EVALUATION OF SOME MULTIFUNCTIONAL MONOMERS FOR USE IN DENTAL PURPOSES

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This study was designed to determine the properties of some dental composite resins achieved with the new monomers synthesized in our group, namely, BisGMA derivative and diacid urethane dimethacrylates, which were photopolymerized at room temperature besides common inorganic fillers. For a number of cured specimens, the equilibrium water uptake, water sorption and contact angle have been measured to establish their behaviour into a wet environment. SEM micrographs recorded on fractured surfaces indicates a good interaction between the partners, conferring them a good balance of all measured properties. Mechanical properties (compressive and diametral tensile strengths), determined for several resins composites, sustain the formation of materials with a hardness comparable to those frequently encountered in dental practice, offering thus an attractive alternative to the existing portfolio of dental monomers.

INTRODUCTION

Within the dental materials arena, the monomer systems used in dental restorative applications have not changed fundamentally, reason for that various copolymers based on photopolymerizable dimethacrylates incorporating diglycidyl methacrylate of bisphenol A (BisGMA) have been extensively used as the organic phase in dental applications for nearly 50 years.[1,2] These dental composite materials typically contain a mixture of rigid and viscous monomers like diglycidyl methacrylate of bisphenol A (BisGMA) taken in combination with reactive diluents such as triethyleneglycol dimethacrylate (TEGDMA) that are filled up to 80 % with inorganic fillers to provide greater rigidity and toughness. Previous studies have shown that through a proper choice of the structures implied in the formation of interpenetrating polymer network and by varying the filler (nature, size, loading, shape, distribution, adhesion, etc) an improvement in the properties of the materials including their clinical performance can be achieved. Despite of several advantages reported in literature, the main

deficiencies encountered in the current resin composites are the high values of the polymerization shrinkage[3-5] and the relatively high percentage of unpolymerized (meth)acrylate functions (25-50 %), both with negative effect on the physical/mechanical properties of the materials, for instance, marginal leakage, insufficient abrasion and inadequate resistance to wear, degradation and fatigue,[6] toxicity,[7] a.s.o, all restricting the service life of them. To respond to these requirements or at least, to diminish the aforementioned drawbacks, novel monomeric systems based on modified Bis-GMA, fluorinated and spiro-orthoester derivatives have been designed and prepared to be tested especially in restorative dentistry.[8,9] Although such resin composites are quite versatile, they adhere poorly to dentin or the tooth structure and for that reason, the realization of a better adhesiveness between restorative materials is of increasing interest. Consequently, new acid monomers with carboxylic or phosphate groups have been developed as adhesives for this area of application.[10] Other strategies aimed at developing urethane di(meth)acrylate (UDMA) alternatives, proposed initially for reducing

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the high viscosity of BisGMA and achieving an adequate conversion in the final composite resins.[11,12] Though a series of urethane acrylate composites have been intensively explored as dental restorative materials with improved properties, up to date, urethane diacrylates chemically modified with carboxyl groups have been not reported. In this regard, it is mentioning our research on the reactive acid functionalized oligomers[13] and non-acid ones,[14] in order to follow the effects of chemical structure of the synthesized macromers, and composition on the photo curing process in some preliminary dental formulations. This work describes our approach to prepare new resin composites employing reactive polymerizable monomers as diacid urethane dimethacrylates and BisGMA
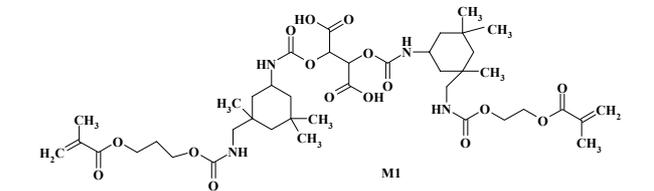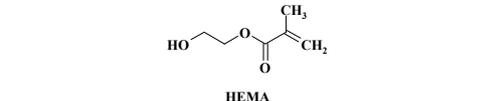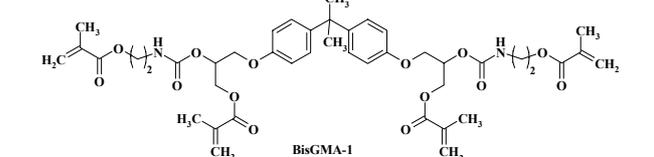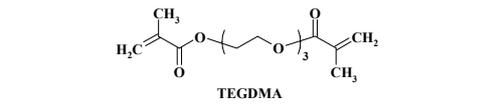
modified with photopolymerizable groups, together with other traditional dental monomers (BisGMA, HEMA, TEGDMA) in the pursuing of specific properties during the formation of polymeric network in the resin composites.

