Elasticity Study of PAAm-κC Composite Prepared in Various κC Content and Measured at Several Temperatures

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Polyacrylamide (PAAm)-kappa carrageenan (κC) composite gels were prepared via free radical crosslinking copolymerization with various (w/v) percentages of κC in the range between 0.5 and 3 (w/v)% of κC. Elasticity properties such as stress, strain and compressive elastic modulus, S of these composite gels were studied in various κC content and at several temperatures. The content and temperature dependence of the compressive elastic modulus, S of the swollen PAAm-κC composite gels due to volume phase transition were produced by using tensile testing technique. It is understood that the compressive elastic modulus was found to decrease up to 1 (w/v)% of κC, and then increase by increasing κC contents, at constant temperatures. The composite preserves the ability to undergo the volume phase transition and its compressive elastic modulus is found to be strongly dependent on the κC content and temperature. It is observed that the compressive elastic modulus increased when temperature is increased up to 40 °C and then decreases below this temperature for all composite gels. However, PAAm-κC composite gel presented lower values for the compressive elastic modulus, showing a minima at 40 °C for 1 (w/v)% of κC content gel.

1. Introduction

Composites have attracted much interest from the point of view of improving the tissue tolerance because of their biocompatibility, biodegradability and non-toxicity, polysaccharides such as carrageenan, alginate and agar. Carrageenans are synthesized by natural based polymers [1]. Carrageenans are sulfated D-galactans extracted from red algae. The κ-carrageenan (κC) is characterized by an alternating disaccharide of α-1, 3-linked D-galactopyranose and β-1-linked 3, 6-anhydro-D-galactopyranose [2]. The presence of hydrophilic sulfate groups with high ionization tendency and less sensitivity to salt solution is the main concept for synthesis of carrageenan based hydrogels. Polyacrylamide (PAAm) hydrogels are usually prepared by copolymerizing acrylamide with the cross-linking monomer in aqueous solution. It is well known that properties of composites depend on the several conditions such as temperature, the ratio of monomers and crosslinker and so on.

The mechanical properties and the swelling behavior of aqueous poly(acrylamide) and poly(acrylamide-Na-acrylate) were investigated [3]. The elastic modulus of such ionic gels did not show decrease with rising swelling ratio, but on the contrary increased up to a fivefold of its value. This behavior was explained by non Gaussian behavior in the network chains. At constant swelling ratio, the modulus of the gels having identical topology decreased with rising degree of hydrolysis. This reflects the influence of the ionic groups on the mean square end to end distance of the free polymer chains. Elastic properties of highly crosslinked polyacrylamide gels have been studied [4]. The elastic modulus was found to increase exponentially with total comonomer concentration, and the modulus passed through a maximum as the crosslinking agent was increased. Compression elastic modulus measurements of neutral, ionic and amphoteric hydrogels based on N-vinylimidazole were performed [5]. A non-Gaussian parameter (β) was introduced to explain that the elastic moduli (G) of samples swollen at equilibrium are larger than predicted by the Gaussian model. Comparison of theory with experiments and relationship between stress, strain, and molecular constitution of polymer networks was developed by Erman and Flory [6].

A review of modeling techniques for predicting the mechanical behavior of polymer nanocomposites was presented [7]. A detailed discussion of computational chemistry and computational mechanics modeling techniques was given. Viscoelastic behavior of carrageenan/milk mixtures was studied at different type of carrageenan types [8]. Iota and kappa carrageenan only have attractive interactions with casein micelles at temperatures below the coil-helix transition temperatures, since only the helix form has a high enough charge density. At higher temperatures the iota and kappa carrageenan/milk systems undergo depletion induced segregative phase separation. Sulphated polysaccharides(kappa- and iota-carrageenan) and sodium alginate added to blue whiting mince were subjected to three different pressure/heat treatments in order to determine the functionality of each one in mince gel [9]. Higher pressure conditions (375 MPa, 37°C, 20 min) induced gels with the lowest

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hardness. The carrageenans (iota or kappa) appeared to form a reticular structure in the heat induced gels. The extraction parameters (pH, temperature, and extraction duration) of seaweeds had been systematically varied in order to produce $k/\imath$- hybrid carrageenans exhibiting a wide range of chemical properties [10]. The relationships between the thermal properties and elasticity of the gels were extensively studied. The compressive elastic modulus and toughness of the swollen PAAm-MWNT composites were studied by us [11], where it was showed that the addition of carbon nanotubes induced and improved elasticity by increase of the temperature from 30 to 60 °C.

