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New urethane dimethacrylates for testing in dental applications. Relational aspects in chemistry and photochemistry of composite materials

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Two urethane dimethacrylate oligomers containing poly(ethylene oxide) spacer of variable length (O-UDMA, UDMA-COOH) and a derivative of bis-GMA modified (bisGMA-ethyl) were synthesized in order to be evaluated as photopolymerizable monomers in dental composites. The photopolymerization of them was monitored by FTIR and fluorescence spectroscopy, and for some cured specimens the water sorption, contact angle have been determined relatively to those in which was incorporated modified/non-modified bis-GMA. If such monomers can provide strong polymers, they could offer alternative to the existing dental monomers.

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1. Introduction

Although the photopolymerizable methacrylate derivatives have been validated as attractive targets for obtaining resin-based restorative dental materials [1, 2], the major organic component remains diglycidyl methacrylate of bisphenol A (bisGMA) used in combination with reactive diluents such as triethyleneglycol dimethacrylate (TEGDMA). One essential feature of these composite resins is that their properties can be tailored through a suitable choice of the structures implied in the three-dimensional network formation as well as by varying the filler, its performance being governed not only by the organic matrix structure, but also by the chemical and physical details of filler (shape, size, distribution, adhesion, etc). Recent advances in this area have provided that there are serious difficulties to differentiate the subtle but important aspects at the surface, since all acrylic formulations undergo thermal shrinkage through polymerization, producing undesired effects to the users [3-5]. Additionally, the relatively high percentage of nonpolymerized acrylate groups (25-50%) deteriorates the physical properties of the materials, for instance, susceptibility to degradation [6] and the toxicity [7]. To compensate these drawbacks, new systems containing modified bisGMA, mesogens, fluorinated or spiro-orthoester monomers, which could produce cross-linked polymers more durable than existent ones, have been reported [8,9].

In connection, the achievement of an adhesive bond between restorative materials and enamel/dentin is of increasing interest, since in the most cases, the use of di(meth)acrylates besides a higher loading of filler yields materials that adhere poorly to dentin or the tooth structure [10]. In order to provide a good adhesion of these materials, new carboxylic acid monomers and phosphor-containing derivatives have been prepared to be tested as dental materials.

Alternatively, a series of urethane di(meth)acrylates (UDMA) has been proposed to realize polymeric composites with improved properties [11-14]. Moreover, a series of multifunctional urethane (meth)acrylate alkoxysilanes as sol-gel precursors have also been developed for the synthesis of ormocer composites, where the mechanical parameters can be modified over a wide range [15-17]. Despite practical results generated by using of urethane acrylate – based composites, little research has been done to understand their behavior in the cured networks through fluorescence spectroscopy.

Therefore, starting from the qualities of these UDMA's used frequently in dental formulations, our group has been undertaken in study synthesis of oligomeric urethane dimethacrylates and bisGMA modified methacrylate derivative, in order to pursue some properties of the formed composites. This work will attempt to discern between the effects of the monomer structure and light-induced polymerization system, in which was incorporated a pyrene derivative as optical probe, following photopolymerization reaction initiated by the well-known couple (camphorquinone/amine). Previously, data on the behavior of carboxylic urethane dimethacrylates in the presence of fluorophore was published [18].

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2. Experimental

Materials. The dimethacrylate monomers used in this study include diglycidyl methacrylate of bisphenol A (bisGMA), triethyleneglycol dimethacrylate (TEGDMA) and 2-hydroxyethyl methacrylate (Sigma-Aldrich Chemical Co.). Polyethylene glycol (PEG, Mw = 400, 1000), L-tartaric acid (TA), isophorone diisocyanate (IPDI), were purchased from Sigma Aldrich Chemical Co. and used without further purification. The initiators used were camphorquinone and 4-(dimethylamino) -phenylacetic acid (DMPheA) (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. Quartz: granulation - 40 μm (about 97%).

