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Developments in denture teeth to prevent softening by food solvents

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Abstract The effect of various food-simulating solvents on the hardness of denture teeth after varying storage times, using a Martens hardness test was determined. Martens hardness (HM) was assessed at baseline and during storage up to 1 month in distilled water (DW), peppermint oil (PO), heptane (HT) and 75% ethanol (ET) for four commercially-available denture teeth; Vivodent (VIV), Double-cross-linked Postaris (DCL), Orthosit (ORT), Candulor porcelain (POR) and two polymer based experimental denture teeth: Experimental 1 (EXP1); a hybrid nanocomposite with two different sized silanated filler particles and Experimental 2 (EXP2); containing an organic copolymer based upon urethanedimethacrylate and polymethyl methacrylate. Hardness [mean (sd)] at baseline was: VIV 142 (1), DCL 142 (1), ORT 209 (9), POR 2926 (101), EXP1 285 (11), and EXP2 146 (12). One-way ANOVA using Tukey's test on polymer-based materials showed that the hardness values of ORT and EXP1 were significantly higher than those of VIV, DCL and EXP2 ($P < 0.05$). Moreover, EXP1 had a significantly higher hardness value than ORT ($P < 0.05$). Except for EXP1, all polymer based materials showed a significant drop in hardness after storage in ET ($P < 0.05$). Specimens stored in water, heptane and peppermint oil showed minor fluctuations in hardness, which were not statistically significant.

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Introduction

The predictable long-term success of implants and implant-retained prostheses (IRP) [1–3] has led to an exponential rise in the provision of this restorative treatment [4], which is set to continue. As with any restorative treatment, long-term maintenance is a major concern. Maintenance needs include repair of fractured clips, dentures, screws, artificial teeth and gold bar. Although some of these problems have been extensively investigated [5–11], an insidious development that clinically is becoming more and more apparent is the high rate of wear in artificial teeth on IRP and opposing conventional dentures. In order to restore worn occlusal surfaces, prostheses have to be remade partially or in total. Such maintenance has considerable clinical and laboratory cost implications.

There are a number of factors that may explain the clinically observed higher wear rate of denture teeth in IRP as compared to conventional complete dentures. These include higher occlusal forces, improved chewing efficiency and changes in the dietary habits of these patients [12–16]. Solvents in the diet may chemically soften denture teeth and be a contributing factor to greater wear.

Foods and drinks contain a number of chemicals, which act as potential solvents. The American Food and Drug Administration (FDA) use food-simulating liquids to test their reaction particularly to plastic containers [17]. The same principle has been used in investigations of solvent resistance of restorative composite resins [18, 19]. The FDA consider that the solubility parameter of solvents contained in foods lies between 1.51×10^{-4} (heptane) to 4.8×10^{-4} $J^{1/2}$ $m^{-3/2}$ (water). 75% ethanol with solubility parameter of 3.1×10^{-4} $J^{1/2}$ $m^{-3/2}$ has been shown to have maximum softening effect on unfilled Bis-GMA [18, 19]. Another potential solvent is peppermint oil, which has been shown to reduce hardness in resins used to cement orthodontic brackets [20, 21].

Most studies investigating the effect of food simulating solvents on hardness have been carried out on composite resins; however, denture teeth are equally susceptible to softening by food-simulating solvents [22].

Since the introduction of resin denture teeth in the mid-20th century, there have been steady developments in order to improve their properties. Currently, there are five broad categories of polymer-based denture teeth available:

1. Polymethylmethacrylate (PMMA)
2. PMMA with filler
3. Cross-linked polymer and matrix (Double Cross-Linked [DCL])
4. Interpenetrating Polymer Network (IPN)
5. Microfilled urethanedimethacrylate (Composite resin based)

All of them except the composite-resin based material contain PMMA as their basic constituent. Various manufacturers have their own brands available within these categories. Additionally, porcelain denture teeth are also available for clinical use.

The materials chosen for this study (Table 1) represent all the above categories with the exception of the IPN. A brief description of the DCL and the Composite resin based material (ORT) is given below.

Double Cross-Linked is an acrylic material constructed using a dough molding procedure in which both the bead pre-polymer and the freshly polymerized monomer are cross-linked. Traditional acrylic materials contain only cross-linked matrix methacrylate and this restricts the beneficial effect of cross-linking. Cross linking both the matrix PMMA and the original bead PMMA offers a potential advantage provided the bead PMMA is not cross-linked to an extent which prevents interpenetrating networks of the matrix and discrete phase polymers.

