

Dedicated to Professor Alexandru T. Balaban
on the occasion of his 85th anniversary

PREPARATION OF POLY(ACRYLIC ACID-*co*-ITACONIC ACID-*co*-N-ACRYLOYL-*L*-ALANINE) GRAFTED WITH METHACRYLATE GROUPS FOR USE IN DENTISTRY

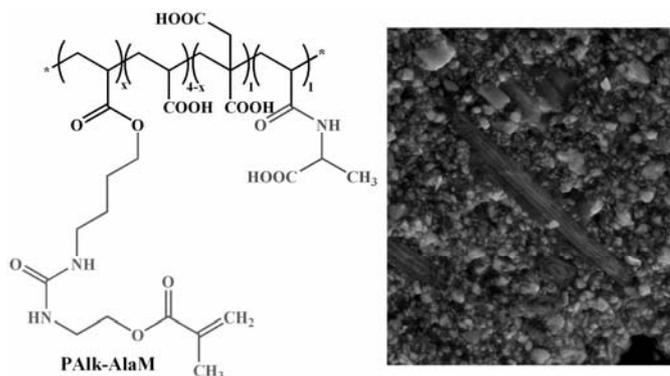
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In this study, a polyalkenoate (PAIk-AlaM) derived from acrylic acid, itaconic acid and N-acryloyl-*L*-alanine was functionalized by using (N-methacryloyloxyethylcarbamoyl-N'-4-hydroxybutyl) urea. The spectroscopic (proton/carbon nuclear magnetic resonance, Fourier transform infrared spectroscopy) characteristics confirmed the proposed structure as well as the functionalization degree of about 15 mol% methacrylate groups. This copolymer was further incorporated in resin-modified glass ionomer compositions besides commercial dental monomers (BisGMA, TEGDMA and HEMA) and studied compared to a similar polyalkenoate based on N-acryloyl-*L*-leucine (PAIk-LeuM). The photopolymerization data obtained by FTIR spectroscopy showed that the conversion degree (53-61.4 %) depends mainly on the amount of copolymer from each formulation. For the preparation of light-curable cements, the organic compositions were mixed with filler (90 wt.% fluoroaluminosilicate/10 wt.% hydroxyapatite) into a 2.7:1 powder/liquid ratio. The light cured specimens were investigated in terms of water sorption/solubility, mechanical parameters and surface morphology, noting that all these features had a more pronounced variation as a function of the amount of modified polyalkenoate added into the formulation and lesser to the type of the amino acid present in the macromolecular chain.



INTRODUCTION

Glass-ionomer cements (GICs) or polyalkenoate cements are nowadays widely used in restorative dentistry owing to their attractive

properties such as good adhesion to moist tooth structure, chemical bonding, thermal compatibility with enamel/dentin, low thermal expansion coefficients, less setting contraction, low shrinkage at the tooth-enamel interface, and anticariogenic

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activity.¹ Typically, this group of versatile materials contains aqueous polymeric acids, namely poly(acrylic acid), poly(acrylic acid-*co*-itaconic acid) or poly(acrylic acid-*co*-maleic acid) and silicate glass powder, and the hardening process is the result of an acid-base reaction between both partners in the presence of water.² Driven by the practical applications and, especially, the lack of strength (brittleness, inferior mechanical characteristics), many efforts have been carried out in order to improve the GICs' strengths through free radical copolymerization of the acid monomers and N-vinyl pyrrolidone³ or (meth)acryloyl-functionalized amino acid monomers, such as L-glutamic acid, β -alanine, glycine, or proline,^{4,5} along with the optimization of the molecular weight of the polyacid and the powder-to-liquid ratio (P/L).

