Oxygen inhibition of autopolymerization of polymethylmethacrylate–glass fibre composite

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The aim of this study was to determine the thickness of the unpolymerized surface layer of autopolymerizing polymethylmethacrylate (PMMA) and PMMA–glass fibre (GF) composite. Powder-to-liquid (P/L) ratios of 10:8, 10:9 and 10:10 by weight of the commercial PMMA was tested and the E-glass fibre weave was used as filler in the PMMA–GF composite. The resin was polymerized between two glass plates at 55 °C in air under an air pressure of 300 kPa. Five samples were polymerized for each test group. The inhibition depth was measured by a light microscopic technique with polarized light. The inhibition depth was affected by the P/L ratio of the PMMA: the mean inhibition depth of the unfilled PMMA with the P/L ratio of 10:10 was 248.6 μm, while it was 175.4 μm in PMMA with the P/L ratio of 10:8 ($p = 0.044$). The inhibition depths were higher in the PMMA–GF composite than in the plain PMMA, which was explained by an inadequate impregnation of the GF weave with the PMMA resin. The results suggest that improper impregnation of the fibre product with autopolymerizing PMMA resin can cause oxygen inhibition of the polymerization reaction which should be taken into account when fibre products are clinically used.

1. Introduction

Polymethylmethacrylate (PMMA) resin has been used in denture fabrication since the 1940s [1]. When dentures are made from heat-cured PMMA, a modified compression-moulding technique is used. In the heat-cured PMMA, the polymerization is initiated by heat, but when the denture is repaired, the heat-cured PMMA is replaced by autopolymerizing PMMA. Polymerization of autopolymerizing PMMA is activated by chemical compounds such as tertiary amine or barbituric acid which allows polymerization to occur at lower temperatures. Because the reactivity of oxygen with free radicals is higher than that with monomers of PMMA, the polymerization reaction of autopolymerized PMMA is inhibited by oxygen [2]. This leads to the formation of an unpolymerized surface layer of the resin which can be examined by microscopic techniques [3–6].

Removable partial or complete dentures often fracture due to the fatigue of the PMMA caused by the occlusal forces during mastication [7, 8]. To avoid fractures, various methods of reinforcing PMMA have been tested [9–22]. The most promising reinforcing methods are based on the fibre composites [17, 18, 22]. Partial fibre reinforcement (PFR) of the denture is placed accurately to the position of the probable fracture initiation, contrary to total fibre reinforcement (TFR) which reinforces the whole denture base. The PFR can be used in denture repairs with autopolymerizing PMMA. By varying the powder-to-liquid (P/L) ratio of dental PMMA, the viscosity, polymerization shrinkage, and thus the impregnation capability of the PMMA resin can be modified [16]. It is possible that inadequately impregnated regions of fibre product with PMMA can cause internal inhibition of polymerization of PMMA. The inhibiting effect of oxygen on the polymerization of the PFR made from PMMA–glass fibre (GF) composite has not, however, been studied so far.

The aim of this study was to determine the inhibiting effect of oxygen on the polymerization of the PMMA–GF composite. The effect of different P/L ratios of the PMMA resin on the oxygen inhibition was also tested.

2. Materials and methods

Clear autopolymerizing PMMA resin (Palapress Vario, liquid batch no 241; powder batch no 1527, Heraeus Kulzer GmbH, Wehrheim, Germany) was used as test material. The PMMA resin was mixed in P/L ratios of 10:8, 10:9 and 10:10 by weight. A drop of each resin mixture was placed on a glass microscope slide (thickness 1.00 mm) and covered with a glass cover slip (thickness 0.14 mm) to prepare unfilled test samples (Fig. 1) [4]. E-glass fibre was used in the form

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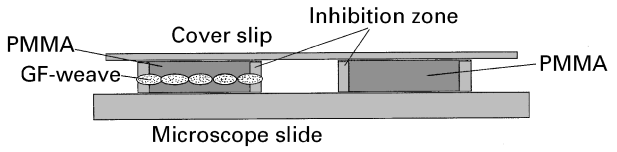

Figure 1 Assembly for measuring thickness of the inhibition layer of PMMA–GF composite and plain PMMA.

of plain fibre weave (No 1080, 48 g m^{-2}, Hexcel, Villeurbanne, France) in preparing the PMMA–GF composite samples. The PMMA–GF composite samples were prepared by dipping a piece of the fibre weave (5×5 mm) in mixtures of PMMA of various P/L ratios. The piece of the fibre weave was then placed between the glass plates for polymerization (Fig. 1). The samples were exposed to air at the boundary between the two glass plates.

