

Synthesis and characterization of methyl methacrylate - glycerol hydrogels by polymerization in acid medium

Síntesis y caracterización de hidrogeles de glicerol-metacrilato obtenido por polimerización en medio ácido

Síntese e caraterização de hidrogéis de glicerol-metacrilato obtidos por polimerização em meio ácido

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Summary. - Hydrogels were prepared from methyl methacrylate, glycerol, and sulfuric or citric acid. A novel route for the synthesis of crosslinked materials using unconventional initiators was evaluated using a 23 factorial experimental design. Effects of independent variables (polymerization time, type, and acid concentration) were statistically analyzed through ANOVA. The synthesis route includes condensation, free-radical and transesterification reactions with modifications of the polymer chemical properties such as the formation of a crosslinking polyester with polymethylmethacrylate (PMMA) and improvement of the mechanical and thermal properties of the hydrogel. A polymerization time of 4-hour produced the highest amount of material when 1.37 g sulfuric acid was used and 3.46 g when citric acid was added. The polymer synthesized with citric acid has a swelling rate up to 214.6%, compared with the materials produced with sulfuric acid that reach up to 31.3% of water absorption.

Keywords: Poly (methyl methacrylate); Glycerol; Sulfuric acid; Citric acid; Cross Linking.

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Resumen. - Los hidrogeles fueron preparados empleando metil metacrilato, glicerol y ácido sulfúrico o cítrico. Una ruta novedosa para la síntesis de materiales entrecruzados empleando iniciadores no convencionales fue evaluada empleando un diseño experimental tipo factorial 2³. Los efectos de las variables independientes (tiempo de polimerización, tipo y concentración de ácido) fue evaluado estadísticamente empleando ANOVA. La ruta de síntesis incluye condensación, radical libre y reacciones de transesterificación con modificaciones de las propiedades químicas del polímero, como la formación de un poliéster entrecruzado con polimetilmetacrilato (PMMA) y mejoras en las propiedades mecánicas y térmicas del hidrogel. Un tiempo de polimerización de 4 horas produjo la mayor cantidad de material: 1.37 g cuando ácido sulfúrico fue empleado y 3.46 g cuando ácido cítrico fue adicionado. El polímero sintetizado con ácido cítrico alcanzó una tasa de absorción de agua del 214.6%, comparado con los materiales producidos con ácido sulfúrico que alcanzan hasta el 31.3% de absorción de agua.

Palabras clave: Poli (metil metacrilato), Glicerol, Ácido sulfúrico, Ácido cítrico, Entrecruzamiento.

Resumo. - Os hidrogéis foram preparados utilizando metacrilato de metilo, glicerol e ácido sulfúrico ou cítrico. Uma nova rota para a síntese de materiais reticulados usando iniciadores não convencionais foi avaliada usando um desenho experimental fatorial 2³. Os efeitos das variáveis independentes (tempo de polimerização, tipo e concentração de ácido) foram avaliados estatisticamente usando ANOVA. A rota de síntese inclui reações de condensação, radicais livres e transesterificação com modificações das propriedades químicas do polímero, tais como a formação de um poliéster reticulado com polimetilmetacrilato (PMMA) e melhorias nas propriedades mecânicas e térmicas do hidrogel. Um tempo de polimerização de 4 horas produziu a maior quantidade de material: 1,37 g quando se utilizou ácido sulfúrico e 3,46 g quando se adicionou ácido cítrico. O polímero sintetizado com ácido cítrico atingiu uma taxa de absorção de água de 214,6%, em comparação com os materiais produzidos com ácido sulfúrico que atingiram até 31,3% de absorção de água.

Palavras-chave: Poli (metacrilato de metilo), Glicerol, Ácido sulfúrico, Ácido cítrico, Reticulação.

1. Introduction. - Hydrogels represent three-dimensional polymeric networks adept at retaining significant amounts of water [1] and, this ability stems from the presence of hydrophilic groups attached to the polymeric chains [2]. They are categorized as either physical or chemical, depending on the nature of their crosslinking [3]. Physical hydrogels rely on electrostatic forces or hydrogen bonding between polymer chains, which can be altered by changes in environmental conditions [4]. Chemical crosslinking involves reactions that often necessitate catalysts or photoinitiators to enhance mechanical strength while potentially compromising material biocompatibility [5].

The crosslinked polymers are typically produced through polymerization or copolymerization of suitable monomers and crosslinking agents, employing free radical polymerization, condensation, or transesterification reactions. Various physical properties, such as swelling capacity and surface characteristics, can be tailored based on the degree of crosslinking and the network formation process. Free radical polymerization, employing chemical initiators [6], biocatalysts [7], or UV light [8], stands out as the predominant method for synthesizing hydrogels from polymethyl methacrylate (PMMA). The polymer configuration is contingent upon the ionization degree of the reaction medium.

