



*Dedicated to the memory of
Professor Ioan Silaghi-Dumitrescu (1950 – 2009)*

NOVEL POLYALKENOATES FUNCTIONALIZED WITH PHOTOPOLYMERIZABLE GROUPS. SYNTHESIS, CHARACTERIZATION AND TESTING IN DENTAL FORMULATIONS

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Modification of poly(acrylic acid-co-itaconic acid) and poly(acrylic acid-co-itaconic acid-co-N-vinylpyrrolidone) with photopolymerizable groups was performed in order to use the resulting copolymers into formulations of dental glass-ionomer type. The chemistry of these materials is based on an esterification reaction of the carboxylic functions from polyacid with 2-hydroxyethyl methacrylate or methacryloyloxyethylcarbamoylamino ethanol, prior prepared in our group. All synthesized structures were characterized by spectral methods, and for a number of restorative materials derived from resin-modified glass ionomer cements other characteristics as wetting properties, water sorption, water solubility and fracture behaviour were determined and investigated by specific measurements. By attaching polymerizable groups on suitable polyalkenoates as part of the liquid component into a dental formulation containing classical monomers (TEGDMA, HEMA) and powder component (quartz glass/hydroxyapatite: 70/30), an improvement of hardness and water sorption properties in the resulting materials was confirmed.

INTRODUCTION

As it is well known, the traditional glass ionomer cements (GICs) or polyalkenoate cements are water based materials, because the classical chemistry of them involves an reactive inorganic glass powder of different particle size/shape/nature containing at least one of di- and multivalent cations, a polyalkenoic acid (usually polyacrylic acid or copolymers of acrylic acid and other monomeric acids), water, and tartaric acid to modify the cement-forming reaction during setting and improve the handling, with major effect on their unique clinical properties.¹⁻³ Therefore, water plays an important role in the formation of the restorative materials by interacting with the polyacid to break the internal hydrogen bonding of the acidic carboxylic moieties, thus allowing a

rapid reaction with the glass, which acts as a base. These GICs have multiple advantages such as, excellent translucency and adhesion to enamel and dentine,^{4,5} biocompatibility,⁶ anticariogenic action,⁷ aesthetic form,⁸ reduced microleakage at the tooth-enamel interface,⁹ to name a few. In addition, working with such materials does not need a dry bonding medium, as in the case of resin composites.^{10,11} Unfortunately, however, other features of the GICs as brittleness, low tensile and flexural strengths together with clinical fracture resistance, are still major problems in this field.¹²

To provide an understanding of the characteristics and limitations of every one system, several strategies have been approached for creating new hybrid materials with improved properties, but most of them are related to modification of the liquid component of the GIC,

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without neglecting the effects resulted from changes in the inorganic glass phase, especially in the light of nanoparticles chemistry.^{13,14} As a first route, the increase of the powder/liquid ratio in GICs, and the use of suitable filler nanoparticles to reinforce the organic matrix was successfully tested in the obtaining of materials with enhanced strength and better fracture toughness.¹⁵ More recently, the concept of copolymers incorporating N-vinylpyrrolidone units (NVP) and amino acid derivatives as spacers between the carboxylic acid groups on the macromolecular chain was also demonstrated as being valid in dentistry.¹⁶⁻¹⁸ Consequently, the generation of a more flexible polymeric backbone had a significant impact on the ionic bond and poly-salt bridge formation within the final ionomer materials.

Another viable alternative taken in study consists of the modification of polyacids with methacrylate functions by means of appropriate monomers, like 2-hydroxyethyl methacrylate (HEMA), case in which the formulation of a new generation of GICs, often called resin-modified glass ionomers, would be favoured by the participation of such polymeric structures at the *in situ* free radical polymerization process.^{19,20} Evidently, all properties of the resulting hybrids are clearly different from those of commercially available GICs. Although a series of significant changes in the basic chemistry and the glass-ionomer liquid formulations properties occurred, the question is still open and all modern material characteristics should be considered, such as mechanical properties, biological effects, and long-term clinical behaviour.

