Hydrophobic Composite Resins Using a Novel Allylic Urethane Monomer as Additive

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Abstract. The purpose of this study is to report the formulation of photopolymerizable composites resins with hydrophobic behavior using a new urethane monomer (ETODC) as additive. The ETODC monomer was used together with Bis-GMA and TEGDMA to formulate a new organic matrix system. Mechanical and hydrophobic behavior were studied, also volumetric shrinkage, polymerization kinetics and cytotoxicity were analyzed. Results were compared with a control resin prepared with Bis-GMA and TEGDMA. The results show that mechanical properties and volumetric shrinkage did not present statistical differences between the studied groups. When compared with the control material, the experimental resin formulated with the ETODC monomer showed higher hydrophobic behavior and higher values of degree of conversion and polymerization rate.
Keywords: Allylic monomer; dental additive; dental composite; resins; photopolymerization.

Resumen. El objetivo de este estudio es reportar la formulación de una resina compuesta fotopolimerizable que presenta comportamiento hidrofóbico, usando un nuevo monómero uretano (ETODC) como aditivo. El monómero ETODC fue usado junto con los monómeros Bis-GMA y TEGDMA para formular un nuevo sistema de matriz orgánica. Los parámetros evaluados en esta investigación fueron, el comportamiento mecánico e hidrofóbico, la contracción volumétrica, cinética de polimerización, así como, la citotoxicidad. Los resultados fueron comparados contra una resina control preparada con Bis-GMA y TEGDMA. Los resultados muestran que las propiedades mecánicas y la contracción volumétrica, no presentan diferencias significativas entre los grupos evaluados. Comparado con el grupo control, la resina experimental, formulada con el monómero ETODC mostró un comportamiento hidrofóbico mayor, mayores valores de grado de conversión y mayor velocidad de polimerización.
Palabras clave: Monómero alílico; aditivo dental; composito dental; resinas; fotopolimerización.

Introduction

Resin composites are increasingly used to restore carious teeth because of their esthetic quality and mechanical performance [1]. These materials were introduced in dentistry more than sixty years ago and, despite that great progress has been made in those years, the current materials used still need to be improved [2]. Resin composites are composed of a polymeric matrix, reinforcing fillers, a coupling agent for binding the filler to the matrix, and chemical compounds (initiators, co-initiators and additives) that promote the polymerization reaction. For the polymeric matrix, typically a mixture of dimethacrylate monomers, like Bisphenol A glycidyl methacrylate (Bis-GMA), triethyleneglycol dimethacrylate (TEGDMA) and urethane dimethacrylate (UDMA) are the most used monomers for this application [3-6].

Bis-GMA biggest problem is its relatively high viscosity that led to low mobility and consequently, a low degree of conversion and low mechanical properties. High viscosity also hinders the incorporation of inorganic filler increasing polymerization shrinkage and affecting other physico-chemical properties [7, 8]. To prevent this, Bis-GMA is commonly diluted with other monomers as TEGDMA or UDMA or a combination of both. This practice eases the incorporation of the inorganic filler and improves mechanical behavior. However, the incorporation of diluent monomers increases volumetric shrinkage during polymerization, property which is considered as the main problem in these restoration materials [7, 9]. In addition, introducing TEGDMA has been found to increase water sorption, accelerating the hydrolytic degradation processes within the material [10].

Advances in the chemistry of dental monomers focused first on the modification of the chemical structure of Bis-GMA, obtaining monomers with improved properties [9, 11]. Also, the use of spiro-orthocarbonate monomers [12], siloranes [13] and ormocers [14, 15] has been incorporated into dental composite formulations to produce composites with less polymerization shrinkage. Also, our workgroup has been working among the last years in the synthesis an evaluation of allylic monomers for dental composites application [16-21], obtaining promising results.

