Research Article

Stimuli-Responsive Hydrogels Based on Polyglycerol Crosslinked with Citric and Fatty Acids

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Polyglycerol-based hydrogels from biodegradable raw materials were synthesized by crosslinking reactions of polyglycerol with citric and fatty acids. Three hydrogels were studied varying molar ratios of crosslinking agent. It was found that crosslink amount, type, and size play a crucial role in swelling, thermal, mechanical, and stimuli-responsive properties. The hydrogels absorption capacity changed in response to temperature and pH external stimuli. The hydrogel with the highest swelling capacity absorbed more than 7 times its own weight at room temperature and pH 5. This material increased 14 times its own weight at pH 10. Creep-recovery tests were performed to study the effect of crosslinking agent on mechanical properties. Deformation and percentage of recovery of synthesized hydrogels were obtained. Formation of hydrogels was confirmed using FTIR, and physicochemical properties were analyzed by Scanning Electron Microscopy (SEM), Differential Scanning Calorimetric (DSC), and Dynamic Mechanical Analysis (DMA). This paper aims to give a contribution to biobased hydrogel knowledge from chemical, physicochemical, and mechanical point of view.

1. Introduction

Hydrogels are polymeric crosslinked, hydrophilic, three–dimensional networks that are not soluble in water but can absorb large quantities of this molecule [1, 2]. Due to their swelling ability, hydrogels have been studied extensively for a variety of applications such as drug delivery [3–6], agricultural applications [7, 8], removal of impurities in aqueous solutions [9, 10], biosensors [11], and spectrophotometric determination of drugs [12]. In these applications, swelling capacity and thermal, mechanical, and stimuli-responsive properties are of most interest. These properties are prescribed by the intrinsic properties of the main chain polymer and the crosslinking characteristics, such as type, amount, and size of crosslinking molecules, as well as environmental conditions. In this work, synthesized hydrogels are based on renewable materials; the main chain polymer is polyglycerol, obtained by glycerol polymerization [13], and citric and

fatty acids are the crosslinking molecules. Polyglycerol has a biocompatible and flexible polyether backbone with a high number of hydrophilic functional groups, which increases polyglycerol versatility and enables the production of hydrogels [14]. Citric acid is a relatively small and multifunctional monomer with pendant functional groups that allow future ester bond-crosslink and hydrogen bonding [15, 16]. Fatty acids are relative long monomers with a carboxylic functional group that with chemical modification of double-double bond of unsaturated fatty acids allows the formation of crosslinked polymer structures [17]. The present study focuses on the synthesis and characterization of novel polymeric materials from biodegradable monomers that respond to pH and temperature stimuli. The effect of type, amount, and size of crosslinking agents on thermal, mechanical, and stimuli-responsive properties was investigated.

Previous studies have reported the synthesis of hydrogels by crosslinking glycerol-derived polyglycerol with

Table 1: Composition of fatty acids used as crosslinking agent. Characterization was made using a gas chromatography system (Agilent Technologies 6890 series), coupled to a FID detector, using an Agilent DB23 column and SUPELCO 38 FAMES as standards.

Fatty acid	Area percentage (%)
Palmitic	9.08
Stearic	8.12
Oleic	32.14
Linoleic	36.31
Linolenic	3.56
Eicosenoic	4.06
Others	6.71

poly(ethylene glycol) diglycidyl ether PEGDE [14]. The resulting hydrogels exhibited pH-dependent swelling behavior with a higher swelling capability at acidic pH value, compared with swelling at neutral and basic pH values. Significant research has been focused on materials that change their properties in response to external physical and chemical stimuli such as pH, electric field, temperature, and ionic strength of the swelling agent, due to acid or basic pendant functional groups present on the polymer backbone [18–21]. Citric acid has been used as crosslinking agent for hydrogels production, for instance, with poly(vinyl alcohol) [22], with varying glycol unit (ethylene glycol, diethylene glycol, and triethylene glycol) [23], and with cellulose [24]. Fatty acids, such as linoleic and oleic acid, have been traditionally used to improve mechanical properties and chemical resistance in polymeric materials [25, 26].