Previously, our group initiated researches concerning the design and synthesis of new photopolymerizable urethane oligomers with and without carboxyl groups to be tested in potential dental formulations.²¹⁻²⁴ In order to continue our work focused on the development of new materials useful in dentistry, this study presents the first results regarding the preparation of two acrylic copolymers, poly (acrylic acid-co-itaconic acid) (*PolyAB*) and poly (acrylic acid-co-itaconic acid-co-N-vinylpyrrolidone) (*PolyAT*) under microwave assisted polymerization conditions, to be organically modified with an urea methacrylate, methacryloyloxyethylcarbamoylamino ethanol (UMA) or HEMA, and further incorporated into glass-ionomer dental restoratives. The selection of the polymerization method as an alternative heat source was motivated by the shorter reaction times, increased yields and purity of the resulting copolymers, comparatively with the thermal

heating using oil baths.²⁵ The purpose of this study being to gain more insight into how a number of photopolymerizable units can often influence the properties of dental formulations based on functionally modified polyalkenoates and other components frequently encountered in this type of application (HEMA, TEGDMA, photoinitiator), we have prepared a number of ionomer composite compositions using as filler a mixture of quartz glass/hydroxyapatite (70:30). Thus, the behaviour of new resin-glass ionomers in the presence of water (contact angle, water sorption, and water solubility) was investigated in tandem with preliminary aspects of crack propagation in some hybrid ionomer materials subjected to Vickers indentation by using polarizing optical microscopy (POM).

RESULTS AND DISCUSSION

Synthesis of new polyacids intended for dental applications, namely poly(acrylic acid-co-itaconic acid) and poly(acrylic acid-co-itaconic acid-co-N-vinylpyrrolidone) containing a small concentration of photopolymerizable groups (10-15%), assumed firstly, the preparation of an appropriate derivative, to be used as organic modifier of the acidic groups on the polymeric backbone. Thus, through a conventional addition reaction of ethanolamine to 2-isocyanatoethylmethacrylate, methacryloyloxyethylcarbamoylamino ethanol (UMA) was obtained (Figure 1), and its structure was confirmed by ¹H-NMR and FTIR spectroscopy.

In the ¹H-NMR spectrum of UMA can be observed signals attributed to the specific groups as follows: the urea NH protons (6.0 ppm), the *trans* and *cis* protons from methacrylate (6.1 and 5.58 ppm, respectively), the proton from the hydroxyl unit (4.65 ppm), the methylene protons attached to the ester group (4.18 ppm), as well as those linked to the hydroxyl group (3.61 ppm). Also, at 3.45 and 3.26 ppm can be remarked the peak of the methylene protons attached to the NH unit, and at 1.91 ppm appeared the protons from the methyl group connected to the methacrylate.

In the FTIR spectrum of UMA (not shown here), absorption bands attributed to the stretching vibration of the hydroxyl group (3367 cm⁻¹), CH₂ stretching (2879-2931 cm⁻¹), carbonyl stretching (1715 cm⁻¹), amide I (1633cm⁻¹), amide II (1542 cm⁻¹), and amide III (1454 cm⁻¹) together with the vibration band characteristic to methacrylate (817 cm⁻¹) were identified, all confirming the expected structure for the synthesized urethane derivative.

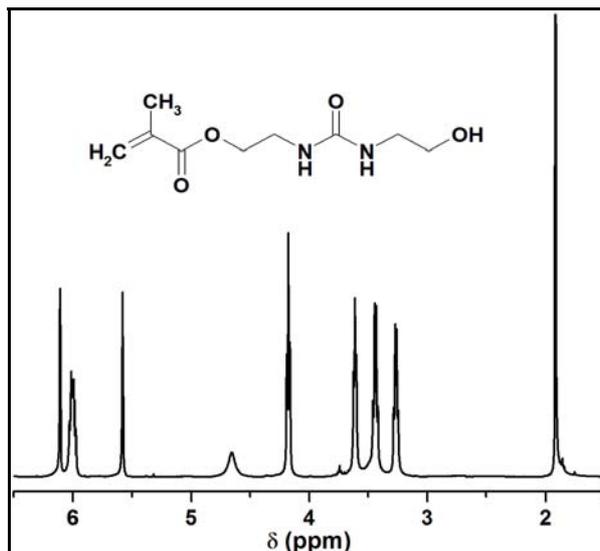


Fig. 1 – Chemical structure and the $^1\text{H-NMR}$ spectrum of methacryloyloxyethylcarbamoylamino ethanol (*UMA*) in CDCl_3 .

