

PROPERTIES OF SOME HYBRID POLYMER COMPOSITES CONTAINING CARBOXYLIC/PHOSPHATE DIMETHACRYLATES AND HYDROXYAPATITE OR CALCIUM PHOSPHATE WITH APPLICATIONS IN DENTISTRY

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Abstract

A series of photopolymerizable dimethacrylates functionalized with carboxylic/phosphate groups have been used as co-monomers in light-curing dental composites incorporating small quantities of inorganic fillers like hydroxyapatite or calcium phosphate. The selected formulations consist of our dimethacrylates and 2,2-bis[4-(2-hydroxy-3-methacryloyloxypropyl)phenyl]propane (BisGMA) or BisGMA analogue, further diluted with triethyleneglycol dimethacrylate (TEGDMA), and reinforced with filler (under 10 wt.%). The photopolymerization rates for experimental formulations varied between 0.104-0.163 s⁻¹, and the degree of conversion ranged among 63.18 and 79.23%. The water sorption values varied from 1.04 to 1.77 wt. %, and water solubility values are in the interval 0.14-0.36 wt %, a higher hydrophilicity being measured for the formulation containing polyethylene oxide chains and carboxyl groups.

1. Introduction

Dental adhesives are extensively employed to realize a better adhesiveness between the restorative materials and dentine/enamel [1,2]. Usually, the dental adhesives are aqueous acidic solutions containing different monomers (acidic, hydrophilic, and hydrophobic monomers) capable to simultaneously etch and infiltrate dental tissues mediating the creation of a bond to the restorative material. Consequently, various new acid monomers with carboxylic and phosphate groups have been developed as adhesives for this area of application [3-5]. Besides the acidic functional group, the adhesive monomers contain one or more polymerizable groups grafted onto a spacer, the most common polymerizable units being the acrylic/methacrylic ones, since their main advantages are related to their easy photopolymerization reaction, as well as to their colourless and tasteless character [6]. In addition to the functional monomers, dental adhesive materials enclose crosslinking monomers (2,2-bis[4-(2-hydroxy-3-methacryloyloxypropyl)phenyl]propane (BisGMA) or triethyleneglycol dimethacrylate (TEGDMA)), necessary for an adequate polymerization of the adhesive layer and to provide the required physico-mechanical strength to the interface.

Sometimes, dental adhesives may include small amounts (below 10 wt. %) of fillers [7], particularly nanofillers, such as colloidal or pyrogenic silica nanoparticles, fluoroaluminosilicate glass, used mainly to modify the viscosity and flow properties of the adhesive. Complementary, they may also improve the strength and elastic modulus of the formed adhesive layer, while, depending on their chemical composition, fillers can also confer fluoride release and radio-opacity.

In this context, the present study addresses the relationships between the acid monomer structure, conversion degree and photopolymerization rates (by differential scanning photo calorimetry), and the specific properties of the resulting dental composites (water sorption, water solubility, hydrophobicity, mechanical parameters). Additionally, the effect of acid groups from some resin composites including a low content of hydroxyapatite or calcium phosphate was tested for adhesive applications.

2. Results and discussions

The chemical structures of the synthesized photopolymerizable monomers to be investigated in dental adhesive formulations are shown in Figure 1. They consist of an urethane dimethacrylate oligomer DMAd-1 with polyethylene glycol soft segment ($M_n = 400$) and carboxyl units previously synthesized in our group [8], an urethane dimethacrylate monomer with carboxyl units without soft segment (DMAd-2) and a photopolymerizable monomer based on castor oil and bearing phosphate units DMAd-3 [5]. Besides the mentioned monomers, three commercially available monomers frequently encountered in dental compositions, namely triethylene glycol dimethacrylate (TEGDMA), 2,2-bis[4-(2-hydroxy-3-methacryloyloxypropyl)phenyl]propane (BisGMA) and 2-hydroxyethyl methacrylate (HEMA), have also been used.