Formation of hydrogels was confirmed using FTIR. Pendant acidic functional groups were identified in the polymer network which either accepts or releases protons as result of changing external pH. The calorimetric analysis was performed to study the effect of amount and size of crosslinking agents on glass transition temperature. Creep-recovery tests were conducted to elucidate structure-property relationship in mechanical properties. Hydrogels swelling behavior was determined at different pH and temperatures. Finally, SEM micrographs were taken to study morphological properties.

2. Materials and Methods

2.1. Materials. Glycerol (85%) and Sulfuric acid (95%) were obtained from Merck. Citric acid (99%) is a commercial product of Suquin Ltda., Bucaramanga, Co. The mixture of fatty acids used in this study was purchased from *Laboratorios León S.A.*, Bucaramanga, Co. Its composition is listed in Table 1.

2.2. Experimental Procedure

2.2.1. Hydrogels Synthesis. Hydrogels synthesis was carried out in two steps using the same reaction system: first step, polymerization reaction of glycerol to produce polyglycerol, and second step, crosslinking reaction of polyglycerol; see Figure 1. The reaction system consisted in a 50 mL glass
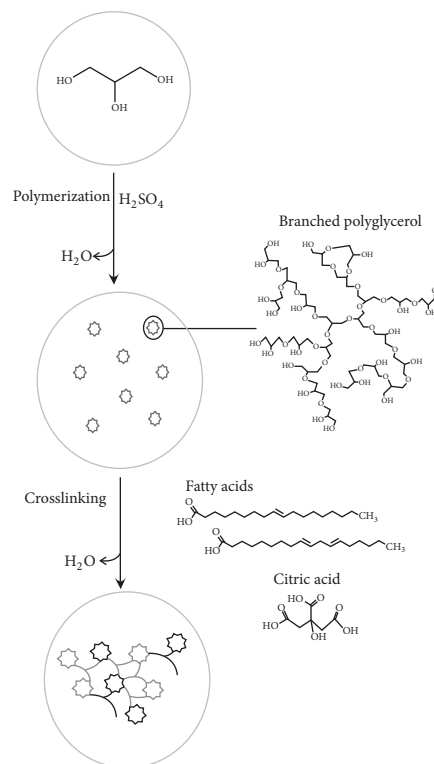

Figure 1: Schematic representation of hydrogel synthesis. First, the glycerol polymerization and the subsequent addition of crosslinking agents.

reactor equipped with a nitrogen inlet, catalyst feeding, thermometer inlet, and a distillation trap to continuously remove water from the reaction mixture. The temperature was maintained at 160°C using a temperature-controlled heating bath. A vacuum pump was attached to the reactor through the condenser. Condensation reactions were carried out at pressure of 22 in Hg. 4.8% w/w of Sulfuric acid was used as a catalyst [13]. The crosslinking agents were added to the reaction mass of polymerized glycerol, just before reaching the gel point, without further addition of catalyst. The reaction proceeded until the hydrogel reached the gel point.

Three different hydrogels were synthesized changing the nature of crosslinking agent: a hydrogel with citric acid as crosslinking agent, a hydrogel with fatty acids as crosslinking agent, and a hydrogel with both citric and fatty acids as crosslinking agent. Molar ratio between polyglycerol hydroxyl groups and crosslinking agents carboxyl groups and molar composition of crosslinking agents of synthesized hydrogels are reported in Table 2. After polymerization and crosslinking process, the hydrogels were washed with distilled water to remove catalyst and unreacted monomers.

2.3. Characterization. The synthesized hydrogels were tested to determinate their swelling behavior as a function of time in distilled water at room conditions. Absorption measurements were also made at 35°C, 55°C, and 85°C and pH 4, 7, and 10 to establish if the synthesized hydrogels have a response to temperature and pH. The absorption tests at different pH

TABLE 2: Samples compositions used for the hydrogels synthesis.