Common crosslinking agents for PMMA include ethylene glycol dimethacrylate (EGDM) [9] and trimethylolpropane triacrylate (TMPTMA) [10], with glycerol remaining relatively underexplored. Glycerol, or propane-1,2,3-triol, garners significant attention in polymer production due to its versatility in yielding diverse polymers with distinct swelling properties and the capacity to form intricate three-dimensional structures [11], [12], [13], [14]. With its three hydrophilic hydroxyl groups capable of intra- and intermolecular hydrogen bonding [15], glycerol exhibits water solubility and a hygroscopic nature, enabling selective manipulation of functional groups to facilitate polymerization using various monomers [11]. In reactions with PMMA, glycerol's hydroxyl groups condense with the acrylate, yielding a network structure suitable for slow-release applications [7].

Vinyl monomer polymerization with strong inorganic acids like nitric acid, hydrochloric acid, or aqueous sulfuric acid as initiating agents achieves reproducible results without requiring high temperatures [16], [17], UV irradiation, or electro initiation. Researchers have investigated the role of oxygen in vinyl polymerizations [18], [19], [20], attributing its effects to peroxide species formed from monomer and dissolved oxygen (present in monomers and solvents). MMA peroxides produced can include an MMA-Oxygen interpolymer with a terminal hydroperoxide group [16], [19]. This compound decomposes into active radicals by action of sulfuric acid, initiating the polymerization of MMA [16]. The radicals are formed according to a reaction as shown in Eq. 1:



An alternative approach to replacing synthetic agents in polymerization reactions involves utilizing carboxylic acids due to their similar chemical structure and advantageous properties, including their organic nature, wide availability, and biodegradability [21], [22], [23]. These acids often serve as compatibilizing agents, enhancing the mechanical, physical, and thermal properties of the resulting materials [22]. Unlike conventional initiators, different acids offer a route to obtaining crosslinked PMMA with glycerol.

Attempts to polymerize sulfuric acid or citric acid with MMA-glycerol over a 4-hour period at room temperature did not yield any products [16]. However, a combination of radical, condensation, and transesterification polymerization pathways could lead to the formation of crosslinked material when acids, glycerol, and MMA are mixed at suitable ratios and temperatures. This study focuses on developing hydrogels from various acids mixed with an MMA-glycerol complex using a two-step polymerization process: (1) PMMA production and (2) crosslinking with glycerol. The effects of acid source, concentration, and reaction time on the resulting polymer were investigated using a 2³ factorial experimental design, with the swelling rate of the material also examined.

Thus, this research presents a novel PMMA material crosslinked with glycerol using either a strong inorganic acid or a carboxylic acid, offering potential applications as a vehicle in slow-release systems.

2 Materials and methods

2.1 Reagents. - Glycerol (> 99%), citric acid (50%)-CA, sulfuric acid (50%)-SA, hydrochloric acid (1N), methanol (> 99.9%), Sodium hydroxide (> 97%) and methyl methacrylate (MMA, > 99%) were purchased from Merck. MMA was purified before use by washing with 10% NaOH solution. Deionized water was obtained from a Synergy® purification system (Merck).

2.2 Synthesis of PMMAG hydrogel. - The polymerization conditions were established based on previous investigations [16], [23], [24]. Evaluation of polymerization time, type and acid concentration were made by duplicate using a 2³ factorial design, where the response variable was the amount of material produced, as shown in Table I and II.

MMA:glycerol ratio was 3:1 for all experiments. Synthesis with SA was carried out in a single stage; while polymerization using CA was made in two stages: First, CA is mixed with glycerol and 0.5% HCl for 1-hour; then, MMA is added, and polymerization time is evaluated. For both experiments, magnetic stirring (250 rpm), temperature control (85 °C) and water reflux system were used. The polymers obtained were washed with methanol and immersed in deionized water for 24-hour to remove excess monomer. Then, the material was dried in an oven at a temperature below 40 °C until stable weight.

Effect	Level	
	Low	High
Acid type	Citric -CA	Sulfuric-SA
Time (h)	2.0	4.0
Acid concentration (%)	0.5	1.0

Table I. Experimental conditions

Run	Acid type	Time (h)	Acid concentration (%)	Material (g)
1	SA	2	0.5	0.72
2	CA	2	0.5	0.00
3	SA	4	0.5	1.25
4	CA	4	0.5	3.02
5	SA	2	1.0	0.85
6	CA	2	1.0	0.00
7	SA	4	1.0	1.37
8	CA	4	1.0	3.46

Table 2. Experimental 2³ factorial design, with results

The statistical software Statgraphics Centurion XVII was used to evaluate the designs of experiments proposed in the document, as well as the statistical parameters, using the analysis of variance (ANOVA) based on *p-value* with a confidence level of 95%.

