

## DIBENZYLIDENE SORBITOL DERIVATIVES FOR IMPROVING DENTAL MATERIALS PROPERTIES

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*Gradul de conversie al monomerilor are un rol foarte important asupra proprietăților fizico-mecanice ale compozitelor dentare. O conversie incompletă poate determina eliberarea de monomer rezidual care poate conduce la diverse probleme clinice precum iritații la nivelul mucoasei orale. Scopul acestui studiu constă în îmbunătățirea gradului de conversie al monomerilor dentari cu ajutorul unor organogelifianți pe bază de 1,3-2,4-bis-O-benziliden-D-sorbitol (DBS). Cercetări anterioare au demonstrat că prin adăugarea DBS crește gradul de conversie al grupărilor vinil din BisGMA etoxilat. Acest fapt se poate datora "efectului de gel Trommsdorff" care sugerează că gradul de polimerizare crește o dată cu creșterea vâscozității.*

*The degree of conversion plays a significant role in determining physical and mechanical properties of final dental composites. Incomplete conversion results in release of unreacted monomers which may cause some clinical problems such as irritations of the oral mucous. The purpose of this research was to improve this condition by using some organogelators based on 1,3-2,4-bis-O-benzylidene-D-sorbitol (DBS). A previous research has revealed that by adding DBS to ethoxylated-BisGMA the vinyl group conversion increases. This may be due to the "Trommsdorff gel effect" which suggests that polymerization rate may increase at high viscosities.*

**Keywords:** degree of conversion, dimethacrylates, organogelators, FTIR

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## 1. Introduction

Dental composites generally are based on methacrylate and dimethacrylate monomers. They are typically composed of two or more monomers, including a relatively viscous dimethacrylate base monomer, such as 2,2-bis-[4-(2-hydroxy-3-methacryloyloxypropoxy)phenyl]propane (Bis-GMA), and a low-viscosity dimethacrylate comonomer, such as triethyleneglycol dimethacrylate (TEGDMA) which is used as a reactive diluter. Another commonly used monomer in commercial dental-resin-based materials is urethane dimethacrylate (UDMA) [1-5].

BisGMA is the most widely used monomer in polymeric matrices of resin-based composites and exhibits many advantages, such as large molecular weight, lower polymerization shrinkage, more rapid hardening and production of stronger and stiffer resins. However, due to intermolecular hydrogen bondings, its high molecular weight and the presence of two aromatic rings in its molecule, this monomer shows a high viscosity and a low mobility, which may influence the degree of conversion of the polymeric matrix. UDMA monomer has a molecular weight nearly equal to that of BisGMA, a lower viscosity and a highly flexible urethane linkage which may improve the toughness of resin composites based on this monomer [6, 7].

Photopolymerization at the ambient temperature is an efficient and convenient cure method and widely used in preparation of dental filling materials. The main drawback is that only a part of the available double bonds is reacting and the unreacted double bonds may either be present in free monomer or as pendant groups attached to the polymer chain backbone. The unreacted groups in the incompletely cured dental resins can cause irritation in the oral mucose and promote allergic reactions [8-16].

In order to investigate new possibilities to improve physico-mechanical properties of dental materials, a systematic study on the photopolymerization reaction of dimethacrylate monomers (BisGMA and UDMA) in the presence of organogelators (dibenzylidene-D-sorbitol, DBS and substituted or functionalized derivatives) was performed. The gelation ability of the organogelator increases vinyl conversion for photopolymerization of dimethacrylate monomers used for dental materials, due to the “gel” effect, also called “Trommsdorff” effect. [17-20].

## 2. Materials and methods

### 2.1 Materials

Experimental formulations were prepared using the dimethacrylate monomers BisGMA and UDMA (Fig. 1) supplied by Sigma Aldrich Chemicals

and were used as received without further purification. 1,3:2,4-bis-O-benzylidene-D-sorbitol (DBS) was supplied by Milliken Chemical Europe, and used without any further modification. Two different functionalized derivatives of DBS, 1,3:2,4-bis-O-(p-methoxybenzylidene)-D-sorbitol (MeO-DBS) and 1,3:2,4-bis-O-benzylidene-5,6-bis-carbonylamino-ethylmethacrylate-D-sorbitol (IEM-DBS), were synthesized according to several procedures described in literature [20].

