

Composition Versus Physico-mechanical Properties of Some Dental Experimental Polymers

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A series of six experimental dental copolymers of different compositions has been prepared from new synthesized Bis-GMA-type oligomers and triethyleneglicol dimethacrylate by photochemical initiation of polymerization. The paper studies the influence of the chemical composition upon the extent of polymerization, mechanical properties and water sorption of the experimental copolymers. The corresponding commercial Bis-GMA-based copolymers were used as control. The extent of the polymerization, determined by FTIR method, ranged between 61.67% for the new copolymers containing 75% bis-GMA-type oligomers and 79.6% for the new copolymers containing 50% bis-GMA-type oligomers in the matrix. From the comparison of the mechanical properties, we came to the conclusion that the values for compressive strengths and diametral tensile strengths were in the same range to those obtained for the corresponding commercial Bis-GMA-based copolymers, while the flexural strength values were higher than the values for to corresponding control copolymers. The water sorption values were in the limit of clinical requirements.

Keywords: dental resins, extent of polymerization, mechanical properties, water sorption

The composition of dental diacrylic resins and the extent of photopolymerization have a pronounced effect on the physico-chemical and mechanical properties of dental adhesives, primers, sealants and restorative resin composites [1-5].

Dimethacrylate monomers used in dental diacrylic resins polymerize to highly crosslinked, three-dimensional networks. As polymerization proceeds, because of the local gel effect, diffusion rates of propagating free radicals and unreacted dimethacrylate molecules are drastically reduced, making 25-50% of the methacrylate groups to remain unreacted [6,7]. The degree of conversion of dimethacrylates may be improved if the distance between the methacrylate groups is long, and the molecular weight is high, respectively. High conversion is not a goal in itself, however. If the monomer is very flexible and not sufficiently bulky, the degree of conversion will be high, but the mechanical properties will be poor. High mechanical properties are particularly important in the process of mastication, where the greatest loads are experienced by the tooth structures. Compressive strength (CS), diametral tensile strength (DTS) and flexural strength (FS) are important parameters for the comparison of dental restorative composites [8-11].

The resin matrix used in dental materials absorbs saliva from the environment. Saliva is mostly water (more than 99 %) and less than 1% solids (macromolecules like proteins, sugars, calcium, sodium and chloride, amino acids, free glucose etc). Water can penetrate in the gaps of the polymer network, reaching around functional groups which are able to deliver hydrogen bonds. Sorption of saliva may precede the physical and chemical processes and

can lead to a change of structure and properties of polymer network [12-15]. The sorption of saliva by acrylic resins is accompanied by dimensional changes, deleterious effects on the structure and function of dental polymers and composites. This behavior affects the restoration life, therefore water sorption of these materials should be as low as possible [16-18].

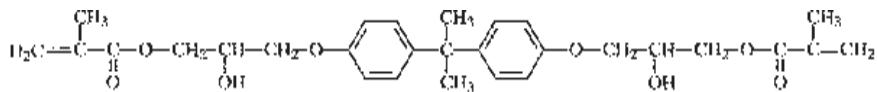
The aim of this paper was to determine the degree of conversion of some new dental resins and to study the relationship between the composition, conversion, strength properties and water sorption of the corresponding copolymer matrices.

Experimental details

Obtaining of the new experimental monomer mixtures

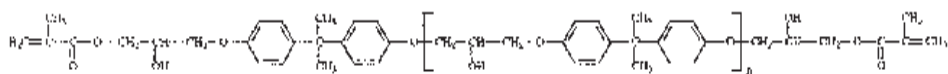
A series of new monomer mixtures have been formulated using two new Bis-GMA-type oligomers synthesized in our laboratory as base monomers and triethyleneglicol dimethacrylate (TEGDMA) as diluting monomer. The new oligomers Bis-GMA336 and Bis-GMA356 have been synthesized from the commercial epoxy resins D.E.R. 336 and D.E.R. 356 (DOW Company) respectively, using the method described in a previous work [19]. The monomer mixture containing the commercial Bis-GMA_{imp} (Merck) and TEGDMA was used as control. In the composition of the monomer mixtures, besides the methacrylic monomers, a photosensitizer, camphorquinone (CQ), in an amount of 0.5%, and an accelerator dimethylaminoethyl methacrylate (DMAEM), in an amount of 1%, were added. Butylated hydroxy toluene (BHT) was added in a quantity of 650 ppm related to the monomer mixtures.