Another approach has been focused on the hybrid materials resulted from the conventional glass-ionomers and composite resins, which involved the incorporation of a small quantity of resin component, frequently 2-hydroxyethyl methacrylate (HEMA), bisphenol A diglycidyl ether methacrylate (BisGMA) and/or urethane dimethacrylate, and diluents (triethylene glycol dimethacrylate, TEGDMA).^{6,7} More impressive than this option, the preparation of polyacids with methacrylate side chains grafted onto the polymer chain to generate visible light-curable polymers and, subsequently, resin-modified glass ionomers (RMGICs) proved to be of great interest in the development of hybrid cements via an acid-base reaction and partly, photochemical polymerization.^{8,9} In fact, a better understanding of the setting chemistry of these materials and their adherence to dental tissues is essential for optimal clinical use.¹⁰

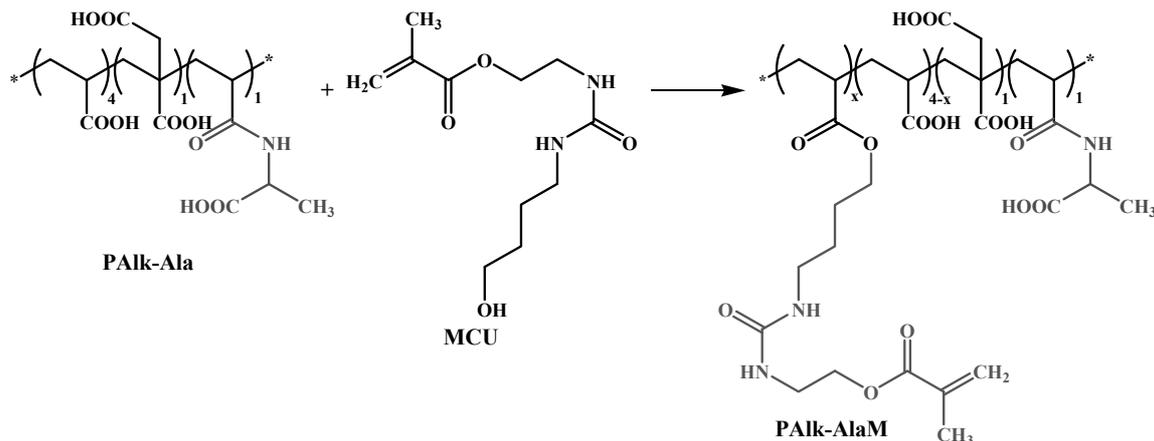
In the course of our continuing studies related to the dental monomers^{11,12} and copolymers,^{13,14} we became interested in the synthesis and exploration of ternary copolymers with photopolymerizable functions capable to form photocrosslinked hybrid polymer networks. With the intention to extend our experience with such structures, we decided to employ N-acryloyl alanine monomer in the obtaining of water soluble ternary copolymers like poly(acrylic acid-*co*-itaconic acid-*co*-N-acryloylalanine) to be further modified with photopolymerizable moieties introduced by means of N-methacryloyloxyethylcarbamoyl-N'-4-hydroxybutyl urea (MCU). The effects of the amino acid and methacrylate units from polyacid on some specific properties of the experimental dental compositions were discussed in comparison

with the materials containing the acid copolymer with leucine residues in its structure.

RESULTS AND DISCUSSION

To prepare L-alanine-containing polyalkenoates chemically modified with methacrylic photopolymerizable units, the synthesis of N-acryloyl-L-alanine (AAla) was firstly performed, according to a previously published protocol.¹⁵ After confirming its proposed structure by the FTIR and ¹H (¹³C) NMR spectra (data given in the experimental part), AAla monomer was polymerized by a free-radical polymerization process with acrylic acid (AA) and itaconic acid (IA) into a feed molar ratio of 4:1:1 (AA:IA:AAla) leading to a novel polyalkenoic acid, poly(acrylic acid-*co*-itaconic acid-*co*-N-acryloyl-L-alanine - **PAIk-Ala**), whose idealized structure is given in Scheme 1. Subsequently, this ternary copolymer was covalently functionalized with photopolymerizable units by means of N-methacryloyloxyethylcarbamoyl-N'-4-hydroxybutyl urea (MCU),¹³ by a conventional esterification reaction, which allowed the obtaining of **PAIk-AlaM** copolymer (Scheme 1).

