

## PROPERTIES OF SOME RESIN-MODIFIED GLASS IONOMERS CONTAINING POLY(ACRYLIC ACID-CO-ITACONIC ACID-CO-N-ACRYLOYL-L-TRYPTOPHAN) FUNCTIONALIZED WITH (METH)ACRYLATE MOIETIES

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### Abstract

New dental ionomer compositions were prepared from diglycidyl methacrylate of bisphenol A (Bis-GMA) or an analogue of Bis-GMA (Bis-GMA-1), triethylene glycol dimethacrylate (TEGDMA) and 2-hydroxyethyl methacrylate (HEMA), and a photocrosslinkable copolymer containing around 10 mol% methacrylate pendant groups. The photocurable polymer was obtained by functionalization with (N-methacryloyloxyethylcarbamoyl-N'-2-hydroxyethyl) urea of a ternary polymer synthesized by a radical polymerization of acrylic acid, itaconic acid and N-acryloyl-L-tryptophan. Light-curable cements, obtained by mixing the above organic compositions with filler (90 wt. % fluoroaluminosilicate/10 wt. % hydroxyapatite), exhibited flexural strength (FS) and compressive strength (CS) varying between 38.08 and 59.12 MPa (FS), and 107.58 and 162.13 MPa (CS), respectively.

### 1. Introduction

Glass polyalkenoates or glass-ionomers cements are bioactive materials that exhibit attractive properties in restorative dentistry such as good adhesion, chemical bonding, thermal compatibility with enamel and dentine, low thermal expansion coefficients, less volumetric setting contraction, low shrinkage at the tooth–enamel interface, and often anticariogenic activity [1]. Usually, the aqueous polymeric acids used for the preparation of these materials are relatively weak acids, such as poly(acrylic acid), poly(acrylic acid-co-itaconic acid) or poly(acrylic acid-co-maleic acid), to name a few. At the same time, it has been demonstrated that (meth)acryloyl-functionalized amino acids monomers, such as L-glutamic acid, β-alanine, glycine or proline can lead to glass-ionomer cement systems with superior properties concerning the compressive strength, diametral tensile strength and flexural strength [2,3]. Another approach has been taken in study the hybrid materials which combine the properties of resin composite with those of the conventional glass-ionomers, the simplest forms incorporating a small quantity of resin component, usually 2-hydroxyethyl methacrylate or bulky monomers, such as bis-glycidyl ether dimethacrylate (Bis-GMA) and/or urethane dimethacrylate, and diluents, such as triethylene glycol dimethacrylate (TEGDMA) [4,5]. In the present study we wish to report herein some resin-modified glass ionomers carrying out poly(acrylic acid-co-itaconic acid-co-N-acryloyl-L-tryptophan) functionalized with

(meth)acrylate moieties, Bis-GMA or its analogue (Bis-GMA-1), TEGDMA and bioactive glass along with their properties including the polymerization rate, degree of conversion, water sorption/solubility, mechanical parameters, surface morphology and fluorescence caused of the tryptophan molecule.