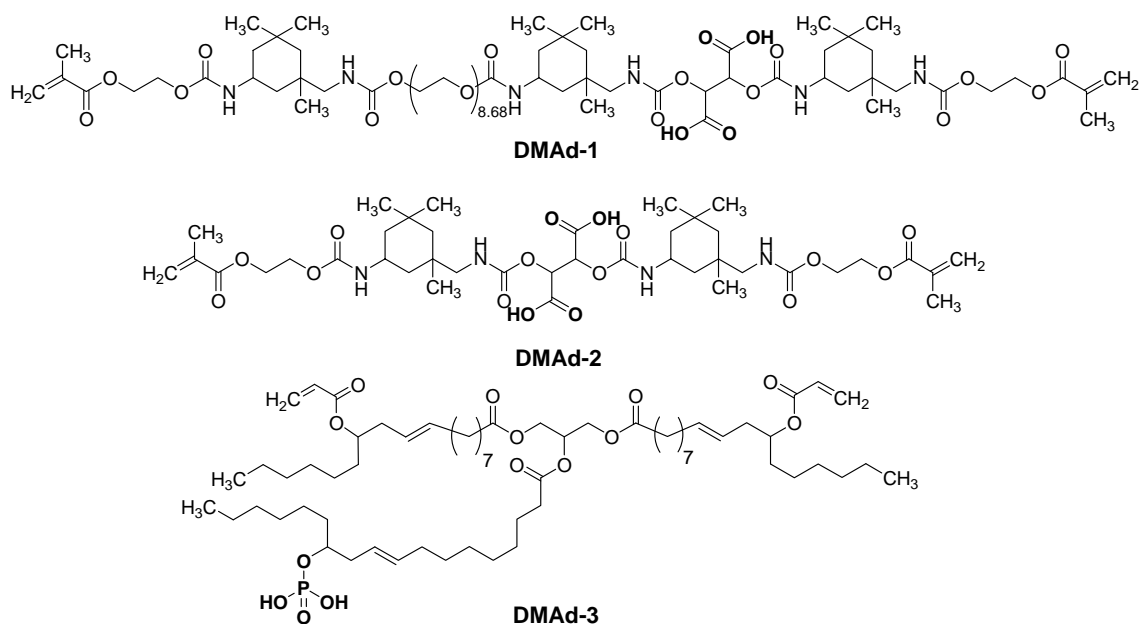


Figure 1. Structures of the monomers used in the study.

The photopolymerization profile of carboxylic/phosphate monomers taken in combination with the commercial dental comonomers were assessed through photoDSC (the gravimetric compositions of the experimental monomer mixtures used to produce the formulations are

listed in Table 1). The photoDSC testing was performed in the presence of 1 wt. % Irgacure 819 added as the photoinitiator to induce monomers polymerization with a light intensity of 4.5 mW/cm². This method was preferred against other systems to monitor the photopolymerization parameters since over time, it has been established that this technique allows a fast evaluation of the most important parameters characterizing the curing kinetics of the photopolymerizable systems which are the rate at the peak maximum (R_{\max}^P) and the degree of double bond conversion (DC).

Formulation	DMAd-1 (wt. %)	DMAd-2 (wt. %)	DMAd-3 (wt. %)	BisGMA (wt. %)	TEGDMA (wt. %)	HEMA (wt. %)
F1	35	-	-	35	15	15
F2	-	35	-	35	15	15
F3	-	-	35	35	15	15
F4	-	-	-	53.8	23.1	23.1

Table 1. Composition (wt.%) of the experimental formulations. Each formulation contains 1 wt. % Irgacure 819.

Figure 2(a,b) shows the photopolymerization rate profile and the double bond conversion for all monomer formulations versus time. In the given figure, it can be noticed that for a thin film where a deeper penetration of the light is reasonably valid, the rate of photopolymerization is lower for the systems including monomers with high soft segment chains (F1 and F3 with DMAd-1 and DMAd-3, respectively), while the F2 formulation incorporating DMAd-2 monomer or the formulation without carboxylic/phosphate units (F4) display increased photopolymerization rates. Therefore, the higher reactive formulation was F4 ($R_{\max}^P = 0.163 \text{ s}^{-1}$) and the lowest photoreactivity was measured for F3 mixture ($R_{\max}^P = 0.104 \text{ s}^{-1}$) with castor oil diacrylate phosphate monomer (DMAd-3). The conversion degree (Figure 2 b) ranged between 63.18 and 79.23 % (after 80 s of UV irradiation). Taking into account the fact that (meth)acrylates polymerization is a diffusion-controlled process, which causes a restricted movement of macroradicals as a function of conversion, between the conversion degree and polymerization rate is a relation of inverse proportionality.