In addition, the use of some additives has been explored to increase the degree of conversion [22], polymerization rate [23], and microhardness [24] of Bis-GMA/TEGDMA based composites. Despite these promising results, the use of additives to improve the properties of these materials does not seem to be widely studied in the scientific literature. Accordingly, the aim of this work is to synthesize of a new urethane monomer with allylic terminal groups and to evaluate its incorporation as an additive (15 wt%) in the formulation of an experimental composite resin. The degree of conversion (DC), polymerization rate (Rp_{max}), polymerization shrinkage (PS), water sorption or hydrophobicity (WS), water solubility (SL), and mechanical properties of this new formulation were investigated, and the results compared with those of a composite formulated with BisGMA/TEGDMA used as a control.
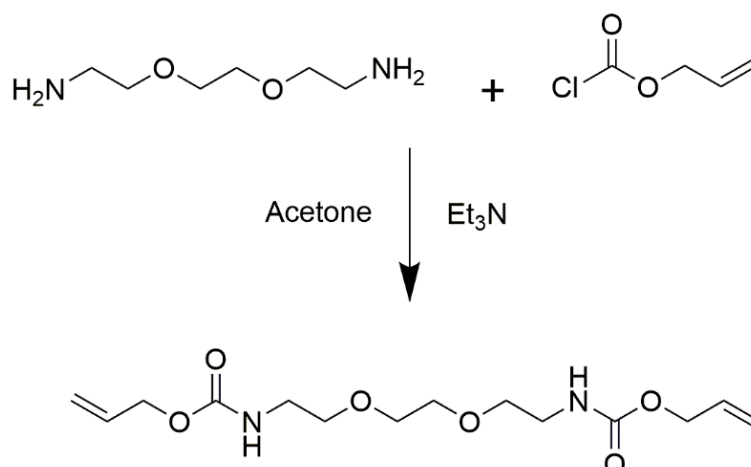
Experimental

Materials and methods

1,2-Bis(2-aminoethoxy)ethane, allylchloroformate, and triethylamine were obtained from Aldrich (USA) and were used without further purification. The solvents used in this work were previously distilled and dried. The infrared (IR) spectra were obtained with a Frontier Perkin Elmer (USA) Infrared spectrophotometer using the attenuated total reflectance (ATR) method. The nuclear magnetic resonance (NMR) spectra were obtained using a 400 MHz Bruker (Germany) nuclear magnetic resonance spectrometer. Chloroform ($CDCl_3$) was used as solvent and tetramethylsilane (TMS) was used as internal reference. The photopolymerizations were made with an Ultra Radii (SDI, Australia) photopolymerization unit equipped with a blue LED visible light (~480 nm) source with an intensity of 1000 mW/cm^2. The dimensions of the specimens were measured using a digital caliper (Mod. CD-6C Mitutoyo Corp., Japan). The three-point bending test was made using a universal mechanical test machine EMIC DL 500 (EMIC, Brazil).

Synthesis of diallyl((ethane-1,2-diylbis(oxy))bis(ethane-2,1-diyl))dicarbamate monomer (ETODC)

25 mL of distilled acetone and 2.5 mL (16.8 mmol) of 1,2-bis(2-aminoethoxy)ethane were placed in a two-necked flask equipped with a stirrer. Subsequently, 5.2 mL of Et$_3$N (37 mmol) and 4 mL (37 mmol) of the allyl chloroformate were added dropwise. The reaction was stirred at 5 °C for 4 h. Then, the solvent was evaporated, and the reaction crude was dissolved in dichloromethane and three washes with distilled water were performed. After the washes, the organic phase was dried over anhydrous sodium sulfate. After evaporation of the solvent, a clear liquid (ETODC) was obtained.

Yield 99%. FTIR/ATR (cm^{-1}) 3337 (δN-H), 2867 (vC-H), 1705 (vC=O), 1658 (vC=C), 1517 (vC=C Ar), 1246 (v-C-O). NMR ^{1}H (400 MHz, CDCl$_3$) δ(ppm). 5.93 (m, 2H, H3), 5.38 (s, 2H, H5), 5.35 (d, *J*=17.17 MHz, 2H, H1), 5.21 (d, *J*=10.5 MHz, 2H, H2), 4.57 (d, *J*=5.67 MHz, 4H, H4), 3.62 (s, 4H, H8), 3.57 (t, *J*=5.13 MHz, 4H, H7), 3.39 (q, *J*=5.34 MHz, 4H, H6). NMR ^{13}C (100 MHz, CDCl$_3$) δ(ppm). 155.9 (C=O), 132.1 (CH$_2$<u>C</u>H=CH$_2$), 70.24 (-CH$_2$-O), 70.13 (-CH$_2$-O), 118.2 (CH$_2$CH=<u>C</u>H$_2$), 65.9 (<u>C</u>H$_2$CH=CH$_2$), 40.53 (CH$_2$-NH).