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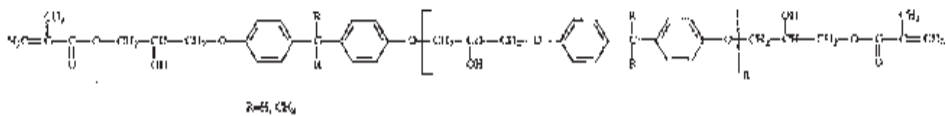
Bis-GMA_{imp}

2,2-bis[4-(2-hydroxy-3-methacryloyloxypropoxy) phenyl]-propane



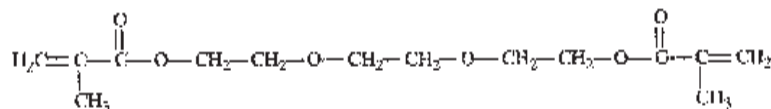
Bis-GMA₃₃₆ (n=0,1)

Dimethacrylic oligomers mixture containing Bis-GMA type monomer - 2,2-bis[4-(2-hydroxy-3-methacryloyloxypropoxy) phenyl]-propane, and the corresponding Bis-GMA type dimer



Bis-GMA₃₅₆ (n=0,1)

Dimethacrylic oligomers mixture containing Bis-GMA type monomers - 2,2-bis[4-(2-hydroxy-3-methacryloyloxypropoxy) phenyl]-propane and bis[4-(2-hydroxy-3-methacryloyloxypropoxy) phenyl]-methane and the corresponding Bis-GMA type dimers



Triethyleneglycol dimethacrylate

No.	Code monomer mixture/copolymer	Bis-GMA _{imp} %	Bis-GMA ₃₃₆ %	Bis-GMA ₃₅₆ %	TEGDMA %
1	A	50	-	-	50
2	B	65	-	-	35
3	C	75	-	-	25
4	D	-	50	-	50
5	E	-	65	-	35
6	F	-	75	-	25
7	G	-	-	50	50
8	H	-	-	65	35
9	I	-	-	75	25

Fig.1. The monomers and oligomers used in the experiments

Table 1
COMPOSITION OF THE
EXPERIMENTAL MONOMERS
MIXTURES AND THEIR
CORRESPONDING
COPOLYMERS

Obtaining of the experimental copolymers

The copolymers were obtained from the corresponding monomer mixtures by exposing to a visible radiation in the wavelength range of 400-500 nm. The radiation was generated by an Optilux dental lamp, produced by Demetron Research Corporation USA.

The composition of the monomer mixtures and the corresponding copolymers are presented in table 1.

Determination of the monomer conversion

The conversion of monomer mixtures was evaluated by determining the residual double bonds using the Infrared Spectroscopy Method. The quantity of unreacted methacrylate groups is determined in percent of the methacrylate groups originally present in the unpolymerized material. The decrease in the intensity of the methacrylate C=C absorbance (A_{meth}) at 1635 -1640