Hydrogel	Molar ratios of OH groups of polyglycerol (PG) : COOH groups of crosslinking agents (CG)	Molar compositions of COOH groups of citric acid (CA) and fatty acids (FFAs)
PG-FFAs	1 : 0.05	100% FFAs
PG-CA	1 : 0.45	100% CA
PG-(CA, FFAs)	1 : 0.5	90% CA-10% FFAs

were performed using *Hanna Instruments* buffer solutions. All measurements were done in triplicate. The hydrogels water absorption was calculated using (1) [14].

$$\% \, S = \frac{W_s - W_d}{W_d} * 100\%, \tag{1}$$

where W_d is the dry hydrogel weight and W_s is the swollen hydrogel weight.

Fourier Transform Infrared Spectroscopy (FTIR) was used to identify functional groups in synthesized hydrogels. The infrared spectra were obtained in transmittance mode in a Thermo Scientific spectrometer (Nicolet 1550 FTIR). Glass transition temperatures were obtained using Differential Scanning Calorimetry (DSC), and measurements were carried out on a DSC Discovery, TA Instruments, Inc. (USA). The samples were subjected to the following thermal schedule: first heating from −80°C to 180°C at 5°C/min to eliminate volatile substances and thermal history of the materials; second, a cooling from 180°C to −90°C at 10°C/min; third, final heating from −90°C to 200°C. All scans were performed under nitrogen purge gas of 50 mL/min. Scanning Electron Microscopy (SEM) measurements were performed to study the morphology of synthesized hydrogels. Samples were pretreated by being fully swollen in distilled water, then frozen in liquid nitrogen, and lyophilized for 72 h. Freeze–dried hydrogels were consequently fractured for morphology visualization. The uncoated environmental SEM images were taken using a Quanta FEG 650 at acceleration voltages of 15 kV. Creep-recovery tests of synthesized hydrogels were tested using Dynamic Mechanical Analysis (DMA), and measurements were carried out on a Q800 dynamic mechanical analyzer, TA Instruments Inc. (USA). The samples were swollen and tests were carried out in water medium. Treatments were compressed at 0.007 MPa during 20 min at three different temperatures; after that, the samples were recovered for 20 min.

3. Results and Discussion

3.1. FTIR Spectral Studies of Polymeric Hydrogels. Fourier Transform Infrared Spectroscopy (FTIR) analysis was conducted to synthesized hydrogels and compared with polyglycerol spectra; see Figure 2. The hydrogels and polyglycerol spectra show hydroxyl group band from 3050 to 3600 cm^{-1} indicative of alcohol groups. Hydrogels O-H stretch exhibits a loss of intensity in comparison with polyglycerol as a consequence of crosslinking linkages. The C-H stretching band was
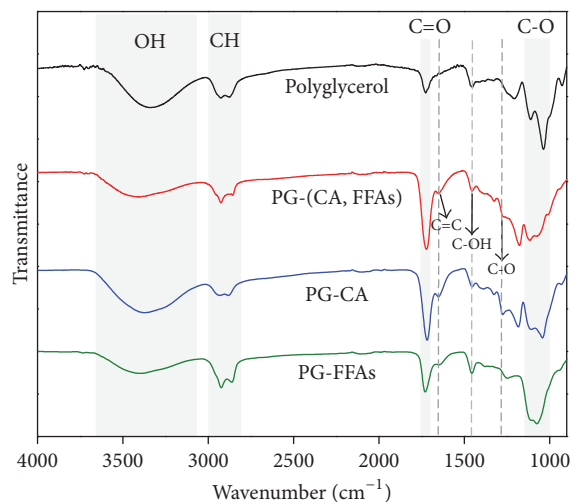

FIGURE 2: FTIR spectra of glycerol-derived polyglycerol and polyglycerol-based hydrogels. The main peaks associated with the structures are highlighted.

observed from 2800 to 3000 cm^{-1} [27]. Hydrogels with fatty acids as crosslinking agents, treatment PG-(CA, FFAs), and treatment PG-FFAs show well-defined C-H stretching as a consequence of hydrocarbon chains of fatty acids. Absorption in the range of 1700–1750 cm^{-1} in hydrogels spectrum is related to C=O stretch of aliphatic esters produced by esterification reactions between polyglycerol hydroxyl groups with carboxylic groups present in citric acid and fatty acids. In the specific case of polyglycerol, this absorption is due to acrolein formation [28]. Absorption at 1650 cm^{-1} is associated with C=C group of both unsaturated fatty acids and undesired products such as acrolein.