Scheme 1. Synthesis of monomer ETODC.

Preparation of composite materials

Two photopolymerizable experimental composite resins were formulated. The resin matrix consisted of 50 wt% of BisGMA, 35 wt% of TEGDMA and 15 wt% of ETODC. As control, BisGMA/TEGDMA in a mass ratio of 50 wt% each one, was used. For both materials, the binary photoinitiation system Camphorquinone/4-dimethylaminobenzoate (CQ/EDAB), 1 and 2 wt% respectively was used. Finally, 65 wt% of glass particles (silanized barium borosilicate) were incorporated using a highspeed mixer SpeedMixer™ DAC 150.1 FV (FlackTek Inc, UK). All the materials were kept in the dark until they were used.

Three points bending test

The flexural strength and the elastic modulus of the experimental composite materials were evaluated based on the point 7.11 of the International Standard ISO-4049 and on the specification no. 27 ANSI/ADA [25, 26].

Bar-shaped specimens (10 x 2 x 2 mm) were prepared by filling the uncured material into stainless-steel molds. The specimens were irradiated on both sides for 20 seconds, giving a total time of 40 seconds. Then, dimensions of the specimens were measured to an accuracy of 0.01 mm using a digital calibrator. The specimens were kept in distilled water at 37° C for 24 hours. The specimens were placed in a universal machine of mechanical tests (EMIC DL 500) on two cylindrical supports of 2 mm in diameter, parallel to each other and at a distance between their centers of 8 mm (N=9). The mechanical test was performed using a load cell of 1 kN, with a head speed of 1 mm per minute. For the data capture, the program used was TESC 1.0.

The flexural strength was calculated using the following formula:

$$\sigma = \frac{3Fl}{2bh^2} \qquad\qquad 1$$

where,

σ = Flexural strength [MPa]; F = Force at the moment of fracture [N]; l = distance between the supports [mm]; b = width of the specimen [mm]; h = height of the specimen [mm].

The flexural modulus was calculated using the following formula:

$$E = \frac{F_1 l^3}{4bh^3 d} \qquad\qquad 2$$

where:

E= Flexural modulus [MPa]; F_1= Force recorded where the deformation stops being directly proportional to the force registered in the graph [N]; b = width of the specimen [mm]; h = height of the specimen [mm]; d= Flexure of the specimen [mm].

Photopolymerization kinetics

The polymerization kinetics from the experimental materials was evaluated with a Fourier Transform Infrared (FTIR) spectrophotometer using an attenuated total reflection (ATR) unit (Frontier, Perkin Elmer). A small sample (~100 mg) of composite resin was placed on the diamond cell window of the ATR unit. Then, a Mylar® strip and a glass slide were placed to reduce the inhibition of the polymerization caused by the oxygen in the air. A spectrum was captured before and after the polymerization process. The degree of conversion was obtained following a method described previously [24] considering the height of the absorption band (% of absorbance) corresponding to the νC=C aliphatic bond at 1638 cm^{-1} and, as internal standard, the height of the absorption band (% of absorbance) corresponding to the νC=C aromatic bond at 1609 cm^{-1}. The absorption band attributed to aromatic νC=C vibration was used as an internal reference because its intensity remained unchanged during the polymerization reaction, and hence, the absorbance was the same before and after the polymerization reaction. The degree of double bond conversion (DC) vs. polymerization reaction time data was plotted and Hill's 1 three-parameter nonlinear regression was performed for curve fitting. The rate of polymerization R_p was calculated considering these data/fitted plots.