RESULTS AND DISCUSSION

The structures of the photopolymerizable monomers proposed to be used in dental formulations are shown in Table 1, in which are included the monomers synthesized by our group, together with the commercial ones.

Table 1

The structures of the employed methacrylates in the formation of resin composites
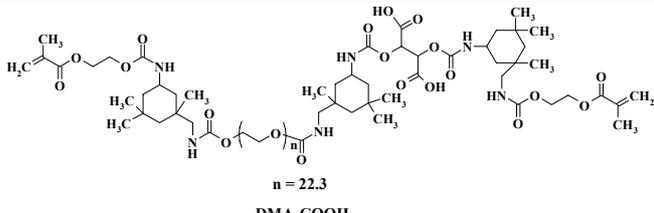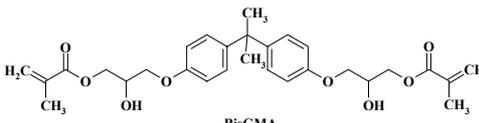
The first acid urethane dimethacrylate is of oligomeric type (DMA-COOH) prepared from polyethylene glycol (PEG, M_w = 1000 g/mol), tartaric acid, isophorone diisocyanate and 2-hydroxyethyl methacrylate (HEMA) used in a molar ratio of 0.5:0.5:2:2, whereas the M1 dimethacrylate is its low molecular homologue without the PEG sequence in its structure. Moreover, in an attempt to reduce the viscosity of BisGMA, mainly attributed to the hydrogen linkages formed between the hydroxyl groups, and also for an increase of the photopolymerizable network density, a certain percent of hydroxyl units was blocked with urethane methacrylic functions, thus obtaining the BisGMA-1 derivative.

The aim of this study was focused on the development of novel acid urethane dimethacrylates and BisGMA substitute, as possible ingredients in the resin composite formulation by mixing them with various glass powders, and to evaluate their possible applicability in dental materials. Consequently, the water contact angles, water sorption/solubility, compressive (CS) and diametral tensile strengths (DTS) for some composite specimens were determined. In Table 2 are presented the percentage composition of the formulations for six composite specimens (S1-S6) obtained from DMA-COOH or M1 and BisGMA or BisGMA-1, together with HEMA, TEGDMA, and 60% Aerosil/Zr-Sr glass (1:1), exposed further to visible irradiation up to

the formation of a hard surface. The initiation system used is composed by 4-(dimethylamino)-phenylacetic acid (DMPheAA, 1 wt.%) and camphorquinone (CQ, 0.5 wt.%).

Table 2

Composition and contact angle values of the prepared composites, initiated with CQ/DMPheAA

Sample*	DMA-COOH	M1	BisGMA-1	BisGMA	TEGDMA	HEMA	Contact angle (°)
	(wt. %)						
S1	15	-	-	40	43.5	-	50.55
S2	-	15	-	40	43.5	-	58.59
S3	15	-	-	40	-	43.5	45.22
S4	15	-	40	-	43.5	-	51.66
S5	-	15	40	-	43.5	-	59.41
S6	15	-	40	-	-	43.5	49.14

*60% Filler

The water contact angle results, which are obviously an indicative of the wetting properties of the composite resins, are presented in Table 2. It can be seen that generally, the modification of carboxyl concentration in composite formulations is not the determining element for a significant variation of the contact angle values. The comparison between the contact angle values measured for the composites S1-S6 allow us to affirm that their hydrophilicity is mainly influenced by the presence of the PEG sequences from the urethane dimethacrylate structure, as well as the incorporation of the HEMA comonomer. For instance, the employing of DMA-COOH oligomer in the preparation of S1 composite had as result the obtaining of a medium contact angle of 50.55°, with 8° lower than for the composite prepared with the M1 monomer, characterized by the absence of PEG blocks. Moreover, the replacement of TEGDMA from the above composites with HEMA causes a decrease of hydrophobicity with more than 5°, due to the hydrophilic nature of the later. In the case of resin composites S4-S6, the use of more hydrophobic modified BisGMA, induces a small increase of the contact angle values comparatively to those containing commercial BisGMA, reason for that, the most hydrophobic formulation seem to be S5, with a contact angle of 59.41°.

