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CHARACTERIZATION OF STRUCTURED ACRYLAMIDE/ACRYLIC ACID HYDROGELS BY TMDSC AND MICROSCOPY

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The thermal behavior of hydrogels synthesized by solution polymerization between acrylamide, acrylic acid and diglycidyl acrylate (DGA) as a crosslinking agent was investigated. The structure of the hydrogel can be tightly controlled with the reaction temperature. This method produces a new type of hydrogels, which exhibit well defined structures at various scales of length simultaneously. These multi-structured hydrogels are hydrophilic, elastic, water insoluble, and soft polymers with an anisotropic optical response. The structure was observed by scanning electron microscopy (SEM), polarized light microscopy (PLM) and macroscopic visualization (CCD camera). In addition, structural transitions in the hydrogels were monitored by temperature modulated differential scanning calorimetry (TMDSC). Severe heating tests in an adiabatic oven were performed to analyze decomposition of the material. Fourier transform infrared (FTIR) spectroscopy was used to qualitatively analyze the hydrogels samples exposed to a sudden thermal treatment.

Keywords: *acrylamide, acrylic acid, polymeric hydrogel, structural transition, TMDSC*

Introduction

Polymers are important materials in modern life and gels are one such type of materials. In a gel, long polymer chains are cross-linked producing a three-dimensional network, which is able to retain a liquid. In many applications, gels hold big quantities of water inside the microscopic network. These materials are known as hydrogels. They can swell in water to an equilibrium volume while preserving their shape and transparency. The nature of polymeric network bonding and functional groups along the chains can be modified by the use of chemical agents, temperature, pH changes, amongst other factors. In general, macroscopic changes in the shape of hydrogel are reversible and produce materials that can be used as 'microscopic sponges' or systems that retain and deliver diverse chemical substances [1–3]. Polymeric hydrogels have many applications and are currently used in hygienic products, paints, food, agriculture, electronic devices, molecular filters and drug delivery systems [1, 4–9].

Nowadays there are just a few kinds of crosslinked hydrogels, which exhibit well-defined micro and macro structures simultaneously [10]. In this work we have developed hydrogels based on acrylamide and acrylic acid, with a singular structural behavior. These multi-structured hydrogels are hydrophilic, elastic, water insoluble, soft polymers with an anisotropic optical response. The structure of the gel is mainly influenced by the synthesis temperature. Structural changes can be detected by thermodynamic and calorimetric techniques. The latter ones are suitable, practical and faster for this determination. Since the 70's, DSC has long been a valuable and powerful technique for many studies of thermal behavior, phase transitions and enthalpies of formation [11–17] and specifically in the analysis of melting and crystallization behavior, as well as the morphology of polymers [18–21]. However, the interpretation of the DSC curve is frequently ambivalent mainly for polymeric systems. TMDSC has been established as an alternative technique to conventional DSC because it allows to obtain more information on thermal transitions [22–26]. Moreover, this experimental method is used to analyze how thermal events relate to the structure of the material, e.g. in polymers [27–30]. The possibility of directly observing the morphological changes of the sample by only measure changes on heat capacity (C_p) as a function of the temperature are an advantage over other techniques [31]. Thermodynamic transition can be identified by discontinuities on properties as C_p or $(\partial C_p/\partial T)_p$ and are reflected as a structural transition (e.g. second or third order transition) [32–37].

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The analysis of thermal and structural properties of hydrogels provides an insight on their macroscopic behavior and final applications. Multi-structured hydrogels can be used as delivery drug systems [1, 2], actuators [9], in bio-molecular separation [38], templates for micro and mesoporous materials, agriculture [39, 40], etc. The hydrogels used in this work were synthesized by aqueous solution polymerization between acrylic acid and acrylamide [41]. The micro/meso/macro structured hydrogels were synthesized following a strict thermal history. Morphological characterization of the samples shows evidence of well-defined structures at different length scales (10^{-6}, 10^{-4} and 10^{-2} m). The structure was observed by SEM, PLM and macroscopic visualization (CCD camera). Additionally, the energy of structural transition was evaluated by a modulated differential scanning calorimeter. Severe heating tests were also performed on these materials. In order to determine the feasibility of the gels for special applications, FTIR spectroscopy was used to qualitatively evaluate material decomposition after thermal treatment of the hydrogel samples.