2.3 Characterization of synthesized hydrogels. - Infrared spectroscopy analyses were performed according to [25], using an FTIR spectrometer (Nicolet 6700 Series) equipped with a single-reflection ATR and a type IIA diamond crystal mounted in tungsten carbide. The diamond ATR had a sampling area of approximately 0.5 mm², where a consistent reproducible pressure was applied to every sample. The infrared spectra were collected at a 4 cm⁻¹ resolution over 128 scans. Scanning electron microscope (SEM) images of the surface morphology were collected using a Hitachi TM-3030 operated at 15 kV. The sample was gold coated and carbon tape support was used during imaging. Thermogravimetric analysis (TGA) was recorded on a Netzsch 209 FI IRIS analyzer at 10 °C min⁻¹ heating rate and nitrogen atmosphere, using 10 mg of sample. Differential scanning calorimetry (DSC) was carried on a Netzsch DSC 204F1 Phoenix at 5 °C min⁻¹ heating rate and nitrogen atmosphere.

2.4 Liquid uptake behavior of the hydrogel. - A dry, pre-weighed hydrogel was placed in deionized water at room temperature. The weight of the hydrating sample was measured for 300 minutes at 60-minute intervals after removing the excess water by gentle blotting. The water uptake percentage was calculated as Eq. 2.

$$P_s = \frac{W_s - W_d}{W_s} \quad (2)$$

where W_s and W_d are weights of swelled and dry samples, respectively.

3 Results and discussion

3.1 Effect of reaction parameters. - Preliminary experiments were carried out to determine the minimum acid concentration and time to produce the polymeric material. The analysis of variance (ANOVA) based on the *p-value* with a confidence level of 95% as shown in the Table III. The statistically significant parameter ($P < 0.05$) on the amount of material produced was time, inducing the formation of polymer chains with reduction of the reagents included in the polymerization process.

Effect	SS	df	MS	p-value
A: Acid type	0.66	1	0.66	0.1235
B: Time	7.09	1	7.09	0.0380
C: Acid concentration	0.06	1	0.06	0.3679
AB	3.69	1	3.69	0.0526
AC	0.01	1	0.01	0.7457
BC	0.02	1	0.02	0.5145
Total error	0.03	1	0.03	
Total	11.5	7		

SS = sequential sums of squares; df = degree of freedom; MS = adjusted mean square.

Table III. ANOVA summary of 2^3 factorial design to the production of polymeric material using acid medium

In the case of SA, heightened acid concentration fosters the formation of a monomer-acid complex characterized by hydrogen bonding, typically initiated at sites exhibiting the greatest surplus of negative charges [26]. The crosslinked structure emerges when favorable configurations arise due to these hydrogen bonds: the initiator radical abstracts hydrogen from adjacent carbons near multiple bonds, thereby instigating polymer chain growth. Polymerizations involving MMA and strong inorganic acids have been documented [16], leading to increased solution viscosity and eventual gelation. The proposed reaction mechanism for PMMA synthesis using SA is depicted in Figure I.

During the reaction, two primary products emerge: the synthesis of PMMA and glycerol, which undergoes a competitive dehydration process via a radical mechanism. This process yields allyl alcohol and triggers the cleavage of bonds to produce acetaldehyde and formaldehyde [15].