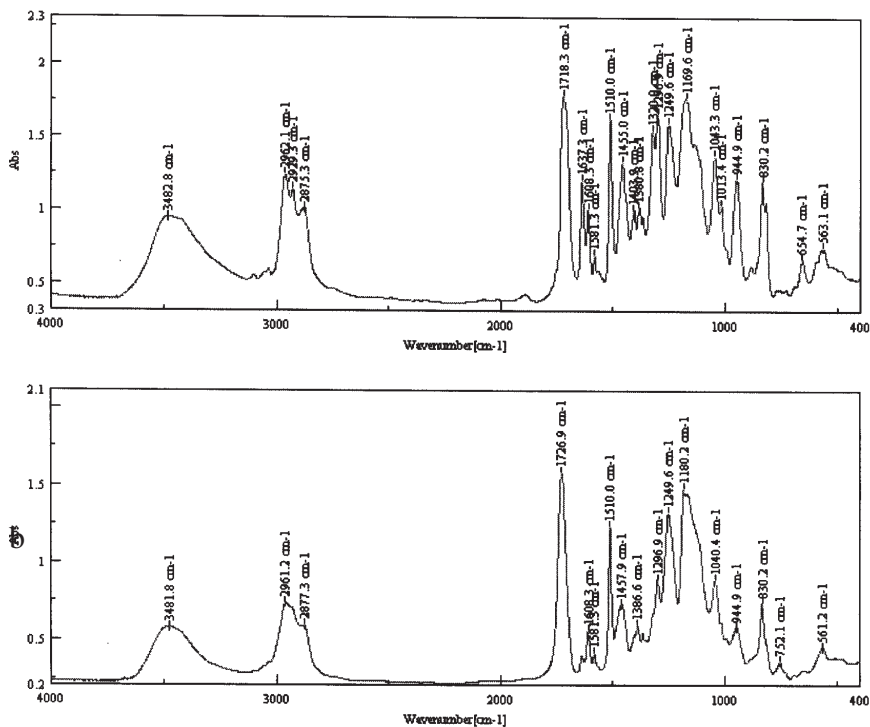


Fig.2. FTIR spectra of 65% Bis-GMA336 and 35% TEGDMA monomer mixture (a) and of the corresponding copolymer (b)

cm⁻¹ was monitored. The phenyl absorbance ($A_{1605-1610}$) at 1605-1610 cm⁻¹ was used as an internal standard [20].

The FTIR spectra of the liquid monomers mixtures prepared as liquid thin films between KBr plates and of the solid corresponding copolymers prepared as KBr pellets were recorded on a JASCO 610 FTIR Spectrophotometer.

As an example, the FTIR spectra of monomer mixture containing 65% Bis-GMA336 and 35% TEGDMA and of the corresponding copolymer are presented in figure 2.

The percentage of double bonds reacted (conversion of double bonds) was calculated from the formula (1):

$$\text{conv \%} = \{1 - [A_{\text{meth}}/A_{\text{arom}}]_{\text{copolymer}} / [A_{\text{meth}}/A_{\text{arom}}]_{\text{monomer}}\} \times 100 \quad (1)$$

Determination of mechanical properties

Compressive Strength

The compressive strength was determined using specimens having the form of cylinders - 8 mm in height and 4 mm in diameter. The specimens were illuminated in their respective molds by the light source (OPTILUX dental lamp, Demetron Research Corporation, USA) in steps of 2mm height, for 40 s each step. The measurements of the compressive strength were made using a Lloyd LR5K Plus mechanical testing apparatus at a 0.5 mm/min pressing speed. The compression strength CS (in MPa) was calculated applying formula (2):

$$\text{CS} = F / 0.785d^2 \quad (2)$$

where: F is the maximum applied load (N) and d is the specimen diameter (mm)