The spectra showed a peak at 1455 cm^{-1} that corresponds to C-OH in-plane bending and CH$_2$ bending [28]. The peaks appearing at 1235–1290 cm^{-1} in hydrogels spectrum are related to C-O vibration of unreacted carboxylic groups. These pendant acidic functional groups will play a crucial role in stimuli-responsive properties. The C-O vibration of unreacted carboxylic groups is highlighted in Figure 3. It is observed that hydrogel PG-FFAs exhibits lower C-O vibration intensity in comparison with hydrogels that have citric acid as crosslinking agent. This result is due to citric acid structure, which has three carboxylic functional groups, and not all of them react in the crosslink reaction. Finally, absorption at 1000–1150 cm^{-1} is related to C-O stretching of the ether groups present in the polyglycerol backbone [14] and etherification reactions between polyglycerol and crosslinking agents. Polyglycerol hydroxyl groups can react by etherification reactions with citric acid hydroxyl group and with fatty acids hydrated carbon-carbon double bonds.

3.2. Thermal Properties. Treatment PG-FFAs exhibits the lowest glass transition at 40.76°C (Figure 4), which is related to the lowest crosslink density and long chain size of fatty acids used as crosslinking agent. Therefore, less temperature is needed to change the hydrogel state from glassy to rubbery.
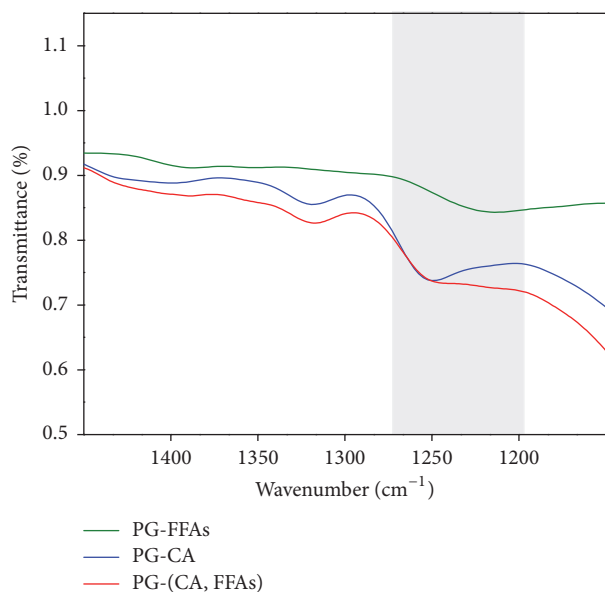
FIGURE 3: Zoom of the FTIR spectra at 1235–1290 cm^{-1} of the three synthesized hydrogels. The highlighted C-O vibration is related to the unreacted carboxylic groups.

On the other hand, treatment PG-CA exhibits the highest glass transition at 50.70°C. This result is due to higher crosslink density and citric acid short chain, which gives less flexibility to the material. In the particular case of hydrogel PG-(CA, FFAs), this material exhibits a glass transition temperature at 42.87°C, which is between the two glass transitions just described. This result can be explained by the combined features of each used crosslinking agent.