To obtain the above mentioned polyacids (*PolyAB* and *PolyAT*), radical copolymerization of the corresponding monomers was carried out under microwave irradiation in the presence of 1,1'-azobis (cyclohexane-1-carbonitrile) used as initiator. Under these experimental conditions, the molar ratios of the co-monomers in these copolymers were AA:AI = 7:3 for *PolyAB*, and respectively, AA:AI:NVP = 7:3:1 for *PolyAT*. The structures and composition of these copolymers were also determined by spectral and analytical methods.

The $^1\text{H-NMR}$ spectrum of *PolyAB* (Figure 2) indicated resonance peaks localized at higher field (1.5-2.4 ppm) which correspond to the aliphatic protons of the macromolecular backbone, whereas those of the methylene protons from itaconic acid are observable at 2.7 ppm.

Compared with *PolyAB*, the $^1\text{H-NMR}$ spectrum of *PolyAT* showed the same signals in the region 1.4-2.2 ppm characteristic for the aliphatic protons from AA and AI, where are overlapped the peaks attributed to methylene protons from NVP. Other resonance signals may be detected at 2.4 ppm (methyne protons from AI), 3.3 ppm (methylene protons linked to amidic carbonyl from NVP) and at 3.96 ppm (methylene and methyne protons attached to nitrogen atom from NVP) (Figure 2). It is obvious to note that in the synthesized copolymers the molar ratio between the monomeric units was found to be of 2.2:1 (*PolyAB*) and respectively, 8:3.5:1 (*PolyAT*), results that sustain the desired structure for polyacids.

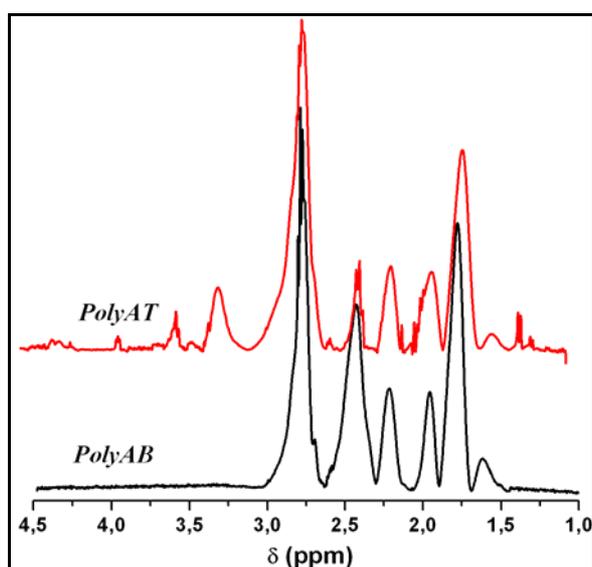


Fig. 2 – $^1\text{H-NMR}$ spectra of *polyAB* and *polyAT* in D_2O .

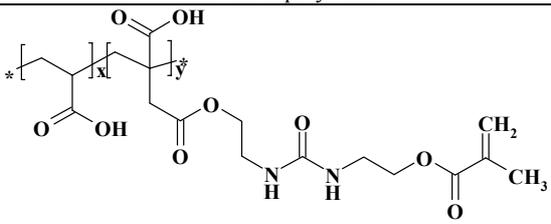
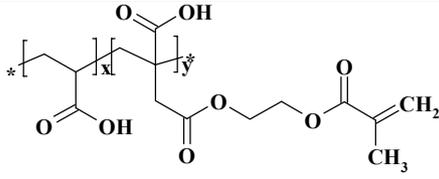
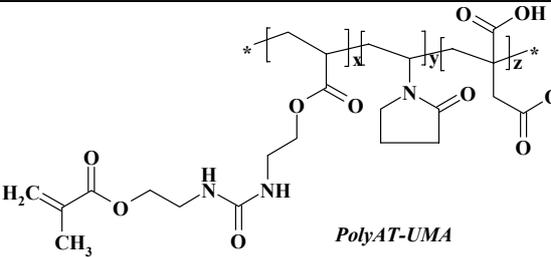
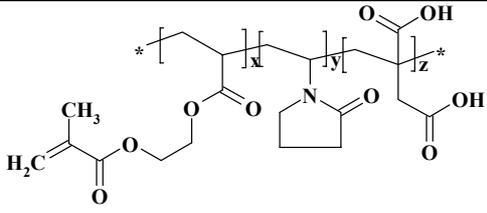
Analysing then the FTIR spectra of both copolymers, specific absorption bands that confirm the anticipated structures can be remarked as follows: for *PolyAB*, the characteristic band for hydroxyl group from carboxylic function ($3500\text{--}3200\text{ cm}^{-1}$), CH stretching vibration ($2969\text{--}2929\text{ cm}^{-1}$), the stretching vibration attributed to the carbonyl group (1708 cm^{-1}), and the deformation vibration of hydroxyl group (1457 cm^{-1}). In the case of *PolyAT*, the FTIR spectra present the same absorption bands like for *PolyAB*, the only difference consisting in a supplementary absorption band of carbonyl stretching appearing at 1633 cm^{-1} (amide I, from NVP).

