

Flexural Strength, Water Sorption and Solubility of a Methylmethacrylate-Free Denture Base Polymer Reinforced with Glass Fibre Reinforcement

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Abstract - A methylmethacrylate-free denture base polymer (Eclipse) in comparison to a conventional denture base polymer (Palapress vario) was evaluated after water saturation and Stick glass fibre reinforcement. The data were analysed with ANOVA at $\alpha=0.05$. Water-storage caused a decrease in the flexural strength and stiffness of the materials ($p>0.05$). Conventional denture base material with fibre reinforcement gave highest flexural strength (201.1 MPa) compared to fibre reinforced Eclipse (79.1 MPa) ($p<0.05$). Water sorption after 76 days was 2,08 % (Palapress vario) and 1,55% (Eclipse). Fibre-reinforcement of methylmethacrylate-free material was not as successful as conventional denture base and needs to be further optimized.

KEYWORDS: Denture base, Fibre reinforced composites, Glass fibres, Flexural strength, Water sorption, Solubility

INTRODUCTION

Poly(methylmethacrylate) (PMMA) has served as a successful denture base polymer since the 1930s and no other material has reached its popularity after its introduction^{1,2}. However, as a denture base it has several shortcomings that need further improvement. PMMA denture bases are susceptible to impact and fatigue fractures³⁻⁶. To improve the impact strength, PMMA denture base polymer have been reinforced with elastomeric particles to act as crack stoppers or various fibres have been incorporated to increase the fatigue life and stiffness of the denture base⁷⁻¹¹. High-impact denture base polymers generally required relatively complex curing cycles or special equipment, which limited their use¹⁰⁻¹².

Attempts to replace the poly(methyl methacrylate) with polymers that have different backbone structure were also made during the last decades but none of the materials have been widely accepted^{1,2,7,8}. A light-cured, urethane acrylate based denture base polymer is currently used. This material has been reported to have superior flexural properties, low water sorption and high polishability. The system also gives the dentist the option to shape the final material in the clinic avoiding the use of modelling wax¹³.

The flexural strength of denture base polymers especially with regard to fatigue is one important weakness and limits the service life under demanding clinical circumstances^{14,15}. Several methods have been suggested for reinforcement and mainly because of the additional cost and additional laboratory steps involved; none of these methods have been universally accepted¹⁴⁻¹⁷. Fibre reinforcement was extensively studied to replace reinforcing metal meshes

used in dentures^{11,15-19}. These reinforcements can be tailor-made for specific patient needs and the cost involved is relatively acceptable, compared to high-impact denture base polymers^{11,19-21}. Use of these fibre reinforcements have not been studied with the MMA-free polymer Eclipse and the reinforcement obtained is not known.

The flexural properties of this material under dry and wet conditions were reported previously¹³ but there are no reports about the water sorption and water solubility of this material and its compatibility with the currently used glass fibre reinforcement system Stick (Stick Tech, Finland).

The aim of this study was to evaluate the flexural properties of two denture base polymers before and after water saturation of the polymers and after application of glass fibre reinforcement with Stick fibres. Water sorption and solubility of these materials were also studied. The working hypothesis of this study was that the different polymers would behave differently after water saturation and fibre reinforcement.

MATERIALS AND METHODS

Materials

One of the polymer systems used in this study was a urethane acrylate based, light cured Eclipse Prosthetic resin, (Dentsply Trubyte, York, USA) (Lot 070213). This material was introduced as a paste, which can be softened for easy manipulation in a warm water bath and after the correct shape is given, light cured in a light curing oven. The conventional control was a poly methylmethacrylate (PMMA) based resin system Palapress vario (Heraeus Kulzer, Hanau, Germany)(Lot 011036 and 012352 for liquid and powder respectively). This second material is a pourable polymer system cured in a pneumatic curing chamber.

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Flexural testing

Specimens were prepared according to ISO 1567 (10 x 65 x 3.3 mm). Six groups were used (n=6) for the tests in each group and the groups and treatments are given in Table 2. The specimens prepared for groups one and two were polymerized in a Pneumatic Curing Unit (Acridense™ IV, GC America Inc.) at 50 °C and 2,00E+04 kg/m², for 20 minutes. The specimens prepared for groups three and four were placed into the preheated mould and then polymerized in Targis Power light-curing unit (Ivoclar Aktiengesellschaft, Schaan, Liechtenstein) (program 3, 2 x 31 minutes only light without heat).