Experimental

Materials

The monomers acrylamide, AM and acrylic acid, AA (purum, 98%), and the initiator system composed by $K_2S_2O_8$ (purum, 99%) and $NaHSO_3$ (puriss.) were purchased from Aldrich Chemical Co. Diglycidyl acrylate (DGA, 90% purity) used as cross-linking agent was purchased from Mexicana Industrial.

Each hydrogel synthesis was carried out in aqueous solution polymerization between the acrylic acid and the acrylamide. The concentrations of cross-linking agent ranged between 0.5–10 mass%. The reaction systems were prepared using acrylamide/acrylic acid (25/25 mass%) in bidistilled and deionized water and the pH was adjusted to a neutral value with 0.2 M KOH solution. The polymerization was initiated by the redox reaction system using 3 mL of a solution (0.1 mass%) of $K_2S_2O_8$ and 3 mL of another solution of $NaHSO_3$ (0.1 mass%).

Methods

Two thermal histories were followed for the synthesis of the hydrogels. In one of them, all components except the initiator were mixed at 298.15 K, homogenized, and then the initiator was added. The system temperature rose to 398.15 K (method 1). On the second approach, all components except the initiator were mixed at 273.15 K, homogenized and left to rest during 24 h at that temperature. Suddenly, the temperature was changed to a preset value, i.e. 293.15 K, and then the initiator was added and the polymerization temperature was controlled (method 2).

Morphological microscopic characterization was carried out using a JEOL JSM 5400 LV SEM, operated at 50 kV. The mesostructure was observed by PLM, with a glucose solution as contrast media, using an Olympus BX50-P polarized light microscope, with a thermostated mechanical stage and a 10× objective lens. The macrostructures were observed with a charge-coupled device (CCD) camera.

The thermal characterization of the hydrogels was carried out using a TA Instruments DSC Q100 differential scanning calorimeter. Measurements were acquired at a scanning rate of 0.1667 K s^{-1}. Commercial pans for solid samples (TA-instruments, T50826 and T51007) were used with 4 or 5 mg of hydrogel. Microscopic rearrangements in the polymer were detected as structural changes, by means of the measurements of heat flow and heat capacity as a function of temperature from scans between 283.15 and 573.15 K. Thermal macroscopic behavior was analyzed using an electric FELISA® oven (with a K-type thermocouple) with 5 g of hydrogel, which was heated to 573.15 K and maintained at this temperature for 4 h.

FTIR spectra were acquired using a Perkin-Elmer Spectrum One FTIR spectrometer. Collected spectra consisted of 300 scans at a resolution of 2 cm^{-1} using a TGS detector. Mass measurements were performed with an Ohaus Explorer EP214 analytical balance.

Results and discussion

The morphological characterization of the samples synthesized by method 1 (without temperature control) revealed hydrogels with no structure. SEM showed flat surfaces, and macroscopically the material obtained looked like plastic foams. On the other hand, method 2 resulted in the production of well defined structures at different scales as we can see Fig. 1a, which reveals a surface with a three-dimensional ribbon-like microstructure with multiple folds with a thickness of 5 μm and length of 100 μm. Figure 1b shows a micrograph obtained by PLM, which once again exhibits regular structure with geometrical shapes that bulge out the surface, at a scale of 10^{-4} cm. Finally, Fig. 1c illustrates a three-dimensional regular structure of a hydrogel sample after 3.5 h in contact with water. The structure is formed by cells-like blocks of 0.5 cm of length.

Hydrogels produced by methods 1 and 2 were analyzed by TMDSC in order to confirm structural changes. The results are shown in Fig. 2. It can be observed from this figure that there is not a significant change in heat flow ($\delta Q/\delta t$) for the hydrogels ob-