The polymerization of the PMMA and the PMMA–GF composite samples was carried out at 55.0 °C ± 1.0 °C for 15 min. To improve thermal conductivity in the samples during polymerization in air, the microscope slides were placed on a brass cylinder (diameter: 50.0 mm, weight 331.2 g) with a temperature of 55.0 °C. The samples were cured in a pneumatic curing unit under an air pressure of 300 kPa. Five ($n = 5$ per group) samples of each PMMA resin mixture with and without the GF-weave were polymerized.

The thickness of the inhibition layer in the samples was measured by using a micrometre bar in a transmission light microscope with polarized light (Orthoplan, Ernst Leitz GmbH, Wetzlar, Germany) with a magnification of ×32. Three measurements were made of each of the samples. The mean values of the measurements were used in the statistical analysis. Micrographs were taken of the samples for visual analysis of the inhibition layer. Cross-sections of the PMMA–GF samples were made to examine the degree of impregnation of the fibre bundles with PMMA. The cross-sections were ground wet with no. 4000 (FEPA) silicon carbide grinding paper and examined under light microscope with a magnification of ×205.

One-way ANOVA was used to determine the statistical differences of the thickness of inhibition layers between the groups of various P/L ratios. Two-way ANOVA was used to analyse the effect of the P/L ratio and incorporation of the GF weave on the thickness of the inhibition layer of PMMA.

3. Results

Mean thickness of the inhibition layer in the samples with P/L ratio of 10 : 10 was 248.6 μm, with P/L ratio of 10 : 9 225.0 μm and with P/L ratio of 10 : 8 175.4 μm ($p = 0.004$) (Fig. 2). The samples of PMMA–GF composite had thickness of the inhibition layer between 248.6 and 218.0 μm ($p = 0.325$). The P/L ratio of the PMMA mixture and the incorporation of the GF weave into the PMMA affected significantly the thickness of the inhibition layer ($p = 0.012$ and $p = 0.028$) (Table I). Fig. 3a and b shows inhibition layers of the

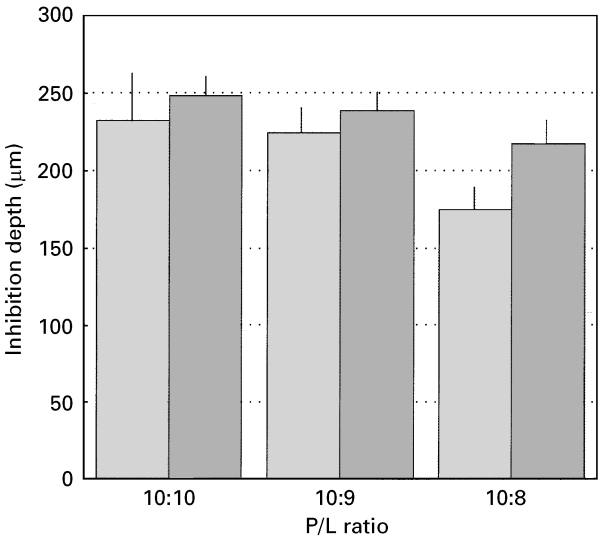

Figure 2 Mean thickness of inhibition layer of the test samples. (□) PMMA; (▩) GF–PMMA.