The resins were activated for visible light polymerization by the addition of camphorquinone (CQ) and ethyl-4(N, N'-dimethylamino) benzoate (4EDMAB) purchased from Sigma Adrich Chemicals.

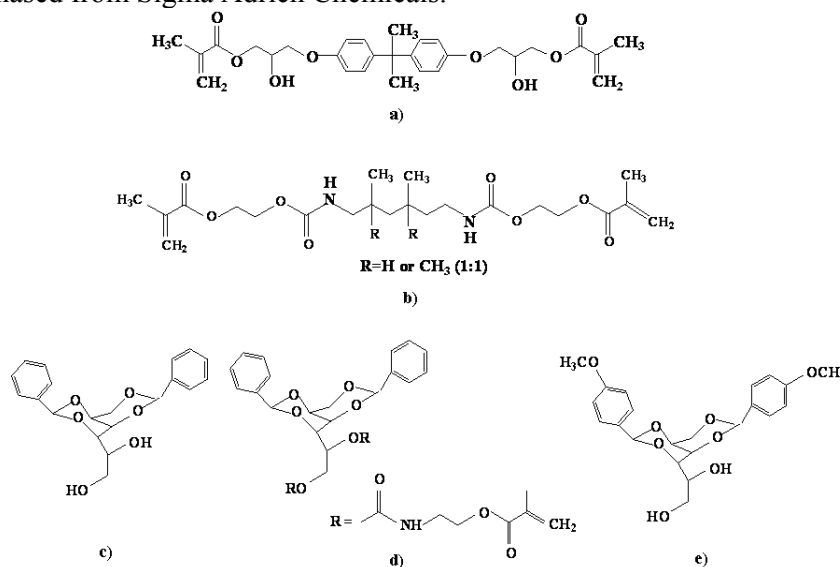


Fig. 1. The chemical structure of raw materials:

a) BisGMA, b) UDMA, c) DBS, d) IEM-DBS, e) MeO-DBS

Several systems were obtained by varying the concentration of dimethacrylate monomers (UDMA, BisGMA) and the content of organogelator (DBS, IEM-DBS and DBS-MeO). (Table 1)

Table 1

The composition of the investigated samples						
Sample code	UDMA (%w)	BisGMA (%w)	organogelator content (%)			
S1	100	-	0	1	2	3
S2	-	100	0	1	2	3
S3	90	10	0	1	2	3
S4	80	20	0	1	2	3
S5	70	30	0	1	2	3

## 2.2 Sample preparation

In order to prepare the organogelator-modified samples, various amounts (0, 1, 2, 3 %w) of different types of organogelator were dissolved into the mixture of dimetacrylate monomers by adding the organogelator to the mixture monomers and storing in an oven at 100°C for 2h. To activate the dimethacrylate mixture for visible light photopolymerization, 0.2% by mass fraction of CQ and 0.8% by mass fraction of 4EDMAB were added to the monomers mixture and mixed until the photoinitiators were completely dissolved [17]. The obtained products were cast in a teflon mould between two glass plates (thickness = 2 mm). The irradiation was performed through the glass plates using a LED (Light Emitting Diode) device (Fig. 2) for 60s, at an angle of 90°. The used device produces visible radiation in the wavelength range from 460-480 nm (blue) and has a light intensity of approximately 700mW/cm<sup>2</sup>.

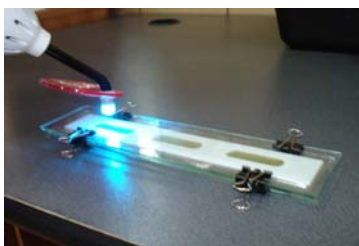


Fig. 2. Light Emitting Diode (LED) device

After photopolymerization, the obtained samples are left in the Teflon mould for 24 h at room temperature and then were characterized.

## 2.3 Sample characterization

*Attenuated total reflection-Fourier Transform Infrared Spectroscopy (ATR-FTIR).*

The FTIR spectra were recorded using 32 scans with a resolution of 4 cm<sup>-1</sup> in 600-4000 cm<sup>-1</sup> region on a VERTEX 70 BRUCKER instrument.

*Optical microscopy (OM).* Microscopic images were recorded on an Olympus SZX10 microscope with a resolution of 600 LP/mm using a high numerical aperture of 0.2, a maximum magnification (126x). A large field of view (69.8 mm) and a long working distance (171 mm) were used.