Synthesis. Oligomeric urethane dimethacrylate (O-UDMA) was prepared by a two-step condensation reaction from poly(ethylene oxide) diol (Mw = 1000) and isophorone diisocyanate, followed by a further reaction with 2-hydroxyethyl methacrylate, as previously reported [19]. For comparison, another macromer with shorter flexible spacer based on poly(ethylene glycol) of 400 average molecular weight bearing two carboxylic acid units in the macromolecular chain was prepared too (UDMA-COOH). As organic comonomer of the resin matrix, was used bisGMA or bisGMA modified with isocyanatoethyl methacrylate, the later being also synthesized by us [20]. The schematic representation of the structures for the synthesized monomers used in the formulations is given in Scheme 1.

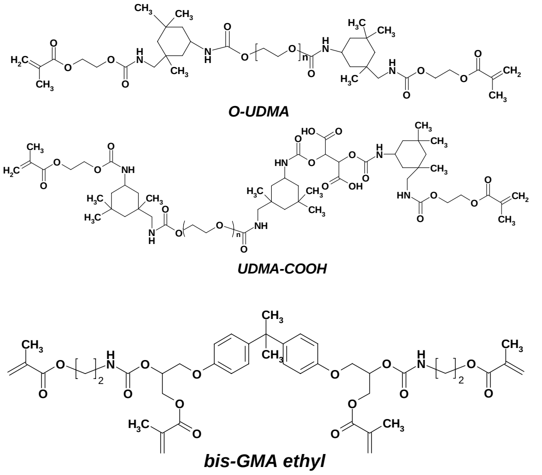
Measurements. The oligomers structures were verified by ^{1}H-NMR and FTIR spectroscopy using a Bruker 400 MHz spectrometer and a Bruker Vertex 70 spectrophotometer, respectively. The fluorescence spectra were obtained at room temperature (without corrections) with an SLM 8000 spectrofluorimeter (Japan) containing a double monochromator with a diffraction network of the GDM-1000 type, a compensatory printer of the K-201 type, and a selective amplifier. UV/visible irradiation were performed with a dental device (LA 500, Blue Light, λ = 400-500 nm, intensity of light 14 mW/cm^2) and the conversion of double bonds was determined by FTIR absorption spectroscopy. Different mixtures of dimethacrylates and photosensitizer [4-(dimethylamino)-phenylacetic acid (1%)/ camphorquinone (0.5%)] was homogenized and coated manually on the KBr plate. The FTIR absorption spectra were measured as a function of irradiation time and the degree of conversion was determined from the difference in absorbance at 1636 cm^{-1} before and after irradiation for a given period. Values obtained were normalized with the difference between absorbance at 1600 cm^{-1}. Under water, contact angle measurements were made on relatively homogeneous surfaces using goniometer (Model 100). The average contact angle was calculated starting from at least ten separate measurements. For the water sorption determinations, three bar shaped specimens of reduced dimensions (2 x 10 x 30 mm) were prepared for each group of oligomer mixtures. The composites were pre-conditioned over a desiccant containing calcium sulfate for 24 h at 37 °C and then weighed (initial weight m_1). Specimens were placed in distilled water at 37 °C for different time intervals and then removed from the water, lightly blotted with a paper to eliminate the surface-adherent water, and weighed (m_2). The water sorption values were calculated employing the equation:

$$\text{Water sorption (wt. \%)} = \frac{m_2 - m_1}{m_1} \text{ X } 100$$

The resin matrix were formulated from the above mentioned monomers and commercial available monomers (bisGMA, TEGDMA), components of the photoinitiator systems consisting of CQ/DMPheA and different fillers.

3. Results and discussion

The structures of the dimethacrylates investigated in this work are shown in Scheme 1.



Scheme 1. Structure of the urethane dimethacrylates used in formulations.

The above structures were employed in the preparation of various formulations in order to monitor the influence of the different oligomers on the composite performances. In table 1 are detailed the formulations composition and some representative physical properties.

Table 1.Characteristics of some dental composite resins initiated with CQ/DMPheA.