In this work, the compressive elastic modulus of the swollen PAAm-κC composites was measured to determine the role of the κC content and temperature on the elasticity. Firstly, elasticity of PAAm-κC composites was characterized by adding different (w/v) percentage of κC. Secondly, tensile testing measurement was performed at a range of temperatures between 25 and 60 °C. The modulus was calculated by means of the model polymer networks [5]. In addition, it was observed that compressive elastic modulus presented lower values at all temperatures for 1 (w/v)% of κC content gel composite, showing a minima at 40 °C.

2. Experiment

2.1. Preparation of PAAm-κC Composites

PAAm-κC composites were prepared by free radical copolymerization as follows: 0.71 g of AAm (acrylamide, Merck), 0.01 g of MBA (N, N'-methylenebisacrylamide, Merck), 0.008 g of APS (ammonium persulfate, Merck) and 2 μl of TEMED (tetramethylethylenediamine, Merck) were dissolved in 5 ml distilled water by heating. The heated mixture solution was held at 80 °C. Then varying percentages (0.5, 1, 1.5, 2, 2.5, and 3 (w/v)% of κC were added. The solution was stirred (200 rpm) for 15 min to achieve a homogeneous solution. All samples were deoxygenated by bubbling nitrogen for 10 min just before the polymerization process [12].

2.2. Mechanical characteristics measurements

After gelation, the composites prepared with various molar monomer percentages were cut into discs with 10 mm in diameter and 4 mm thickness. Before the compression measurements, the composites were maintained in water at different temperatures to achieve swelling equilibrium. A final wash of all samples with distilled water was carried out for 1 week, at a desired temperature to remove unreacted monomers and to allow the gel to achieve swelling equilibrium. The mechanical experiments of the PAAm- κC composites were performed at temperatures of 25, 30, 40, 50, and 60 °C, respectively. A Hounsfield H5K-S model tensile testing machine, settled a crosshead speed of 1.0 mm/min and load cell of 5N sensibility were used to perform uniaxial compression experiments on the samples of each type of composites.

Figure 1 shows the behaviors of 0.5 (w/v)% of κC in the copolymer before and after applying the uniaxial compression. Figure 1a corresponds to initial state, i.e., zero loads and, Fig. 1b presents the gel under 5N, respectively. Loss of water and changes in temperature during the measurements were not detected because the compression period was less than 1 min. There was no deswelling during the compressive deformation stage, which means that our experiment corresponds to the case in which we can assume a compressive elastic modulus, S.
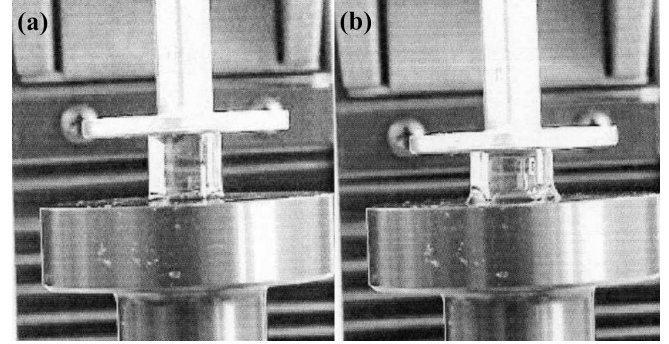

Fig. 1. Compression process of (w/v)% of κC (a) initial (f = 0.0 N) and (b) final states (f = 5.0 N), respectively.