*Scanning electron microscopy (SEM).* The morphology of the obtained systems was examined on a SEM Quanta Inspect F equipment at an accelerating voltage of 30 kV. Prior to SEM examination, the specimens were fractured using liquid nitrogen and sputter-coated with a thin layer of gold in order to avoid charge accumulation and to obtain various images.

*Contact angle measurements.* The surface wettability was determined using KSV Instruments's CAM 100 by measuring the contact angle on the surface of the films.

*Mechanical properties (Compression strength).* The mechanical properties of the samples were measured on an Instron 3382 instrument, equipped with a 2 kN cell at room temperature ( $25 \pm 1^\circ\text{C}$ ) and  $50 \pm 10\%$  relative humidity. The square-shaped (10 mm . 10 mm) samples of 5-6 mm thickness were placed on the lower plate and compressed by the upper plate at a constant compression rate of 1 mm/min until fragmentation of the studied sample occurred. Measurements were replicated 4 times for each sample and the average value was calculated and reported.

### 3. Results and discussion

#### 3.1 The degree of conversion calculated from ATR-FTIR

ATR-FTIR is a useful tool for studying the chemical structure of polymers because of the vibrational frequencies of polymer molecules in the infrared range and to study the cure reaction of thermoset polymers, such as degree of conversion [8].

The progress of the curing reactions for the dimethacrylate based-systems was monitored using the intensity for the characteristic IR bands of methacrylic groups at  $1638\text{ cm}^{-1}$  ( $\nu_{\text{C}=\text{C}}$ ) consumed during the process.

For the obtained specimens it was monitored the degree of conversion of methacrylic groups using ATR-FTIR at different reaction times (before curing, after 60s curing, after 24h) (Fig. 3).

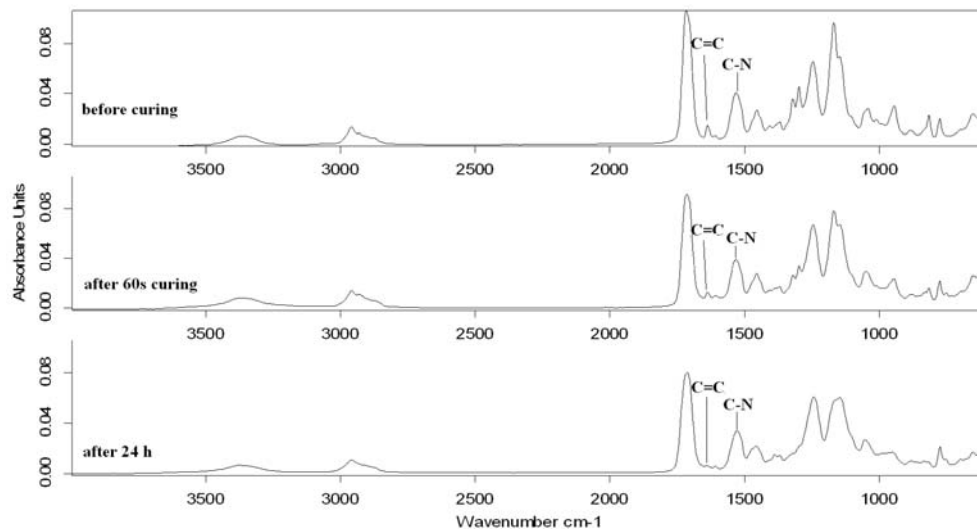


Fig. 3. ATR-FTIR spectra during photopolymerization of S3 + 2%DBS

The degree of conversion was determined from the ratio of the areas of absorption peaks at  $1638\text{ cm}^{-1}$  (assigned to  $\nu_{\text{C}=\text{C}}$ ) and  $1532\text{ cm}^{-1}$  (corresponding to  $\nu_{\text{C}-\text{N}}$ ) for uncured and cured samples. The amide absorption remains constant during polymerization and serves as an internal reference absorption band. The progress of curing reaction was evaluated using the following equation:

$$\eta = \left[ 1 - \frac{\left( \frac{A_{1638}}{A_{1532}} \right)_t}{\left( \frac{A_{1638}}{A_{1532}} \right)_0} \right] \times 100 \quad (1)$$

where:  $\eta$  – conversion,

$(A_{1638})_t$  =  $1638\text{ cm}^{-1}$  peak area at time  $t$ ;

$(A_{1638})_0$  =  $1638\text{ cm}^{-1}$  peak area at time 0;

$(A_{1532})_t$  =  $1532\text{ cm}^{-1}$  peak area at time  $t$ ;

$(A_{1532})_0$  =  $1532\text{ cm}^{-1}$  peak area at time 0;

### 3.2 The influence of organogelator type and concentration on the degree of conversion

Fig. 4 shows the influence of organogelator content (%w) on the degree of conversion of the methacrylic groups.