¹H NMR spectroscopy was used to elucidate the copolymers structure. Fig. 1 shows the ¹H NMR spectra of PAlk-Ala and its corresponding modified form. The signals of the methyl protons (1.42 ppm), methylene/methine protons (1.5 – 2.5 ppm), methylene protons (2.7 ppm), methine protons close to carboxylic groups from alanine (4.32 ppm) and carboxylic protons (12.33 ppm) were assigned to PAlk-Ala. From the integral ratio of the methine (4.32 ppm) and methylene protons (2.7 ppm), the copolymer composition was estimated to be 4:1:1 (AA:IA:AAla), in excellent agreement with the experimental ratio used in synthesis. In the case of PAlk-AlaM other peaks appeared at 1.39 ppm (CH₂-CH₂ from butyl), 1.95 ppm (CH₃ from methacrylate), 3.1 ppm (CH₂ close to urea unit), 3.4 ppm (CH₂ from ester), 5.69 and 6.06 ppm (unsaturated protons) and at 5.98 ppm (urea protons). The methacrylate grafting degree of the PAlk-AlaM copolymer was estimated following the integral ratio between the unsaturated (5.69 and 6.06 ppm) or methyl protons (1.42 ppm) and the methylene (2.7 ppm) protons from the principal backbone. According to the NMR analysis about 15 mol.% of the carboxylic moieties from the PAlk-Ala were functionalized with methacrylic moieties.



Scheme 1 – The synthesis route for the grafting of PAlk-Ala copolymer with photopolymerizable moieties.

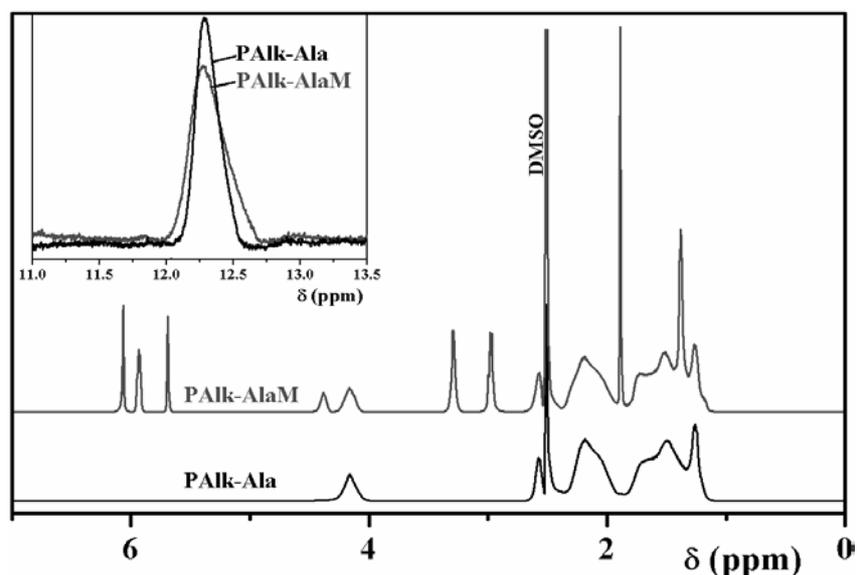


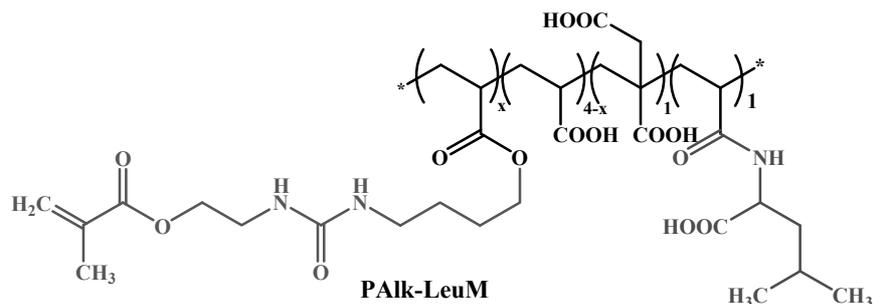
Fig. 1 – ^1H NMR spectra for PAlk-Ala and PAlk-AlaM copolymers recorded in DMSO-d_6 and the signal for the carboxylic protons (inset).

Both copolymers were soluble in water and organic solvents, such as ethanol, *N,N*-dimethylformamide, dimethyl sulfoxide, and 1,4-dioxane. It is important to note that the chemical modification of PAlk-Ala does not alter the solubility of PAlk-AlaM in water, allowing solution-phase processing required at the attaining of polymer/reactive glass/hydroxyapatite compositions taken in mixture with dental monomers.

In order to achieve a comparative study involving the PAlk-AlaM, which contains a more hydrophilic amino acid, its analogue (PAlk-LeuM) based on acrylic acid, itaconic acid and *N*-acryloyl-*L*-leucine synthesized by our group¹³ was selected for our investigations (structure illustrated in Scheme 2).