Tensile strength

The tensile strength was measured using the diametral compression test (the indirect test of determining the tensile strength). The general technique of preparing and testing the copolymer specimens was similar with the one described when determining the compression strength, with the only difference that the cylindrical specimens had 4mm in thickness (T) and 6mm in diameter (D). The specimens were subjected to compression along the cylinder generator. The F force that acts on the cylinder,

caught between the pans of the apparatus, determines the appearance of the tensile efforts on the vertical diameter plane. The tensile strength DTS (in MPa) was calculated applying the formula (3):

$$\text{DTS} = 2 \times F / \pi \times D \times T \quad (3)$$

Flexural Strength

The flexural strength was determined using specimens having rectangular form (length 25.0 mm, height 2.0 mm and width 2.0 mm), according to ISO 4049/2000 [21]. The general technique of preparing the copolymer specimens was similar with the one used at the determination of compressive strength. After the measurement of height *a* and width *b*, the specimens were subjected to three-point loading with *l*=20 mm between the supports. The crosshead speed of the testing machine was 1.0 mm/min. The flexural strengths FS were calculated as:

$$\text{FS} = 2 \times F \times l / 2 \times b \times a^2 \quad (4)$$

Determination of water sorption

Disk specimens of copolymers 15±1mm diameter, 1±0.1mm thickness were prepared in a mold by exposing each side to a visible radiation in the range of 400-500 nm for 40 sec using a dental lamp.

Water sorption values were determined according to ISO 4049/2000 [21] at 1, 2, 3, 4, 7, 14, 21 and 30 days of storage in artificial saliva.

The values for water sorption (Wsp), for each of the specimens were calculated using the formula:

$$\text{Wsp} = M1 - M2 / V \quad (5)$$

M1 - the mass of the specimen after immersion in artificial saliva [μg],

M2 - the mass of the specimen after removing from the artificial saliva and drying [μg],

V- volume of the specimen [mm³]

The structures of copolymers before and after immersion in artificial saliva were examined using a FEI scanning electron microscope (SEM).