Sample	Formulation	Contact angle (^{0})	Water sorption (wt. %)
S1	O-UDMA - 18.43 % bisGMA – 48.84 % TEGDMA – 32.17 %	44.62	4.92
S2	O-UDMA – 67.45 % TEGDMA – 32.54 %	13.11	17.6
S3	O-UDMA – 46 % UDMA-COOH– 5.5 % bisGMA – 48.5 %	62.23	3.25
S4	O-UDMA – 46 % UDMA-COOH– 5.5 % bisGMA ethyl– 48.5 %	24.81	4.25
S5	UDMA-COOH– 51.5 % bisGMA ethyl– 48.5 %	33.54	5.24

Since many factors will influence the interactions of various partners including the material surface topography, it needs to know hydrophilicity that can be evaluated from the contact angle test. From the above data we can affirm that when a dental composite which contain an important quantity of poly(ethylene oxide) is in contact with a drop of bidistilled water, a substantial decreasing in contact angle value is achieved due to the hydrophilic nature of the polymeric sequence. The experimental results shows us that the angle values and implicitly the hydrophobicity can be increased if in the formulation is incorporated a certain proportion of modified and unmodified bisGMA as observed in Table 1.

It is a well known issue that water sorption in the case of dental composites is considered one of the key properties given that their chemical stability in a wet environment is crucial to guarantee the viability of these materials by ensuring adequate mechanical properties and a non-porous and smooth surface. Additionally, water sorption is a diffusion-controlled process that occurs in the organic resin matrixes and mainly depends on hydrophobicity [21] and crosslinking density of cured resins [22]. The analysis of data regarding water sorption included in Table 1 allows us to affirm that the dental composite resins comprising only the urethane dimethacrylate oligomer without the addition of any percent of bisGMA or modified bisGMA shows an important amount of water sorption comparatively to the samples that incorporate and bis-GMA monomer. This behavior is a consequence of the high hydrophilicity induced by the poly(ethylene oxide) sequences which haft to be compensated with variable quantities of bisGMA or other hydrophobic derivative.

Another crucial parameter in the development of dental composites is represented by the double bond conversion which leads the formation of crosslinked polymeric networks applicable as dental materials. The conversion degree (DC) for the methacrylic function was determined by FTIR spectroscopy from the difference in absorbance at 1635 cm^{-1} before and after irradiation for a particular time. In figure 1 is represented the monotonically decay of the double bond absorption after defined irradiation intervals recorded for sample S2.

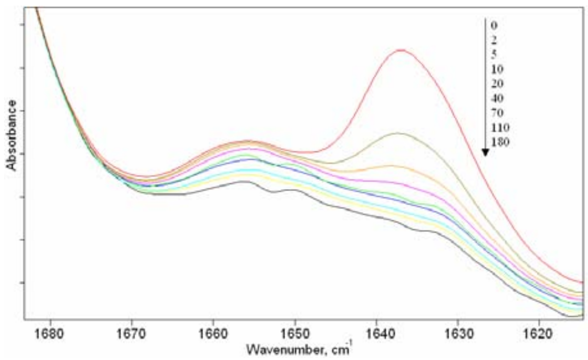


Fig. 1. Changes in the FTIR spectrum for the absorption band of double bond into a dental formulation containing O-UDMA/TEGDMA (1/2) and DMPheA/CQ upon irradiation.

It may be observed that by irradiation, the absorption band at 1636 cm^{-1} is completely vanished after 180 s with the formation of the resin network. This data indicates that the studied systems exhibit a similar trend to other multifunctional dimethacrylates and upon photopolymerization they form complex polymeric networks in which the spacer connects rigid polymethacrylate main chains. Subsequently, the DC for the investigated dimethacrylates is about 45 % after 40 s of irradiation, a satisfactory result for the dimethacrylate urethane dental composites.