The photopolymerization behaviour of some reactive monomer mixtures incorporating methacryloyl-modified polyalkenoates (dissolved in ethanol) and dental commercial monomers, such as

BisGMA, TEGDMA and HEMA (compositions given in Table 1) was evaluated. The appreciation of the conversion degree by FTIR spectroscopy has been taken into consideration the fact that, upon the exposure to visible light irradiation, the stretching vibration characteristic to double bonds at about 1637 cm^{-1} and the bending vibration in the 815 cm^{-1} region are progressively diminished. Thus, the graphical representation displayed in Fig. 2, illustrates the gradual decay of the double bond absorption band in case of the F2 experimental mixture with irradiation time, so that after 180 seconds of visible light irradiation, the intensity of the absorption band is reduced to almost 60%. This value indicates satisfactory photocuring because, frequently, the conversion degree in dental systems based on commercial monomers without polyacids does not exceed 70%.¹⁶



Scheme 2 – Structure of the PAlk-LeuM copolymer.

Table 1

Composition (wt.%) of the experimental formulations (each mixture contains 1 wt.% Irgacure 819).

Formulation	PAlk-AlaM	PAlk-LeuM	Water	BisGMA	TEGDMA	HEMA
F1	50		25	12.5	6.25	6.25
F2	46.66		23.33	15	7.5	7.5
F3	40		20	20	10	10
F4		50	25	12.5	6.25	6.25
F5		46.66	23.33	15	7.5	7.5
F6		40	20	20	10	10

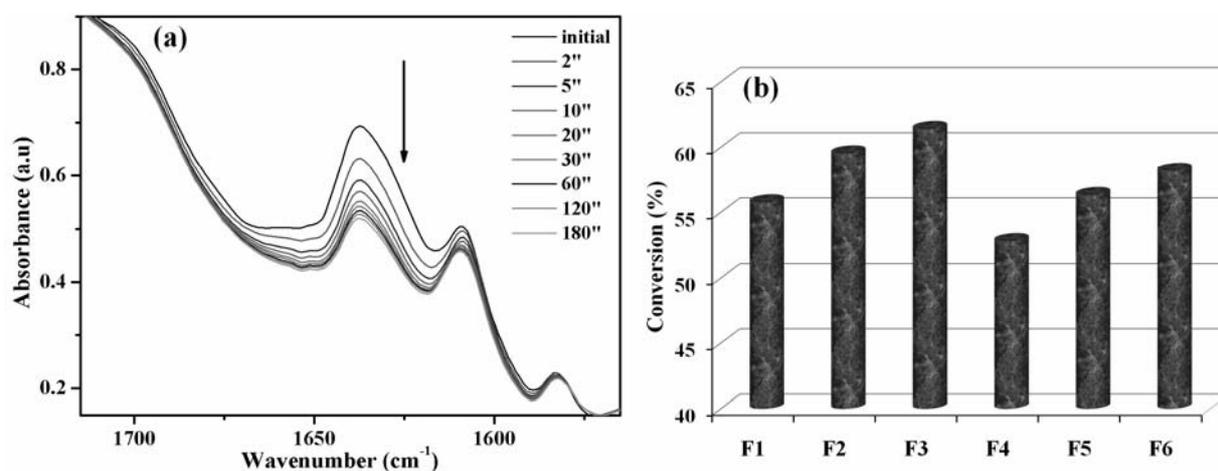


Fig. 2 – Evolution of the double bond absorption band from F2 formulation (a) and the double bond conversion for the photopolymerized samples (b) under irradiation with visible light.

The degree of conversion measured for all experimental formulations after 180 seconds of irradiation with visible light (Fig. 2, b) shows that this parameter varied between 53 % (F4) and 61.4 % (F3). It should be noted that the polyalkenoates comprising amino acid residues with different hydrophilicity have no major effect on the conversion degree, although the system viscosity

decreased and by increasing the amount of PAlk-AlaM incorporated in the sample. Such photoresponse can be assigned to the fact that the photopolymerization process in such materials takes place in parallel to some acid–base reactions triggered by the hydrophilic nature of polyacids, which often induce opacity to the samples.