Orthosit (ORT) is a composite resin based material and contains an inorganic filler based primarily on silica. Although the filler is silanated, there is little scope for bonding of the filler and resin matrix with this material.

The two experimental teeth included (EXP1 and EXP2) are being developed in order to improve mechanical properties especially the wear resistance of denture teeth. EXP 1 is a type of ''hybrid nanocomposite'' designed to overcome problems of filler-matrix bonding experienced with ORT. EXP1 has two main types of fillers, which are both silanated with γ methacryloxypropyltrimethoxysilane. The first group of particles are <20 nm and the second group >100 nm. The resin phase consists of an organic copolymer which is a splintered organic polymer made in a mix of PMMA and urethanedimethacrylate. The formulation of filler and copolymer is designed to achieve optimum bonding between the discrete and continuous phases in the composite structure.

EXP2 contains an organic copolymer filler based upon UDMA and PMMA and is designed to give an even rate of wear with minimal surface roughening. The formulation is designed to reduce wear of both the material and the counterface, which comes into contact with the material.

The aims of this study were to test the effect of various food simulating solvents on the hardness of artificial denture teeth. The hypothesis to be tested was that the polymer-based denture tooth specimens will be softened after storage in 75% ethanol and peppermint oil but that the modified compositions of the experimental teeth would reduce this effect.

Materials and methods

Four commercially-available and two experimental prototype denture tooth materials were investigated (Table 1). The materials were tested for Martens hardness (HM). HM measurements were made on a Martens testing machine with hardness measurement head (Zwick Z 2.5, Zwick GmbH & Co, Ulm, Germany) using a previously described method (Shahdad et al. 2005, accepted).

The manufacturer (Ivoclar Vivadent, Schaan, Liechtenstein) produced samples of denture teeth as circular disc specimens suitable for hardness testing. The details of

Table 1 Materials included in the study

Code	Material details
VIV	Vivodent (polymethylmethacrylate)
DCL	Postaris (double-cross-linked polymethylmethacrylate)
ORT	Orthosit (micro-filled composite resin; urethanedimethacrylate with SiO_2 filler)
POR	Candulor (porcelain)
EXP1	Experimental 1 (micro-filled composite resin; urethanedimethacrylate with specially surface treated SiO_2 filler)
EXP2	Experimental 2 (polymethylmethacrylate and 20% urethanedimethacrylate pre-polymer)

Ivoclar Vivadent, Schaan, Liechtenstein, manufactured all the specimens specimen production have also been previously described by the authors (Shahdad et al. 2005, accepted).

The effect of various food simulating solvents on specimen hardness was tested. Three different food simulating solvents were chosen to broadly cover the spectrum of solvent effects. These were peppermint oil, 75% ethanol and heptane. Distilled water was used as a control storage medium.

The effect of storage time in these solutions was tested. One specimen from each material group was stored in each solvent for 1 min, 5 min, 1 h, 24 h, 1 week and 1 month respectively. One specimen from each group was also tested dry (stored in air) to establish the baseline HM value.

All specimens were tested within 15 min of removal from the solvent. The specimens were blotted dry before testing at ambient temperature. Four indentations were made on each specimen.

The HM was calculated automatically by software (TestXpert®, Zwick GmbH & Co, Ulm, Germany) and was expressed as test force F (50N) divided by the surface area of the indenter $A_s(h)$ penetrating beyond the zero-point of the contact and was expressed as N/mm^2.

The results of the hardness tests of dry specimens were analysed using one-way ANOVA. Significant differences between materials were determined using Tukey's test. Any significant differences in the hardness after storage in solvents were also tested using one-way ANOVA. A value of $P < 0.05$ was regarded as significant.

Results

The means and standard deviations of Marten's hardness (HM) for the six materials tested dry are shown in Table 2. The hardness values of POR were approximately 10 times higher than any of the polymer-based materials and hence were excluded from the one-way ANOVA. Tukey's test showed that EXP1 was the hardest polymer based material being significantly harder than ORT. Both ORT and EXP1 were significantly harder than VIV, DCL and EXP2 ($P < 0.05$).