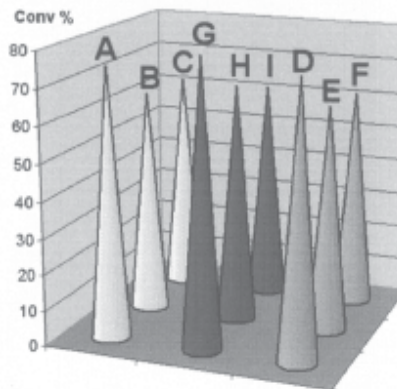


Fig.3. Conversion of double bonds in the dental copolymers

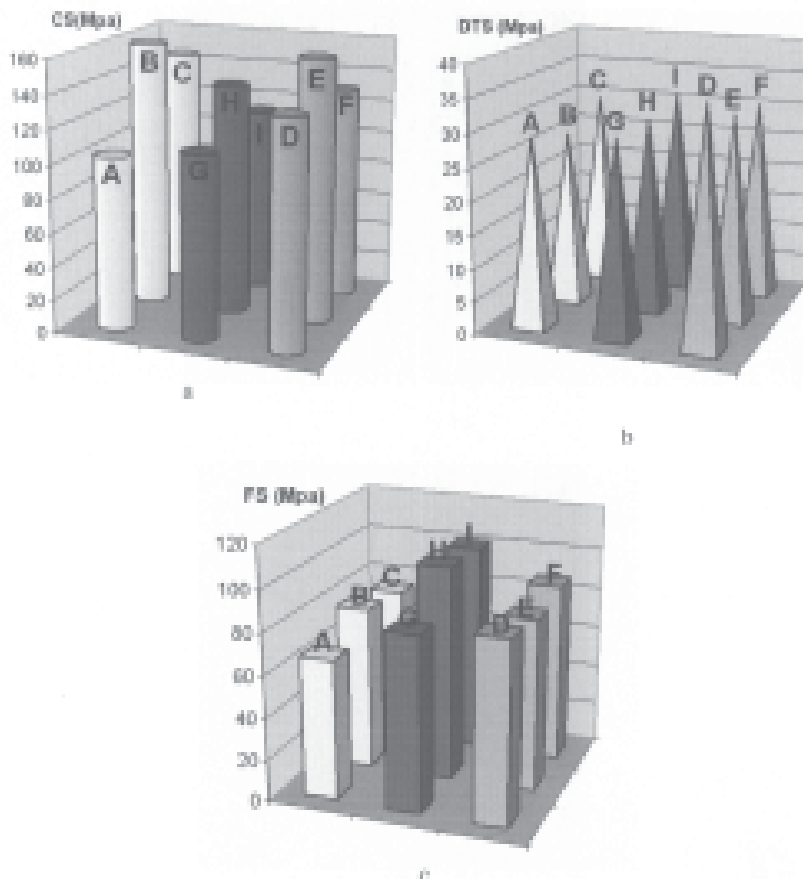


Fig.4. Compressive strengths (a) diametral tensile strengths (b) and flexural strengths (c) for the new dental copolymers

Results and discussions

Determination of monomer conversion

Conversion of double bonds in the new dental copolymers is shown in figure 3. The results show that in the case of the three Bis-GMA type oligomers, the degree of conversion is influenced mainly by the Bis-GMA-type oligomer/TEGDMA ratio and secondly by the Bis-GMA-type oligomer chemical structure. The decreasing of conversion of double bonds with the increasing of the Bis-GMA type monomer, respectively with the decreasing of the TEGDMA content in the mixture can be explained by the effect of physical and chemical properties of the two types of monomers, which are derived from their structural features, upon the evolution of polymerization.

The aromatic Bis-GMA-type oligomers, having large rigid molecules with reduced mobility, characterized by a very high viscosity, reach the gel state in a very short time after the beginning of reaction. After their polymerization, a large number of double bonds remain unreacted. The aliphatic TEGDMA monomer, having an increased flexibility of the chain due to the ether linkages, a great mobility of the molecules and much lower viscosity, reaches the gel state after a longer period of time than the aromatic oligomers, time enough for a greater number of methacrylate groups to react.

From the figure 3 there can be noticed that in all cases the copolymers with 65% Bis-GMA type oligomers presented a significant decrease of conversion compared to the copolymers containing 50% Bis-GMA type oligomers ($\Delta\text{conv.} = 12.9\%$ for Bis-GMA₃₃₆-based copolymers; $\Delta\text{conv} = 12.8\%$ for Bis-GMA₃₅₆-based copolymers and $\Delta\text{RDB} = 12.03\%$ for Bis-GMA_{imp}-based copolymers). For the copolymers containing 75% Bis-GMA type oligomers, the values of conversion were closed to the values recorded for the copolymers with 65% Bis-GMA type oligomers, Δconv varying between 1 and 5%.

Determination of mechanical properties

Compressive strengths, diametral tensile strengths and flexural strengths of the new dental copolymers as function of composition is shown in figures 4a, 4b and 4c.

The results presented in figure 4 show that the mechanical properties are highly influenced by the type of Bis-GMA oligomer presented in copolymer.

The compressive strengths obtained for Bis-GMA_{imp}-based copolymers were in the range of 103.21 and 159.71 MPa, the CSs for Bis-GMA₃₃₆-based copolymers ranged between 130.2 and 158.27 MPa, and the CS values were between 110.3 and 138.29 MPa for Bis-GMA₃₅₆-based copolymers. The highest values of CS in all cases were obtained for an amount of 65% Bis-GMA type oligomer in the copolymer. The values of CS recorded for Bis-GMA₃₃₆-based copolymers are high and closed to the CSs values obtained for Bis-GMA_{imp}-based copolymers, the series of Bis-GMA₃₅₆-based copolymers presented smaller values for this property.

The diametral tensile strengths are relatively high and about in the same ranges for all three series of copolymers (30.62-36.04 MPa for Bis-GMA₃₃₆-based copolymers, 29.7-31.1 MPa in the case of Bis-GMA₃₅₆-based copolymers and 26.43-29.76 MPa for Bis-GMA_{imp}-based copolymers).

The flexural strengths are very high for the copolymers containing the synthesized oligomers.