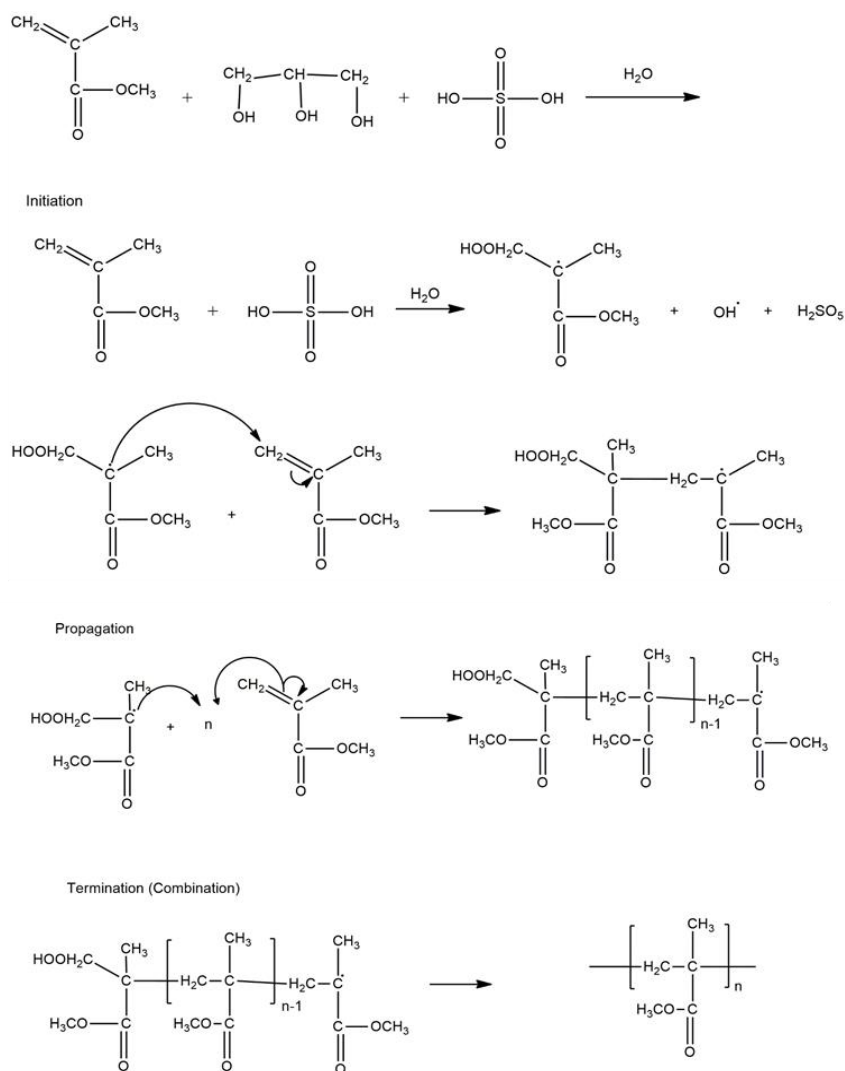


Figure I. Possible reaction mechanism to obtain PMMA using SA.

Citric acid (CA) was chosen as a polyfunctional reagent due to its non-toxic nature and metabolic production by microorganisms. It serves as a crosslinking agent by facilitating hydrogen bond interactions within a polymeric network [27]. Glycerol was selected as a trifunctional monomer to enhance the hydrogel's properties, leveraging its flexibility and absorption characteristics. Hydrochloric acid (HCl) was employed to introduce an excess of protons and activate carbonation, initiating the polymerization reaction. The addition of CA to the MMA-glycerol mixture at temperatures ranging between 22-30 °C for a 4-hour duration did not induce polymerization. However, employing a radical/condensation/transesterification polymerization approach resulted in the formation of a physically crosslinked material when glycerol and CA were added in a suitable ratio to MMA at temperatures exceeding 60 °C. Figure II elucidate the proposed reaction mechanism and, structurally, the material derived from CA comprises primary chains of PMMA, side chains originating from crosslinking with glycerol-citrate, and residual components such as monomer, glycerol, and unreacted CA. The network's structure and chemical composition play pivotal roles in determining the material's properties.