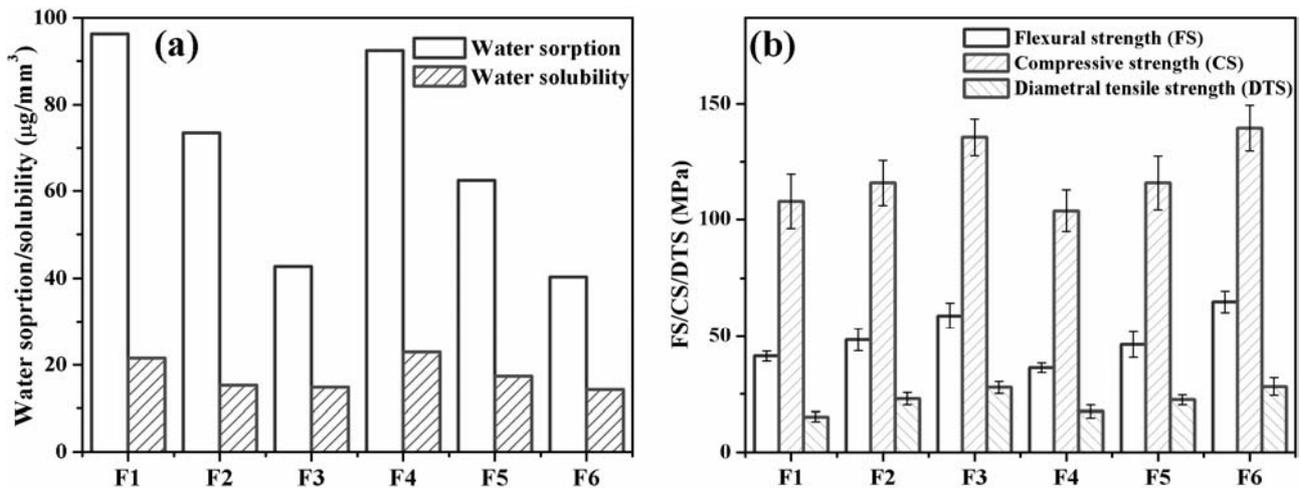


Fig. 3 – Evaluation of the water sorption/solubility (a) and mechanical parameters (b) for the materials filled with 90 wt.% fluoroaluminosilicate/10 wt.% hydroxyapatite.

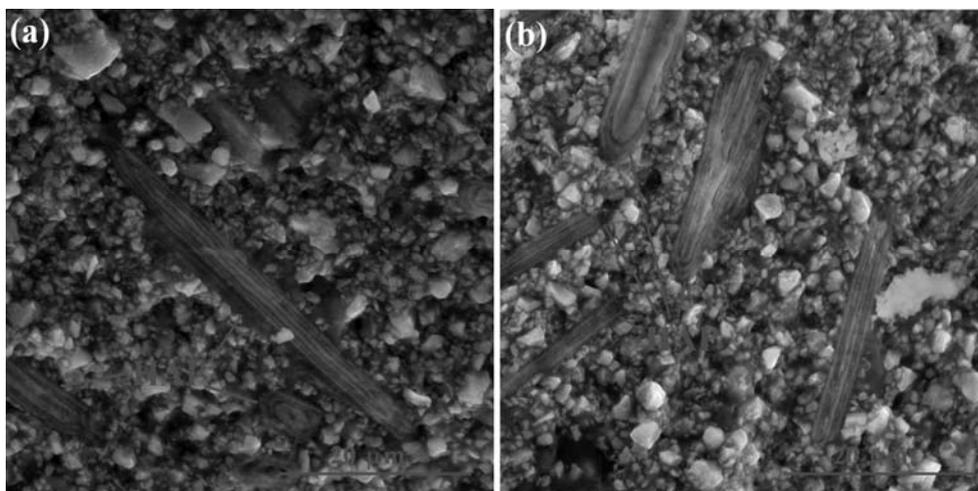


Fig. 4 – SEM images for the F2 (a) and F5 (b) filled formulations in fracture.

