Light Cured Fluoride Filled Denture-Coating Materials

Panarat Kodkeaw,[1] Piyawat Phankosol,[2] Nantana Jiratumnukul[3]

[1]*Dental Biomaterials Science, Graduate School, Chulalongkorn University, Bangkok 10330, Thailand*
[2]*Faculty of Dentistry, Department of Prosthodontics, Chulalongkorn University, Bangkok 10330, Thailand*
[3]*Faculty of Science, Department of Materials Science, Chulalongkorn University, Bangkok 10330, Thailand*

Received 18 February 2009; accepted 9 September 2009
DOI 10.1002/app.31558
Published online 10 December 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Light cured denture-coating materials were prepared by formulating an acrylate monomer with a photoinitiator system (camphorquinone and dimethylaminoethyl methacrylate) using one of three base monomers [bisphenol A glycerolate diacrylate (Bis-GDA), glycerol 1,3-diglycerolate diacrylate (GDA), and diurethane dimethacrylate (DU-DMA)] each with four diluents [triethylene glycol dimethacrylate (TEGDMA), di(ethylene glycol) methyl ether methacrylate, 2-hydroxyethyl methacrylate (HEMA), and methacrylic acid (MAA)] at a fixed 1 : 1 molar ratio of base monomer to diluent. The twelve formulations were then evaluated for their surface hardness and water sorption as coating materials. The DU-DMA/MAA, DU-DMA/HEMA, Bis-GDA/HEMA, and GDA/MAA based coatings provided a high level of both surface hardness and water sorption properties. When sodium fluoride (NaF) or calcium fluoride (CaF_2) was incorporated into those formulations, the fluoride ion release rate from all four NaF containing coating materials was extremely high in the first week, decreasing sharply in the second week and then decreasing in the later 2 weeks. In contrast, the CaF_2 containing coating materials showed a slower sustained rate of fluoride ion release over the 4-week test period, with the DU-DMA/HEMA based coating having a fluoride ion release pattern that meets the requirements for dental use.
 J Appl Polym Sci 116: 743–747, 2010

Key words: radiation cured coating; denture; fluoride

INTRODUCTION

Fluoride is well-known for its efficiency in the prevention of dental caries (cavities). The major effect of fluoride is the mineralization of dental hard tissues, which continues throughout the life time of the tooth.[1] Fluoride ions at a low level (0.1–2.0 ppm) in oral fluids can markedly inhibit tooth demineralization during acid attack.[1–5] Although brushing of the teeth with fluoride tooth paste (1,000 ppm) has been strongly linked to the reduction in the prevalence of caries, the fluoride content in saliva decreases rapidly after cleaning and returns to the base line within 1–2 h.[1] The resultant extended time period of a low localized oral fluoride concentration, and thus low protection from dental caries, could be of concern, especially in the case of removable denture users.

Removable partial dentures are a noninvasive and low cost treatment for the prosthetic rehabilitation of tooth loss. However, wearing removable partial dentures is one of the additional risk factors for dental carries development in elderly people,[6] where the incidence of new and recurrent caries, as well as the average severity of root caries, is greater in users of removable partial dentures, especially in those people who wear removable partial dentures in both jaws.[7–9]

Acrylic-based removable partial dentures are often used in developing countries because they are a noninvasive, fast to work with, and provide a low cost solution for prosthetic rehabilitation. However, this type of prosthesis has serious drawbacks with regards to the prognosis of the remaining teeth, which could be the result of having a high contact area with the neighboring teeth which makes for both cleaning difficulty and large surface area to harbor plaque, and thus allows for an inability or inattention to maintain good oral hygiene, with subsequent enhanced cavity formation in the neighboring teeth.[6]

Denture-coating materials are widely used in dental application for esthetic purposes, such as, coating the polished surface of acrylic denture base or the coating materials can serve to fill up tiny holes on the surface of the acrylic and to enhance its resistance to plaque build up.[10–12] In addition, the ability of denture-coating materials to seal the surface of acrylic-based polymers can help to reduce the level of residual monomers that are released.[13]

Correspondence to: N. Jiratumnukul (jnantana@sc.chula.ac.th).