Another option to monitor the photopolymerization process is the use of fluorescence probe that give information about the rotational mobility of the molecules, in the surrounding matrix. In a highly viscous medium in which the mobility of the molecules or molecular fragments is strongly reduced, it is of interest to observe the changes in fluorescence intensity that accompanies the slow-down in the fluorophore mobility as the matrix viscosity increased upon completion of the curing reaction in the dental resin formulations. Photopolymerization, going from a monomer of relatively low viscosity to a polymeric network, causes large changes in the mobility of the molecules that comprise the medium. Consequently, an increase in monomer fluorescence intensity as the irradiation time increased was remarked. This response reflects the extent of photocuring in such composites, where only viscosity changes owing to the polymerization reaction may be invoked to explain such a trend.

On the other hand, the ratio of pyrene monomer fluorescence intensity at 377 nm (I_1) to that at 397 nm (I_3), defined as I_1/I_3 ratio, provides information about its local environment of the pyrene into the polymeric network. Therefore, if the magnitude of I_1/I_3 suggests small changes in the intensity ratio of the first and third vibrational bands, this places the pyrene in a more hydrophobic environment of the polymeric matrix.

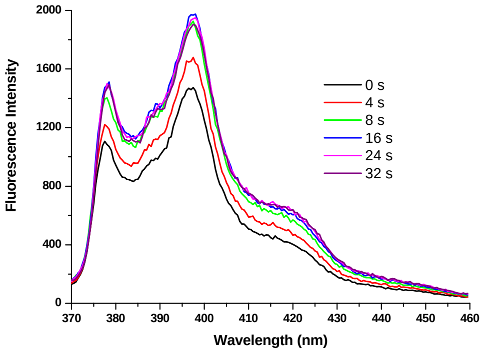


Fig. 2. Fluorescence spectrum for the formulation S1, Aerosil/Sr - Zr glass (1:1), and pyrene derivative irradiated with visible light (λ_{exc}: 353 nm)

As can be seen in Figure 2, for a formulation consisting of O-UDMA(18.43 %), bisGMA (48.84 %) and triethylene glycol dimethacrylate (TEGDMA, 32.17 %) initiated with 4-(dimethylamino)-phenylacetic acid (DMPheA, 1 %) and camphorquinone (0.5 %), in which about 50% filler (Aerosil/Sr-Zr glasss, 1:1) was added, the partitioning of pyrene into hydrophobic environments can be followed by an increase in pyrene monomer emission. Hence, by gradual exposure to visible light irradiation (conducted with a curing light dental device, BLUE SWAN led) the monomers start to polymerize with the formation of a clear and hard glassy solid (after 40 sec). Figure 3 reveals the change in monomer fluorescence intensity of the pyrene, excited at 353 nm, with the curing time for a formulation containing O-UDMA/ TEGDMA, DMPheA/CQ, Aerosil/Sr - Zr glass (1:1) and pyrene derivative as a function of curing time (visible light), excited at 353 nm (a) and (b), plot of the deconvolution results.

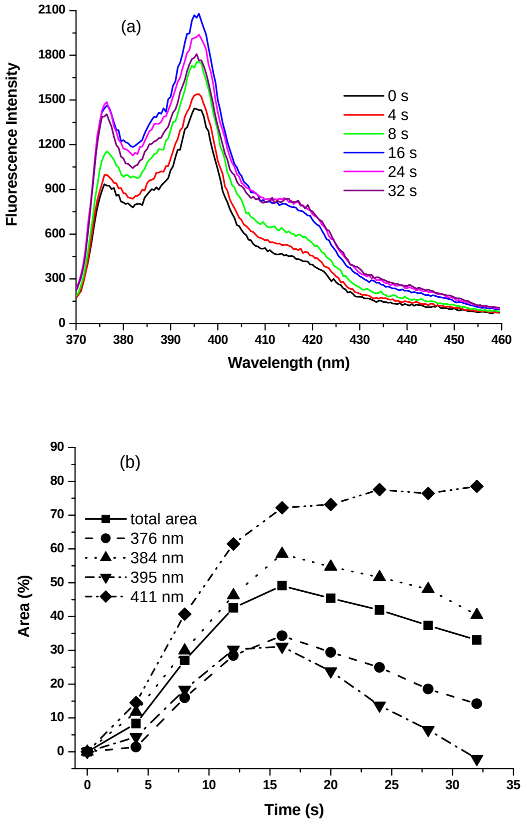


Fig. 3. Fluorescence spectrum for a formulation based on S2, Aerosil/Sr - Zr glass (1:1) and pyrene derivative as a function of curing time (visible light), excited at 353 nm (a) and (b), plot of the deconvolution results.