After storage in 75% ethanol for 1 month all polymer based materials except EXP1 showed a statistically significant reduction in hardness (Table 3). The percentage reduction in hardness values of VIV, DCL and EXP2 after 1 month were remarkably high (96, 85 and 90% respectively). There was also a marked reduction of 68% in hardness of ORT after 1 month storage in 75% ethanol. On the contrary, EXP1 showed only a 30% reduction in its hardness. Despite this drop the values at 1 month were greater than the values of VIV, DCL and EXP2 at baseline. The most marked drop in hardness of all the materials occurred between the 1 week and 1 month time period (Fig. 1) except for ORT which also showed a significant ($P > 0.05$) drop between 24 h and 1 week time period.

Specimens stored in water, heptane and peppermint oil showed minor fluctuations in hardness, which were not statistically significant.

None of the solvents had any effect on the hardness of the porcelain specimens.

Table 2 Mean hardness (HM) values of dry specimens

Material	HM (sd)
VIV	142 (1)[a]
DCL	142 (1)[a]
ORT	209 (9)[b]
POR	2926 (101)[d]
EXP1	285 (11)[c]
EXP2	146 (12)[a]

(sd) standard deviation

Mean values of materials with the same superscript are not statistically significantly different ($P < 0.05$)

Table 3 Percentage reduction in hardness after storage for one month in 75% ethanol

Material	HMi (sd)	HMf (sd)	HMi–HMf/Hmi%
VIV	142 (1)	6 (1)*	96%
DCL	142 (1)	21 (2)*	85%
ORT	209 (9)	67 (5)*	68%
POR	2926 (101)	3008 (94)	No change
EXP1	285 (11)	200 (30)	30%
EXP2	146 (12)	14 (2)*	90%

HMi: Initial Martens hardness

HMf: Final Martens hardness

* Significant reduction in hardness ($P > 0.05$)

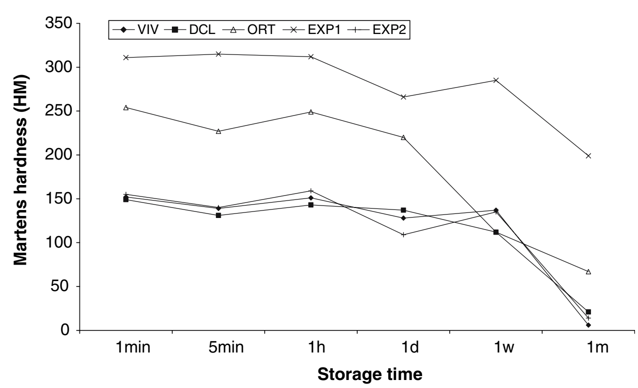

Fig. 1 Changes in hardness at various time points after storage in 75% ethanol

Discussion

As was hypothesised, all of the resin-based materials were softened by 75% ethanol albeit to varying degrees. The formulation of EXP1 provided the highest level of hardness and greatest resistance to solvent softening. Not surprisingly, POR produced the highest HM values, which remained unaffected by any of the solvents.

Six different denture tooth materials were included in the study. The composition of these materials covered the range of denture teeth available to clinicians plus two prototype materials. Acrylic denture teeth have been criticised for years due to their low wear resistance [23, 24] compared with porcelain teeth. However, porcelain has its own disadvantages that include brittleness, lack of bonding to the denture base and contact clicking sound during function. Also, once the porcelain surface glaze is lost, it becomes very abrasive [25]. Several attempts have been made to develop denture tooth materials with properties between those of acrylic and porcelain. In vitro and in vivo studies have shown improvement in hardness and wear resistance of these new generations of improved denture teeth [22, 26–30].

The Martens hardness test is suitable for hardness testing of most solid materials. The reason is that the hardness value comes from the indentation depth under working load and is therefore less affected by the material's visco-elastic and optical properties (Shahdad et al. 2005, accepted). It includes the effects of both elastic and plastic deformation and visco-elastic effects during loading. Also the geometry of the indenter, which is identical to the Vicker's pyramidal diamond indenter, makes the result theoretically independent of the test force chosen [31], which has also been previously confirmed in denture teeth (Shahdad et al. 2005, accepted). The variation of hardness with load is a well-known artefact of traditional hardness testing and is often known as the indentation size effect [32]. Martens hardness is much less susceptible to such indentation size effects as it is based on the Oliver and Pharr method [33] which corrects for the effects of elastic recovery whereas traditional Vickers testing does not.

