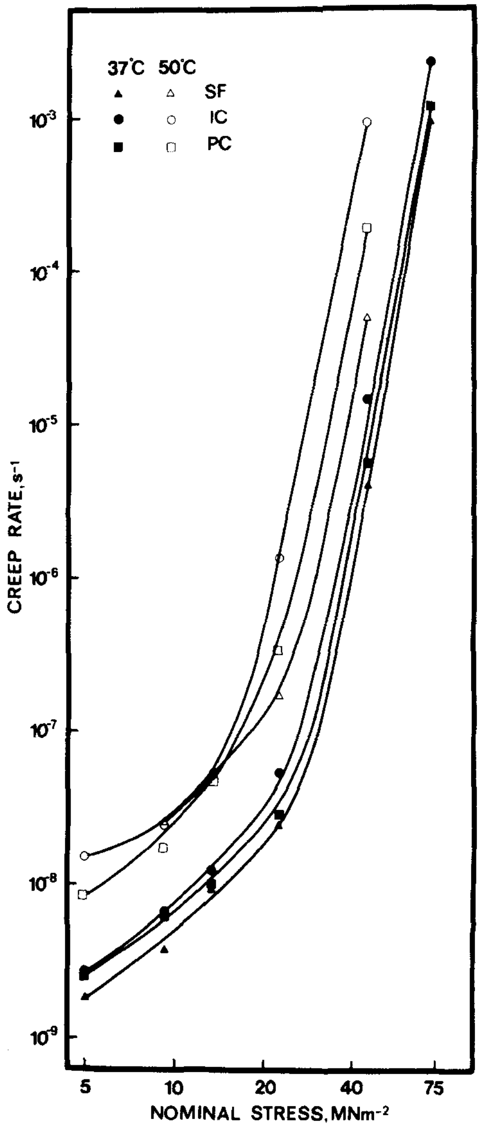

Fig. 8. Secondary creep rates as a function of stress at 37 and 50°C for auto-polymerized pour type materials with 9.0% EGDMA, IC; 2.5% EGDMA, SF; and 4.4% 1,4-BDMA, PC, in their monomer liquids.

A comparison of the secondary steady state creep rates of materials with 3 to 5 per cent of the cross-linking agent 1,4-butanediol dimethacrylate (1,4-BDMA) in the monomer liquid (11, 13) demonstrates that the creep rates are related to the processing conditions (Fig. 5). This dependence on the processing conditions is also evident for the materials with 8 to 9 per cent of the cross-linking agent ethylene glycol dimethacrylate (EGDMA) in the monomer liquids (11, 13) (Fig. 6). The apparent irregular crossing of the curves of the auto-polymerized dough (Q10) and pour type materials (IC) is probably due to different composition of the pol-