3.3. Mechanical Properties. The adequacy of hydrogels for specific applications depends on their mechanical properties and response times [29]. In this work, mechanical properties were evaluated by a creep-recovery test at different temperatures: 35°C, 55°C, and 70°C. Tests were performed in water medium simulating a typical condition of hydrogels in their applications. Results are shown in Figure 5. In general, all hydrogels have a small transition before a flat equilibrium region. Hydrogels deformation and percentage of strain recovery (SR) at different temperatures depend strongly on crosslink density, size, and type of crosslink agent. PG-FFAs present the highest deformation at all temperatures. This hydrogel has a slight variation of deformation at 35°C and 55°C and a significant increase in deformation at 70°C due to high molecular mobility at temperatures above glass transition temperature. Percentages of recovery of PG-FFAs are relatively low, 38.41, 41.45%, and 27.55% at 35°C, 55°C, and 70°C, respectively. High deformations and relatively low percentages of recovery of PG-FFAs hydrogel are due to low crosslink density and long chains of fatty acids used to form the network. High crosslink density and short chains of citric acid resulted in PG-CA hydrogels with relatively low deformation related to PG-FFA hydrogel. PG-CA hydrogel presented an increase in deformation and decrease in the
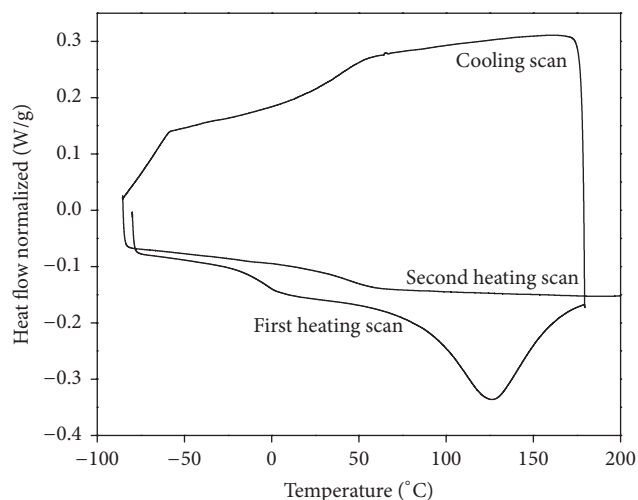
(a)
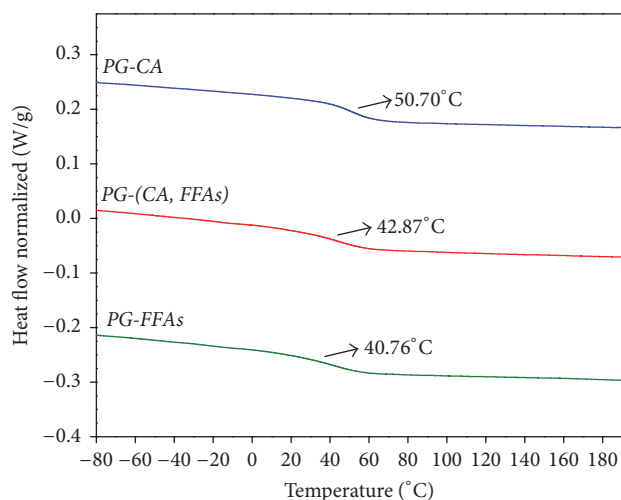
(b)

FIGURE 4: (a) First and second heating scan DSC result for hydrogels synthesized. (b) Hydrogels glass transition temperatures found in the second heating scan.

percentage of recovery as temperature increases. This result may be related to hydrogel chains mobility since glass transition temperature is 50°C. Finally, PG-(CA, FFAs) hydrogel has above 55°C the lowest deformation and the highest percentage of recovery of all hydrogels at this temperature.