TABLE I Two-way ANOVA analysis of the P/L ratio and the incorporation of the glass fibre (GF) weave on the inhibition depth of autopolymerizing PMMA

Variable	SS	MS	d.f.	*F*	*p*
P/L ratio	11024.1	5512.0	2	5.4	0.012
GF weave	4200.6	4200.6	1	4.1	0.028
Interaction	1357.3	678.7	2	0.7	0.528
Within cells	25517.2	1021.6	24		

SS, sum of squares; MS, mean squares; d.f., degrees of freedom.

samples. Microscopical analysis of the cross-sections of the samples showed inadequately impregnated bundles of the fibres of the weaves with PMMA of various P/L ratios (Fig. 4).

4. Discussion

The inhibiting effect of oxygen on the polymerization of autopolymerizing PMMA–GF composite was demonstrated in this study. It has been shown that filler particles incorporated into resin diminish the effect of oxygen inhibition [6] by changing the viscosity of the resin. This is in agreement with the Nernst–Einstein relation which states that gas diffusion in liquid has a direct relation to the viscosity of the liquid [23].

Denture PMMA consists of prepolymerized powder beads and methylmethacrylate (MMA) monomer liquid which after the setting period forms a gel. The viscosity of the PMMA–MMA mixture before gel formation can be regulated by changing the P/L ratio of the mixture. The viscosity of the PMMA mixture affects the degree of impregnation of fibre product with PMMA [20]. Inadequate degree of impregnation has been reported to be one of the shortcomings of the PMMA–fibre composites used in dentures [15, 16, 24]. The inadequate degree of impregnation affects initially mechanical properties of the composite