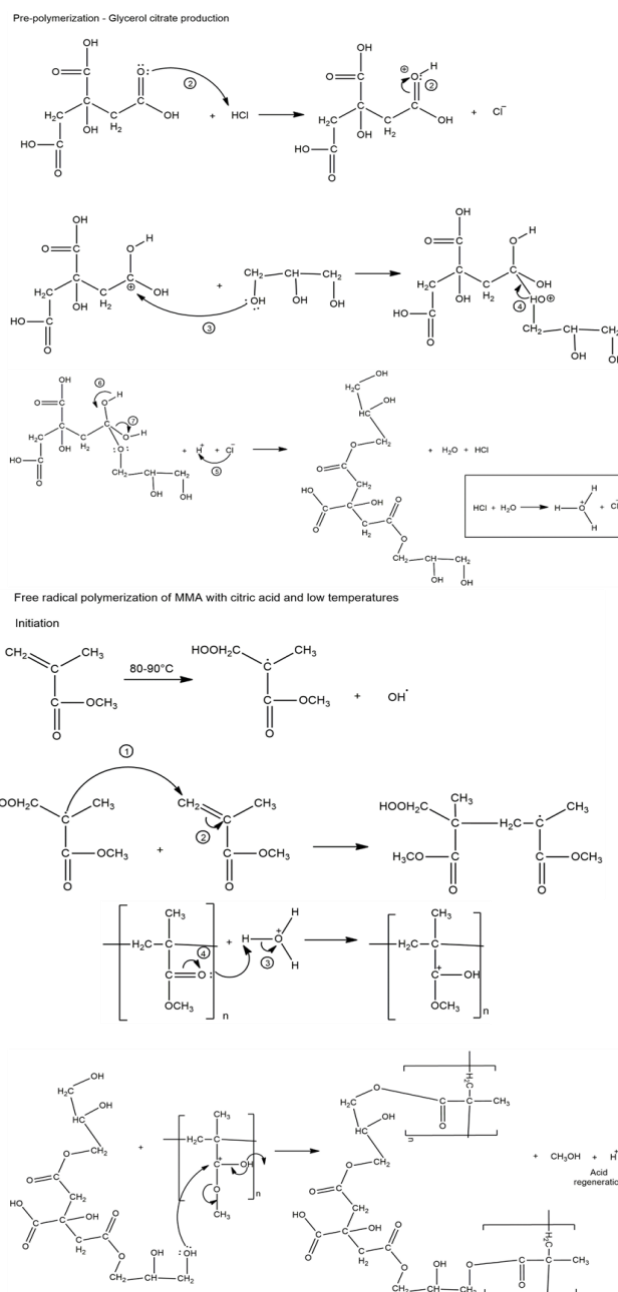


Figure II. Possible reaction mechanism to obtain crosslinking glycerol citrate- PMMA using AC.

When the polymerization process with SA or CA does not have enough reaction time, it is likely to obtain a different configuration because the formation of hydrogen bonds that crosslink intermolecular carboxyl groups does not occur [23]. The effectiveness of crosslinking in the polymerization process indicates that the main route for crosslinking between macromolecules is associated with the chain sequence of the addition reaction between macro radicals [28]. The ideal conditions to produce material suggested by the software are shown in Table IV: 1% CA and 4-hour process, can produce 3.4 g of crosslinked material from MMA and glycerol.

Effect	Low	High	Ideal
Acid type	SA	CA	CA
Time (h)	2.0	4.0	4.0
Acid concentration (%)	0.5	1.0	1.0
Amount of material produced at ideal parameters 3.40 g			

Table IV. Ideal values of polymeric material process variables

3.2 Characterization of synthesized hydrogels. - The FTIR spectra of the samples obtained with SA, CA and different reaction parameters are like those reported in the literature for PMMA [29] with changes due to reaction mechanism and the presence of glycerol in the reaction. When working with CA, the 2-hour process produced nonpolymeric structure; thus, only the 4-hour samples were evaluated (Figure III).

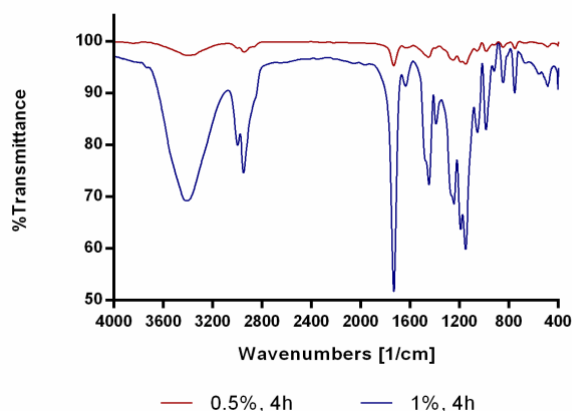


Figure III. FTIR spectra of polymeric material obtained with different concentrations of CA and 4-hour process.

In the materials obtained with 0.5% CA, the difference in the bands confirms the importance of the concentration of acid in the formation of glycerol-citrate. Bands at 2949 and 1446 cm^{-1} show the stretching and flexing vibration of the CH_2 group, respectively. At 3406 cm^{-1} indicates the presence of an OH group of glycerol and its decrease suggests the formation of the ester, confirmed with the band due to stretching $\text{C}=\text{O}$ at 1732 cm^{-1} , as well as signs of $\text{C}-\text{O}-\text{C}$ stretching at 1054 cm^{-1} . When 0.5% CA was used, higher production of glycerol-citrate was complete without achieving adequate crosslinking with the PMMA chains.

In the samples obtained using SA (Figure IV), the band located at 2992 cm^{-1} belongs to the stretching vibration of $\text{O}-\text{CH}_3$ and CH , 2949 cm^{-1} to the stretching vibration of $\text{C}-\text{CH}_3$ and CH , 1729 cm^{-1} to the stretching vibration of the $\text{C}=\text{O}$ of the polymer and compounds formed in the dehydration of glycerol, 1447 cm^{-1} to the flexion of $\text{O}-\text{CH}_3$, 1260-1040 cm^{-1} to the vibration of the $\text{C}-\text{O}-\text{C}$ bond, that is characteristic of PMMA samples [30].