In specimens groups five and six, the Stick glass fibres were first impregnated in liquid Palapress for 30 min before the Palapress material (group five) was placed into the mould and polymerized in Pneumatic Curing Unit (Acridense™) or the Eclipse Prosthetic resin (group six) was then placed in to the mould and gently heated. Polymerization was completed in Targis Power light-curing unit (Ivoclar) (program 3, 2 x 31 minutes only light without heat). The surfaces were polished with 1200 grit SiC – paper.

The specimens from the groups one and three were stored at room temperature (22 ± 0.2°C) for 5 days before testing.

The tests were made according to a 3-point bending test ISO 1567 with a universal testing machine (Lloyd Model LRX, Lloyd instruments, Fareham, England). The height and width of all specimens were measured before testing. Ultimate flexural strength (σ) (MPa) of the samples was calculated using the formula:

$$\sigma = \frac{3FL}{2bd^2}$$

where F is the load at fracture, L the span, b the width, and d the thickness of the specimens.

Flexural modulus (E) (MPa) was calculated from the graph with the following formula:

$$E = \frac{F}{D} \frac{L^3}{4bd^3}$$

where L is the span, b the width, b the height and F/D the slope of the linear region of the load-displacement curve.

Water sorption and solubility

Flexural strength samples were used for determining water sorption and solubility. After polymerization, the water uptake by weight was measured by an analytical balance (AT261 Deltarange Mettler Toledo, 0.1 mg resolution) after 1, 2, 6, 12, 19, 26, 33, 40, 47, 54, 62, 69, 76 days.

The specimens for the Solubility-groups were taken from the Water stored-groups after performing the 3-point bending test. The specimens were dehydrated in an oven at 50°C for 40 days. The weight change was measured at 2, 7, 13, 33,35,37,40 days. Water sorption (WS) and water solubility (SL) was calculated using the formulas:

$$WS\% = \frac{m_2 - m_3}{m_1} \times 100 \quad SL\% = \frac{m_1 - m_3}{m_1} \times 100$$

where m_1 is the initial mass, m_2 is the mass after water immersion and m_3 is the mass after dehydration.

Table 1. Materials used in the study.

Brand names (Code)	Manufacturer	Composition	Processing method
Eclipse	Dentsply Trubyte, York, PA	Urethane methacrylate, Stearyl acrylate	Soften the material in the conditioning unit for 1-1,5 minutes to allow manipulation. After application, cure in the Dentsply curing unit.
Palapress Vario	Heraeus Kulzer, Hanau, Germany	PMMA (powder), MMA, 1,4-BDMA (liquid)	Pourable polymer system;55°C at 2,00E+04 kg/m ² pressure/15 min
Stick	Stick Tec, Turku, Finland	E-glass fibres preimpregnated with PMMA	Wet the Stick fibres with the monomer and cure with the denture base polymer

PMMA= Poly(methyl methacrylate)
MMA= Methyl methacrylate
1,4-BDMA= 1,4-Butanediol dimethacrylate

Table 2. Groups and treatments used in the study.

Group	Material	Treatment/storage	Fibre reinforcement
1	Palapress	None/Dry stored	None
2	Palapress	None/Water stored at 37 °C for 77 days (18 Ω purity distilled water)	None
3	Eclipse	None/Dry stored at (22 ± 0.2 °C)	None
4	Eclipse	None/Water stored at 37 °C for 77 days (18 Ω purity distilled water)	None
5	Palapress	Glass fibres/Dry stored (22 ± 0.2 °C)	Unidirectional Stick, Longitudinal, Centre of the specimen
6	Eclipse	Glass fibres/Dry stored	Unidirectional Stick, Longitudinal, Centre of the specimen

Scanning Electric Microscopy

Scanning electron microscopy analysis were done after polishing of the fracture surfaces up to 4000-grit (FEPA) and carbon sputtering (SCD 050; Bal-Tec, Balzers, Liechtenstein). Then, the FRC materials were examined with a scanning electron microscope (SEM) (JSM-5500; Jeol Ltd., Tokyo, Japan) to determine impregnation of the fibre by the resin.

Statistical Analysis

Statistical analysis was performed using SPSS (Statistical package for social science, SPSS Inc., Chicago, IL). One-way analysis of variance was carried out for flexural strength, flexural modulus and water sorption values.