3.4. Swelling Properties. The hydrogel with the highest swelling degree is PG-(CA, FFAs). It absorbs more than seven times its own weight; see Figure 6. This swelling behavior may be related to the contribution of both crosslinking agents; fatty acids long chains may contribute to large pore sizes, and unreacted hydroxyl groups of citric acid in addition to unreacted polyglycerol hydroxyl groups increase water affinity. Hydrogel PG-CA probably has smaller pore sizes for holding water caused by citric acid short chains. Finally, hydrogel PG-FFAS has only fatty acids that, despite its long
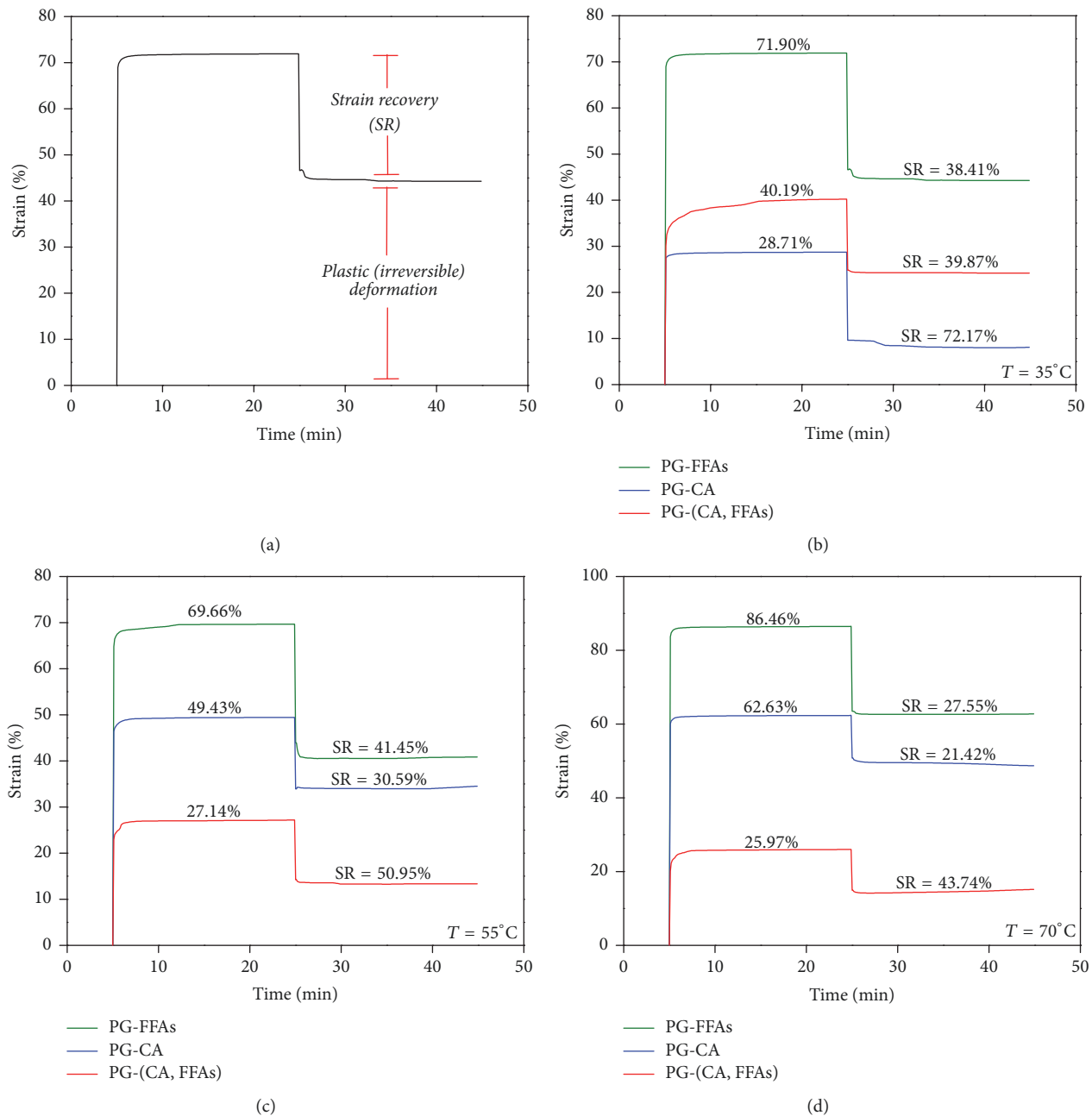
FIGURE 5: Submersion-compression creep for treatments PG-FFAs, PG-CA, and PG-(CA, FFAs) in DMA at 35°C, 55°C, and 70°C.

chain size, its crosslinking degree is low holding limited water molecules within its structure.

3.4.1. Effect of pH on Swelling Behavior. The swelling behavior of hydrogels was studied after 60 minutes of water absorption at pH 4, 5, 7, and 10. From the results, it was concluded that the hydrogels swelling behavior depends on external pH; see Figure 7. The greater swelling capability of hydrogel PG-(CA, FFAs) is observed when the pH value is 10, in which the hydrogel absorbs more than 13.7 times its own weight. At pH 4 and 7, the hydrogel also increases its swelling capability absorbing 8.6 and 10 times their own weights, respectively.