## 2. EXPERIMENTAL

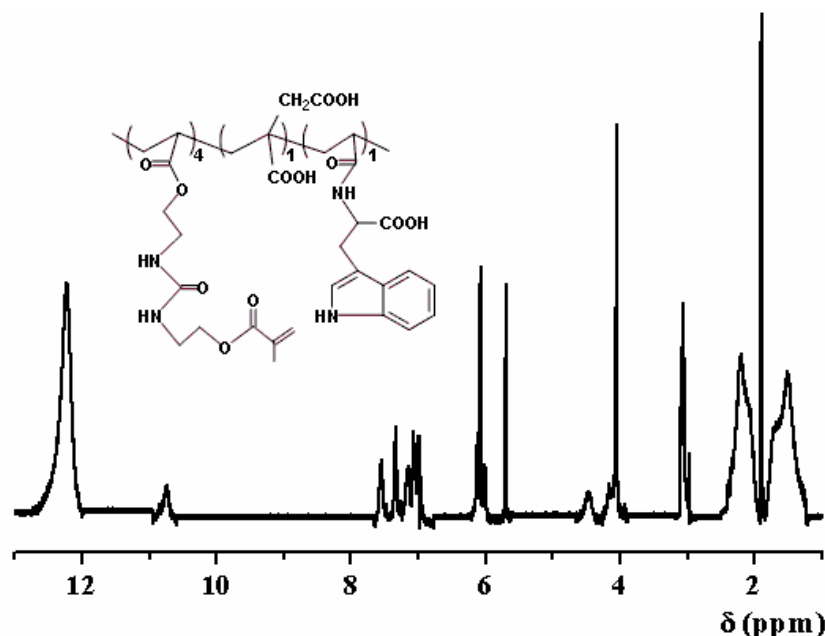
*Synthesis of N-acryloyl-L-tryptophan.* The acryloyl amino-acid derivative was synthesized by a Schotten–Baumann reaction [6]. Briefly, to a two-neck flask containing L-tryptophan and NaOH aqueous solution, acryloyl chloride was added dropwise with stirring at the temperature below 0°C. The mixture was stirred for 24 hours at room temperature. The solution was acidified to pH 2 with HCl (37%) and the formed precipitate was filtered, washed with water and dried in vacuum at ambient temperature. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>), δ (ppm): 3.06 (m, 2H, -CH<sub>2</sub>CHCOOH), 4.56 (d, 1H, -NHCHCOOH), 5.5–6.1 (dd, 2H, -CH=CH<sub>2</sub>), 6.2 (m, 1H, -CH=CH<sub>2</sub>), 6.9–7.6 (m, 5H, indole ring), 8.4 (s, 1H, -CHNHC from indole ring), 10.8 (s, 1H, NHCHCOOH). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>), δ (ppm): 27.6 (-CH<sub>2</sub>CHCOOH), 54.4 (-NHCHCOOH), 109.3–112.4 (indole ring), 118.2–127.8 (indole ring and -CH=CH<sub>2</sub>), 164.8 (-C=O), 174.3 (-COOH).

*Synthesis of (N-methacryloyloxyethylcarbamoyl-N'-2-hydroxyethyl)urea.* To a 50 mL two-necked flask containing methylene dichloride and 2-amino-1-ethanol, 2-isocyanatoethyl methacrylate was added dropwise. The resulting solution was kept under stirring at room temperature for 24 h. Complete conversion of the starting isocyanate was confirmed by FTIR spectroscopy through complete disappearance of intensity band at 2265 cm<sup>-1</sup> ascribed to NCO group. The solution was concentrated in vacuum to give methacryloyloxyethylcarbamoylamino ethanol as a yellowish viscous liquid. <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ (ppm): 1.91 (s, 3H, CH<sub>3</sub>), 3.10-3.20 (s, 2H, CH<sub>2</sub> adjacent to NH), 3.41-3.47 (m, 2H, CH<sub>2</sub> near to OH), 3.67 (d, 2H, CH<sub>2</sub> adjacent to urea), 4.17-4.20 (d, 2H, CH<sub>2</sub>-OCO), 5.58 (s, 1H, =CH *cis*), 5.99 (m, 2H, NH), 6.10 (s, 1H, =CH *trans*). <sup>13</sup>C NMR (CDCl<sub>3</sub>), δ, ppm: 167.61 (CO acrylate), 158.66 (CO urea), 136.00 (C=), 126.03 (=CH<sub>2</sub>), 64.19 (CH<sub>2</sub>-O), 62.19 (C-OH), 40.08 (C-N), 39.37 (C-N), 29.66 (CH<sub>2</sub>), 26.81 (CH<sub>2</sub>), 18.24 (CH<sub>3</sub>).

*Synthesis of the ternary copolymer.* Acrylic acid, itaconic acid and *N-acryloyl-L-tryptophan* were copolymerized in the 4:1:1 molar ratio in 1,4-dioxane solution. Radical polymerization was initiated by 1,1'-azobis(cyclohexanecarbonitrile) (0.2% with respect to the amount of monomers) and performed at 80 °C for 72 h after degassing and purging the monomers solution with nitrogen in cylindrical glass tubes [7]. The copolymer was precipitated in a large excess of ethyl ether and a fine yellow powder was obtained after drying at 60 °C for 12 h. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>), δ (ppm): 12.25 (broad, COOH), 10.5–10.7 (s, 1H, -NHCO), 6.9–8.5 (m, 6H, indole ring), 4.5-4.6 (s, 1H, -CHCO), 3.40-3.65 (w, CH<sub>2</sub> and CH from itaconic acid and tryptophan residue), 2.58 (m, CH, acrylic acid), 2.09-2.18 (w, CH<sub>2</sub>, acrylic acid). The copolymer exhibited the fluorescence emission at 367.4 nm in water, when excited at 280 nm.