Such behavior confirms that there is no excimer in the obtained glassy materials and the variation of I_1/I_3 with the irradiation time is similar to that observed in the first figure. In such a case, the total area (I_1-I_4) of the fluorescence intensity increased more than 45% (Table 2) compared to the non-irradiated sample, effect probably arising from a diminishing in collision-induced fluorescence quenching [23].

Table 2. Parameters of the Gaussian curves resulting from monomer fluorescence spectral deconvolution for S2, Aerosil/Sr-Zr glass (1:1) and pyrene derivative

Time (sec)	Total Area	I_1 376 nm	I_2 384 nm	I_3 395 nm	I_4 411 nm
0	40452	6190	6322	14897	13043
4	43830	6275	7066	15553	14936
8	51379	7176	8214	17634	18355
12	57665	7953	9248	19403	21061
16	60321	8315	10020	19531	22455
20	58816	8010	9782	18443	22581
24	57414	7735	9583	16937	23159
28	55571	7338	9363	15862	23008
32	53817	7068	8878	14587	23284

Since the hardening time is dependent on composition, in the later formulation a modification was operated. If Aerosil/quartz (1:1) is incorporated as filler, the I_1/I_3 value changed from 0.42 to 0.48 and the total area (I_1-I_4) of the fluorescence intensity increased with 44%. This finding suggests that the filler nature has not as effect a qualitative difference in pyrene fluorescence, where the viscous O-UDMA/bisGMA monomers exhibit almost the same effective activation energy. When the system based on O-UDMA (67.45 %) and TEGDMA (32.54 %) initiated of CQ/DMPheA does not contain bisGMA, the I_1/I_3 ratio presented comparable values with those found for the formulation in which the bisGMA was included. Figure 4 shows the influence of composition on the fluorescence profile vs. irradiation time for the S2 formulation with the Aerosil/quartz filler system.

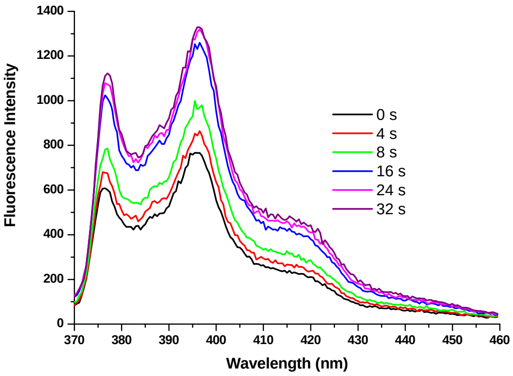


Fig. 4. Effect of the filler (Aerosil/quartz: 1:1) on the fluorescence spectrum for the S2 formulation with pyrene derivative during irradiation with visible light and excited at 353 nm.

The obtained result indicates a significant enhancing of the curing process compared to Aerosil/Sr and Zr glasss, where the total area (I_1-I_4) increased just with 50% (Figure 5 and Table 3).

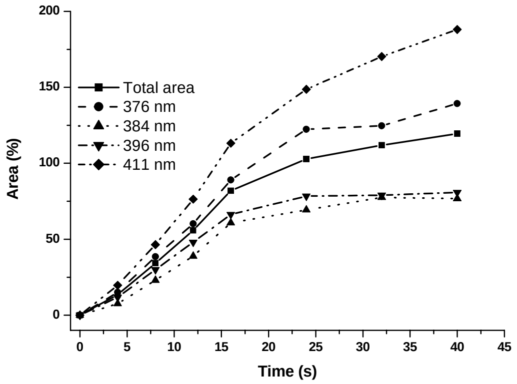


Fig. 5. Plot of the deconvolution for the S2 formulation with Aerosil/quartz 1:1 filler and pyrene monomer.