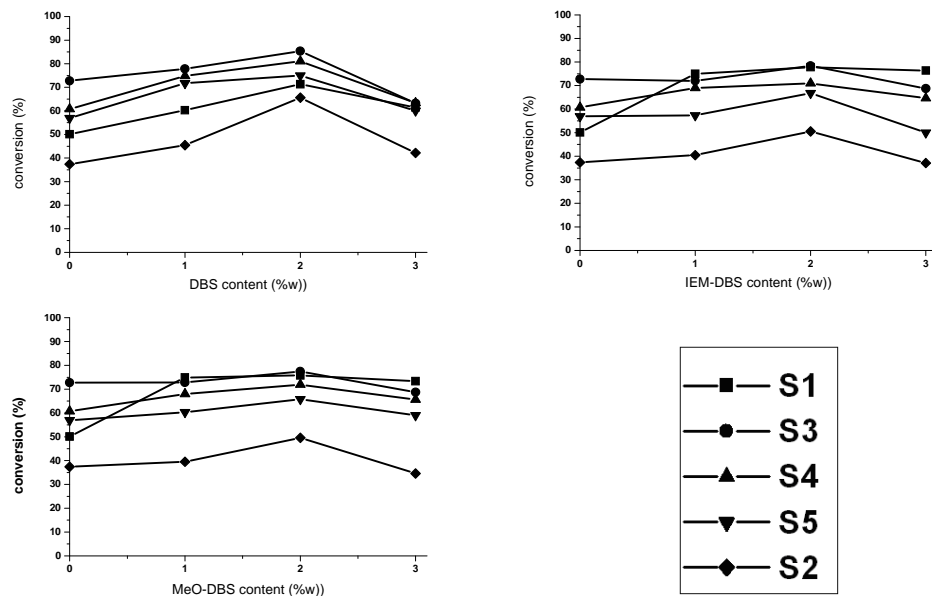


Fig. 4. The dependence of methacrylic groups conversion against organogelator content

From the dependencies of conversion against time, for all the studied systems, it was observed that the highest conversion was obtained for the system S3 with 2% organogelator, independently of the type of functionalized derivatives of DBS was used.

The literature survey concerning the organogelators effect on the conversion degree reveals that this kind of information is extremely brief. Previous efforts have revealed that DBS is capable of gelation in a wide variety of dental monomers [21]. A recently study indicate that adding DBS to ethoxylated BisGMA leads to a statistically significant increase in vinyl group conversion. This may be due to the “gel” effect (“Trommsdorff” effect) which suggests that polymerization rate may increase at high viscosities due to a reduction in chain termination accompanying the decreased mobility of the polymer radicals. Organogelators, by causing physical gelation of the monomer, may also reduce the mobility of the chain ends, thereby enhancing free radical propagation and vinyl conversion [17].

Also, it was noticed that at higher concentrations (3% organogelator) the conversion degree decreases, according with the results obtained by Wilder et al. [17]. In order to establish the reason of this behavior, an advanced morphological characterization by OM, SEM and contact angle was performed.

### *3.3 The influence of organogelator type and concentration on the morphological structure*

The OM images show the structure of S3 system containing different amounts (0, 1, 2, 3 % w) of DBS/ IEM-DBS/MeO-DBS (Fig. 5).

The samples with organogelator (DBS, IEM-DBS or MeO-DBS) include many spherical pores that were formed by air introduced during the mixing process. At higher concentrations of organogelator (3%) the mixture becomes too viscous and many spherical voids remain trapped within the mixture and the positive effects of gelation were cancelled by inhibition of the propagation step during polymerization [17]. This fact can cause a reduction of the conversion degree for the methacrylic groups when a higher amount of organogelator is added. In the future, an improved technique will be used in the processing of the samples in order to eliminate the voids.

Unlike the systems with DBS or MeO-DBS, the samples based on IEM-DBS (2%) exhibit a compact structure. This is probably due to the presence of other supplementary methacrylic groups (from IEM-DBS) giving a better compatibility with polymer matrix.