As reported in other studies [20, 30], an explanation for these results is that at basic pH values, the unreacted carboxylic groups become ionized producing carboxylate ions ($RCOO^-$), and H^+ combines with OH^- from basic solution forming H_2O. Negative charges of carboxylate ions create an electrostatic repulsion between the polymer chains forcing the hydrogel to uncoil, increasing free volumes in the hydrogel network.

In the specific case of treatment PG-FFAs, its swelling degree at high pH is lower in comparison with the other two treatments because this material presents less unreacted carboxylic groups; see Figure 3. A different trend result was
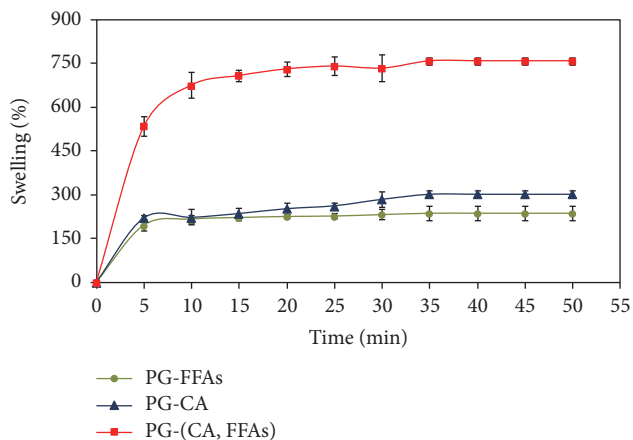
FIGURE 6: Swelling behavior of treatments PG-FFAs (●), PG-CA (▲), and PG-(CA, FFAs) (■). Measurements were taken at 20°C and pH 5 using (1).

FIGURE 8: The temperature-dependent swelling behavior of treatments PG-FFAs (●), PG-CA (▲) and PG-(CA, FFAs) (■). Swelling percentage was calculated using (1).
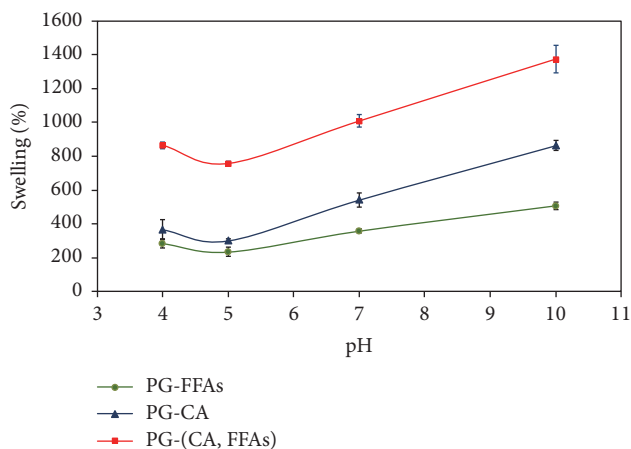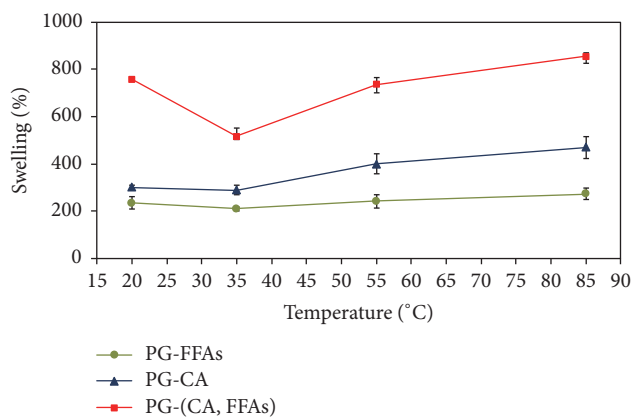

FIGURE 7: pH-dependent swelling behavior of treatments PG-FFAs (●), PG-CA (▲), and PG-(CA, FFAs) (■), measured at 25°C. Swelling percentage was calculated using (1).