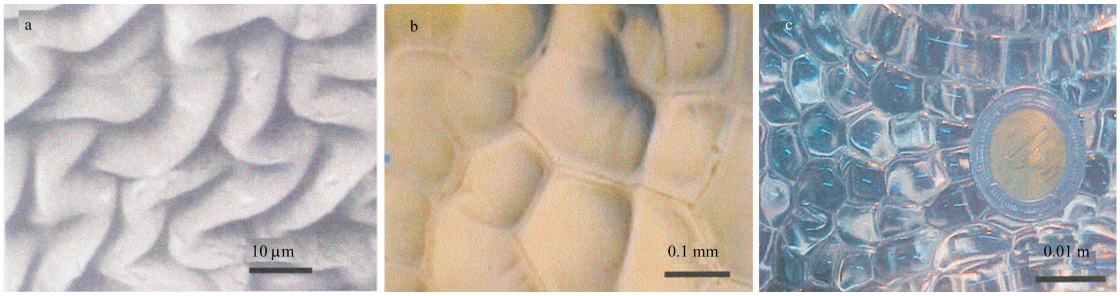

Fig. 1 Hierarchical structure of hydrogels obtained by method 2, a – microstructure by SEM, b – mesostructure by PLM and c – macrostructure CCD camera

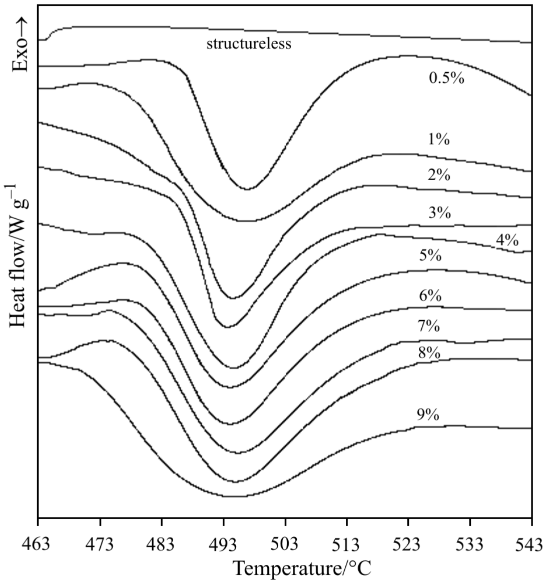

Fig. 2 TMDSC diagram of heat flow as function of the temperature for the synthesized hydrogels by method 1 (structureless) and for all concentrations of DGA (method 2)

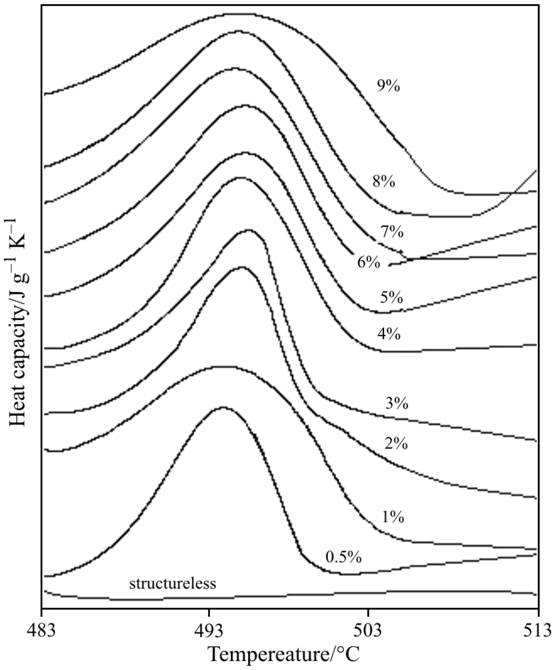

Fig. 3 Heat capacity as function of temperature and DGA content

tained by method 1, however, a slight energy absorption can be observed for method 2. This absorption was about 35–40 J g^{-1} near 493.15 K, for all experiments and crosslinking agent percentages, showing no dependence on DGA content. This energy can be attributed to the fact that the hydrogels synthesized were cross-linked polymers; therefore the absorbed energy is not needed for fusion (first order transition), but rather for structure rearrangement. From the morphological observations it can be concluded that the hydrogels have characteristic structures at different scales, or a hierarchical structure. Also, it can be inferred that when a hydrogel is placed at high temperatures, the free chains are induced to join the main polymer network, causing a rearrangement similar to that classic polymer crystallization. Furthermore, C_p changes were registered at the same temperature of