RESULTS

Flexural strength and flexural modulus results are shown in Table 2 and 3. The initial flexural strength of Eclipse was 101.5 (± 20.2) MPa. Water storage and fibre reinforcement both caused a decrease in the flexural strength (92.2 (± 15.1) and 79.1 (± 21.9) MPa respectively). However, this change was not significant ($P > 0.05$). Palapress had an initial flexural strength of 97.3 (± 13.1) MPa which decreased to 69.7 (15.5) MPa after water storage. Fibre reinforcement of Palapress resulted in an increase in flexural strength to 201.1 (± 618) MPa from the initial value of 973 (± 13.1) MPa ($P < 0.05$).

The flexural modulus of bending was also influenced by treatments. Water storage caused a slight decrease in the flexural modulus of the two unreinforced polymers. Flexural modulus of Eclipse decreased to 1.9 GPa from an initial value of 2.8 GPa ($P > 0.05$) and flexural modulus of Palapress decreased to 1.9 GPa from and initial value of 2.4 GPa ($P > 0.05$). Fibre reinforcement of Palapress resulted in a significant increase of flexural modulus to 3.7 GPa compared to the initial value ($P < 0.05$).

Water sorption and solubility values are presented in Figures 3 and 4 respectively. Percent water absorption was 2.08 for Palapress and 1.55 for Eclipse and these values were not statistically significant ($P = 0.077$) at 76 days. The water sorption of Palapress was higher until 12 days, and then slowed down and reached equilibrium after about 54 days. Eclipse, on the other hand, continued absorbing water and the absorption slowed down but still did not stop after 54 days. The solubility by weight is similar between the materials and at the level of 0.22 (± 0.08) and 0.20 (± 0.01) percent respectively for Palapress and Eclipse.

SEM images revealed that there were spaces between the matrix and the glass fibres in Eclipse and the impregnation of the fibres were only partly successful. Palapress specimen showed almost continuous contact between fibres and the matrix with very few empty spaces.

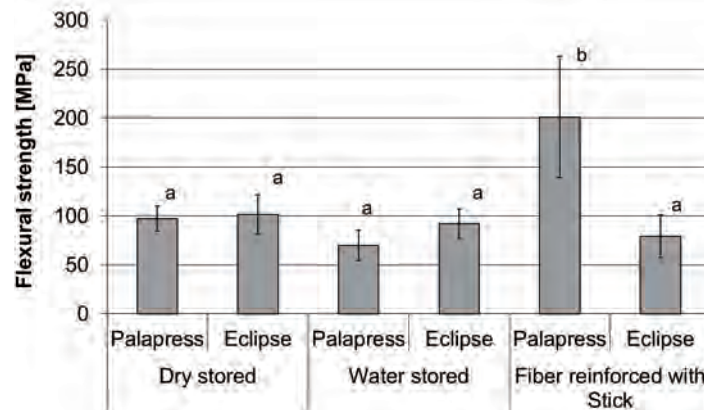


Figure 1. Flexural strength of the materials. Letters represent significant group.

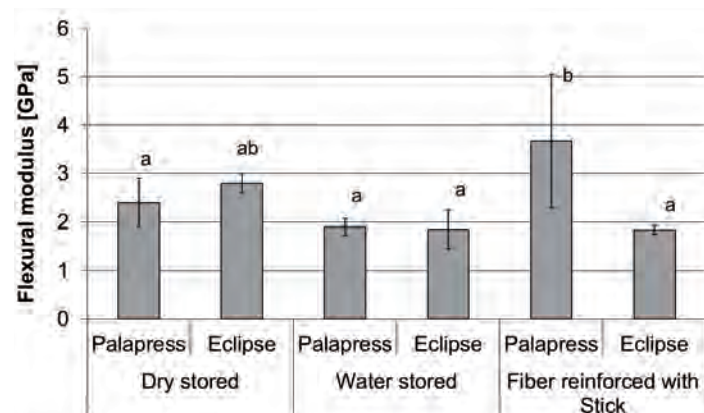


Figure 2. Flexural modulus. Letters represent significant groups.