Another major consideration is absorption of water and leaching of small molecules, two processes which take place simultaneously, when the composite resins are in contact with water and oral fluids. For this reason, water sorption is a key parameter to guarantee viability and quality of these materials. Moreover, water sorption is a diffusion-controlled process that produces in the organic resin matrixes and mainly depends on hydrophilicity and crosslinking density of the cured resins. Hence, the hydrophilic constituents clearly increased water sorption values, reason for that it is expected that the composites enclosing dicarboxylic urethane dimethacrylate of oligomer or monomer type to behave adequately. From this perspective, the analysis of data included in Figure 1 allows us to affirm that the dental composite resins comprising the urethane dimethacrylate macromer show a higher percent of water sorption comparatively to the samples in which was incorporated the low molecular monomer (M1).
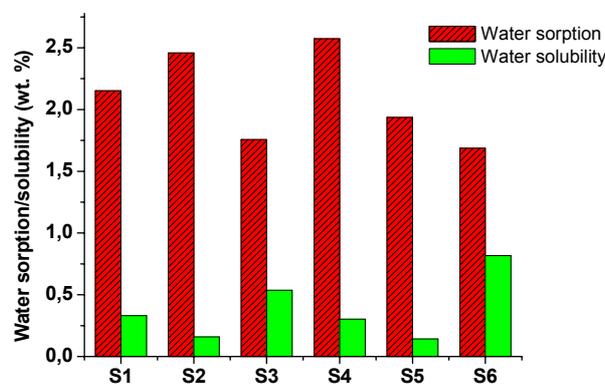

Fig. 1 – Water sorption and water solubility characteristics of the experimental resin composites.

Regarding the water solubility experiments, the obtained values are comparable with data reported in the literature[15] and these may be correlated with the water sorption and contact angle data. Thus, the composites incorporating the HEMA as comonomer (S3 and S6) presented the higher percent of water solubility caused probably of itself hydrophilic nature. Additionally, HEMA having a small molecule that contains only a single double bond it could favour the significant leaching out of the monomer from the formed material.

Within this context, the morphology of the resin composites were examined by SEM analysis in fracture, the resulting surfaces revealing a regular and homogeneous appearance (Figure 2 a, b), where the formation of porous cavities due to filler

debonding seems to be minimal. Moreover, the filler distribution into the organic matrix is relatively uniform, in fracture being observed only few filler particles with dimensions under 5 μm. This result indicates a favourable adhesion between filler and matrix on one hand, and a good interaction between the filler (Aerosil/Zr-Sr glass) and the urethane dimethacrylate by means of the carboxyl groups situated along an oligomeric backbone. However, it may be noticed that for the S3 composite (with HEMA in formulation), the fractured surface has an elevated rugosity as compared with S1 sample, observation which confirm also the high water sorption/solubility of the composites containing HEMA.
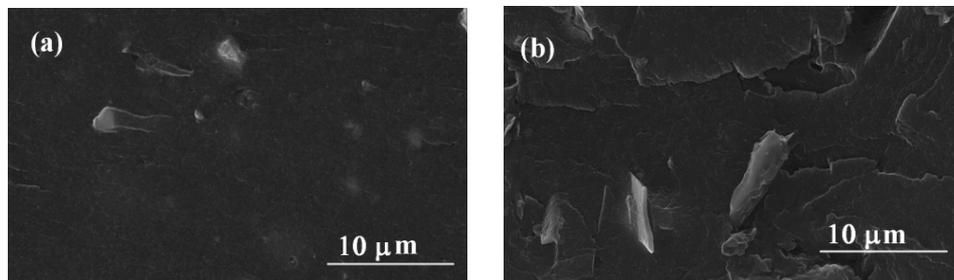

Fig. 2 – SEM micrographs of the resin composites S1 (a) and S3 (b) in fracture.

Diametral tensile strength (DTS) and compressive strength (CS) are commonly used in the evaluation of dental material formulations[16]. The composites containing the dimethacrylate urethane carboxylic oligomer and low molecular urethane monomer mixed with BisGMA, BisGMA-1, HEMA or TEGDMA together with 60 % inorganic filler (Aerosil/Zr and Sr glass) were tested to evaluate their mechanical parameters. The results