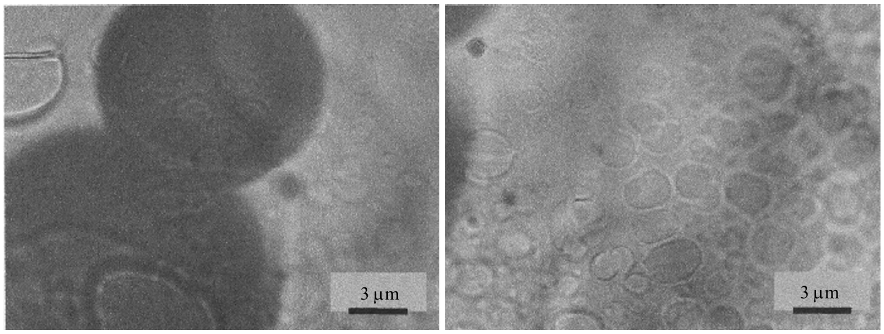

Fig. 4 Mesoscopic photographs after dynamic scans by TMDSC

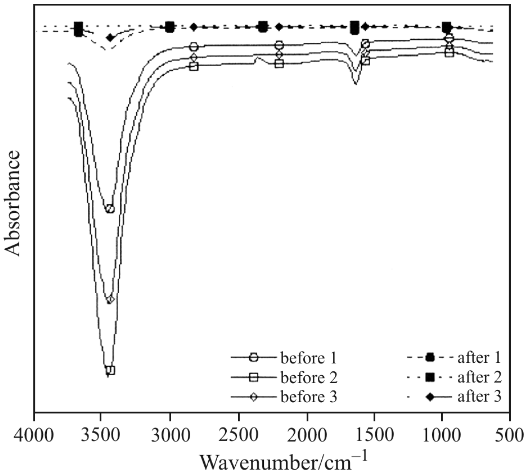

Fig. 5 FTIR spectra before and after severe thermal treatment

493.15 K (Fig. 3). From this information, we evaluated $(\partial C_p/\partial T)_p$, which represents another thermodynamic criterion for second or third order transitions, and observed that at 493.15 K exist a discontinuity as function of temperature, which confirms that there is a structural change at this temperature. This phenomenon was found to be non-reversible, as evidenced by a second TMDSC scan, which included a reverse scanning, and no signal was detected for this step. There is no correlation between the percentage of crosslinking agent and energy absorption, so it can be concluded that the transformation occurring at the detected absorption energy was due to a microscopic structural rearrangement.

All TMDSC experiments were carried out to a maximum of 573 K, temperature at which the material