3.5. Morphological Properties. Morphology of hydrogel PG-(CA, FFAs) is shown in Figure 9. It was found that the hydrogel exhibits an uneven, rough, heterogeneous, and slightly porous structure. The observed hydrogel pore heterogeneity (pore diameters from 2 to 62 μm) could be related to the randomness of crosslinking reactions between polyglycerol and citric-fatty acids which have different chain lengths and functional groups. Furthermore, the porous structure has interconnected pores forming open channels for capillary absorption of water; see Figure 9(b).

This material looks like a sponge and its swelling process follows the same principle, keeping the water within its structure due to its free volumes. This hydrogel may be considered as macroporous material according to IUPAC [31].

4. Conclusions

The effect of type, amount, and size of crosslinking molecules such as citric and fatty acids on thermal, mechanical, swelling, and stimuli-responsive polyglycerol-based hydrogel properties was studied. The small citric acid molecule used as crosslinking agent produced high crosslink density which manifested itself in higher glass transition temperature, relatively low hydrogel deformation, and higher amount of unreacted carboxylic functional groups that propitiated stimuli-responsive properties. On the other hand, large fatty acids molecules used as crosslinking agent produced low crosslink density which manifested itself in lower glass transition temperature, higher hydrogen deformation, and less unreacted carboxylic functional groups. It was concluded that it is possible to tune hydrogel properties by the judicial combination of citric and fatty acids crosslinking agents. The resulted hydrogel combining both crosslink agents has an intermediate glass transition temperature, relative short deformation with high recovery, and unreacted carboxylic functional groups that improved stimuli-responsive properties in comparison with hydrogels with uncombined crosslinking agents.

obtained at pH 4 where hydrogels showed higher swelling behavior than that at pH 5; this can be related to the attraction of H$^+$ ions to hydroxyl and ether groups, as reported before [14]. Swelling results at different pH correlate with unreacted carboxylic groups reported previously in FTIR results; see Figure 3; hydrogels with more free unreacted carboxylic groups have a greater response to changes in pH.

3.4.2. Effect of Temperature on Swelling Behavior. Hydrogels swelling behavior was studied after 60 minutes of water absorption at 20, 35, 55, and 85°C (Figure 8). Results show that at 35°C the three hydrogels present the lowest swelling degree. At this temperature, all hydrogels are below glass transition temperature as shown in Figure 4. At temperatures above 55°C, all hydrogels are above glass transition temperature. As a result, hydrogels chain mobility increases water absorption. The greater swelling capability is observed at 85°C where the PG-(CA, FFAs) hydrogel absorbs water 8.5 times its own weight.
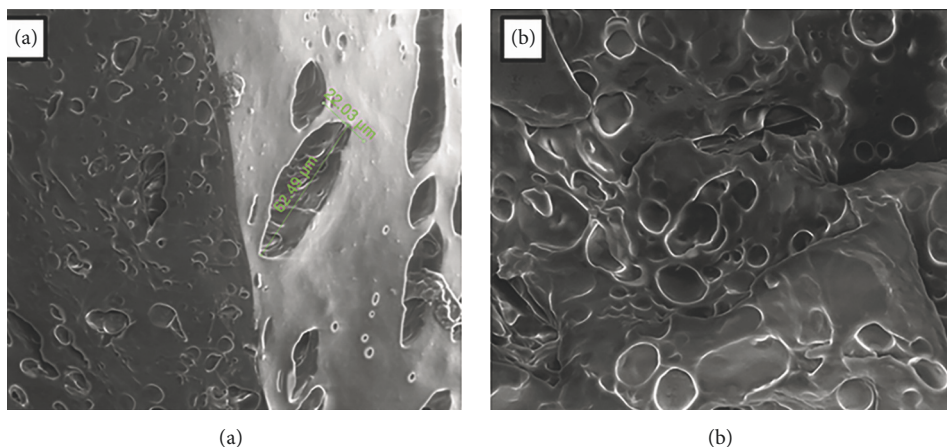
FIGURE 9: SEM micrographs of the hydrogel PG-(CA, FFAs).

Conflicts of Interest

The authors declare that they do not have any conflicts of interest.

Acknowledgments

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