obtained for the composites S1 - S6 concerning the diametral tensile and compressive strengths are illustrated in Figure 3. It may be remarked that the lower values for the diametral tensile and compressive strengths are recorded in the case of composites that contain HEMA, followed by those comprising the M1 monomer, when is supposed that the short molecular chains induced an inferior cohesion between the organic and inorganic matrixes.
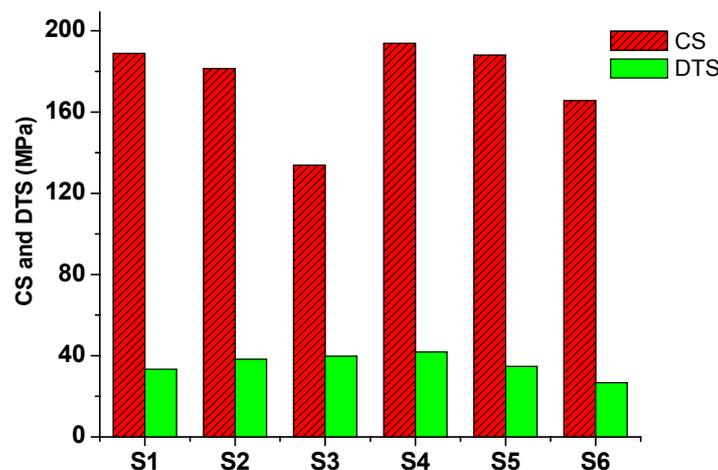

Fig. 3 – Compressive (CS) and diametral tensile strength (DTS) for the experimental resins.

On the other hand, the inclusion of modified bis-GMA, namely bisGMA-1 determines a slight increasing of the mechanical parameters, comparative to the resin composites prepared by using commercial BisGMA, results attributed to an augmented concentration of double bonds. However, it can conclude that the mechanical parameters obtained for the investigated composites are rather closer to those reported in the literature for some glass ionomer cements,[17] without to neglect the relatively lower filler amount (60 %) and to the ionic nature of the urethane oligomer and monomer.

EXPERIMENTAL

Materials. The dimethacrylate monomers BisGMA, TEGDMA and HEMA, as well as the compounds used in the synthesis (polyethylene glycol, Mw = 1000), L-tartaric acid, isophorone diisocyanate), were purchased from Sigma Aldrich Chemical Co. and used without further purification. The initiators used were camphorquinone and 4-(dimethylamino)-phenylacetic acid (DMPheAA) (from Sigma-Aldrich Chemical Co.). Aerosil (Degussa): content in SiO_2 99.6%; specific surface 180 m^2/g; refraction index 1.46; particle medium diameter 0,04μm. Zr and Sr glass (1:1): granulation under 5 μm (about 97%); density 2,9 g/cm^3.

Synthesis. The urethane dimethacrylate oligomer with carboxylic groups (DMA-COOH) was prepared according previously reported method.[13] For comparison, the corresponding low molecular dimethacrylate (M1) bearing two carboxylic acid units in structure were prepared too. As organic co-monomer of the resin matrix, was used both Bis-GMA and BisGMA modified with urethane-acrylic moiety (BisGMA-1), the later being also prepared by us through the reaction of hydroxyl groups with 2- isocyanatoethyl methacrylate.[18]

Measurements. Surface microstructure of the composites was examined under scanning electron microscopy, SEM (Carl Zeiss DSM-950, Heidenheim, Germany), the specimens being sputter-coated with gold. Water contact angle measurements were made on relatively homogeneous surface using goniometer (Model 100). The average contact angle was calculated starting from at least ten separate measurements. For the water sorption determinations, four disk specimens of reduced dimensions (15 ± 0.1mm diameter, 1 ± 0.1mm thickness) were prepared for each group of mixtures.[15] Compressive (CS) and diametral tensile strengths (DTS) were measured using a Shimadzu AGS-J testing machine, with a 5 kN load cell at a crosshead speed of 1 mm/min. The compressive strength was calculated from the equation $CS = P/\pi r^2$, where P is the load at fracture and r the radius of the sample cylinder. Diametral tensile strength was determined from the relationship $DTS = 2P/\pi dt$, where d is the diameter and t the thickness, respectively, of the cylinder.

CONCLUSION

In this investigation, the effects of the chemical structure of urethane dimethacrylates with and without poly(ethylene oxide) sequences and composition on some specific properties for dental resin composites were studied. The obtained values for contact angle and water sorption/solubility confirmed the hydrophilic nature of the prepared composites, due principally to the PEG segments from the urethane dimethacrylate as well as to HEMA component enclosed into a part of them. The mechanical properties of the formed composites that contain small quantities of urethane dimethacrylates situate them closer to the glass ionomer resins family.

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