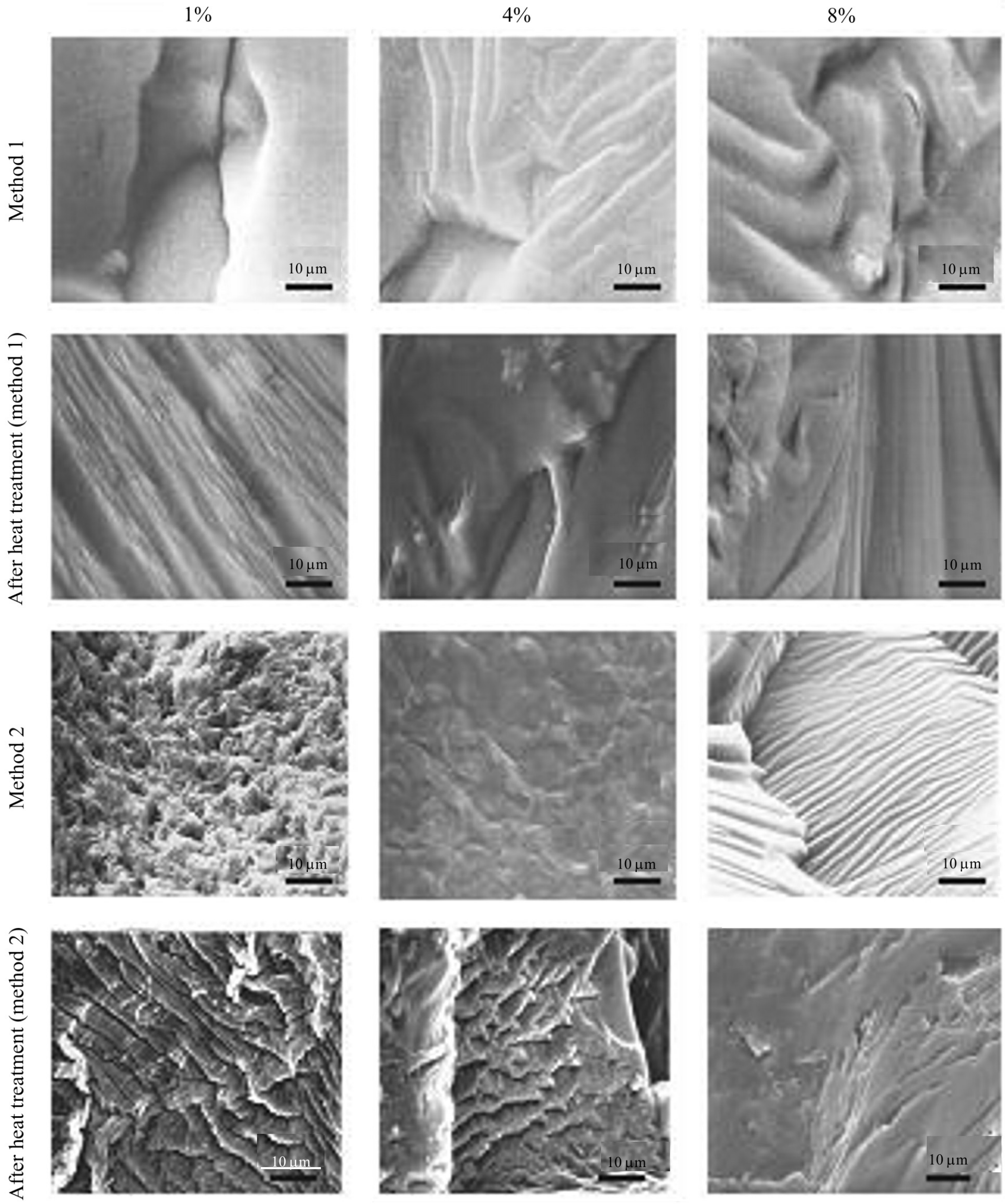

Fig. 6 SEM micrographs as function of DGA content (without temperature control for method, and with temperature control for method 2)

degraded, but part of the hydrogel preserves certain properties, thus creating a sponge-like material. Figure 4 shows the mesoscopic structure by PLM of the materials after the temperature scans, detecting that the hydrogel preserves some structure, and spherical shadow pores are created due to decomposition of the material.

In order to analyze the macroscopic thermal behavior and hydrogel decomposition, severe heating treatment was executed in the adiabatic oven. FTIR spectra were collected before and after severe heating treatment. Figure 5 shows IR spectra in the 500–3800 cm^{-1} range for three hydrogel samples. Two characteristic absorptions can be observed, at 3200–3400 and 1650 cm^{-1} corresponding to $–NH_2$ group, and at 1650–1800 cm^{-1} corresponding to the C=O group. The results show changes on these peaks, which means that when the material decomposes, it is mainly by the formation of CO_2 from the C=O moieties and ammonia from amines. Due to the liberation of these gases, a sponge-like material was obtained at the end of thermal treatment (big pores observed in Fig. 4). Furthermore, we obtained SEM micrographs (Fig. 6) for the different contents of crosslinking agent, as well as, before and after severe heating testing for both synthesis methods. In the figure it can be observed that at microscopic scale part of the material is not decomposed, but the original characteristics are lost.

Conclusions

Polymeric hydrogels based on acrylamide and acrylic acid under controlled polymerization temperature exhibit well-defined micro, meso and macrostructures. The temperature is a critical parameter in order to obtain hierarchically structured hydrogels, since the thermal behavior and creation of structure of the materials strongly depends on the synthesis conditions. The obtained hydrogels showed energy absorptions of microscopic rearrangement, which corresponded to a structural third order transition evaluated from TMDSC measurements. This rearrangement transition is similar to polymer crystallization and there is no dependence on the quantity of crosslinking agent. Severe change of temperature in the material triggers polymer chains rupture and functional groups like $–NH_2$ and C=O react causing the decomposition of the material.

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