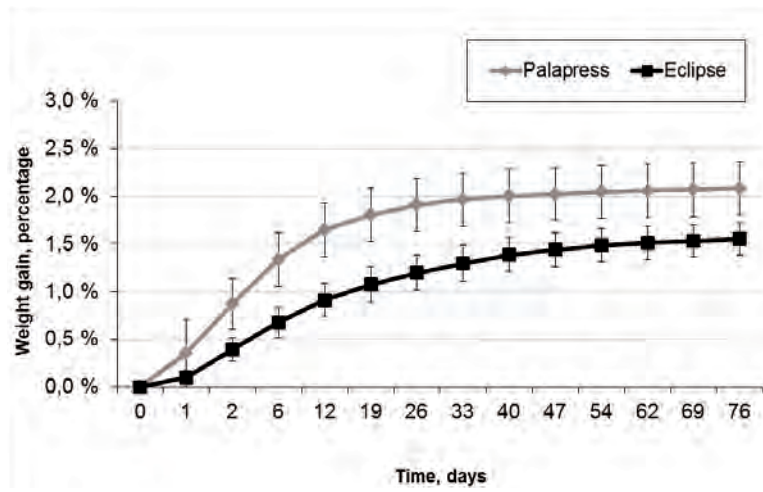


Figure 3. Weight gain of the materials as a result of water immersion at 37°C.

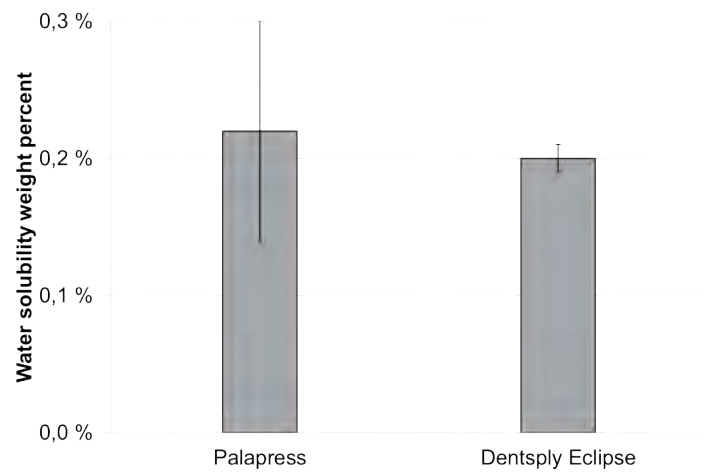


Figure 4. Water solubility of the materials after 72 days.

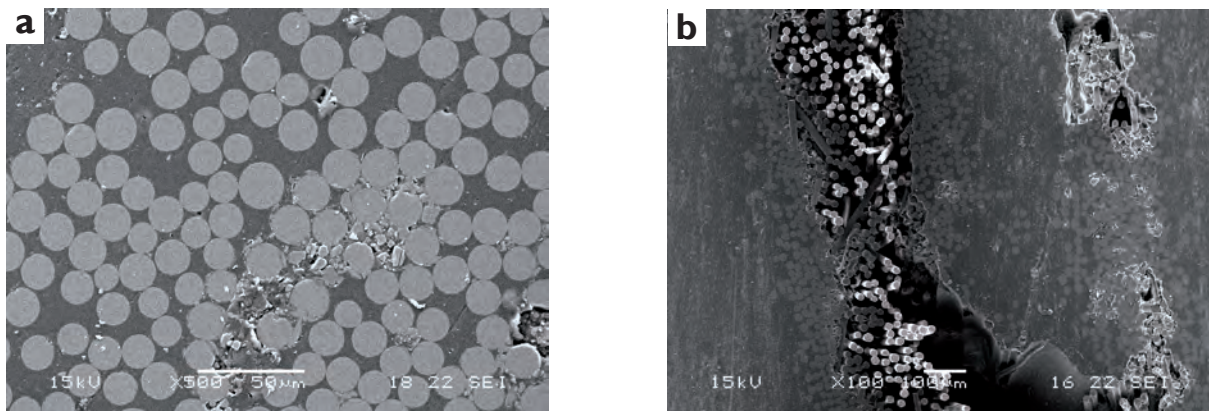


Figure 5a,b. SEM image of (a) Palapress Vario and (b) Eclipse after glass fibre reinforcement. Note the improper wetting/impregnation of the fibres in Eclipse.

DISCUSSION

Palapress was cured in a pressurized chamber in the existence of heat. Although this curing technique is different compared to the compression molding technique, the chemical composition is very similar to the conventional heat-cured denture base polymer¹². Therefore, this denture base polymer was used to compare different aspects of denture base polymer performance to that of Eclipse prosthetic resin.

In the current study, the test samples were immersed in distilled water for 76 days. By plotting the weight gain in time in a graph (Fig. 3), it was shown that the two materials approached equilibrium in time. Water content of a polymer affects the mechanical properties. For PMMA, water diffuses throughout the polymer resulting in a plasticizing effect and increased water content decreases the modulus of elasticity of the polymer²¹. Therefore, testing the mechanical properties of a denture base polymer after water saturation will give valuable information about how the material will behave in the oral environment.