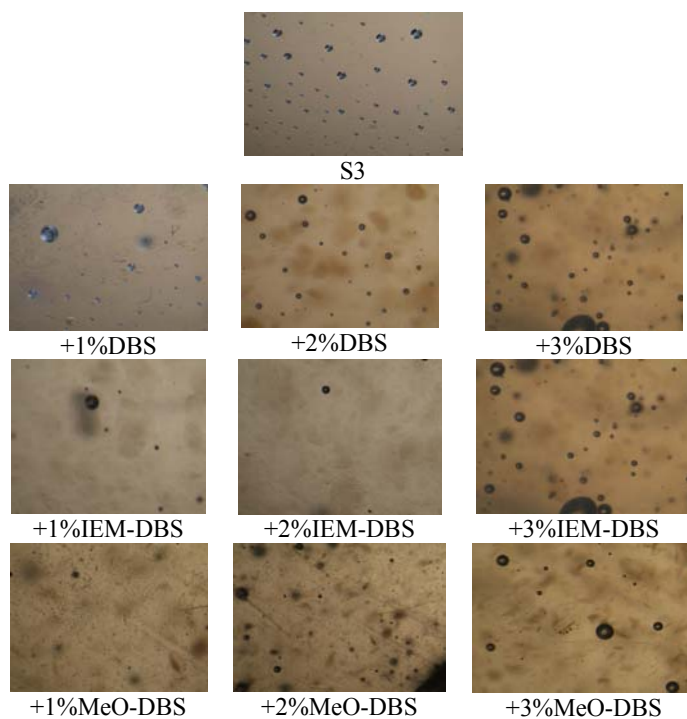


Fig. 5. OM images (2x10x3.6 zoom) for S3 without /with different amounts of organogelator

This statement is confirmed by SEM images which reveal a clear difference between the morphology of the samples with or without IEM-DBS (Fig. 6).

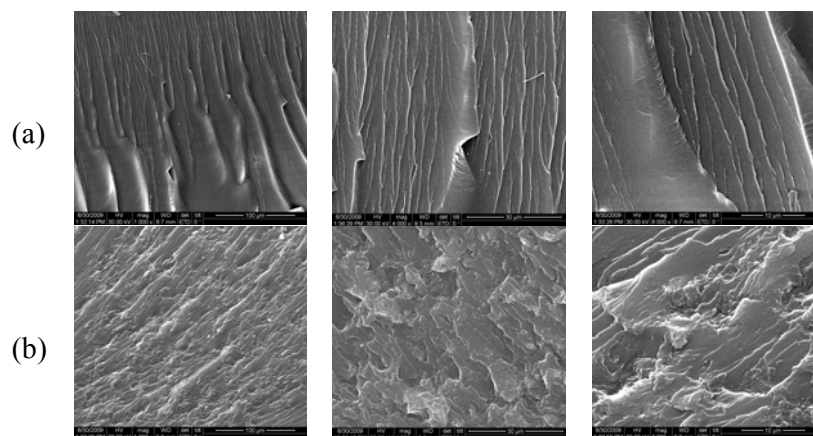


Fig. 6. SEM micrographs of S3: without (a) and with 2% IEM-DBS (b)



Supplementary, another rapid and convenient method to characterize surfaces and to determine the “wettability” is contact angle measurement [22].

In Fig 7. one can be seen the changes in water-surface contact angles from the S3 specimens with different amount of IEM-DBS organogelator. The contact angles of water with the surfaces slightly decrease with the increasing of IEM-DBS content. Such a change can signify an increase in surface hydrophilicity probably caused by the additional oxygen atoms supplied by the organogelator.

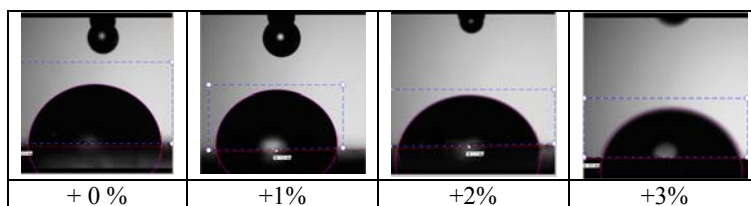


Fig. 7. Visual changes in water-surface contact angles on the samples S3 with IEM-DBS (0, 1, 2, 3%)

The same decreasing tendency of contact angle values was also observed in the case of substrate S3 with DBS and MeO-DBS organogelators. The results are shown in Table 2.