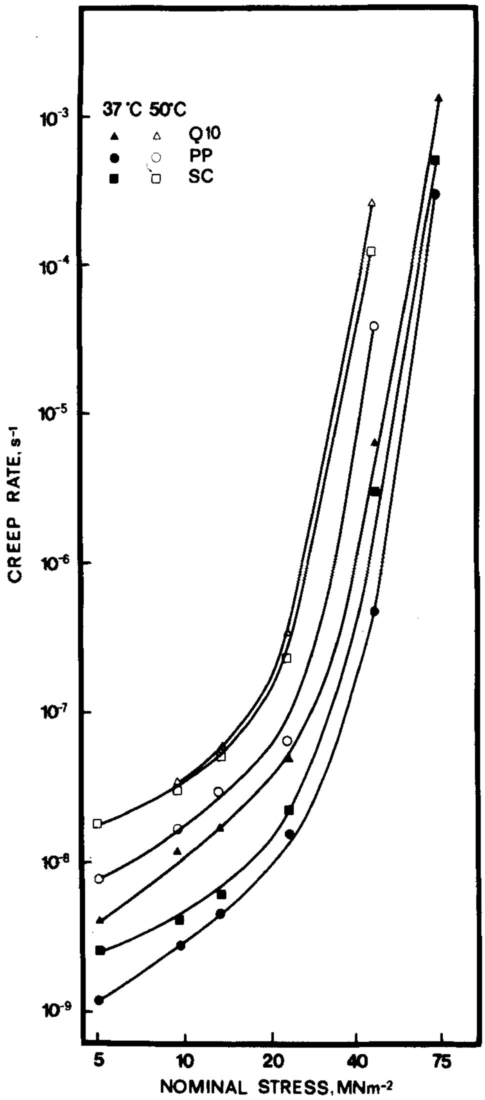

Fig. 9. Secondary creep rates as a function of stress at 37 and 50°C for auto-polymerized dough type materials with 8% EGDMA, Q10; 2.0% EGDMA, SC; and 4.7% 1,4-BDMA, PP, in their monomer liquids.

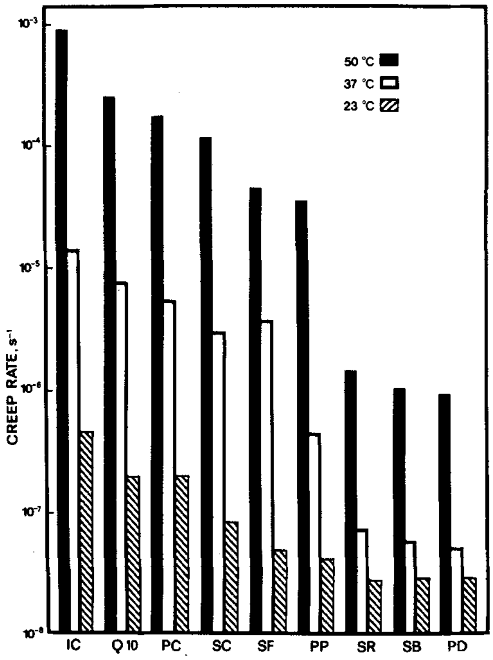

Fig. 10. Secondary creep rates as a function of temperature for all denture polymers investigated, when subjected to a nominal stress of 46 MNm^{-2}.

ymer beads. The beads of IC are of PMMA, whereas those of Q10 are a copolymer of MMA and approximately 20 per cent ethyl methacrylate (EMA) (12). It is known that the compressive yield stress (17) and softening point (3) decreases with increasing size of the ester group in methacrylate ester polymers. Accordingly the creep of a polymer should increase with increasing amounts of the ethyl methacrylate units, as demonstrated by increased creep rates at low stresses for Q10.

The heat-polymerized materials showed only minor differences with respect to creep rate, at both low and high stress levels and at different temperatures. It was, however, observed that the material PD, with 3.3 per cent 1,4-BDMA as cross-linking agent (11, 13) had the lowest creep rates at low stress values both at 37 and 50°C (Fig. 7).

At low stress the pour type materials had creep rates of about the same magnitude. However, at higher stress the differences increased, especially at 50°C. These differences can be correlated to the cross-linking agents in their monomer liquids. The material IC with 9 per cent EGDMA (11) had the highest creep rate, and the material SF with 2.5 per cent EDGMA (11) had the lowest creep rate (Fig. 8).

The degree of conversion of monomers to polymer is determined by the polymerization temperature. Pendant methacrylate groups will remain both in the matrix and IPN of the resulting polymeric network system which may have a plasticizing effect at low deformation rates (13). With increasing content of cross-linking agent the amounts of pendant methacrylate groups should increase. This was noted at higher stress values for IC and also for the auto-polymerized dough type material Q10. Of the auto-polymerized dough type materials tested at 37°C, Q10 had higher creep rates at low stress values than SC and PP (Fig. 9). This was probably due to the polymer beads in Q10 which are copolymers of MMA and EMA (12). The high content of EGDMA in the monomer liquid of Q10 (11, 13) may, in addition, contribute to the high creep rates seen at high stress levels. At 50°C the material SC, with 8 per cent dibutyl phtalate in the monomer liquid (13), also had relatively high creep rates at the low stress values. This was probably due to the plasticizing effect of dibutyl phtalate at this temperature.

The slope at the lower part of the curves in Figs. 5 to 9 may represent a «bulk» deformation implying a relatively homogeneous deformation at low stress levels.