In order to obtain light-curable functionally modified polyacids used in dental restoratives of glass-ionomer type, we consider that through moderate conversion of the carboxyl groups in

photopolymerizable ester acrylic functional groups will generate new materials with improved properties. Generally, such materials can be prepared by the addition of methacrylate components to the polyacids, which are initially settled by light-activated polymerization, accompanied by an acid–base reaction, induced through water sorption. Within this context, we have realized the modification of carboxyl groups from *PolyAB* and *PolyAT* using methacryloyloxyethylcarbamoyl amino ethanol (UMA) or 2-hydroxyethylmethacrylate (HEMA), via conventional esterification reaction. The idealized chemical structure of copolymers thus functionalized with photopolymerizable groups in the side chain, as well as their spectral characteristics are given in Table 1.

Table 1

The structures of the polyacids modified with methacrylic functions and the spectral data ($^1\text{H-NMR}$ and FTIR)

Modified copolymers	$^1\text{H-NMR}$ (δ , ppm)	FTIR (ν , cm^{-1})
 <p><i>PolyAB-UMA</i></p>	$-\text{COOH}$ (7.93); $\text{CH}_2=\text{CH}$ (cis-5.64, trans-6.04); COO-CH_2 (4.03); $\text{CH}_2\text{-NH-CO-NH-CH}_2$ (3.3, 3.4); $\text{CH}_2\text{-COO-}$ and CH-COOH (2.1-2.2); CH_3 (1.88); $\text{CH}_2\text{-CH}$ (1.2-1.8).	$-\text{OH}$, NH ($3500\text{--}3300$); CH (2934); CO (1722); amide I (1653); $\text{CH}_2=\text{C-}$ (820).
 <p><i>PolyAB-HEMA</i></p>	$-\text{COOH}$ (8); $\text{CH}_2=\text{CH}$ (cis-5.68, trans-6.06); COO-CH_2 (4.1-4.25); $\text{CH}_2\text{-COO-}$ and CH-COOH (2.23); CH_3 (1.88); $\text{CH}_2\text{-CH}$ (1.25-1.8).	$-\text{OH}$, NH ($3500\text{--}3300$); CH (2845 and 2926); CO (1734); amide I (1631); $\text{CH}_2=\text{C-}$ (817).
 <p><i>PolyAT-UMA</i></p>	$-\text{COOH}$ (7.95); $\text{CH}_2=\text{CH}$ (cis-5.68, trans-6.06); COO-CH_2 (4.05); N-CH and N-CH_2 (3.93); $\text{CH}_2\text{-NH-CO-NH-CH}_2$ (3.3); $\text{CH}_2\text{-COO-}$ and CH-COOH (2.1-2.3); CH_3 (1.88); $\text{CH}_2\text{-CH}$ (1.2-1.8).	$-\text{OH}$, NH ($3460\text{--}3300$); CH (2850 and 2933); CO (1722); amide I (1651); $\text{CH}_2=\text{C-}$ (814).
 <p><i>PolyAT-HEMA</i></p>	$-\text{COOH}$ (7.96); $\text{CH}_2=\text{CH}$ (cis-5.68, trans-6.06); COO-CH_2 (4.1-4.27); N-CH and N-CH_2 (3.93); $\text{CH}_2\text{-COO-}$ and CH-COOH (2.1-2.35); CH_3 (1.89); $\text{CH}_2\text{-CH}$ (1.25-1.8).	$-\text{OH}$, NH ($3460\text{--}3300$); CH (2934); CO (1731); amide I (1650); $\text{CH}_2=\text{C-}$ (813).