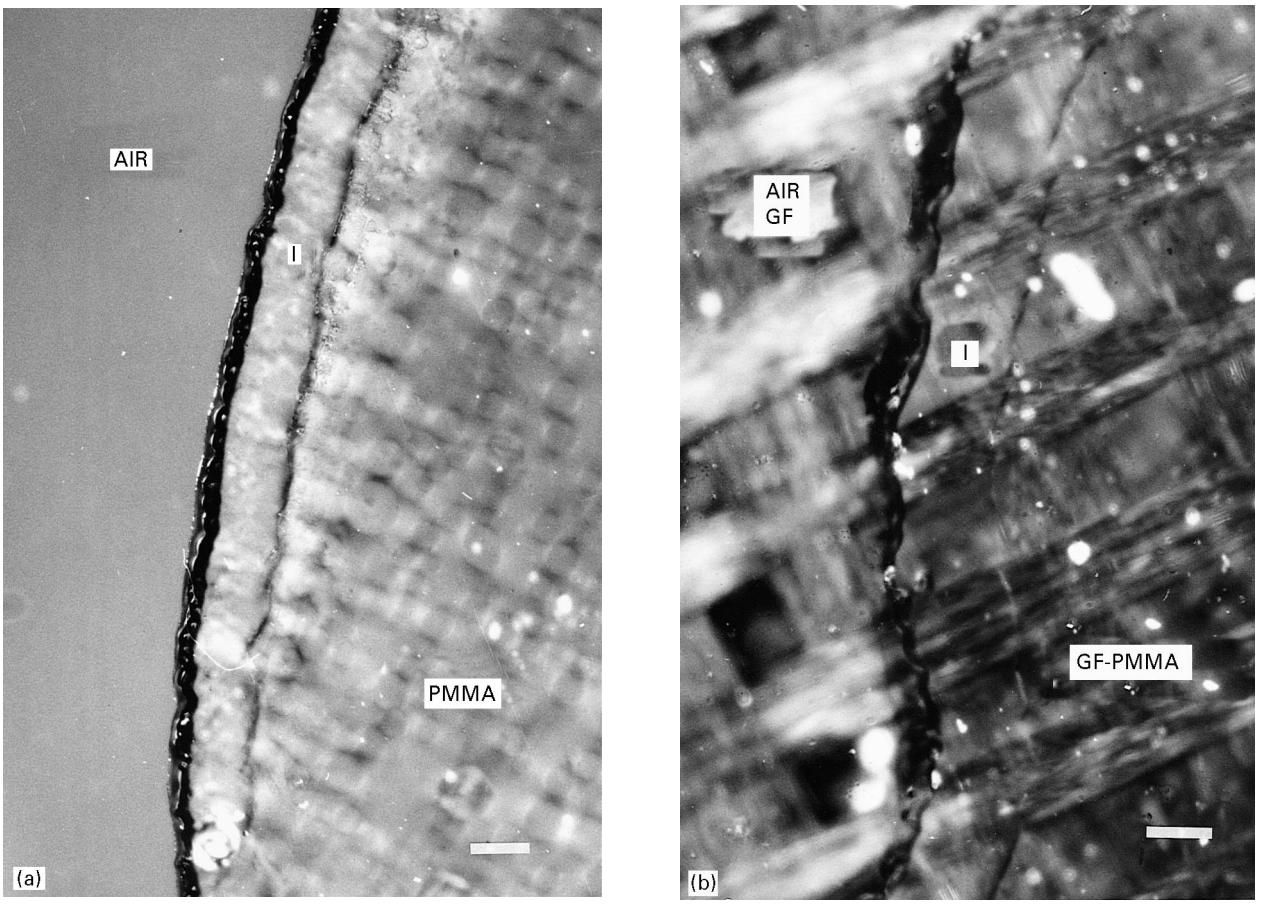

Figure 3 Micrographs of the inhibition layer of (a) plain PMMA and (b) PMMA–GF composite (GF, glass fibre; PMMA, polymethylmethacrylate resin; I, inhibition layer). Original magnification 32×, bar = 200 μm.

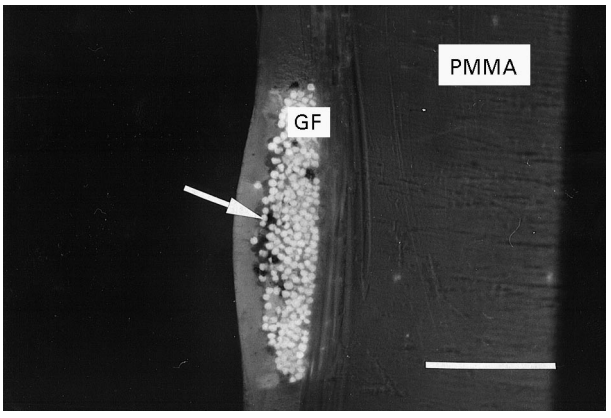

Figure 4 Cross-section of the PMMA–GF composite sample. Arrow indicates the poorly impregnated fibre bundle of the glass fibre weave. Original magnification 205×, bar = 100 μm.

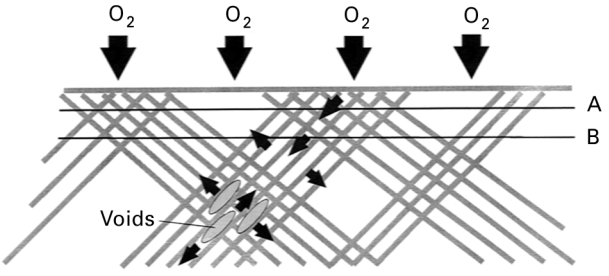

Figure 5 Schematic diagram of the oxygen inhibition in PMMA–GF composite. Line A shows the inhibition depth of plain PMMA and line B of poorly impregnated PMMA–GF composite. Voids in the structure of the composite act as oxygen reserves and cause internal inhibition of the polymerization.

but it also allows oral microbes to grow in the voids of the poorly impregnated composite. Acidic fermentation products of some of the oral microbes which grow in the voids of the PFR can cause corrosion of the GF surface, destroy the interface of polymer matrix and fibres, and thus decrease the strength of the PFR. This might lead to an unexpected fracture of the denture.