Table 2

Contact angle measurements for S3 specimen with organogelator

DBS content (%)	Contact angle (°)	IEM-DBS content (%)	Contact angle (°)	MeO-DBS content (%)	Contact angle (°)
0	83.23	0	83.23	0	83.23
1	81.41	1	82.94	1	80.49
2	78.74	2	79.91	2	80.39
3	73.93	3	69.39	3	76.61

### 3.5 Mechanical properties. Compression strength

In the case of dental materials it is very useful to characterize them in terms of mechanical properties namely the compression strength, since these materials are designed to operate under cyclic mechanical stress caused by mastication forces.

The mechanical data obtained (Fig. 10, Table 3) are in good agreement with the values obtained from ATR-FTIR. The systems with DBS and IEM-DBS exhibit the highest compression strength. These systems exhibit the highest conversion as well. Therefore it can be said that the increasing conversion degree leads to improved mechanical properties (compression strength). However, the system with MeO-DBS exhibits the lowest compression strength.

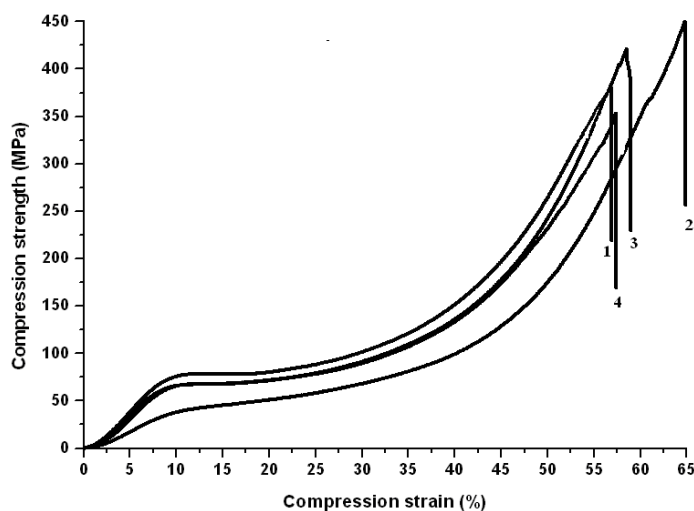


Fig. 8. Compression strength for: (1) substrate S3; (2) S3+2%DBS; (3) S3+2%IEM-DBS; (4) S3+2%MeO-DBS

Table 3

The compression strength values for the S3 sample with different types of organogelator

Code	Samples	Compression strength (MPa)
1	S3	394
2	S3 + 2%DBS	450
3	S3 + 2%IEM-DBS	421
4	S3 + 2%MeO-DBS	332

#### 4. Conclusion

The gelation ability of the organogelator increases vinyl conversion for photopolymerization of dimethacrylate monomers used for dental materials, due to the “gel” effect (“Trommsdorff” effect). The curing degree from ATR-FTIR confirms that the addition of a certain amount (2% w) of organogelator, leads to a higher conversion of methacrylic groups.

The highest conversion was obtained for the system S3, based on 90%UDMA and 10%BisGMA, with 2% organogelator, regardless the type of organogelator used. This composition of monomers (S3) was chosen in order to observe the influence of organogelator type and concentration on the morphological structure and the mechanical properties.

Unlike the samples with DBS or MeO-DBS, the samples based on IEM-DBS (2%) exhibit a compact structure. This is probably due to the presence of other supplementary methacrylic groups (from IEM-DBS) giving a better compatibility with polymer matrix. This statement is confirmed by SEM images which reveal a clear difference between the morphology of the samples with or without IEM-DBS.

The contact angle measurements prove that with increasing of the organogelator content, the hydrophilicity of the studied system consecutively increases.

The mechanical data obtained are in good correlation with ATR-FTIR data. The systems with DBS and IEM-DBS exhibit the highest compression strength and also the highest conversion which means that in all cases by increasing the vinyl conversion degree the mechanical properties are enhanced.

### Acknowledgements

The National University Research Council, from the Romanian Ministry of Education, Research and Youth is gratefully acknowledged for the financial support of the research through the exploratory project "Low shrinkage dental materials mediated by organogelators", PN-II-Idei-2008-2, number 725/2009, code 1718.

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