Measurement of polymerization shrinkage

Volumetric shrinkage due to polymerization was determined by measuring the density of the materials before and after polymerization using the Archimedes' principle [27]. The measurements were made using an analytical balance (OHAUS) coupled with a density determination kit. To obtain measurements, the following procedure took place in a humidity-free room with controlled temperature. Unpolymerized resin spheres were weighted in air and in a solvent as quickly as possible to avoid the solvent to flow through the sample. Specimens were polymerized and weighted immediately in air and after in water.

The following formula was used to determine the density of the spheres,

$$\rho = \frac{m_{air} \times \rho_{solvent}}{m_{air} - m_{solvent}} \qquad\qquad 4$$

where:

ρ = is the density of the material; $m_{solvent}$ = is the mass of the sample in water in grams; m_{air} = is the mass of the sample in air in grams; $\rho_{solvent}$ = is the density of hexane at the temperature the measurement was taken.

Based on the results, the following equation was applied to determine the volumetric contraction:

$$S = \left(\frac{\rho_{pol} - \rho_{unpol}}{\rho_{pol}} \right) \times 100 \qquad\qquad 5$$

where:

S = is the percentage of volume change (contraction); ρ_{pol} = is the density of the polymerized samples; ρ_{unpol} = is the density of the unpolymerized samples.

Water sorption and solubility

Water sorption and solubility of the composite materials were evaluated in accordance to that which is established in section 7.12 of the ISO No. 4049 International Standard[26]. Samples were polymerized in a silicon mold with a 5 mm diameter and 1 mm thickness. Once polymerized, the specimens were placed in a vertical support inside a desiccator to eliminate humidity. They were weighted daily until their mass remained constant (±0.01), this mass was registered as m_1. After obtaining m_1, the thickness and diameter of the specimens were measured to obtain the volume of each one (V). After, all the specimens were immersed in distilled water at 37 °C for a week and weighted to obtain m_2. After this time, the specimens were introduced again in a desiccator to eliminate water, and they were weighted daily until their mass remained constant. This mass was registered as m_3.

The water sorption (W_{sp}) and solubility (W_{sl}) were calculated using the following equation:

$$W_{sp} = \frac{m_2 - m_3}{V} \qquad\qquad 6$$

$$W_{sl} = \frac{m_1 - m_3}{V} \qquad\qquad 7$$

where:

m_1 = mass of the sample before immersion (µg); m_2 = mass of the sample after immersion in water for seven days (µg); m_3 = mass of the reconditioned sample (µg); V = volume of the sample (mm^3).

Cytotoxicity assay

Cell viability ratio was evaluated by the WST-1 colorimetric assay. Disc-shaped specimens (5x1 mm) were prepared and placed in 24-well plates with DMEM and stored at 37 °C for 24 h. Volume of DMEM for each plate was calculated following the specifications provided by the ISO 10993:12 standard. After this incubation period, the conditioned medium supposed to contain the eluent released by the experimental and control materials. Mouse fibroblast cells (L929) were cultured at a density of 2x104 cells in 96-well plates containing DMEM (Dulbecco's Modified Eagle's medium) media supplemented with 10% L-glutamine, 10% fetal bovine serum (FBS), penicillin (100 U/mL) and streptomycin (100 U/mL). Cells were incubated at 37ºC under 95% air and 5% CO_2 for 24h.

After incubation, the culture medium was replaced with 200 µL of the conditioned medium from each specimen. The plate was then incubated (37 °C, 5% CO_2) for a period of 24h. After this period, the medium was aspirated, and the WST-1 solution was applied. The results were read in a spectrophotometer with a wavelength of 450nm, where absorbance values were considered as an indicator of cell viability. WST-1 is a water-soluble Tetrazolium salt that is reduced outside the cells and its product, a water-soluble formazan salt, is an indicator of cell viability which can be red after an incubation time of 2h.

Results and discussion

Monomer synthesis and characterization

The chemical structure of the new monomer ETODC was confirmed by FTIR, ^{1}H and ^{13}C NMR spectroscopy. The synthetic route of the monomer ETODC is depicted in Scheme 1, and the data relevant to their structure is summarized in the experimental section.

