Analysis of a Hydrogel using both a Q-Series and a Nano DSC

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Abstract

Gelatin-based hydrogels consist of a mixture of water-soluble polypeptides and are generally used in the food, cosmetics, pharmaceutical and biomedical industries. The hydrogel formation mechanism of gelatin, which is also called gelation, results in the formation of a physical network through hydrogen bonding. Using Differential Scanning Calorimetery (DSC) it is possible to determine the energy released or absorbed by gel formation or melt, respectively. TA Instruments manufactures many DSC models that differ in design and sensitivity that can be used for the same application. Heat flow results obtained on two DSC models, Q2000™ and Nano DSC™, using a common gelatin material will be demonstrated.

Introduction

Hydrogels are generally made from natural or synthetic polymers dissolved in aqueous solution. Natural gelatin consists of a mixture of water-soluble polypeptides of high molecular weight derived from collagen. The water content of a hydrogel material can be as high as 99%. In industry, hydrogels are mainly used in drug delivery systems, as tissue scaffolds, in wound healing patches, and in food and cosmetics products.[1-7] Upon cooling a gelatin solution to lower temperatures, a hydrogel can form by polypeptide chain association, which results in the formation of more rigid triple-helix structures.[8] This gelation mechanism is usually a thermo-reversible process. When the gelatin-based hydrogel is heated, the helical structure dissociates and the gel 'melts' or collapses.[9]

Depending on the gelation mechanism, a hydrogel can have diverse thermal and mechanical properties. For consistent hydrogel formation it is important to understand the chemistry of gelation and be able to quantitatively analyze these properties. Analytical techniques such as thermal analysis (e.g., DSC) and rheology can be utilized to better understand the properties of gelatin hydrogel formation.

Experimental

Dry gelatin [type A from porcine skin] powder was purchased from Sigma Aldrich (Milwaukee, WI). Type A gelatin is derived from acid-cured tissue with an average molecular weight of 40,000-50,000. Gelatin solutions were prepared in warm (approx. 60 °C) reagent grade deionized water (Ricca Chemical Co., Arlington, TX) at concentrations ranging from 1-10 % w/v.

The Nano DSC™ was equilibrated at 60 °C and the gelatin solution was warmed to ~60 °C prior to loading the sample capillary cell. Deionized water was loaded into the reference capillary. Following pressurization to 3 Atm, the Nano DSC™ was programmed to first cool the sample to 1 °C and then reheat to 60 °C at 1 °C/min.

The Q-Series DSC, Q2000™, and the Nano DSC™ were used to analyze the gelation and melt transitions of the hydrogel. For the Q2000™ experiments, warm gelatin solutions weighing between 5-20 mg were loaded into Tzero® hermetic pans and sealed. An empty pan served as the reference. The Q-series DSC was equilibrated at 80 °C, then cooled and reheated at 5 °C/min between 80 and -10 °C.

Results and Discussion

Gelatin hydrogels form by thermally reversible polymer chain association. DSC was shown to be a useful tool to determine the energies of the gelation process. Figures 1 and 2 display the gelatin solution heating and cooling results, respectively, obtained on a Nano DSC™. The heat flow signals are not baseline-corrected, but are offset on the Y-axis for presentation. There is a large concentration-dependent shift in the gelation transition upon cooling (10-19°C) compared to the melt transition upon heating (25-27°C). These results indicate that there is a concentration-dependent effect on the gelation mechanism, which can be explained by the need of three polypeptide chains to associate for gel formation.[9] When melted, the helical structure of gelatin totally dissociates and the polypeptide chains revert to random coils.[9]