*Synthesis of copolymer with pendant methacrylate groups.* To a solution of copolymer in 1,4-dioxane was added a solution of N,N'-dicyclohexylcarbodiimide (DCC) and a solution of (*N-methacryloyloxyethylcarbamoyl-N'-2-hydroxyethyl*)urea in the same solvent. During addition the activating agent and functionalization reagent, the reaction flask was kept in a cold water bath. The reaction mixture was stirred for 24 h, at room temperature and for 2 h at 32 °C, in a dry nitrogen atmosphere. The dicyclohexylurea formed was filtered off. The solution was poured into a large amount of ethyl ether, and the polymer precipitated. The crude product was separated by decantation and dried in vacuum for 12 h. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>), δ (ppm): 1.37-1.39 (m, 5H, CH<sub>2</sub> and CH from itaconic acid and tryptophan backbone), 1.51-1.66 (broad, CH<sub>2</sub>, acrylic acid), 1.89 (s, 3H, CH<sub>3</sub>), 1.95-2.05 (broad, CH<sub>2</sub> from tryptophan and methacrylate), 2.57 (s, CH, acrylic acid), 2.95-3.10 (2H, CH<sub>2</sub> from itaconic acid side chain),

3.25-3.28 (m, CH<sub>2</sub>-N, methacrylate), 4.19-4.27 (br, CH<sub>2</sub>-O, methacrylate), 4.41 (s, 1H, CH-N, tryptophan pendant), 5.73 (s, =CH *cis*), 5.89 (s, NH, methacrylate), 6.09 (s, =CH *trans*), 6.9-8.7 (m, indole ring), 10.5-10.7 (s, NH). In Figure 1 is presented the <sup>1</sup>H NMR spectrum of the above copolymer modified with 10 mol% pendant methacrylate groups and its structure (PAlk-TrpM).



**Figure 1.** The <sup>1</sup>H NMR spectrum of the photopolymerizable ternary copolymer and its structure (PAlk-TrpM).

*Preparation of light-curable hybrid materials.* The resin-modified glass ionomer (RMGICs) specimens used for photopolymerization study, mechanical characterization, water sorption/solubility and contact angle surface morphology (SEM) were prepared using a two-component system in a powder/liquid ratio of **2.7/1**. The composition of the organic liquid matrix is given in Table 1, each sample containing polyacid dissolved in distilled water (**1:0.5** by weight), dental monomers and 1 wt.% Irgacure 819 as the initiator system, while the inorganic filler consists in **90** wt.% fluoroaluminosilicate glass Fuji II LC Improved and **10** wt.% hydroxyapatite.

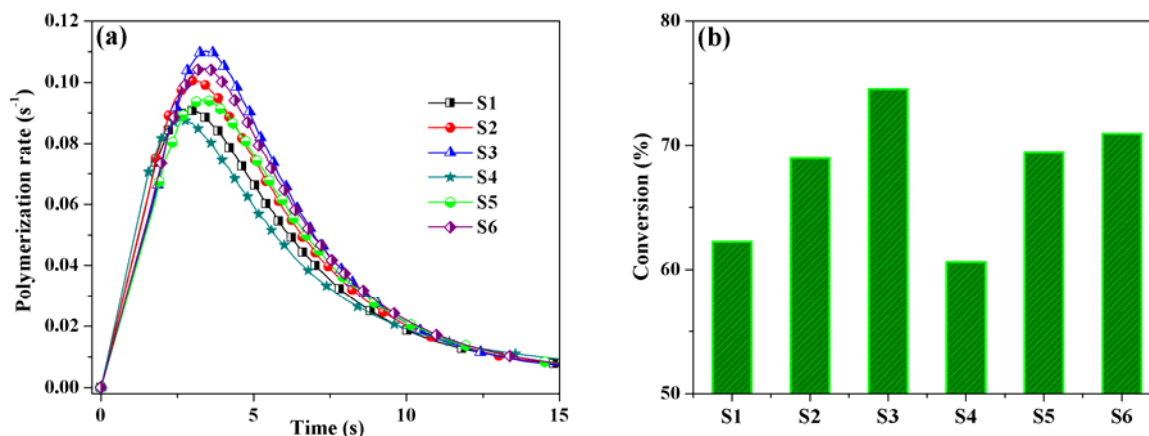
| Sample | PAlk-TrpM<br>(wt. %) | Bis-GMA<br>(wt. %) | Bis-GMA-<br>1 (wt. %) | TEGDMA<br>(wt. %) | HEMA<br>(wt. %) | Water<br>(wt. %) |
|--------|----------------------|--------------------|-----------------------|-------------------|-----------------|------------------|
| S1     | 50                   | 12.5               | -                     | 6.25              | 6.25            | 25               |
| S2     | 45                   | 16.3               | -                     | 8.1               | 8.1             | 22.5             |
| S3     | 40                   | 20                 | -                     | 10                | 10              | 20               |
| S4     | 50                   | -                  | 12.5                  | 6.25              | 6.25            | 25               |
| S5     | 45                   | -                  | 16.3                  | 8.1               | 8.1             | 22.5             |
| S6     | 40                   | -                  | 20                    | 10                | 10              | 20               |