As mentioned before, for creating light-curable resin-modified glass ionomer hybrid materials the decisive components for this kind of products such as the photopolymerizable partners (modified copolymers and dental comonomers), water and reactive glass powder were integrated in dental compositions. To well realize these hybrid compositions, the powder/organic phase ratio was kept at 2.7:1, which is recommended in the majority of the studies reported on these materials. Therefore, six formulations obtained by mixing the aqueous solution of PAlk-AlaM (F1-F3) or PAlk-LeuM (F4-F6) with BisGMA, TEGDMA, HEMA and filler (90 wt.% fluoroaluminosilicate/10 wt.% hydroxyapatite) were subjected to photopolymerization followed by salt-bridge formation in water as a result of additional curing for 1 day.

Useful information concerning the ability of the final RMGICs to be employed as dental materials

is provided through the quantification of their performance into a wet environment, for which reason the water sorption and water solubility values were determined after seven days of storage in water at 37 °C (Fig. 3, a).

Given the hydrophilic nature of the polyalkenoates and the presence of HEMA monomer in formulations, the water sorption for the experimental samples ranged from 40.36 $\mu\text{g}/\text{mm}^3$ (F6) to 96.28 $\mu\text{g}/\text{mm}^3$ (F1). However, water was absorbed in higher amounts in the specimens containing PAlk-Ala derivative (F1-F3), and evidently in the F1 sample incorporating the larger percent of PAlk-Ala (50 wt. %). Likewise, it can be remarked that an increase of the polyalkenoate content with 10 wt. % induces almost a doubling of the absorbed water, fact that illustrates the importance of the polyacids into the later achievement of RMGIC materials. In the literature, it

has been demonstrated that the RMGICs absorb more water than the resin composites,¹⁷ for instance the water sorption for Fuji II LC Improved was found to be $152.37 \mu\text{g}/\text{mm}^3$.¹⁸

On the other hand, the assessment of water solubility indicates that the leaching of small molecules is more evident in the materials containing 50 wt. % polyacids (F1: $21.54 \mu\text{g}/\text{mm}^3$; F4: $23.03 \mu\text{g}/\text{mm}^3$), while the lowest water solubility was found for F6 sample ($14.28 \mu\text{g}/\text{mm}^3$). Water sorption and water solubility are two simultaneous processes that took place when dental materials are in contact with water or other oral fluids and strongly depend on the hydrophilicity and the crosslinking degree of the cured resin. In our case, besides the increased hydrophilicity induced by the selected organic matrix, the crosslinking density expressed mainly through the photopolymerization conversion degree seems to influence to a larger extent the behaviour of the RMGICs in water.

Over time, various RMGIC formulations were proposed in order to improve the mechanical characteristics as well as to diminish the accentuated moisture sensitivity of some conventional glass ionomer materials. Still, their low mechanical strength combined with a poor wear-resistance as compared to other dental materials has restricted their use into the oral cavity. Since the most appropriate way to assess the strength of glass ionomer composites refers to flexural strength that offers simultaneous information about three types of stresses (tensile at one surface, compression at the other surface and shear strengths),¹⁹ this feature was preferred for the identification of the better ionomer composition achieved from the methacrylate modified amino acid polyalkenoates. The flexural strength values, graphically represented in Fig. 3, b, show that the lowest FS value was attained for F4 composition (36.4 MPa), while the higher value was reached for F6 sample (64.8 MPa) with an increased crosslinking density of the sample triggered by the increasing amount of photopolymerizable components. Such mechanical parameter for the composites incorporating larger amounts of polyalkenoates can be presumably ascribed to the formation of a small number of ionic/covalent crosslinking on the (photo)curing phase caused by the appearance of some interferences between the two processes reported in the literature.²⁰ However, it is obvious that the modification of the copolymer structure through the variation of the amino acid nature has not significantly influenced

the FS values, since for the same amount of polyalkenoate, the FS variation is minor.

The same trend was found in the case of compressive (CS) or diametral tensile (DTS) strength (Fig. 3, b). It is obvious that the inclusion of increased amounts of photopolymerizable monomers favoured the improvement of mechanical parameters (higher CS and DTS values for F6 RMCIC), while the modification of polyalkenoates into the experimental resin ionomers produced negligible differences.

The homogeneous distribution of the inorganic fillers (fluoroaluminosilicate and hydroxyapatite) into the photocrosslinked polymer networks was established by registering the scanning electron microscopy (SEM) images for the experimental RMGICs in fracture (Fig. 4, a, b).