It is difficult to explain the contribution of the Aerosil/quartz filler and its interactions that seems responsible for the highest fluorescence intensity as the monomers continue to react for the formation of highly cross-linked, rigid, and glassy polymeric network in the absence of bisGMA.

Table 3. Parameters of the Gaussian curves resulting from monomer fluorescence spectral deconvolution for S2 formulation with Aerosil/quartz (1:1) as filler and pyrene derivative.

Time (sec)	Total Area	I_1 376 nm	I_2 384 nm	I_3 396 nm	I_4 411 nm
0	20837	2512	5292	6687	6346
4	23661	2891	5695	7476	7599
8	27975	3479	6509	8692	9295
12	32467	4025	7348	9901	11193
16	37910	4747	8510	11123	13530
24	42259	5586	8960	11930	15783
32	44158	5644	9394	11970	17150
40	45738	6011	9353	12093	18281

A totally different behavior was encountered for the dental formulations obtained by the inclusion of a small amount of dimethacrylate urethane with carboxyl groups UDMA-COOH. In figure 6 is presented the fluorescence spectrum for the S3 composite with Aerosil/Zr-Sr glass and pyrene methanol as fluorescent probe.

During irradiation, the fluorescence intensity is decreasing probably due to the ability of the carboxyl groups interact with the cations liberated from the filler that allow the formation of carboxylate units which can act as fluorescence quenchers. The obtained results are in agreement with our previous research on this field [18].

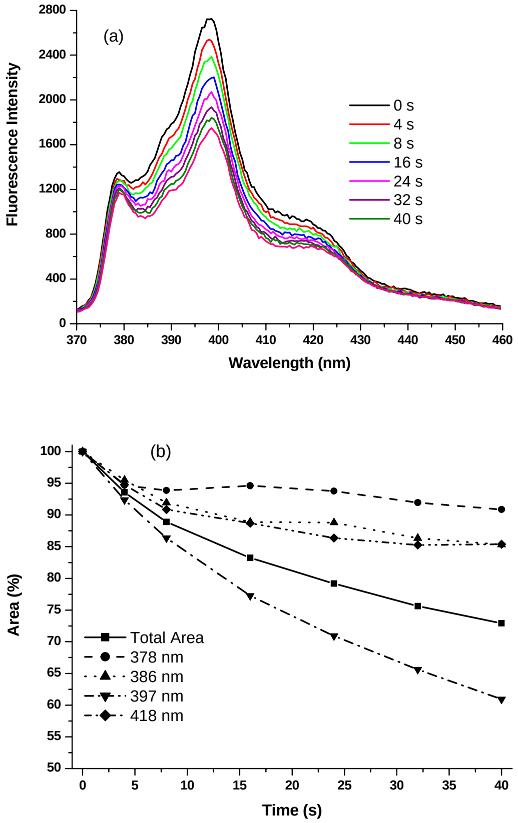


Fig. 6. Monitoring the photopolymerization of S3 formulation Aerosil/Zr-Sr glass (1:1) via fluorescence probe (pyrene methanol) at λ_{exc} = 353 nm (a), and (b), the evolution of the monomer fluorescence intensity area.

It should be emphasized that the fluorescence data regarding the photopolymerization kinetic for all studied formulations are in good agreement with those determined by FTIR spectroscopy and this fact is in favor of the development of oligomer urethane dimethacrylates to be used in the curing reaction for obtaining of dental polymeric networks. Future studies will be focused on preparing of multi-methacrylates with various functions used to formulate them in composite resins with improved properties.

4. Conclusions

A carboxylic acid urethane dimethacrylate with polyethylene oxide in its structure and a non-carboxylic one were synthesized and photocopolymerized with other monomers including a modified bisGMA, demonstrating the potential of them for making dental composite resins with good adhesive properties.

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