Contract grant sponsors: Chulalongkorn University, King's Dental Innovation Center.

The objective of this research was to study the physical properties of light curable denture-coating materials and their fluoride release rate with a view to potentially using fluoride-filled polymeric coatings on dentures to supply fluoride ions for the adjacent teeth to the denture for prevention of cavity formation.

EXPERIMENTAL

Materials

The three base monomers, bisphenol A glycerolate diacrylate (Bis-GDA), glycerol 1,3-diglycerolate diacrylate (GDA), and diurethane dimethacrylate (DU-DMA) were purchased from Sigma-Aldrich. The four diluents were purchased as follows: triethylene glycol dimethacrylate (TEGDMA) from Fluka Chemicals, di(ethylene glycol) methyl ether methacrylate (DEGME-MA) and 2-hydroxyethyl methacrylate (HEMA) from Sigma-Aldrich, and methacrylic acid (MAA) from Merck. Camphorquinone (CQ) was purchased from Fluka Chemicals and (2-dimethylaminoethyl) methacrylate (DMAEMA) was purchased from Merck. Sodium fluoride (NaF) and calcium fluoride (CaF_2) were purchased from Merck.

Coating formulation preparation

The twelve coating formulations were prepared using the combination of the three base monomers and the four diluents in 1 : 1 molar ratio (Table I). To all twelve formulations, the visible light photoinitiator system [0.5% (w/w) CQ and 1.0% (w/w) DMAEMA] was added. Subsequentially, 5% (w/w) NaF or 4.6% (w/w) CaF_2 was added into those coating formulations found to have both a high surface hardness and water sorption, so as to obtain NaF-filled and CaF_2-filled light curable coating materials for studying the possibility of controlled *in situ* fluoride ion release.

Specimen preparation

The 10 disk-shaped specimens (13 mm diameter and 0.5 mm thickness) were prepared from each formulation according to ISO 4049[14] and then cured in a light-curing chamber (POLYLUX-P/PT; DREVE-Dentamid GmbH) for 5 min on each side of the disk. Polymerized specimens were removed from the molds and the edge was polished to remove flash and irregularities using No. 1000 grit abrasive paper. The specimens were then cleaned with an ultrasonic cleanser and deionized water, and dried before testing.

Surface hardness testing

The surface hardness of specimens was measured according to ASTM E384-05a[15] using a microhardness tester and Knoop indenter (FM-700e Type D, FUTURE–TECH, Japan) with 50 g of load for 15 s. Three measurements were taken on each specimen and the mean values were calculated.

Water sorption testing

The water sorption of specimens was measured according to ISO 10477.[16] The specimen's weight after soaking in 2 mL of DI water for 4 weeks was measured. The percentage of water sorption was calculated.

Fluoride releasing measurement

The fluoride releasing properties of NaF- and CaF_2-filled coating materials were measured according to ASTM D1179-04[17] using an ion selective electrode and pH/Ion meter to measure the fluoride ion releasing of specimens after soaking in the water for 1 week. The measurement was done by correlation with a standard curve using serial dilutions of a standard fluoride solution (Fluoride standard 100 ppm F^- Orion 940907, Orion ionplus® Application Solution, Thermo electron Corporation).

RESULTS AND DISCUSSION

Surface hardness

The surface hardness of unfilled coating materials were tested according to the American Society for Testing and Materials, and the results are summarized in Figure 1. The hardness was clearly dependent upon both the diluent and the base monomer used and ranged from as low as 1.4 to 27.5 HK values.

The hardness of coating should match with that of the denture base material, which according to the literature is about 18–20 HK.[18] From the obtained results (Fig. 1), the formulations of DU-DMA/MAA, GDA/MAA, DU-DMA/HEMA, Bis-GDA/TEGDMA, Bis-GDA/HEMA, and DU-DMA/TEGDMA, in order of the hardest first, provided a surface hardness of greater than HK value of 18, ranging from 27.5 to 18.3, respectively.