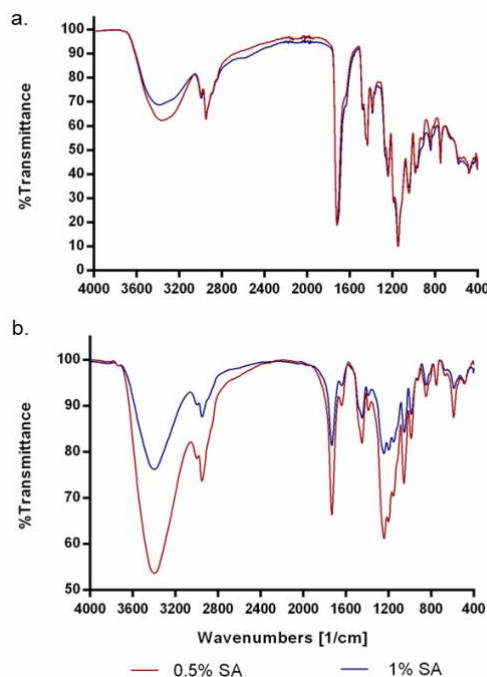


Figure IV. FTIR spectra of polymeric material obtained with different concentrations of SA and a. 2-hour and b. 4-hour.

The band located near to 3395 cm^{-1} is due to the OH stretch of glycerol, showing the presence of different amounts of residual glycerol within the polymer network. Concentration of the acid affects the dehydration process of glycerol since a weak incorporation of glycerol was noticed in the samples obtained with 1% SA compared to the ones with 0.5% SA. In the samples obtained with different acids, the presence of the band between $1719\text{--}1732\text{ cm}^{-1}$ is related to the stretching of the acrylate of the material and it is dependent on the type of acid included in the process. The polymer contains residual reagents, as the band corresponding to $1641\text{--}1637\text{ cm}^{-1}$ C-C of the MMA is characteristic of the monomer, and the band of $1146\text{--}1153\text{ cm}^{-1}$ evidence unreacted glycerol. These results are described in previous studies for materials obtained from glycerol [35] or MMA with different polymerization mechanisms [31], [32].

The surface of the polymer changes according to the process conditions: different profiles are observed when CA is used. Some irregular pores are observed on the rough area of the material with 0.5% CA (Figure Va). Researchers established that the presence of pores on the surface is an ideal characteristic in the application of polymers with a similar structure as those obtained from CA-Glycerol, due to these pores increment the area of the network, developing contact points between the hydrophilic and solvent chains, facilitating the entry and absorption of liquids within the polymer matrix. Also have a smooth laminar appearance (Figure Vb) with granules on the surface, attributable to reaction residues of CA.

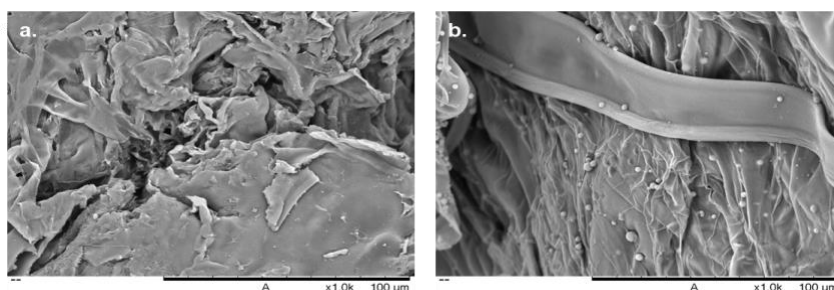


Figure V. SEM images of the samples obtained with 4-hour and CA: a. 0.5%; b. 1%.

In materials obtained from 0.5% SA and 2-hour, there is an association between the spherical shapes and the agglutination which could have formed during the polymerization process (Figure VIa). A fibrous material with irregular structure was obtained from 1% SA and 2-hour reaction (Figure VIc); in contrast, a different polymer was obtained with the same concentration of acid over a 4-hour reaction, which has a network structure attributed to dissolved oxygen in the solution that modifies the assemble of the pores during polymerization (Figure VIb). Results suggest that the acid concentration and synthesis time directly affect the appearance of the material polymeric network.