The acquired micrographs proved a good compatibility between the organic phase and the inorganic fillers and are typical for this kind of hard materials. Moreover, SEM micrographs display the existence of HAP rod-like structures with a maximum length of $20 \mu\text{m}$ and about $5 \mu\text{m}$ in thickness embedded into the organic matrix, while the smaller bright spots are furnished by the fluoroaluminosilicate glass from Fuji II LC Improved, which are smaller in size.

EXPERIMENTAL

Materials. Itaconic acid (IA), 4-amino-1-butanol, N,N' -dicyclohexylcarbodiimide (DCC), isocyanatoethyl methacrylate, L-alanine, acryloyl chloride, 1,1'-azobis(cyclohexanecarbonitrile) (ABCN), HEMA, BisGMA, TEGDMA, Irgacure 819 and hydroxyapatite were purchased from Sigma Aldrich Chemical Co. (Taufkirchen, Germany) and used without further purification. Acrylic acid (AA) was also purchased from Sigma Aldrich Chemical Co. (Taufkirchen, Germany) and was purified by vacuum distillation before use. The GC Fuji II LC Improved powder was purchased from GC Corporation, Tokyo, Japan.

Synthesis of AAla. The synthesis procedure of AAla derivative was previously reported.¹⁵ Acryloyl chloride (4.5 mL, 0.055 mol) and sodium hydroxide solution (2.0 g, 0.05 mol) were simultaneously dropwise added to a well stirred solution of L-alanine (0.05 mol, 4.45 g) and sodium hydroxide (2.0 g, 0.05 mol) at 0°C . Further, the solution was stirred at room temperature for 24 h and then neutralized with HCl solution to an acidic pH. The resulting white solid was filtered off and dried at room temperature. Yield: 5.7 g, (80%). FTIR (KBr, cm^{-1}): 3309 (N-H), 2992-2882 (C-H), 1732 (C=O), 1653 (amide I), 1619 and 815 (C=C), 1550 (amide II), 1223 (C-O). ^1H NMR ($\text{DMSO}-d_6$, δ , ppm): 12.63 (carboxyl), 8.45 (1H, NH), 6.31 (1H, CH-CO), 6.10 (1H, =CH trans), 5.60 (1H, =CH cis), 4.28 (1H, CH-N), 1.30 (3H, CH_3). ^{13}C NMR (D_2O , δ , ppm): 179.4 (COO), 171.10 (CO), 132.21 (=CH₂), 131.09 (=CH), 51.64 (C-N), 19.01 (-CH₃).

Synthesis of PAlk-Ala copolymer. AA (5.76 g), IA (2.6 g) and AAla (2.86 g) were copolymerized into a molar ratio of 4:1:1, in dioxane solution. The radical polymerization, initiated by ABCN, was performed at 80 °C for 72 h after degassing and purging the monomer solution with nitrogen. The formed terpolymer (PAlk-AAla) was precipitated in diethyl ether, a fine powder being obtained after drying in vacuum for 12 h. Yield: 87 % (9.8 g).

Synthesis of PAlk-AlaM. Firstly, 8 g of PAlk-Ala copolymer was dissolved in dioxane and cooled in an ice bath under stirring. Then, 2.86 g (13 mmol) DCC and 3.39 g (13.9 mmol) MCU (prepared according to a previously published procedure¹³) were added, keeping the temperature around 0 °C for about 2 hours. Further, the reaction mixture was heated to room temperature and stirred for 24 h under a dry nitrogen atmosphere. The resulting dicyclohexylurea was filtered off and the polymer was precipitated into a large amount of diethyl ether. The crude product was separated by decantation and dried in vacuum for 12 h. Yield: 59% (6.7 g). FTIR (cm⁻¹): 3381 (N-H), 2973 (C-H), 1722 (C=O), 1639 (NH-CO, amidă I), 1637 (C=C), 1570 (NH-CO, amidă II), 1184 (C-OH), 815 (C=C).

Measurements. Fourier transform infrared (FTIR) spectra were recorded using a Bruker Vertex 70 FT-IR spectrometer, and ¹H (¹³C) NMR spectra were recorded using a Bruker AC 400 instrument. The FTIR photopolymerization experiments were performed on the organic formulations (detailed in Table 1; the polyacid was dissolved in ethanol) subjected to blue light using a dental-curing unit (LA 500, Model Blue-light, Apoza Enterprise Co, Taiwan), and recording the FT-IR absorption spectra after different irradiation times. The conversion degree was determined from the differences appeared in the C=C stretching vibration at 1637 cm⁻¹ after various curing periods. For all samples, the average DC values of three specimens under each curing time were reported.