From the $^1\text{H-NMR}$ spectra of all modified polyacids the functionalization degree of these copolymers was estimated following the integral ratio between the unsaturated or methyl protons and the methylene/methyne protons from the backbone. As result, the modified copolymers (PolyAB-UMA, PolyAB-HEMA, PolyAT-UMA, PolyAT-HEMA) contain methacrylate side chains between 5 and 7 %.

To make possible the generation of new dental materials formulated with polyalkenoates modified with photopolymerizable methacrylate groups, we have explored some properties of experimental

formulations subjected to irradiation with visible light. Consequently, we have realized a set of 4 formulations based on 30 % modified polyalkenoates (dissolved in distilled water 1:1 wt./wt.), 10 % TEGDMA and 30 % HEMA, which were gently mixed by hand with 70% quartz glass and 30% hydroxyapatite, and with 0.5 (by weight) of CQ and 1.0 % (by weight) of DMPheAA as the classical photoinitiator system. Additionally, for comparison we have also prepared two formulations comprising only unmodified *PolyAB* and *PolyAT* mixed with quartz glass /hydroxyapatite (70/30) powder (Table 2).

Table 2

Contact angles and Vickers hardness of modified copolymer formulations (each contain 70 % wt. filler (quartz glass/hydroxyapatite: 70/30))

Sample	Formulation*	Angle value (°)	H _v
S1	30 % <i>PolyAB-UMA</i>	31.30	64.65
S2	30 % <i>PolyAB-HEMA</i>	27.20	80.3
S3	30 % <i>PolyAT-UMA</i>	28.65	73.96
S4	30 % <i>PolyAT-HEMA</i>	24.33	40.6
S5	30 % <i>PolyAB</i>	35.9	44
S6	30 % <i>PolyAT</i>	33.56	31.4

*each formulation contain 30 wt.% HEMA, 10 wt.% TEGDMA and is initiated with 0.5 wt.% CQ and 1 wt.% DMPheAA

The water contact angle determinations, which are indicative of the wetting properties of the resin-modified composites, are presented in Table 2. It can be observed that the surfaces of all composites are hydrophilic with a contact angle between 24.33 and 35.9°, values mainly attributed to the presence of a high concentration of carboxylic units on the polymer backbone. Also, we can remark that the formulations based on the ternary polyalkenoate are more hydrophilic than those comprising binary polyacid, behaviour owing to the presence of N-vinylpyrrolidone units in the latter. Therefore, the cyclic amide ring from NVP could be responsible for the strong hydrophilic domains, which probably caused the decreased water contact angle of this type of formulations.²⁶

Also, it is clear that water sorption in the case of dental restorations is one of the key element, because the 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. Hence, the hydrophilic constituents in polymer chains expose the composites to hydrolytic degradation, which results in material breakdown. For this reason, it is expected that the formulations of improved GICs dental restoratives enclosing

modified polyalkenoates, TEGDMA and HEMA to behave adequately. Water sorption is a diffusion-controlled process that occurs in the organic resin matrixes and mainly depends on hydrophobicity and crosslinking density of cured resins. From this perspective, the analysis of data given in Figure 3 allows us to state that, generally, the formulations incorporating the modified polyacids presents a lower water sorption percent (2.2-2.9 wt%) comparatively to the unmodified polyalkenoates of binary (4.1 wt%) or ternary type (2.9 wt%), finding which can be ascribed to a higher crosslinking degree of the organic matrix.

While literature data for other glass ionomer cement indicated a lower water sorption (1.0-2.5 wt. %),²⁰ in our case the use of the polymerizable polyacids in combination with the above monomers including HEMA, and a relatively high fraction of hydroxyapatite could be responsible for the observed effect. For minimizing these values, it is necessary to reduce the amount of HEMA as well as the concentration of carboxylic groups from copolymers. Moreover, the incorporation of hydroxyapatite characterized through a certain particle size distribution that could now react with the polyacid, may also explain the absence of important differences related to this parameter.