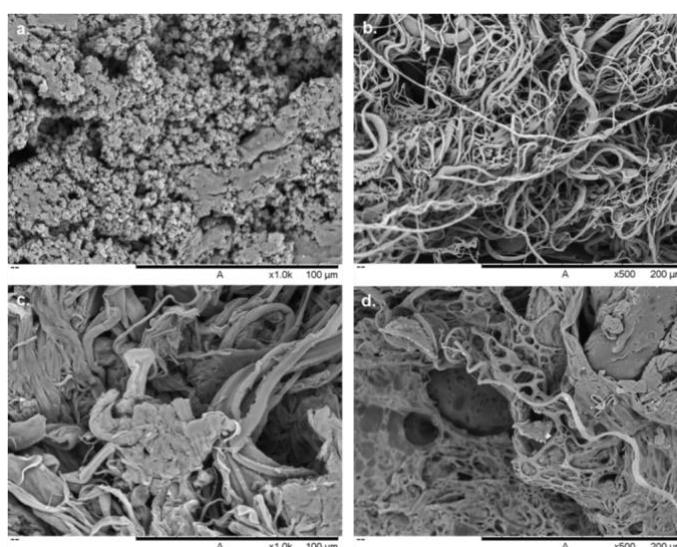


Figure VI. SEM images of the material obtained using SA. a. 0,5%, 2-hour; b. 0,5%, 4-hour; c. 1%, 2-hour; d. 1% 4-hour.

Figure VII shows the TGA and DTG curves for the polymers produced with different polymerization conditions. In Table 5, residual mass, T_d and T_g glass of the polymers obtained are reported. The exact values of the residual mass at the different temperatures were determined from the DTG curve of the polymers produced in 4-hour varying the type and acid concentration.

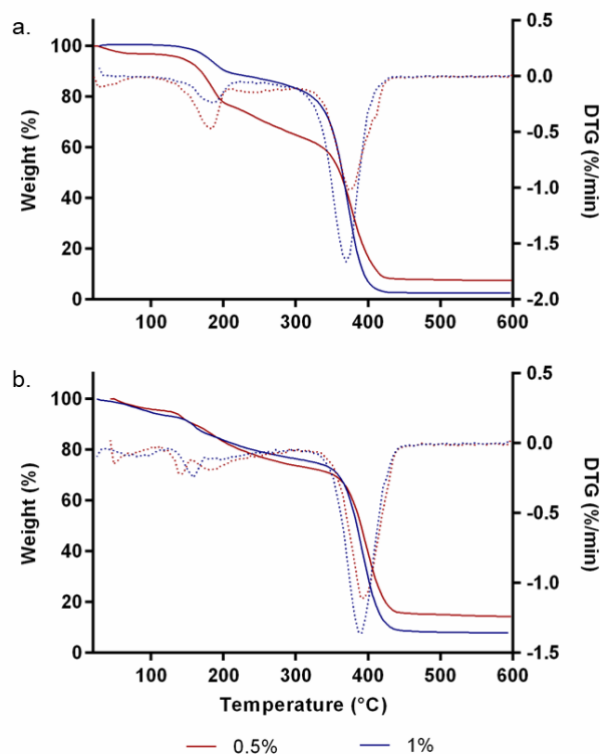


Figure VII. Thermogravimetric analysis for material obtained with different types of acids varying concentration and 4-hour of polymerization: a. CA; b. SA.

Sample	T_d (°C)	Residual mass (%)					T_g (°C)
		150	250	350	450	>500	
CA 0,5%	376.8	94.2	71.2	55.1	8.04	7.59	110.5
CA 1%	369.60	98.9	87.0	67.7	2.73	2.55	118.2
SA 0.5%	389.75	90.8	77.1	70.32	15.73	14.53	163.1
SA 1%	391.12	90.6	79.1	72.0	8.70	7.95	148.3

Table 5. Thermal behavior of the synthesized material with different operational conditions and 4-hour of polymerization.

Thermal decomposition of the samples obtained with SA or CA follow two stages. In the first stage, up to 16% of the sample was decomposed due to the vaporization and degradation of glycerol, and the remaining unreacted monomer. In the second stage, 80% of the samples with SA decomposed between 390–450°C; whereas the polymer obtained with CA breaking down between 369–434°C, this related to the decomposition of the principal polymeric chains and the crosslinked structure (Table 1). Decomposition percentage during the first stage indicates that a higher amount of glycerol-citrate is crosslinked in the polymer network when 0.5% CA mixture is added to the reaction.