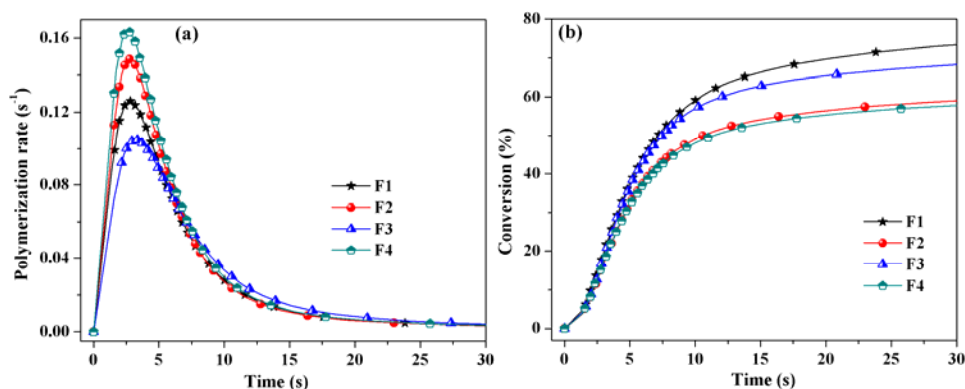


Figure 2. PhotoDSC rate profiles for the experimental formulations (a) and double bond conversion for the hybrid materials during the UV irradiation (b).

Water sorption and water solubility are two processes which normally take place in the oral environment, reason for that their quantification is very important to predict the feasibility of this type of materials. Water sorption and water solubility measurements were performed in distilled water at 37 °C, on photopolymerized samples containing additional 10 % filler (hydroxyapatite - HAP or calcium phosphate $\text{Ca}_3(\text{PO}_4)_2$ - CaP). The analysis of the data illustrated in Figure 3 a showed that the water sorption values varied from 1.04 to 1.77 wt. %, and water solubility values varied from 0.04 to 0.12 wt. %.

and water solubility values are in the interval 0.14-0.36 wt %. Therefore, the more hydrophilic formulation (F1) contains polyethylene oxide chains and carboxyl groups that may caused the increased water sorption values, as compared to the samples with DMAAd-3 component (F3) or that without acid monomer (F4). Regarding the water solubility, the highest values were determined for the filled composites, probably due to the structural defects bring by the filler particles on the organic photocrosslinked matrix arrangement.

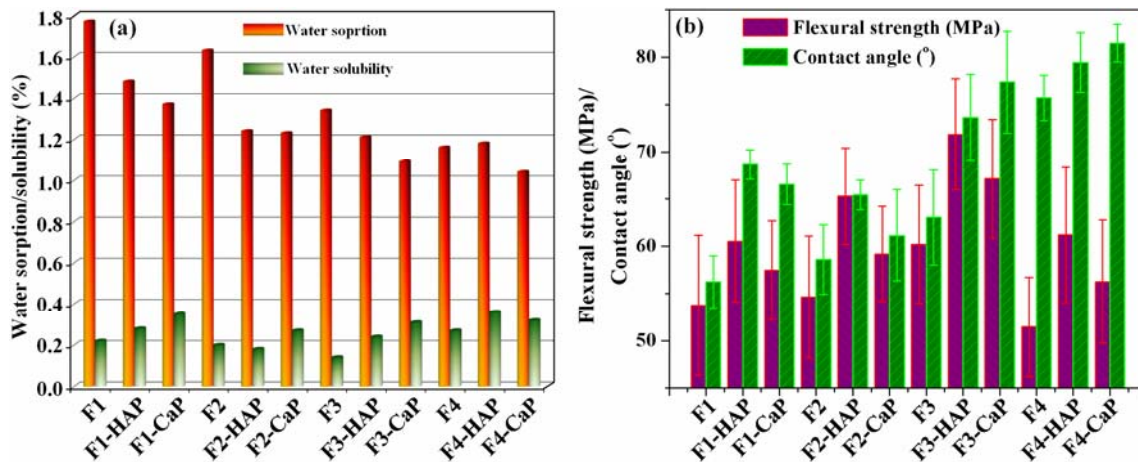


Figure 3. Percent of water sorption and water solubility for the photopolymerized matrixes (a) and contact angle/flexural strength values for the experimental samples (b).