They ranged from 83.47 to 87.47 MPa in the case of Bis-GMA₃₃₆-based copolymers and 83.74 to 102.94 MPa for Bis-GMA₃₅₆-based copolymers compared to 66.91-78.15 MPa obtained for Bis-GMA_{imp}-based copolymers. The highest values were obtained for 65% Bis-GMA₃₃₆ containing copolymer (102.94 MPa).

Despite the resultant decrease in degree of conversion (fig.3), an increasing content of Bis-GMA type oligomers does not result in a reduction in strengths properties. This lack of correlation between conversion and strengths could be explained by the fact that flexible TEGDMA is substituted by the much stiffer Bis-GMA type oligomer in the polymer network. The relative stiffness of Bis-GMA type oligomers is related to the bulky, aromatic groups of the central part of the molecule, causing much larger barriers to rotation about the bonds.

Among the synthesized Bis-GMA type oligomers, Bis-GMA₃₃₆ leads to the obtaining of copolymers with highest CS and DTS. FS values for the copolymers containing Bis-GMA₃₃₆ and Bis-GMA₃₅₆ are much higher comparing with the FSs obtained for Bis-GMA_{imp} containing copolymers.

Determination of water sorption

Analyzing the strength properties values, there were selected for water sorption tests the copolymers containing 65% Bis-GMA type oligomers: 65%Bis-GMA₃₃₆- based copolymer, 65%Bis-GMA₃₅₆- based copolymer, and 65%Bis-GMA_{imp}- based copolymer, respectively. Water sorption values of the selected dental copolymers as function of storage time were presented in figure 5.

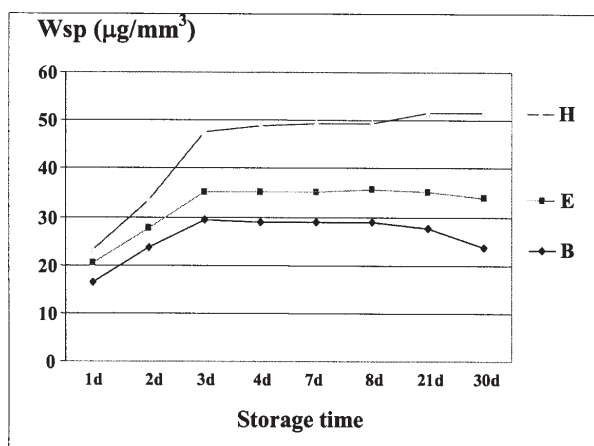


Fig. 5 Water sorption of copolymers as function of storage time

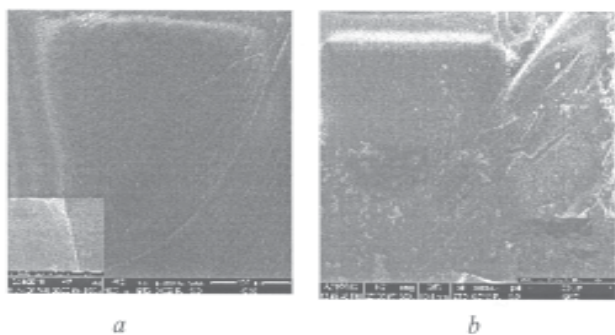


Fig.6. SEM photomicrographs (x 800/3000) illustrating fracture surface of B copolymer prior to immersion (a) and after 30 days of storage in artificial saliva (b)

The water sorption values increase until the third day of storage for all three copolymers, then remains about at the same level until the 8th day, when the values for Bis-GMA₃₃₆- based copolymer and Bis-GMA_{imp}- based copolymer slightly decrease. Maximum values for sorption (29.44 µg/mm³ for copolymer B after three days; 35.6 µg/mm³ for copolymer E after three days) were lower than 40 µg/mm³. Bis-GMA₃₅₆- based copolymer shows a maximum sorption value (50.9 µg/mm³) after 21 days of storage. SEM photomicrographs illustrating fractured surfaces of Bis-