The FTIR spectra of the monomer ETODC is according to its expected structure. The appearance of the band assigned to the carbonyl group is the most important evidence confirming the monomer obtention. Further corroboration was acquired from ^{1}H NMR spectra, in which the integration, multiplicity, and assignments are according to the monomer structure. The main evidence of the obtaining of the ETODC monomer are the signals which correspond to the different kind of protons for the allylic groups Fig. 1. These signals can be observed in the range between 4.5 and 6 ppm. The presence of the signals at high frequencies corresponding to methylene protons ends up confirming the obtaining of the monomer.
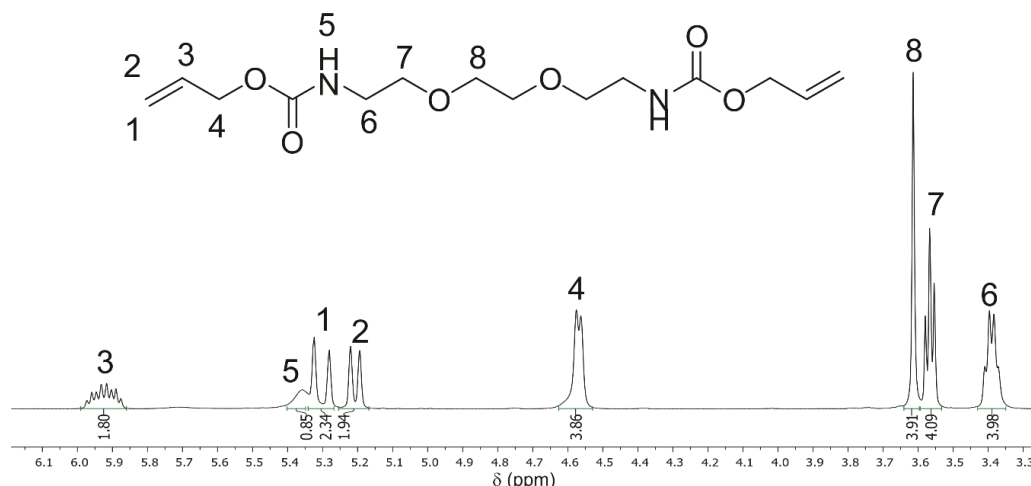

Fig. 1. ^{1}H NMR spectra of monomer ETODC.

Flexural Strength and Elastic Modulus

Fig. 2 shows the arithmetic means values for the flexural strength and elastic modulus of the evaluated composites. According to the statistical analysis, there are no differences between the evaluated groups in both properties ($p > 0.05$). Although the ETODC monomer has two terminal allylic groups, and these monomers are known to have a process of self-inhibition of the polymerization reaction, the flexural strength of the experimental material was comparable to that of the control resin [18, 19]. According to ISO 4049:2009 standard, the materials formulated in this study are classified as Type 1, Class 2, Group 1 materials, which corresponds to polymer-based restorative materials suitable for restorations involving occlusal surfaces whose setting is achieved by the application of an external source which is applied intra-orally. Such standard also specifies that, for this type of materials, the minimal flexural strength shall be equal or greater than 80 MPa, value that was achieved for both experimental and control materials.
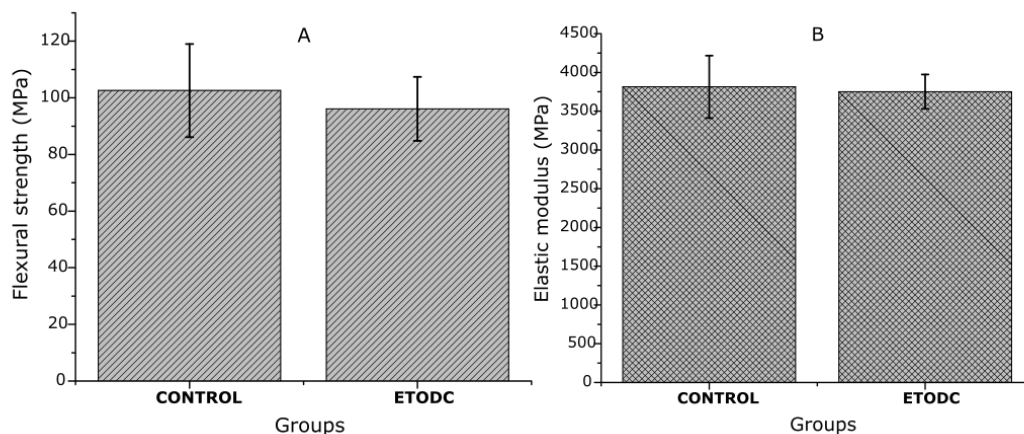
Fig. 2. Flexural strength (A) and elastic modulus (B) of composites resins evaluated.