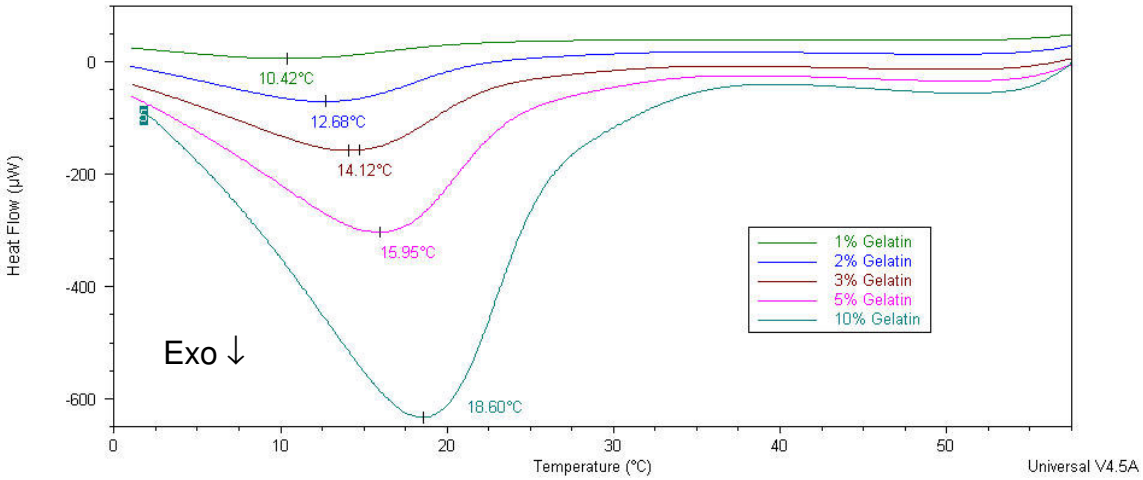

Figure 1: Nano DSC™ cooling segment

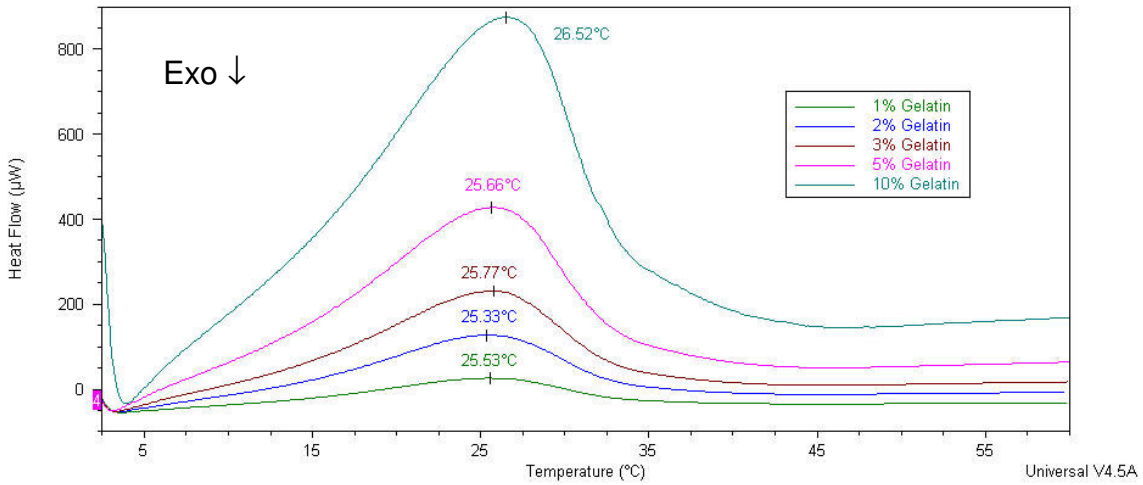

Figure 2: Nano DSC™ heating segment

Figures 3 and 4 show the gelatin solution temperature ramp results obtained on a Q2000™. Upon cooling (Fig. 3), the gelatin solution forms a hydrogel below 22-24°C. Since the formation of the triple-helix is a kinetically controlled process, higher cooling rates result in lower temperature transitions compared to those observed from the Nano DSC, whereas the melt transition (Figure 4) is relatively unaffected (~28-30°C). Using these conditions, the Q-Series DSC could detect the gelation/melt processes at a sample concentration of 3% w/v.