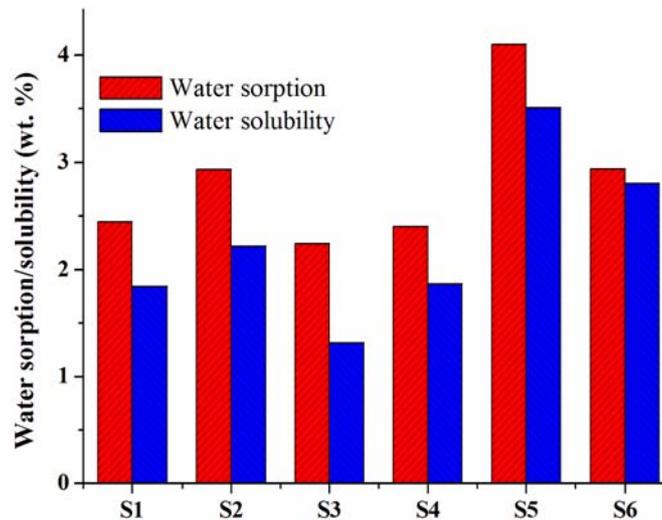


Fig. 3 – Water sorption and water solubility characteristics of the experimental formulations containing modified polyacids.

Since the leaching of small molecules in the presence of water is a usually occurring process taking place when dental materials are in contact with water and oral fluids, water solubility of our formulations has to be investigated. Indeed, in agreement with water sorption, the values for water solubility in the case of samples S1-S6 (1.3-3.5 wt. %) were found to be greater than that of ionomer glass (0.3-0.58 wt. %) formulated with copolymers of acrylic and citraconic acids, and fluoroaluminosilicate as filler.²⁷

The surface hardness determinations represent a convenient method to evaluate the mechanical properties of dental composites. It has been previously observed that the composition of the resin matrix, the nature of the interface between the organic monomers and inorganic phase, as well as the particle size distribution of the inorganic fillers have a major impact on the hardness of the

resulting materials.²⁸ As can be remarked from the data included in Table 2, the values for Vickers hardness are situated in the range of 40.6 to 80.3 (Table 2), mentioning that generally, these are higher for the modified composites comparatively with the non-modified ones. Subsequently, the probability of interconnectivity between the modified polyacids and the inorganic phase within the final materials would be significantly increased being higher than that reported for some conventional glass-ionomer restorative materials reinforced with short glass fibers.¹²

In order to quantify the surface damage caused by the Vickers indentation performed on some dental specimens incorporating our modified copolymers, a first optical examination of the surface was employed, namely, by polarizing optical microscopy (POM).

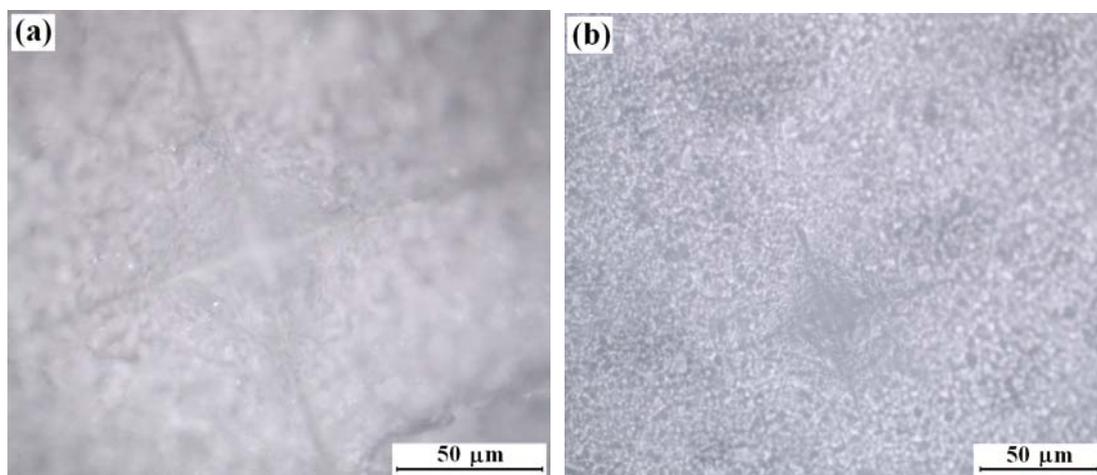


Fig. 4 – Optical microscopic image of the Vickers indentations in resin composite S1 (a) and S2 (b).

The optical microscopy images of the resin composites S1 and S2 depicted in Figure 4 (a, b) showed the characteristic Vickers indents on the composite surface, where four specific line are visible, but these are not capable to produce at microscopic level the radial and lateral cracks alongside the four main lines generated of indentation. Since such observation is crucial for explaining the first cracks developed in dental resin composite, additional investigations will be further taken into consideration in our laboratory.