Polymerization kinetics

The degree of conversion (DC) of the experimental resin formulated with the ETODC monomer as additive showed higher values than those of the control resin (Table 3). This behavior could be explained because of two factors, first, the presence of the allylic group in the structure monomer and second, the presence of the NH of the carbamate group. Previous works have reported DC values close to 100% using allylic monomers when formulating dental composite resins, and it might be explained because of the flexibility of the functional group that enhances the diffusion of free radicals getting higher values of DC [16, 18, 19]. Moreover, NH groups in monomer ETODC can increase the mobility of radical sites on the polymer structure by a chain transfer reaction [1, 28].

Fig. 3 shows the graphics of polymerization rate. The R_p(max) value is slightly higher for the resin formulated with ETODC monomer. This behavior could be also explained because of the presence of NH groups. Autoacceleration of polymerization is higher in the experimental resin must probably because of the labile bond of N-H groups, which, favor the chain transfer reactions [1, 28]. The higher R_p(max) obtained with the experimental group also suggests rapid gelation of the polymer, which could restrict the diffusion of growing chains in the dental composite [29].

As the degree of conversion is positively related to most of the properties of the photopolymerizable materials, is extremely important to keep their polymerization as efficient as possible. Following this, the use of ETODC monomer could guarantee higher stability for Bis-GMA/TEGDMA based composites.
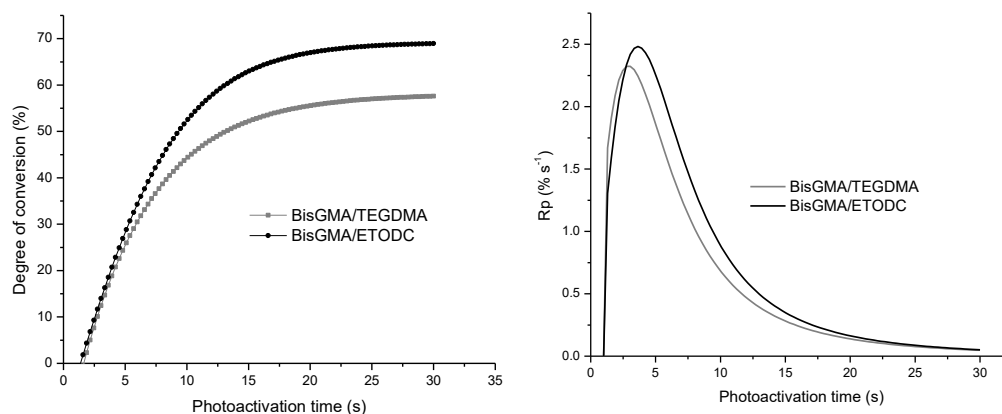

Fig. 3. Photopolymerization kinetics from the experimental materials.