Based on the results of the flexural tests, the hypothesis that the different denture base polymers will behave differently was partly rejected. The initial flexural strength of Eclipse material was higher than Palapress. However, the difference was not significant. The flexural strength values obtained from the current study is in accordance with previous publications testing the initial flexural strength of Eclipse^{8,22}.

Water storage for 76 days resulted in a decrease in flexural strength for both the material types. This is expected because the effect of water on the elastic modulus of polymers in general is well known²¹. At the time of testing, the samples used in this study contained about 1,5 to 2 % water. This may have affected the flexural strength by softening the material. Previous reports about the water-immersed samples of Eclipse report higher flexural strength results^{23,24}. This may be due to difference in the testing protocols. The previous tests were done after 30 days of water immersion. In the present study, 76 days was used. The water sorption chart shows that for PMMA based Palapress, equilibrium is reached after 50-60 days and for Eclipse, after 70 days the water absorption slowed down and the material approached equilibrium. A 30 day period is certainly not enough for these materials to reach equilibrium, especially for Eclipse.

MMA-free polymer Eclipse had significantly higher flexural modulus before water immersion and water immersion decreased the stiffness resulting in similar flexural modulus compared to PMMA-based denture base polymer. This decrease in stiffness may have long-term consequences when fatigue and longer-term water immersion is involved. A comparison with PMMA-based denture base with regard to endurance strength under flexural fatigue could be useful in predicting the behaviour of these materials under clinical settings.

Fibre reinforcement of PMMA denture base with glass fibres is a popular concept and is recommended where a higher flexural modulus and fatigue resistance is needed^{10,11}. The results obtained from the current study with reinforcement of Palapress with Stick fibres is in good agreement with a previous study where Palapress was reinforced with Stick fibres and tested under similar conditions⁶. The flexural strength of the fibre reinforced Palapress was significantly higher than the initial strength of the unreinforced Palapress. However, for Eclipse, such an increase was not observed. The flexural strength of glass fibre reinforced Eclipse was lower, showing that the fibre reinforcement did not succeed. Also, the SEM images of the fracture surfaces reveal that wetting of the fibre bundles and proper impregnation was not obtained with Eclipse (Fig. 5a,b). The high viscosity of the Eclipse could be the reason. Previously, similar problems were reported because of the highly viscous denture base polymers²⁵⁻²⁸. Energy dissipation mechanism of a fibre reinforced composite relies on the bond strength between fibres and the matrix. Poor impregnation will allow the fibres to be pulled out without friction, resulting in lower fracture toughness. Thus, using the currently recommended methods, Stick fibres will not have a reinforcing effect with Eclipse.

Palapress and Eclipse differed with regard to the amount of water they absorbed after 76 days of water immersion (Fig. 3). It can be seen that Palapress had a steeper curve during the first twelve days. Eclipse had a more gradual increase of water content. This shows that PMMA absorbs water faster. The urethane acrylate based Eclipse has a slower rate of water sorption, but reaches a similar level at the time of equilibrium.

CONCLUSIONS

The results of this study revealed that modifications with regard to application technique are needed to obtain the reinforcing effect of Stick fibres with MMA-free denture base polymer. With regard to water sorption and solubility, Eclipse resin showed slower water sorption rate and comparable equilibrium water-uptake results to that of a conventional PMMA denture base polymer.

ACKNOWLEDGEMENTS

The authors would like to thank Genevieve Alfont for her help in technical assistance and specimen preparation.