EXPERIMENTAL

Materials. The commercial monomers used in this study are 2-hydroxyethyl methacrylate (HEMA) and triethyleneglycol dimethacrylate (TEGDMA) (Sigma-Aldrich Chemical Co.). Acrylic acid, itaconic acid, N-vinylpyrrolidone, 1,1'-azobis(cyclohexane-carbonitrile), 2-isocyanatoethyl methacrylate, ethanolamine, N,N'-dicyclohexylcarbodiimide were purchased from Sigma Aldrich Chemical Co. and used without further purification. The initiators used were camphorquinone (CQ) and 4-(dimethylamino)-phenylacetic acid (DMPheAA) (from Sigma-Aldrich Chemical Co.). The filler used was hydroxyapatite (Sigma-Aldrich Chemical Co.) and quartz granulation - 40 μ m (about 97%).

Synthesis of methacryloyloxyethylcarbamoylamino ethanolic acid (UMA). 2.9 mL (0.02 mol) 2-isocyanatoethyl methacrylate was treated with 1.18 mL (0.02 mol) ethanolamine, dissolved in THF, at room temperature for 24 hours. After the reaction is complete, the UMA is collected by rotary evaporation under vacuum.

Synthesis of poly (acrylic acid-co-itaconic acid) (PolyAB) and poly (acrylic-co-itaconic acid-co-N-vinyl pyrrolidone) (PolyAT). The microwave assisted polymerizations were performed in the same conditions for both copolymers, *PolyAB* and *PolyAT*, using a single mode microwave system Discover (CEM, Inc.). Therefore, for the *PolyAB* synthesis, 1.3 mL (1.37 g, 0.019 mol) acrylic acid, 0.62 g (0.047 mol) itaconic acid and 0.004 g (0.2 %) 1,1'-azobis(cyclohexane-carbonitrile) as initiator were firstly dissolved in 3.7 mL dioxane in a special vial. The tube was saturated with purified nitrogen, positioned in the CEM system and irradiated at 80 °C for 30 min. The resulted polymer was precipitated in diethyl ether and dried under reduced pressure at 60 °C for 48 h. Similarly, was obtained a ternary copolymer (*PolyAT*) starting from 0.95 mL (1 g, 0.13 mol) acrylic acid, 0.77 g (0.06 mol) itaconic acid, 0.21 mL (0.22 g, 0.02 mol) N-vinyl pyrrolidone and 0.004 g (0.2 %) 1,1'-azobis(cyclohexane-carbonitrile).

Synthesis of PolyAB-UMA, PolyAB-HEMA, PolyTB-UMA, PolyTB-HEMA. Since for the modification of polyalkenates the same method was employed, we present here only the synthesis of *PolyAB-UMA*.

2 g *PolyAB* dissolved in 25 mL dry dioxane were reacted with 0.2 g UM at room temperature for 24 hours. The resulting polymer was collected by precipitation in diethyl ether and removal of the residual solvent under vacuum.

Measurements. The structures of all synthesized derivatives were verified by ¹H-NMR and FTIR spectroscopy using a Bruker 400 MHz spectrometer and a Bruker Vertex

70 spectrophotometer, respectively. Water contact angle measurements were made on relatively homogeneous surface using goniometer KSV Cam 200. The average contact angle was calculated starting from at least ten separate measurements. Water sorption, water solubility and Vickers indentations determinations were performed as previously described.²³ The resulting indentations were evaluated with an optical microscope (Leica DM 2500 M).

CONCLUSIONS

In this study poly(acrylic acid-co-itaconic acid) and poly(acrylic acid-co-itaconic acid-co-N-vinylpyrrolidone) modified with 5-7% methacrylate groups were synthesized, characterized and incorporated into dental formulations to obtain materials of resin-glass ionomers type. It was concluded that, both modified acrylic copolymers added besides other photopolymerizable monomers (HEMA, TEGDMA) and 70% filler (quartz glass/hydroxyapatite: 70/30) led to restorative dental materials with enhanced properties.