Mass loss is the main difference among TGA curves, this indicates the effect of type and acid concentration to initiate the polymerization process. This variation modifies the molecular weight, the end groups of the chain [33], and the degree of crosslinking achieved by glycerol-citrate affecting the rate of thermal decomposition observed in each degradation stage (Figure VII). The polymer obtained with 0.5% SA has higher thermal stability than the other samples due to a relatively larger volume and increased distance between the cross-linked bonds in the polymer chains. The

complete degradation of the linear PMMA is close to 450°C [34], while the obtained material decomposes after 500°C where there are residues of the polymer (Figure VII); this proves enhanced thermal stability of the synthesized crosslinked material.

T_g was 148.3°C in samples with 1% SA with a thermal stability lower than material with 0.5% SA, which reached T_g of 163°C. Polymers produced with 1% CA reported higher T_g, 118.29°C. A possible explanation of the thermal stability observed in the synthesized materials is the formation of a crosslinking network that affects the mobility of the macromolecule, decreasing the probability of a change in the conformation, and increasing the glass transition temperature of the materials.

Swelling capacity can be determined by the amount of space available within the polymer network to accommodate the solvents [35]. Polymer-solvent interaction forces define the water retention capacity [36]. Swelling speed of the sample depends on the chemical nature of the sample and the functions along the polymer chain, achieving different types of crosslinked bonds (covalent, ionic, or physical) [37]. The process of cross-linking is performed by controlling variables such as temperature, type and amount of crosslinking agent, and external factors such as oxygen, presence of water and others [38]. Evidence of crosslinks is related to the swelling of the polymer matrix when it contacts a solvent. Samples required up to 300 min to stabilize water absorption and maintain constant weight. None showed fragmentation or loss of material when it reached the maximum swelling capacity.

Figure VIII shows the swelling behavior of the obtained polymers. Samples produced with SA reached up to 33.13% of water absorption, in contrast, samples with 0.5% CA, reached up to 215.85%. Materials with 1% CA and different times achieved similar results of swelling capacity, confirming the affinity between the polymer and the solvent. In the case of the polymer obtained with 0.5% CA, reaction time affects the amount of material produced and its further physical behavior, indicating that swelling capacity is related to the formation of crosslinked bonds between the polymer chains.

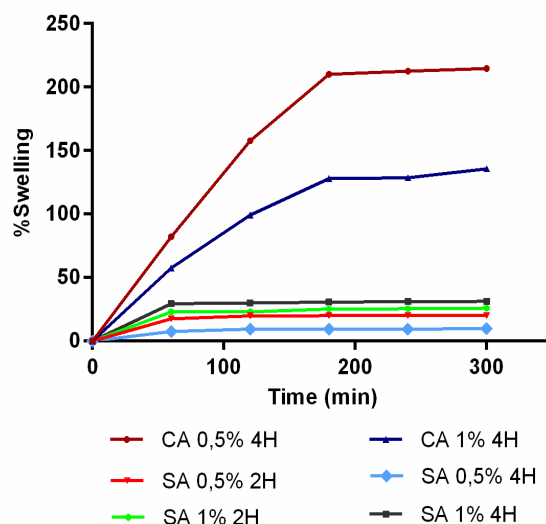


Figure VIII. Swelling behavior of cross-linked polymer, using different acids and polymerization time.

Data indicate that low concentrations of CA and 4-hour of polymerization result in a crosslinking of the monomer with glycerol that produces a better water absorption, compared to the material obtained with 1% of CA and different polymerization time. Presence of SA leads to formation of more free radicals to induce the formation of PMMA, without achieving enough crosslinking with glycerol that stimulates water retention in the material.

4 Conclusions. - The polymerization processes that include MMA, glycerol, and commercial acids such as sulfuric acid or citric acid can produce polymers with different characteristics due to variations of operational conditions. In polymers obtained with CA, a glycerol-citrate pre-polymer was formed and then cross-linked with the developed

PMMA, exhibiting modification of the thermal and mechanical properties when compared with those obtained with SA that have higher thermal stability. Surface of the sample with SA shows branched structures and some pores formed by the oxygen involved in the polymerization process. On the other hand, materials with CA show irregular pores that can facilitate the entry of liquids into the polymer matrix. Glycerol citrate (like the pre-polymer formed in the materials obtained with CA) improves the water absorption properties. Glycerol is a hydrophilic substance that forms three-dimensional structures when it is used to obtain hydrogels, and CA acts as a compatibilizing agent that promotes the union of the formed PMMA chains with the pre-polymer.

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Nota contribución de los autores:

1. Concepción y diseño del estudio
2. Adquisición de datos
3. Análisis de datos
4. Discusión de los resultados
5. Redacción del manuscrito
6. Aprobación de la versión final del manuscrito

LTV ha contribuido en: 1, 2, 3, 4, 5 y 6.

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