Water sorption

The water sorption is related to the ability of the water to diffuse into the material, dissolve, and carry out the fluoride ions to the surface. Materials with a high water sorption can promote fluoride ion release from their matrix. The water sorption of all twelve

TABLE I
Coating Formulations

Formulation	1	2	3	4	5	6	7	8	9	10	11	12
Base monomer (mol)												
Bis-GDA	1	1	1	1	–	–	–	–	–	–	–	–
GDA	–	–	–	–	1	1	1	1	–	–	–	–
DU-DMA	–	–	–	–	–	–	–	–	1	1	1	1
Diluents (mol)												
TEGDMA	1	–	–	–	1	–	–	–	1	–	–	–
DEGME-MA	–	1	–	–	–	1	–	–	–	1	–	–
HEMA	–	–	1	–	–	–	1	–	–	–	1	–
MAA	–	–	–	1	–	–	–	1	–	–	–	1
Photoinitiator (% by wt)												
CQ	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
DMAEMA	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0

unfilled coating formulations was mostly related to the base monomer used, and specifically to the hydrophilic properties of the monomer used in the formulation, although the diluent used also played a significant role too (Fig. 2).

The coating materials containing the GDA base monomer provided the highest water sorption properties relative to others, and within these four formulations, those containing HEMA showed the highest sorption levels follow by DEGME-MA, MAA, and TEGDMA, respectively. Although the coating materials containing Bis-GDA or DU-DMA base monomer showed approximately the same lower levels of water sorption and were almost independent of the diluent used. Taking into account both the surface hardness and water sorption properties of the coating materials, led to the exclusion of Bis-GDA/TEGDMA and DU-DMA/TEGDMA because of their low water sorption, and so the four remaining formulation (GDA/MAA, Bis-GDA/HEMA, DU-DMA/HEMA, and DU-DMA/MAA) were chosen to further characterize their fluoride release rates.

Fluoride releasing properties of coatings

The four base monomer/diluents systems (GDA/MAA, Bis-GDA/HEMA, DU-DMA/HEMA, and DU-DMA/MAA) selected on the basis of surface hardness and water sorption properties were remade as in Table I, except for the incorporation of either NaF or CaF_2, and then evaluated for their resultant release of fluoride ions as coating materials.[17] The results of the fluoride ion release kinetics from NaF- and CaF_2-filled coating materials are shown in Figures 3 and 4, respectively, and are distinctly different. All NaF-filled coating materials showed a high initial fluoride ion release in the first week, which then decreased sharply in the second week and almost leveled-off in the third and fourth week, as shown in Figure 3. This might be because NaF, in

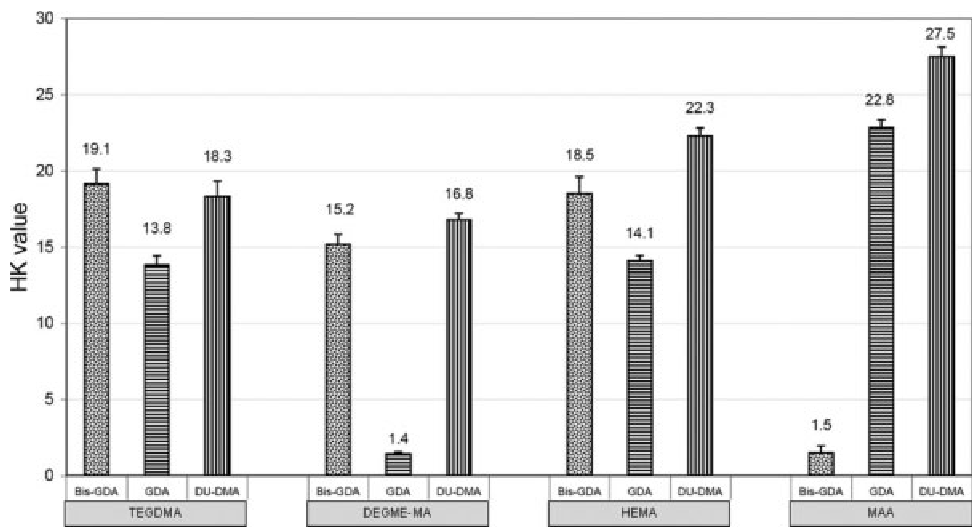

Figure 1 The surface hardness of unfilled coating materials.