3. Results and discussion

Forces (f) or loads corresponding to compression (mm) were obtained from the original curves of uniaxial compression experiments. The force, f(N) versus compression (mm) curves for 1 and 2 (w/v)% of κC contents at 50 °C are shown in Fig. 2a, where it is seen that the repulsive force between monomers increases rapidly when the bond length is shortened with respect to the equilibrium position. It is also seen that when κC content is increased to higher values, then repulsive force increased as presented in Fig. 2a.

The compression measurements were analyzed through plots of the applied stress, τ, ($\tau = f/A$ with f being the acting force and A — the cross-section of the undeformed swollen specimen) versus $\lambda - \lambda^{-2}$, where $\lambda = L/L_0$ is the relative deformation caused by compression of the length of the swollen sample along the direction of the stress (L), with respect to the initial length (L_0) of the swollen but undistorted sample. They show the typical curvature at the smallest range of deformation that is generally assigned to imperfect geometry of the surface of the gel specimen [5]. The elastic modulus was determined by linear regression, as the slope of such plots as given in Eq. (1):

$$S \approx \frac{(f/A)}{\alpha - \alpha^{-2}}. \tag{1}$$

Stress (Pa)–(α–α^{-2}) plots were drawn by using the data obtained from the plots of f(N) versus compression curves for 1, and 2 (w/v)% κC contents at 50 °C in Fig. 2b.
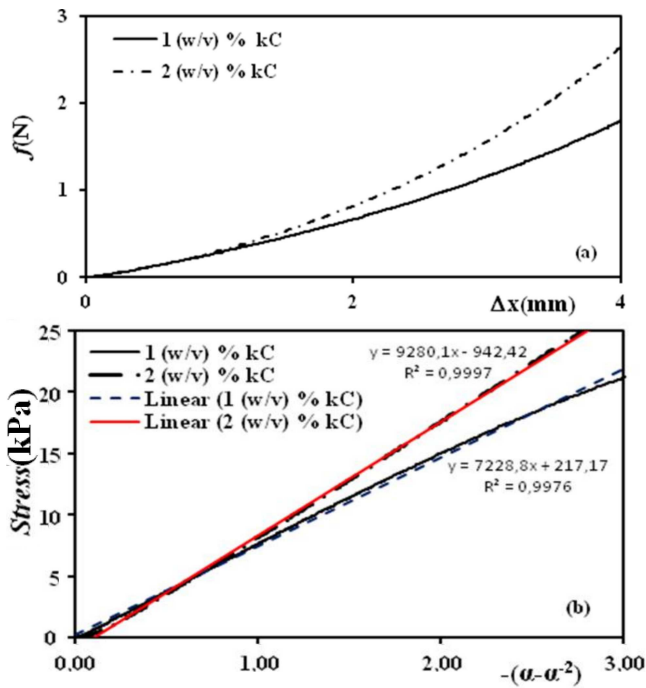
Fig. 2. (a) The force $f(N)$ and compression (mm) curves, and (b) stress and $-(\alpha-\alpha^{-2})$ curves for 1 and 2 (w/v)% of κC contents at 50 °C, respectively.

Pure PAAm gel is found to possess approximately twice larger modulus than PAAm-κC composite sample at 1 (w/v)% of κC which is the minimum value for the composite. It is also seen in Fig. 2b that 1 (w/v)% of κC content composite present smaller initial slope than 2 (w/v)% of κC content composites and the stress of 2 (w/v)% of κC in the composite increases dramatically where the κC monomers are in change of this behavior. In this case, it appears that an increase in the viscosity of the medium hinders the movement of free radicals and monomers molecules and enhanced the chance of chain transfer between PAAm and κC molecules [13] which play an important role for getting the different onset behavior.
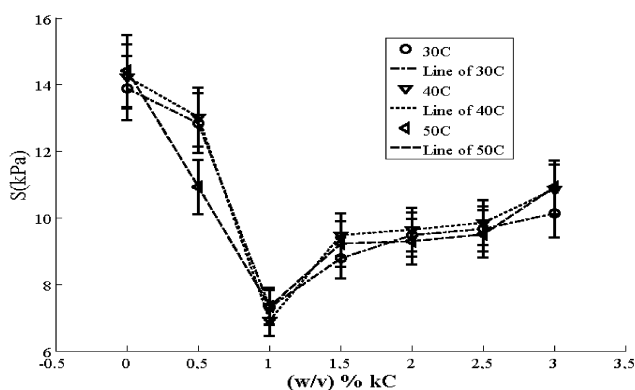

Fig. 3. Effect of various (w/v)% of κC on the compressive elastic modulus of PAAm-κC composite at 30, 40, and 50 °C, respectively.