**Table 1.** Composition (wt.%) of the experimental formulations (S1-S6). Each monomer mixture contains 1 wt.% Irgacure 819.

### 3. RESULTS AND DISCUSSION

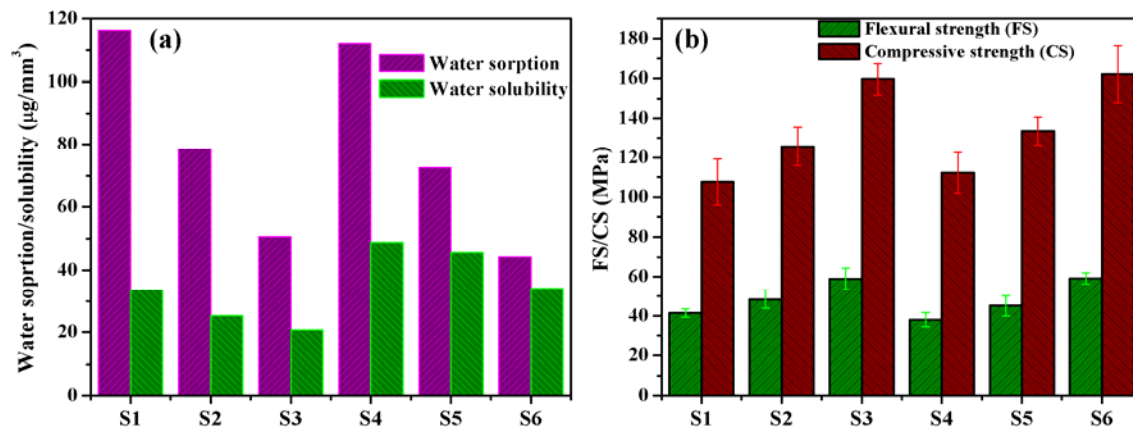
The photopolymerization rate of the six experimental formulations upon exposure to UV light was evaluated by photoDSC (Figure 2a) and the degree of conversion of the C=C double bond is graphical illustrated in Figure 2b. Now, regarding the evolution of such parameters it

is clear that these have values close to those encountered in the field of dental monomers. Unexpectedly, the replacement of Bis-GMA with Bis-GMA-1 that contains additionally 90% urethane methacrylate groups had no important consequences on the system photoreactivity.



**Figure 2.** PhotoDSC rate profiles for the S1-S6 formulations with 1 wt. % Irgacure 819 (a) and double bond conversion after 3 minutes of UV irradiation (b).