Water Sorption and Solubility

The mean values for water sorption and solubility of the evaluated resins are shown in Table 1. According to results, the experimental resin is hydrophobic because of it exhibits lower values of water sorption (p=0.035), the values obtained are below the maximum limit allowed by the ISO 4049:2009 standard (< 40 $\mu g/mm^3$ for water sorption and < 7.5 $\mu g/mm^3$ for solubility). The incorporation of new ETODC monomer increases the polymer crosslinking in the organic matrix. Therefore, the organic matrix is able to decrease the interaction with water molecules by dipole interactions or by hydrogen bonds. It has been previously demonstrated that higher values of double bond conversion led to lower water sorption values[30]. The sorption phenomenon and solubility in resins may trigger a variety of chemical and physical processes, which may create complications and degeneration in the structure and function of the polymeric material. For example, these processes may include volumetric changes such as swelling, physical changes such as softening and plasticization, and chemical changes such as oxidation and hydrolysis. Thus, it is important to obtain monomers useful in the fabrication of composite resins with low sorption and solubility levels.

Table 1. Physical-chemical properties evaluated in this work.

Group	Water Sorption ($\mu g/mm^3$)	Solubility ($\mu g/mm^3$)	Degree of conversion (%)	Volumetric Shrinkage (%)
BisGMA/TEGDMA	38.69(4.12)[a]	6.2 (0.65)[a]	70.88 (0.68)[a]	4.48 (0.27)[a]
BisGMA/TEGDMA/ ETODC	25.14(3.0)[b]	4.66 (0.77)[b]	84.09 (1.81)[b]	4.22 (0.55)[a]

Same superscript [ab] letters in each column indicates that there are no statistically significant differences

Polymerization Shrinkage

The mean value of polymerization shrinkage obtained for the experimental composite containing ETODC monomer was lower than the values obtained for the material used as the control, however, the difference was not statistically significant. The slight differences between the materials could be explained by two facts, first, the monomer ETODC has a higher molecular weight than TEGDMA, and second, the presence of carbamate functional group must probably confer stiffness to the chemical structure. Some authors have reported greater shrinkage due to polymerization when using monomer with lowest molecular weight [31].

Although there are no differences in the volumetric shrinkage means of the groups evaluated, it is worth mentioning that the lower shrinkage values obtained when the additive monomer ETODC was used it could make the material less prone to the generation of internal tensions which may cause the production of microfractures or microbubbles, which ones could make weaker the polymer formed [3, 32].

Cytotoxicity Assay

Fig. 4 shows the viability of L929 cells that were cultured with the extraction medium from different resin systems prepared with BisGMA/TEGDMA/ETDOC and BisGMA/TEGDMA. According to the statistical analysis, there were no statistical differences among the groups evaluated (p>0.05). Experimental system formulated with the monomer ETODC showed cell viability close to 100%, which according to ISO 10993, is considered non cytotoxic. In this study, Filtek® Z350XT (3MESPE) was used as reference material since this material meets the requirements stablished by ISO 10993 standards.
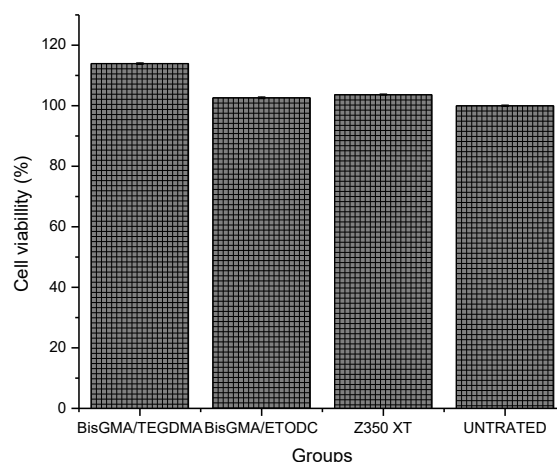
Fig. 4. Cell viability/proliferation of fibroblast L929 cells.

Conclusion

A new allylic urethane monomer (ETODC) was synthesized and used as an additive in the formulation of an experimental composite resin. According with the results, the experimental composite resin showed mechanical behavior similar to a control resin formulated without the additive. Besides, the experimental material showed a better hydrolytic behavior, higher double bond conversion, higher polymerization rate (Rp) and less polymerization shrinkage. Cytotoxicity assay shows that the experimental resin is nontoxic against fibroblast cells. Considering this, the use of the ETODC monomer as an additive, results a promising approach for the formulation of composite resins with enhanced behavior.

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