The water contact angles of the formulations without filler or enclosing 10 wt. % filler were measured using the sessile droplet method, and the obtained values are graphically represented in Figure 3 b. The contact angle values ranged from 56.22° (F1) to 81.49° (F4-CaP) and are dependent on the content of the carboxyl/phosphate groups and filler in the photopolymerized films.

The mechanical parameters exemplified in this study by flexural strength that offers simultaneously information on three types of stresses (tensile at one surface, compression at the other surface, and shear strengths) are likewise illustrated in Figure 3 b. It can be observed that flexural strength values ranged between 51.45 MPa (F4) and 71.85 MPa (F3-HAP) and are higher in the filled composites.

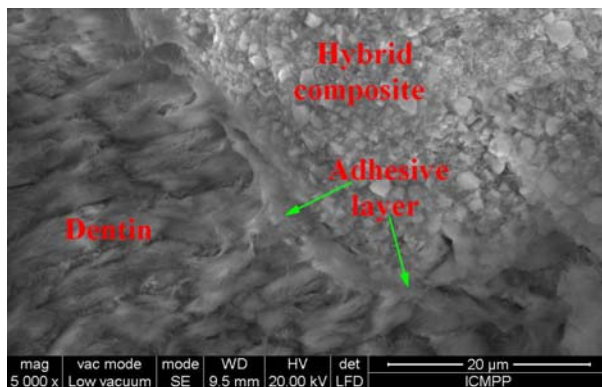


Figure 4. SEM image of the interfaces between the dentin and a commercial resin composite after treatment with the F3 experimental adhesive.

The scanning electron microscopy (SEM) investigation showed that the adhesive system based on F3 formulation produced a hybrid layer without defects (Figure 4) when employed between the a resin composite and dentin.

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References

- [1] K. L. Van Landuyt, J. Snauwaert, J. De Munck, M. Peumans, Y. Yoshida, A. Poitevin, E. Coutinho, K. Suzuki, P. Lambrechts and B. Van Meerbeek. Systematic review of the chemical composition of contemporary dental adhesives. *Biomaterials*, 28(26):3757-3785, 2007.
- [2] K. Ikemura, T. Endo and Y. Kadoma. A review of the developments of multi-purpose primers and adhesives comprising novel dithiooctanoate monomers and phosphonic acid monomers. *Dental Materials Journal*, 31(1):1-25, 2012.
- [3] G. Sahin, A. Z. Albayrak, Z. S. Bilgici and D. Avci. Synthesis and evaluation of new dental monomers with both phosphonic and carboxylic acid functional groups. *Journal of Polymer Science, Part A: Polymer Chemistry*, 47(7):1953-1965, 2009.
- [4] X. Xu, R. Wang, L. Ling and J. O. Burgess. Synthesis and stability study of dental monomers containing methacrylamidoethyl phosphonic acids. *Journal of Polymer Science, Part A: Polymer Chemistry*, 45(1):99-110, 2007.
- [5] V. Melinte, T. Buruiana, H. Aldea, S. Matiut, M. Silion, and E. C. Buruiana. Photopolymerizable phosphate acrylates as comonomers in dental adhesives with or without triclosan monomer units. *Materials Science and Engineering C*, 34:176-185, 2014.
- [6] N. Moszner and T. Hirt. New polymer-chemical developments in clinical dental polymer materials: enamel–dentin adhesives and restorative composites. *Journal of Polymer Science, Part A: Polymer Chemistry*, 50(21):4369-4402, 2012.
- [7] M. Sadat-Shojai, M. Atai, A. Nodehi and L. N. Khanlar. Hydroxyapatite nanorods as novel fillers for improving the properties of dental adhesives: Synthesis and application. *Dental Materials*, 26():471-482, 2010.
- [8] T. Buruiana, V. Melinte, L. Stroea and E. C. Buruiana. Urethane dimethacrylates with carboxylic groups as potential dental monomers. Synthesis and properties. *Polymer Journal*, 41(11):978-987, 2009.