Figure 3 shows the plot of compressive elastic modulus, S versus (w/v)% κC content in the composite, where compressive elastic modulus decreases up to 1 (w/v)% of κC content, and then increases with increase of (w/v)% of κC content, indicating that there is a sudden change in the material elasticity at 1 (w/v)% of κC content composite. The change in S predicts that the copolymers have reached a super elastic percolation network above 1 (w/v)% of κC content composite [14]. The reason behind the changes of compressive elastic modulus, S as shown in Fig. 3 can be explained by increase of κC content which enhances the hydrophilicity network below 1 (w/v)% of κC content.

In addition, the hydrophobicity of network significantly improves the stress relaxation of the composite above 1 (w/v)% of κC content due to its small size in the hydrated state when the double helices can cluster together; this promotes the aggregation, which improves the elasticity of the composite structure. This must suggest that the viscose medium has a network structure with flexible polymer chains just as swollen medium [15]. Lastly, as it was predicted, the elastic properties of PAAm-κC composite are highly dependent on the (w/v)% of κC content, which directly influences monomer interactions between PAAm and κC in the composite. Such monomer interactions will play a critical role in load transfer and interfacial bonding that determines elastic properties of the composites. The variations in the κC content in the resultant composite could be the major reason for this phenomenon. In addition, lower κC (below 1 (w/v)% of κC) content enhances the hydrophilicity of the hydrogel in PAAm-κC composite. A further increase in κC content (above 1 (w/v)% of κC content), however, results in decreased absorbancy [15]. This is probably due to an increase in the viscosity of the medium, which hinders the movement of free radicals and monomers molecules and the enhanced chance of chain transfer between PAAm and κC monomer molecules [13]. Thus, κC can show a significant effect in the PAAm-κC composite. This is due to its small part in the hydrated state when the double helices can cluster together, which results in higher elasticity of the composite system [16].

The force, $f(N)$ versus compression (mm) curves at 30 and 40 °C for 2.5 (w/v)% of κC are presented in Fig. 4a. It is seen in Fig. 4a that when temperature increases for high κC content composites, then repulsive force presents larger numbers. This is because the repulsive interaction between monomers of composites of the swollen state is much stronger than that of the collapsed state. In other words, the composites are easily affected by deformation [17].

Stress (Pa)–$(\alpha-\alpha^{-2})$ plots for 2.5 (w/v)% of κC content composites were drawn in Fig. 4b by using the data observed in the plots of $f(N)$ versus compression curves in Fig. 4a at 30 and 40 °C, respectively. The stress for the 2.5 (w/v)% of κC composites at 40 °C increases dramatically. From above observations it can be predicted that the stress as well as the composite content can affect

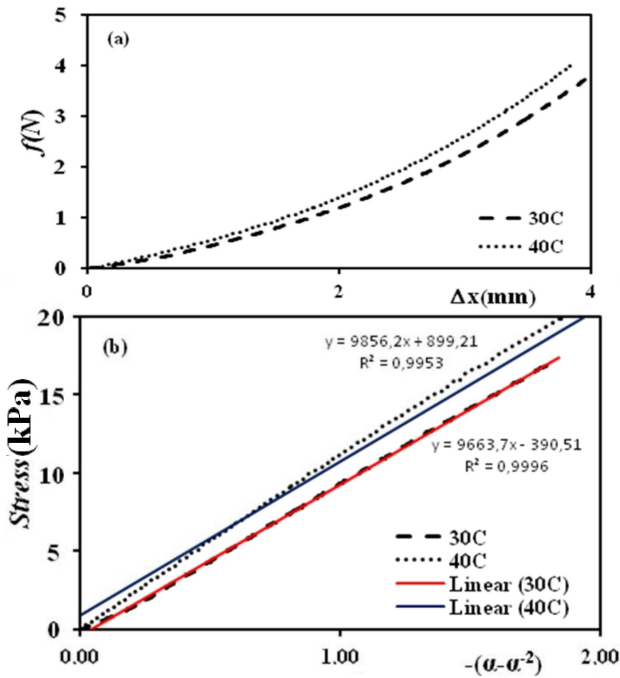the stability of stress–$(\alpha-\alpha^{-2})$ curve and thus enhance the transverse interchain interaction [17].