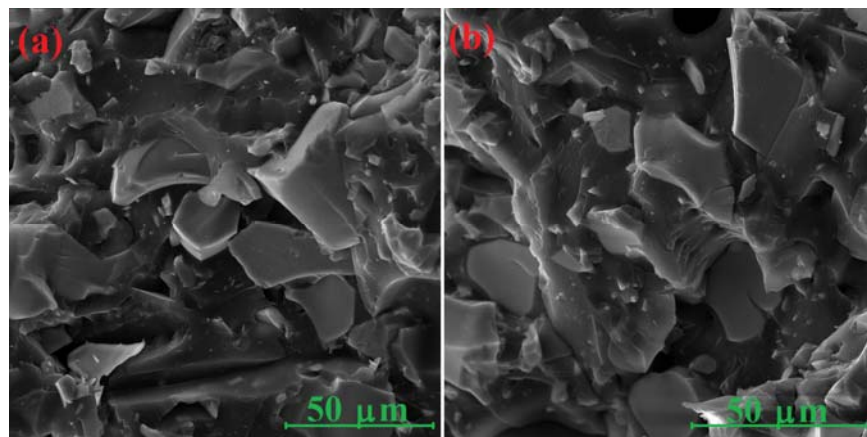
Water sorption and water solubility of the resin-modified glass ionomer cements (S1-S6) were determined after seven days of storage in water at 37 °C, and the experimental values plotted against time are given in Figure 3a. Depending on the composition of each formulation, water sorption ranged from 44.27 (S6) to 116.28  $\mu\text{g}/\text{mm}^3$  (S1), whereas water solubility varied between 20.79 (S3) and 48.93  $\mu\text{g}/\text{mm}^3$  (S4). As reported in the literature [8] such materials absorb more water than the resin composites for example, water sorption for Fuji II LC Improved was determined to be 152.37  $\mu\text{g}/\text{mm}^3$ . The flexural strength (FS) and compressive strength (CS) were measured with a testing machine using a 5 kN load cell (Figure 3b). It can be seen the FS lowest value was found for S4 (38.08 MPa) and for S6 (59.12 MPa) the highest value. Analysis of the CS values shows that the S1 specimen had a lower value (107.58 MPa) than the S6 (162.13 MPa).



**Figure 3.** Evaluation of water sorption and water solubility for the prepared RMGICs (a) and flexural strength (FS) / compressive strength for the filled materials (b).

Scanning electron micrographs for S1 (Figure 4a) and S4 (Figure 4b) specimens were recorded after fracture in the presence of hydroxyapatite microcrystals intimately mixed with

the fluoroaluminosilicate glass from Fuji II LC Improved linked together with the organic matrix due to a good compatibility between the both inorganic and organic components.



**Figure 4.** SEM micrographs of S1 (a) and S4 (b) resin-modified glass ionomers containing GC Fuji II LC Improved powder, in fracture.

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#### References

- [1] U. Lohbauer. Dental Glass Ionomer Cements as Permanent Filling Materials? — Properties, Limitations and Future Trends. *Materials*, 3:76-96, 2010.
- [2] A. Moshaverinia, N. Roohpour., J. A. Darr, I. U. Rehman. Synthesis of a proline-modified acrylic acid copolymer in supercritical CO<sub>2</sub> for glass-ionomer dental cement applications. *Acta Biomaterialia*, 5(5):1656–1662, 2009.
- [3] W. Wu, D. Xie, A. Puckett, J. W. Mays. Synthesis of amino acid-containing polyacids and their application in self-cured glass-ionomer cement. *Eur. Polym. J.*, 39:959-968, 2003.
- [4] R. Di Nicoló, L. K. Shintome, S. I. Myaki, M. P. Nagayassu. Bond strength of resin modified glass ionomer cement to primary dentin after cutting with different bur types and dentin conditioning. *J. Appl. Oral Sci.*, 15:459–464, 2007.
- [5] J. W. Nicholson, B. Czarnecka. The biocompatibility of resin-modified glass-ionomer cements for dentistry. *Dent. Mater.*, 24:1702–1708, 2008.
- [6] S. Gingter, E. Bezdushna and H. Ritter. Chiral Recognition of Poly(*N*-isopropylacrylamide-co-(D or L)-*N*-tryptophan-acrylamide) with Methylated  $\beta$ -Cyclodextrin. *Macromolecules*, 43(7):3128-3131, 2010.
- [7] A. Piletsky, E. V. Piletska, K. Karim, K. W. Freebairn, C. H. Legge, A. P. F. Turner. Polymer Cookery: Influence of Polymerization Conditions on the Performance of Molecularly Imprinted Polymers. *Macromolecules*, 35:7499-7504, 2002.
- [8] A. Yap. Resin-modified glass ionomer cements: a comparison of water sorption characteristics. *Biomaterials*, 17:1897-1900, 1996.