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REFERENCES

1. Jagger DC, Harrison A, Jandt KD. The reinforcement of dentures. *J. Oral Rehabil.*, 1999; **26**:185.94.
2. Rueggeberg FA. From vulcanite to vinyl, a history of resins in restorative dentistry. *J. Prosthet. Dent.*, 2002; **87**:364.79.
3. Vallittu PK, Alakuijala P, Lassila VP, Lappalainen R. In vitro fatigue fracture of an acrylic resin-based partial denture: an exploratory study. *J. Prosthet. Dent.*, 1994; **72**:289.95.
4. Vallittu PK, Lassila VP, Lappalainen R. Transverse strength and fatigue of denture acrylic-glass fibre composite. *Dent. Mater.*, 1994; **10**:116.21.
7. Vallittu PK, Lassila VP, Lappalainen R. Evaluation of damage to removable dentures in two cities in Finland. *Acta Odontol. Scand.*, 1993; **51**:363.9.
8. Narva KK, Lassila LV, Vallittu PK. The static strength and modulus of fibre reinforced denture base polymer. *Dent. Mater.*, 2005; **21**:421.8.
9. Jagger DC, Jagger RG, Allen SM, Harrison A. An investigation into the transverse and impact strength of "high strength" denture base acrylic resins. *J. Oral Rehabil.*, 2002; **29**:263.7.
10. Machado C, Sanchez E, Azer SS, Uribe JM. Comparative study of the transverse strength of three denture base materials. *J. Dent.*, 2007; **35**:930.3.
11. Pfeiffer P, Rolleke C, Sherif L. Flexural strength and moduli of hypoallergenic denture base materials. *J. Prosthet. Dent.*, 2005; **93**:372.7.
12. Vallittu PK. A review of fibre-reinforced denture base resins. *J. Prosthodont.*, 1996; **5**:270.6.
13. Vallittu PK. A review of methods used to reinforce polymethyl methacrylate resin. *J. Prosthodont.*, 1995; **4**:183.7.
14. Mutluay MM, Ruyter IE. Evaluation of adhesion of chairside hard relining materials to denture base polymers. *J. Prosthet. Dent.*, 2005; **94**:445.52.
15. Mumcu E, Cilingir A, Gencil B, Sülün T. Flexural properties of a light-cure and a self-cure denture base materials compared to conventional alternatives. *J. Adv. Prosthodont.*, 2011; **3**:136.9.
16. Jagger DC, Harrison A, Jandt KD. The reinforcement of dentures. *J. Oral Rehabil.*, 1999; **26**:185.94.
17. Rached RN, de Souza EM, Dyer SR, Ferracane JL. Dynamic and static strength of an implant-supported overdenture model reinforced with metal and nonmetal strengtheners. *J. Prosthet. Dent.*, 2011; **106**:297.304.
18. Polat TN, Karacaer O, Tezvergil A, Lassila LV, Vallittu PK. Water sorption, solubility and dimensional changes of denture base polymers reinforced with short glass fibres. *J. Biomater. Appl.*, 2003; **17**:321.35.
19. Karacaer O, Polat TN, Tezvergil A, Lassila LV, Vallittu PK. The effect of length and concentration of glass fibres on the mechanical properties of an injection- and a compression-molded denture base polymer. *J. Prosthet. Dent.*, 2003; **90**:385.93.
20. Tezvergil A, Lassila LV, Vallittu PK. The effect of fibre orientation on the thermal expansion coefficients of fibre-reinforced composites. *Dent. Mater.*, 2003; **19**:471.7.
21. Vallittu PK. A review of fibre-reinforced denture base resins. *J. Prosthodont.*, 1996; **5**:270.6.
22. Kangasniemi I, Vallittu P, Meiers J, Dyer SR, Rosentritt M. Consensus statement on fibre-reinforced polymers: current status, future directions, and how they can be used to enhance dental care. *Int. J. Prosthodont.*, 2003; **16**:209.
23. Takahashi Y, Chai J, Kawaguchi M. Effect of water sorption on the resistance to plastic deformation of a denture base material relined with four different denture reline materials. *Int. J. Prosthodont.*, 1998; **11**:49.54.
24. Pfeiffer P, An N, Schmage P. Repair strength of hypoallergenic denture base materials. *J. Prosthet. Dent.*, 2008; **100**:292.301.
25. Diaz-Arnold AM, Vargas MA, Shaul KL, Laffoon JE, Qian F. Flexural and fatigue strengths of denture base resin. *J. Prosthet. Dent.*, 2008; **100**:47.51.
26. Ali IL, Yunus N, Abu-Hassan MI. Hardness, flexural strength, and flexural modulus comparisons of three differently cured denture base systems. *J. Prosthodont.*, 2008; **17**:545.9.
27. Vallittu PK. Acrylic resin-fibre composite - Part II: the effect of polymerization shrinkage of polymethyl methacrylate applied to fibre roving on the transverse strength. *J. Prosthet. Dent.*, 1994; **71**:613.617.
28. Vallittu PK. The effect of void space and polymerization time on transverse strength of acrylic - glass fibre composite. *J. Oral Rehabil.*, 1995; **22**:257.261.
29. Vallittu PK. Impregnation of glass fibres with polymethylmethacrylate by using a powder coating method. *Applied Composite Materials*, 1995; **2**:51.58.
30. Vallittu PK. Flexural properties of acrylic polymers reinforced with unidirectional and woven glass fibres. *J. Prosthet. Dent.*, 1999; **81**:318.326.