Fig. 4. (a) The force f(N) and compression (mm) curves and (b) stress versus $(\alpha-\alpha^{-2})$ curves for 2.5 (w/v)% of κC contents at 30 and 40 °C, respectively.
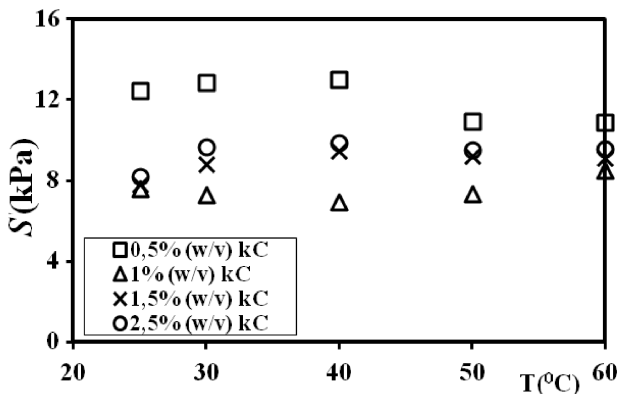

Fig. 5. Effect of temperature on the compressive elastic modulus of PAAm-κC composite for 0.5, 1, 1.5, and 2.5 (w/v)% of κC content composites, respectively.

The compressive elastic modulus, S of various (w/v)% of κC contents composites at several temperatures were produced from the linear regions, observed from the plots of stress–$(\alpha-\alpha^{-2})$ curves which are shown in Fig. 5. The modulus for all composites increases up to 40 °C, and then decreases between 40 and 60 °C, κC presenting maxima at 40 °C. However, compressive elastic modulus presented a minimum at 40 °C, for 1 (w/v)% of κC content sample. The change in compressive elastic modulus in the initial stage may originate from the greater availability of monomer molecules in the vicinity of the chain

propagating sites of κC in PAAm-κC composite. Because these gels were recognized to be affected by the alkaline hydrolysis which can be explained by the low osmotic pressure that increases up to 40 °C, then decreases again from 40 °C to 60 °C. Practically, most of acrylamide-based polymers are actually partially hydrolyzed to introduce some carboxylic groups into the chain. The presence of these charged units improves water solubility and increases hydrodynamic volume of the chain due to the mutual repulsion of the negative charges. In other words, the presence of κC in the PAAm gel at 40 °C creates larger water absorbing volumes, which then result in maximum compressive elasticity for below and above of 1 (w/v)% of κC content composites [14, 18, 19]. On the other hand, the behavior of S for the 1 (w/v)% of κC content composite can be understood by the super elastic network property of the gel system [14].

4. Conclusion

Tensile testing technique can be used to define the elastic behavior of PAAm-κC composite for various (w/v)% of κC content. This technique was employed to measure force versus compression, and $-(\alpha-\alpha^{-2})$ for the composite. It is important to note that compressive elastic modulus of the composite is much higher for low (below 1 (w/v)% of κC) and high κC (above 1 (w/v)% of κC) content regions of the composite, producing a critical value at 1 (w/v)% of κC content.

The temperature effect on the elasticity of PAAm-κC composites was also studied. It is observed that the low compressive elastic modulus was achieved at 40 °C and 1 (w/v)% of κC content. On the other hand, high compressive elastic modulus was obtained below and above 1 (w/v)% of κC at 40 °C. The elasticity of the composites was recognized to be affected by the alkaline hydrolysis and osmotic pressure, in turn, results in carboxylate anion increment and consequently, absorbancy enhancement.

Acknowledgments

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