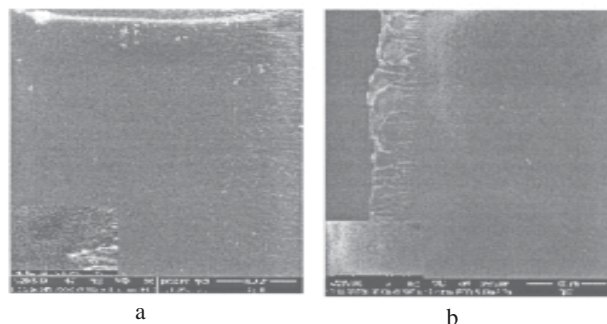


Fig.7. SEM photomicrographs (x 800/3000) illustrating fracture surface of E copolymer prior to immersion (a) and after 30 days of storage in artificial saliva (b)

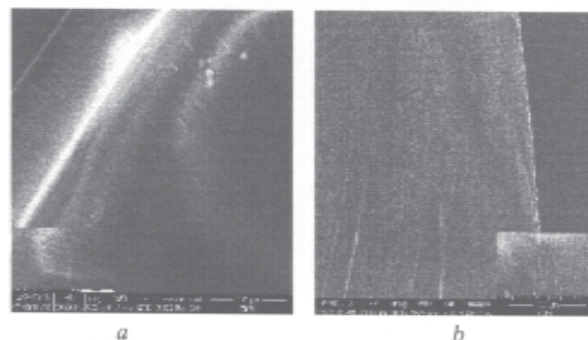


Fig.8. SEM photomicrographs (x 800/3000) illustrating fracture surface of H copolymer prior to immersion (a) and after 30 days of storage in artificial saliva (b)

GMA- based copolymer specimens prior (a) and after 30 days of storage in artificial saliva (b) are shown in figure 6.

SEM photomicrographs of copolymers in the fractured surfaces prior to immersion in artificial saliva (fig. 6a, 7a, 8a) show a homogeneous structure with fine striations due to fractures. After 30 days of storage in artificial saliva, B and E copolymers showed surfaces with unessential modifications (fig. 6b, 7b). In the case of H copolymer (fig.8b), the surface is slightly deteriorated due to an increased content of absorbed water.

Conclusions

A series of six experimental dental monomer mixtures of different compositions were prepared in order to obtain the corresponding copolymers by photochemical initiation of polymerization. The monomer mixtures were obtained from two new Bis-GMA-type oligomers (Bis-GMA336 and Bis-GMA356), synthesized in our laboratory from the commercial epoxy resins D.E.R. 336 and D.E.R. 356 (DOW), and triethyleneglicol dimethacrylate in different ratios.

The copolymers have been investigated by FTIR spectroscopy method in order to evaluate the extent of polymerization of the monomers. The obtained results pointed out as a general conclusion that conversion decreases with the increase of the amount of Bis-GMA-type oligomer in the mixture and presents closed values for the same amount of Bis-GMA-type oligomers in the mixture.

The mechanical properties, compressive strengths, diametral tensile strengths and flexural strengths were determined. The highest value for CS (158.27 MPa) was recorded for the 65% Bis-GMA₃₃₆- based copolymer and the highest values for FS (102.94 MPa) was obtained in the case of the 65% Bis-GMA₃₅₆- based copolymer. The diametral tensile strengths were relatively high and about in the same ranges for the two series of copolymers (30.62-

36.04 MPa for Bis-GMA₃₃₆- based copolymers and 29.7-31.1 MPa in the case of Bis-GMA₃₅₆- based copolymers)

Comparing the new copolymers containing 65% Bis-GMA type oligomers, we found out that the smallest water sorption values recorded during the 30 days of storage in artificial saliva were the ones of the Bis-GMA₃₃₆- based copolymer.

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