The resin-modified glass ionomer specimens for contact angle, water sorption/solubility, and mechanical determinations were prepared by using a two component system (liquid and powder) having a powder/liquid ratio (P/L, by weight) 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, while the inorganic filler consists in 90 wt. % fluoroaluminosilicate glass Fuji II LC Improved and 10 wt. % hydroxyapatite.

Flexural (FS), compressive (CS), and diametral tensile strengths (DTS) were measured using a Shimadzu AGS-J testing machine, with a 5 kN load cell. Cylindrical specimens were prepared in glass tubing with dimensions of 4 mm diameter x 8 mm length for compressive strength (CS) and of 4 mm diameter x 2 mm length for diametral tensile strength (DTS) investigation. A Teflon mould was used to fabricate the specimens for flexural strength (3 mm in width x 3 mm in thickness x 25 mm in length). Specimens were blue-light irradiated for 30 s on each side, removed from the mould after 15 min in 100% humidity, and conditioned in distilled water at 37 °C for 24 h prior to testing. A crosshead speed of 1 mm/min was applied in these tests. The compressive strength was calculated from the equation $CS = P/\pi r^2$, where P is the load at fracture and r the radius of the sample cylinder. DTS was estimated from the relationship $DTS = 2P/\pi dt$, where d is the diameter and t the thickness, respectively, of the cylinder. The flexural strength in three-point bending was obtained

using the expression $FS = 3Pl/2bd^2$, where l is the distance between the two supports, b the width and d the thickness of the specimen.

For water sorption/solubility measurements, six disk specimens of reduced dimensions (6 ± 0.1 mm diameter, 2 ± 0.1 mm thickness) for each group of mixtures were prepared. The specimens were hardened by exposing to blue light for 30 s on each side and then allowed to set for 15 minutes in 100 % humidity at 37 °C before removing from the moulds. The samples were pre-conditioned over a desiccant containing calcium sulfate at 37 °C until their weight remains constant (initial weight m_1). The specimens were placed in distilled water at 37 °C for 7 days and then removed from the water, lightly blotted with a paper to eliminate the surface-adherent water, and weighed (m_2). Further, the specimens were dried into an oven at 50 °C until their weight was constant again (m_3). The water sorption for each sample was determined using the equation (1):

$$\text{Water sorption } (\mu\text{g mm}^{-3}) = \frac{m_2 - m_1}{V} \quad (1)$$

$$\text{Water solubility } (\mu\text{g mm}^{-3}) = \frac{m_1 - m_3}{V} \quad (2)$$

The water solubility was calculated employing equation (2): where m_1 is the initial weight of the specimen, m_2 is the weight after keeping in water, m_3 is the weight of the sample dried at 50 °C and V is the specimen volume.

The microstructure of the cured samples in fracture was examined by using an environmental scanning electron microscope QUANTA200 (FEI Company, Hillsboro, USA). The composites were examined in low vacuum mode operating at 20 kV using an LFD detector.

CONCLUSIONS

In summary, this study describes the achieving of a random copolymer based on acrylic acid, itaconic acid and N-acryloyl-L-alanine which was subsequently partially functionalized with methacrylate moieties. A methacrylate grafted polyalkenoate containing N-acryloyl-L-leucine derivative was employed for comparison, and photoreactive experimental mixtures of resin-modified glass ionomer type were formulated together with commercial monomers BisGMA, TEGDMA and HEMA. Further, the photobehaviour of the unfilled composites was evaluated through FTIR spectroscopy. Light-curable cements were prepared from aqueous solutions of dental ionomer compositions together with dental monomers and filler (90 wt.% fluoroaluminosilicate/10 wt.% hydroxyapatite) using a powder/liquid ratio of 2.7:1. The mechanical properties and water sorption/solubility depend on the amount of copolymers, the best values being determined for the materials with the lowest amount of modified polyalkenoates. Also, the variation in the amino acid nature (L-alanine,

L-leucine) did not have major influence on the investigated parameters.

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