The results of the present study showed that the oxygen inhibition layer was thicker in the samples with the GF weave than in those without the GF weave. The explanation is likely in the inadequately impregnated GF bundles with the PMMA resin which left some voids between the fibres. Voids between the single fibres were oxygen reserves which allowed oxygen to inhibit polymerization deeper in the structure of the composite than in the plain PMMA, i.e. polymer without the voids (Fig. 5). This hypothesis might explain also some of the results of the previous studies, in which the mechanical properties of PMMA–GF composite with voids in the structure were investigated [15, 16, 24]. Consequently, the low strength of the inadequately impregnated autopolymerizing PMMA–GF composite might be caused by improper contact with the PMMA resin and the GF and by the

internal oxygen inhibition of the PMMA–GF composite at the regions of the voids.

From the clinical perspective, the results of the present study emphasize the importance of the good impregnation of the PFR and the TFR with the autopolymerizing PMMA. Poor impregnation leads to decreased mechanical properties of the dentures due to internal oxygen inhibition of the PFR or the TFR, which cannot be affected e.g. by polymerizing the denture in water. To obtain well-impregnated PFRs and TFRs for dentures, a novel type of fibre reinforcement which easily can be impregnated with PMMA resin should be developed. The internal oxygen inhibition should be taken into account also when other dental resins such as BISGMA (bisphenol-A-glycidyldimethacrylate) and TEGDMA (triethyleneglycoldimethacrylate) copolymer are used in order to make restoration or periodontal splints of fibre composite.

References

1. R. W. PHILLIPS, In "Skinner's science of dental materials", edited by R. W. Phillips (W.B. Saunders Company, Philadelphia, 1991) p. 177.
2. G. V. SHULZ and G. HENRICI, *Makromol. Chem.* **18/19** (1956) 437.
3. W. FINGER and K. D. JÖRGENSEN, *Schweizt. Monatsschr. Zahnheilk.* **86** (1976) 812.
4. I. E. RUYTER, *Acta Odontol. Scand.* **39** (1981) 27.
5. M. P. LEKKA, L. PAPAGIANNOULIS, G. C. ELIADES and A. A. CAPUTO, *J. Oral Rehabil.* **16** (1989) 287.
6. F. A. RUEGGEBERG and D. H. MARGESON, *J. Dent. Res.* **69** (1990) 1652.
7. D. C. SMITH, *Brit. Dent. J.* **110** (1961) 257.
8. P. K. VALLITTU, V. P. LASSILA and R. LAPPALAINEN, *Acta Odontol. Scand.* **51** (1993) 363.
9. C. E. CARROL and J. A. von FRAUNHOFER, *J. Prosthet. Dent.* **52** (1984) 639.
10. A. R. RUFFINO, *ibid.* **54** (1985) 75.
11. C. K. SCHREIBER, *Brit. Dent. J.* **130** (1971) 29.
12. D. L. GUTTERIDGE, *J. Dent.* **20** (1993) 50.
13. A. J. GOLDBERG and C. J. BURSTONE, *Dent. Mater.* **1** (1985) 66.
14. N. H. LADIZESKY, Y. Y. CHENG, T. W. CHOW and I. M. WARD, *ibid.* **9** (1993) 128.
15. P. K. VALLITTU, V. P. LASSILA and R. LAPPALAINEN, *J. Prosthet. Dent.* **71** (1994) 607.
16. P. K. VALLITTU, *ibid.* **71** (1994) 613.
17. P. K. VALLITTU, V. P. LASSILA and R. LAPPALAINEN, *Dent. Mater.* **10** (1994) 116.
18. P. K. VALLITTU, *J. Prosthodont.* **5** (1996) 270.
19. P. K. VALLITTU, H. VOJTKOVA and V. P. LASSILA, *Acta Odontol. Scand.* **53** (1995) 392.
20. P. K. VALLITTU, *J. Oral Rehabil.* **22** (1995) 257.
21. N. H. LADIZESKY and T. W. CHOW, *Clin. Mater.* **6** (1990) 209.
22. N. H. LADIZESKY, C. F. HO and T. W. CHOW, *J. Prosthet. Dent.* **68** (1992) 934.
23. W. JOST, In "Diffusion in solids, liquids, and gases" (Academic Press, New York, 1960) p. 459.
24. P. K. VALLITTU, *Appl. Compos. Mater.* **2** (1995) 51.

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