REFERENCES

1. J.W. Nicholson, *Biomaterials*, **1998**, *19*, 485-494.
2. R.L. Bowen and W.A. Marjenhoff, *Adv. Dent. Res.*, **1992**, *6*, 44-49.
3. E. Larraz, S. Deb, C. Elvira and J. San Roman, *Dent. Mater.*, **2006**, *22*, 506-514.
4. A.D. Wilson and B.E. Kent, *J. Appl. Chem. Biotechnol.*, **1971**, *21*, 313-318.
5. M.J. Tyas and M.F. Burrow, *Aust. Dent. J.*, **2004**, *49*, 112-121.
6. Y.W. Gu, A.U.J. Yap, P. Cheang and K.A. Khor, *Biomaterials*, **2005**, *26*, 713-720.
7. K. Nakajo, S. Imazato, Y. Takahashi, W. Kiba, S. Ebisu and N. Takahashi, *Dent. Mater.*, **2009**, *25*, 703-708.
8. R. Bagheri, M.F. Burrow and M.J. Tyas, *J. Oral Rehabil.*, **2007**, *34*, 68-76.
9. E. Magni, L. Zhang, R. Hickel, M. Bossu, A. Polimeni and M. Ferrari, *J. Dent.*, **2008**, *36*, 885-891.
10. C.K.Y. Yiu, F.R. Tay, N.M. King, D.H. Pashley, S.K. Sidhu, J.C.L. Neo, M. Toledano and S.L. Wong, *J. Dent. Res.*, **2004**, *83*, 283-289.
11. F.R. Tay, S.K. Sidhu, T.F. Watson and D.H. Pashley, *J. Dent. Res.*, **2004**, *83*, 644-649.
12. I.M. Hammouda, *J. Mech. Behav. Biomed. Mater.*, **2009**, *2*, 73-81.
13. E. Coutinho, M.V. Cardoso, J. De Munck, A.A. Neves, K.L. Van Landuyt, A. Poitevin, M. Peumans, P. Lambrechts and B. Van Meerbeek, *Dent. Mater.*, **2009**, *25*, 1347-1357.
14. A. Moshaverinia, S. Ansari, M. Moshaverinia, N. Roohpour, J.A. Darr and I. Rehman, *Acta Biomaterialia*, **2008**, *4*, 432-440.
15. L.H. Prentice, M.J. Tyas and M.F. Burrow, *Dent. Mater.*, **2006**, *22*, 746-751.
16. B.M. Culbertson, *J. Dent.*, **2006**, *34*, 556-565.

17. W. Wu, D. Xie, A. Puckett and J.W. Mays, *Eur. Polym. J.*, **2003**, *39*, 959-968.
18. A. Moshaverinia, N. Roohpour, J.A. Darr and I.U. Rehman, *Acta Biomaterialia*, **2009**, *5*, 1656-1662.
19. J.W. Nicholson and B. Czarnecka, *Dent. Mater.*, **2008**, *24*, 1702-1708.
20. L. Rojo, B. Vazquez, J. San Roman and S. Deb, *Dent. Mater.*, **2008**, *24*, 1709-1716.
21. T. Buruiană, E.C. Buruiană, V. Melinte, A. Colceriu and M. Moldovan, *Polym. Eng. Sci.*, **2009**, *49*, 1127-1135.
22. E.C. Buruiană, T. Buruiană, V. Melinte, M. Zamfir, A. Colceriu and M. Moldovan, *J. Polym. Sci. Part A: Polym. Chem.*, **2007**, *45*, 1956-1967.
23. T. Buruiană, V. Melinte, L. Stroea and E.C. Buruiană, *Polym. J.*, **2009**, *41*, 978-987.
24. T. Buruiană, V. Melinte, F. Jitaru and E.C. Buruiană, *Rev. Roum. Chim.*, **2009**, *54*, 1001-1005.
25. C. Costa, A.F. Santos, M. Fortuny, P.H.H. Araújo and C. Sayer, *Mater. Sci. Eng. C*, **2009**, *29*, 415-419.
26. A. Moshaverinia, N. Roohpour, S. Ansari, M. Moshaverinia, S. Schricker, J.A. Darr and I.U. Rehman, *Dent. Mater.*, **2009**, *25*, 1240-1247.
27. M. Keyanpour, *Iran. Polym. J.*, **1998**, *7*, 271-275.
28. J. Manhart, K.H. Kunzelmann, H.Y. Chen and R. Hickel, *J. Biomed. Mater. Res.*, **2000**, *53*, 353-361.