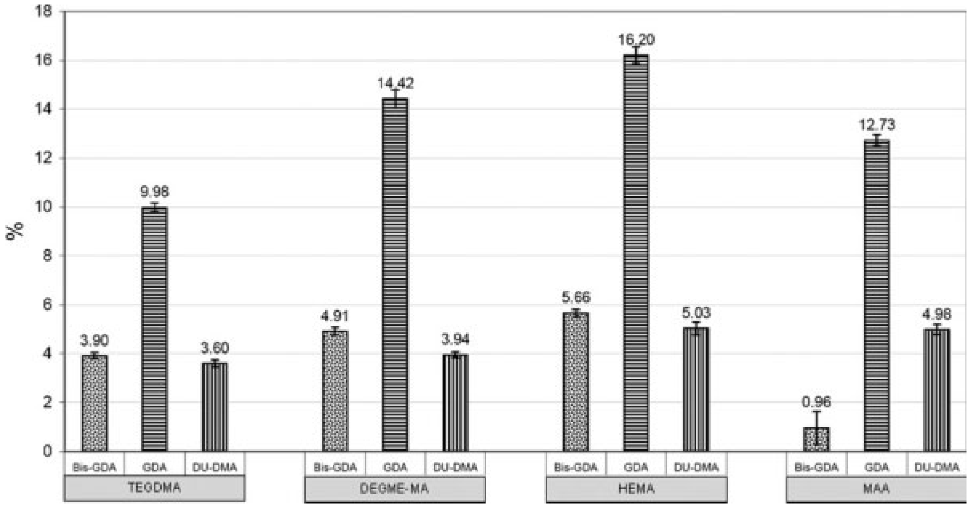

Figure 2 The water sorption of unfilled coating materials.

general, is water soluble and significantly more than that of CaF_2.

In contrast, the rate of fluoride ion release from the four CaF_2-filled coating materials (Fig. 4) was much lower than NaF-filled coating. As mentioned earlier, this is likely to be because CaF_2 is only slightly water soluble (0.016 g/L at18°C) relative to NaF (42 g/L at 20°C). Regardless, the formulations of DU-DMA/MAA and Bis-GDA/HEMA both provided an almost constant rate of fluoride ion release through the whole period of 4-week study period, whereas the DU-DMA/HEMA coating showed the highest level of fluoride ion release which increased significantly (~ 1.4-fold) between the first and second week, and then gradually increased from the second week to the fourth week.

Indeed, for DU-DMA/HEMA, a release of almost 5 ppm/week was attained by the fourth week compared with the limitation of the water solubility of CaF_2 imposing a maximal ion release of 8 ppm. However, the amount of fluoride ion needed for caries prevention is much lower, at around 0.1–2.0 ppm.[1–5] As a result, the fluoride ion release rate from all four of the tested CaF_2-filled coating materials was sufficient for prevention of dental caries formation, at least over this 4-week period. We conclude that DU-DMA/HEMA is a candidate polymer matrix for making CaF_2-filled denture-coating materials.

CONCLUSIONS

Light cured denture-coating materials with fluoride ions releasing properties can be formulated using DU-DMA as a base monomer and HEMA as the diluent monomer in a molar ratio of 1 : 1, using a visible light photoinitiator system [0.5% (w/w) CQ and 1.0% (w/w) DMAEMA] and CaF_2 filler. This coating material provided a surface hardness that is slightly higher than the acrylic denture base materials and with moderate water sorption. The fluoride ion

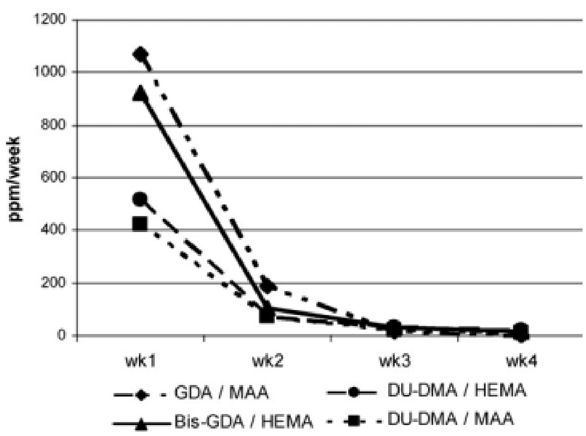

Figure 3 The fluoride released from NaF-filled coating materials.