At $2.8 \cdot 10^{-2}$ strain in a uniaxial compression fine diffuse shear zones or micro bands initiate flaws in the PMMA, whereas broad diffuse shear bands were observed at strains of about $6 \cdot 10^{-2}$ (10). In multiphase systems like denture base polymers, there is a high probability for local stress concentrations to occur.

Secondary creep at high stress levels, represented by the slope at the upper part of the curves (Figs. 5–9), may be ascribed to an inhomogeneous deformation mechanism. This means that the strain is localized in certain local regions, i.e. the shear bands. In these shear bands strain softening may take place, resulting in increased creep rates.

At high creep values there was an apparent irreversibel deformation at isothermal conditions. In the shear bands it is assumed to be an orientation on the molecular level. When annealed above the glass transition temperature, sufficient thermal energy is introduced into the material to restore the original molecular statistical disorder. It is known that a deformed glassy polymer test specimen may recover its original dimensions when heat-treated above its glass transition temperature (7).

At high stress levels the creep rates are highly temperature dependent. The differences in creep rates between materials investigated increased with increasing temperature (Fig. 10). These circumstances may be explained by increased thermal motions of the pendant methacrylate groups, which separate the main chain segments of the polymer backbones. However, the heat-polymerized polymers had the lowest creep rates at all temperatures and stress levels, irrespective of composition.

REFERENCES

1. Bevan, L. Crazing under applied compression. J. Mater. Sci. 1978, 13, 216 – 217
2. Braden, M. Polymeric prosthetic materials. In: von Fraunhofer, J.A. ed. Scientific aspects of dental materials. Butterworths, London and Boston 1975, pp 425 – 458
3. Crawford, J.W.C. The properties of some *higher polymethacrylic esters*. J. Soc. Chem. Ind. 1949, 68, 201 – 208
4. Glantz, P.-O. & Bates, J.F. Creep in some acrylic dental resins. Odontol. Revy 1973, 24, 283 – 292
5. Glantz, P.-O. & Stafford, G.D. Recovery of some acrylic resins after repeated loading. 1. Laboratory study. Swed. Dent. J. 1973, 66, 129 – 134
6. Glantz, P.-O. & Stafford, G.D. Recovery of some acrylic resins after repeated loading. 2. Clinical study. Swed. Dent. J. 1973, 66, 137 – 142
7. Haward, R.N. The post-yield behaviour of amorphous plastics. In: Haward, R.N. ed. The physics of glassy polymers. Applied Science Publishers Ltd., London 1973, pp 340 – 393

8. Jagger, R.G. & Huggett, R. The effect of cross-linking on indentation resistance, creep and recovery of an acrylic resin denture base material. J. Dent. 1975, 3, 15 – 18
9. Menges, G., Riess, R. & Suchanek, H.-J. Einfluss korrosiver Flüssigkeiten auf mechanisch beanspruchte Thermoplaste. Kunstst. 1974, 64, 200 – 204
10. Nugent, H. & Bevan, L. Deformation of PMMA samples containing a stress-raising flow. Polym. 1979, 20, 661 – 662
11. Ruyter, I.E. Release of formaldehyde from denture base polymers. Acta Odontol. Scand. 1980, 38, 17 – 27
12. Ruyter, I.E. & Pedersen, B. Composition of denture base materials. 1979. In preparation
13. Ruyter, I.E. & Svendsen, S.A. Flexural properties of denture base polymers. J. Prosthet. Dent. 1980, 43, 95 – 104
14. Stafford, G.D., Bates, J.F., Huggett, R. & Glantz, P.-O. Creep in denture base polymers. J. Dent. 1975, 3, 193 – 197
15. Stafford, G.D. & Huggett, R. Creep and hardness testing of some denture base polymers. J. Prosthet. Dent. 1978, 39, 682 – 687
16. Turner, S. Creep in glassy polymers. In: Haward, R.N. ed. The physics of glassy polymers. Applied Science Publishers Ltd., London 1973, pp 223 – 278
17. Vincent, P.I. Methacrylate ester polymers. Plast. 1962, 27, 105 – 110