The solvents selected in this study have been previously used by other investigators and would be a fair representative, if not a rigorous test, of food and drinks [18–21, 34, 35]. The 75% ethanol concentration has a solubility parameter of 3.1×10^{-4} $J^{1/2}$ $m^{-3/2}$ which has been shown to have maximum softening effect on unfilled Bis-GMA. Peppermint oil was chosen based on the previous findings, which have shown to reduce hardness in resins used to cement orthodontic brackets, while heptane represents the vegetable oils, meats and fats.

The higher HM values of ORT and EXP1 in this study are explained by the incorporation of silica microfiller. These materials are similar in that they both contain UDMA cross-linking agent reinforced with inorganic silica microfillers. However, EXP1 has two different sized fillers and a reformulated resin phase designed to achieve optimum bonding between the discrete and continuous phases in the composite structure. This study demonstrates that these modifications have rendered EXP1 statistically significantly harder than its structurally similar counterpart, ORT even after storage in 75% ethanol for 1 month. Moreover, the degree of softening of EXP1 after a month was less than half that seen for ORT. On the other hand, the formulation of EXP2 was not successful in improving hardness and resistance to solvent softening and produced similar results to other polymer-based materials

The effect of food-simulating solvents on hardness of restorative materials has previously been investigated [18, 19, 36]. In this study 75% ethanol (representing a stringent test of alcohol-containing food and drink) significantly affected the hardness of polymer-based materials, with VIV the worst affected and EXP1 the least affected. After one-month immersion VIV specimens retained only 4% of the initial hardness value whereas EXP1 retained 70% of its initial hardness value. Such softening is in agreement with previous investigators [18, 19, 22, 35]. Wu and McKinney [19], reported that immersion of composite resin material in 75% ethanol for 2-weeks reduced the hardness value by approximately 65%. Mair [37], questioned the relevance of storage in 75% ethanol before determining the hardness of restorative materials. He commented that even the strongest of alcoholic drinks rarely approach 25% ethanol, and hence it could safely be assumed that the exposure time of a restoration to this environment is negligible in the vast majority of the population. Although this is generally true, nonetheless, various spirits available for consumption do contain alcohol in excess of 40%. Certainly, low concentration alcohol solutions (9%) do accelerate three-body wear compared with water [38]. Furthermore, rather than simulate average conditions, tests should represent the harshest conditions in order to evaluate materials for their long-term durability for use in vivo.

Storage in heptane did not reduce the hardness of any materials tested but gave some slight, although not statistically significant, increases in the hardness of VIV, ORT, and EXP1. This finding has also been previously reported [18, 34, 35], and has been attributed to the effects of heptane in reducing the oxygen inhibition during post curing. However, in case of denture teeth, it is unlikely that the phenomenon of post curing would have any great effect because of the optimal curing process that denture teeth undergo during the manufacturing process. Nonetheless, heptane may reduce the leaching out of silica and metal ions from composite filler particles following specimen storage in aqueous solutions.

The inclusion of peppermint oil as one of the solvents was based on findings by earlier investigators [20, 21]. They reported that peppermint oil may soften the resin used in the bonding of orthodontic brackets and that the degree of softening was influenced by storage time. Additionally, there is anecdotal evidence that many edentulous patients wearing dentures routinely suck on sweets containing peppermint. However, peppermint oil did not reduce the hardness of any of the denture teeth tested in our study. The composition and polymerisation method of denture teeth and orthodontic resin are significantly different and it is fair to assume that these factors may render denture teeth resistant to softening by peppermint oil. Hence, the hypothesis that peppermint oil would soften denture teeth was rejected.

Finally, the greatest drop in HM was noticed between one week and one-month storage in 75% ethanol (Fig. 1). It is unclear whether this change in hardness is gradual over this three-week period or whether the change is sudden after a specific time period of storage. Our study was designed with frequent early measurements to determine if softening occurred rapidly following solvent immersion, which did not appear to be the case. Further research is recommended to test the specimens at other intervals in order to study this behaviour in detail.

Conclusions

Based on the results of this study, we conclude that EXP1, which is a type of a hybrid nanocomposite resin based material, is significantly harder than other polymer-based materials tested in this study. Moreover, storage in 75% ethanol significantly reduced the hardness of all polymer-based materials except EXP1 with some materials showing greater reduction than others.

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