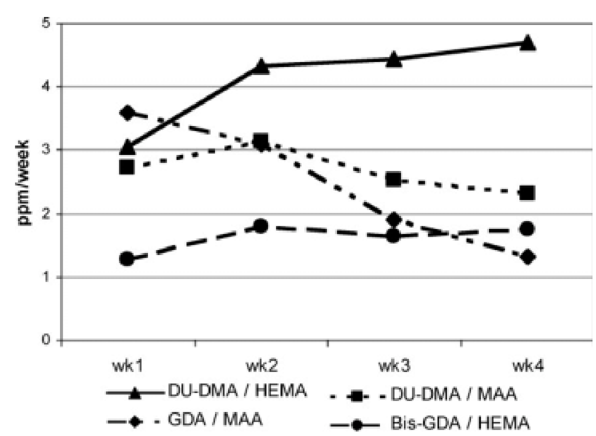

Figure 4 The fluoride released from CaF_2-filled coating materials.

release rate was consistent, at least over a 4-week period, and the level of release was in the range required for dental caries prevention.

References

1. Fejerskov, O.; Ekstrand, J.; Burt, B. A. Fluoride in Dentistry; Munksgaard: Copenhagen, 1996.
2. Yamazaki, H.; Litman, A.; Margolis, H. C. Arch Oral Biol 2007, 52, 110.
3. Carey, C. M.; Gove, R.; Eichmiller, F. C. J Dent Res (Special Issue A) 2004, 83, 19.
4. Margolis, H. C.; Moreno, E. C.; Murphy, B. J. J Dent Res 1986, 65, 23.
5. ten Cate, J. M.; Duijsters, P. P. E. Caries Res 1983, 17, 513.
6. Budtz-Jørensen, E.; Müller, F. In Improving Oral Health for the Eldery; Lamster, I. B., Northridge, M. E., Eds.; Springer: New York, 2008; Chapter 13.
7. Jepson, N. J. A.; Moynihan, P. J.; Kelly, P. J.; Watson, G. W.; Thomason, J. M. Br Dent J 2001, 1991, 140.
8. Tuominen, R.; Ranta, K.; Paunio, I. J Oral Rehabil 1988, 15, 515.
9. Yamaga, T.; Komoda, Y.; Soga, K.; Ono, M.; Asada, T.; Itosaka, N.; Nokubi, T. J Osaka Univ Dent Sch 1994, 34, 65.
10. Budtz-Jørgensen, E.; Kaaber, S. Scand J Dent Res 1986, 94, 569.
11. Monsenego, P. J Oral Rehabil 2000, 27, 708.
12. Sesma, N.; Lagana, D. C.; Morimoto, S.; Gil, C. Braz Dent J 2005, 16, 129.
13. Vallittu, P. K. Acta Odontol Scand 1996, 54, 188.
14. International Organization for Standardization. Dentistry-Polymer-Based Filling, Restorative and Luting Materials, ISO 4049; International Organization for Standardization: Switzerland, 2000.
15. ASTM E384-05a. Standard Test Method for Microindentation Hardness of Materials; American Society for Testing and Materials: West Conshohocken, PA, 2006.
16. International Organization for Standardization. Dentistry—Polymer-Based Crown and Bridge Materials, ISO 10477; International Organization for Standardization: Geneva, 2004.
17. ASTM D1179-04. Standard Test Methods for Fluoride Ion in Water; American Society for Testing and Materials: West Conshohocken, PA, 2006.
18. Rawls, H. R. In Phillips' Science of Dental Materials; Anusavice, K. J., Ed.; Saunders: St. Louis, 2003; Chapter 7.