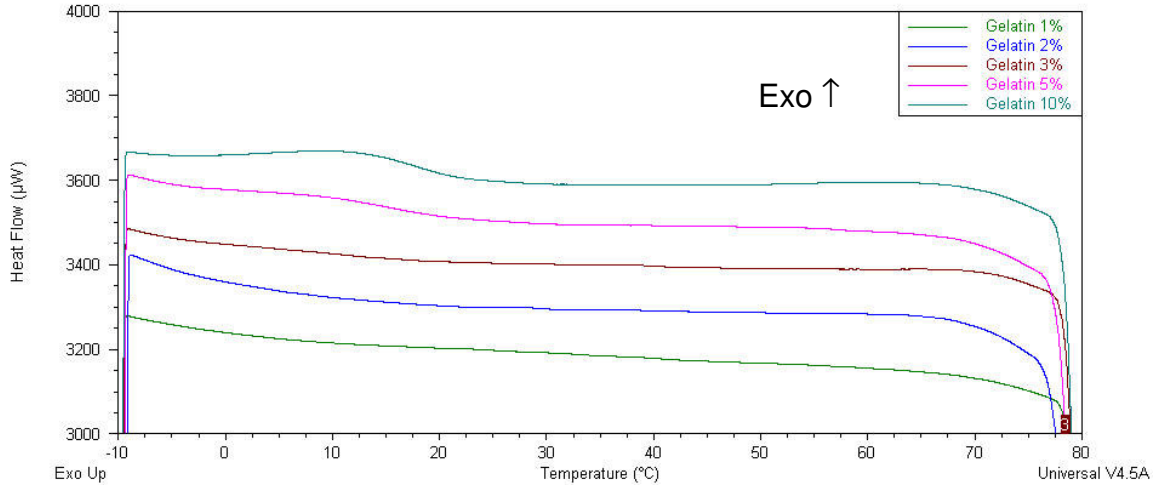

Figure 3: Q-series DSC cooling segment

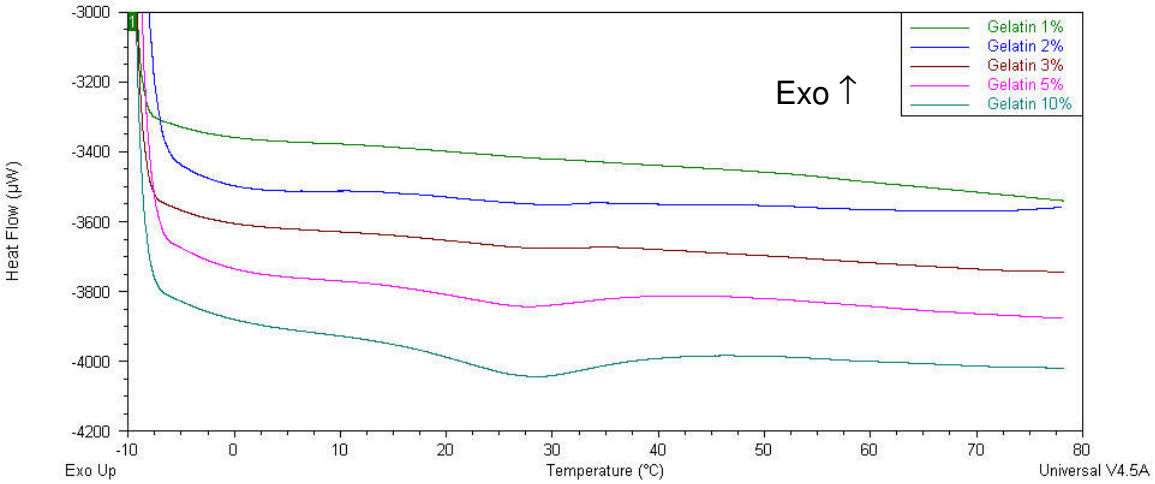

Figure 4: Q-series DSC heating segment

Conclusions

In order to better understand the thermal properties of hydrogels such as gelatin, thermal analysis techniques can be used to monitor gel formation and melting processes at different temperatures. DSC is a useful technique for studying the enthalpic properties of hydrogel materials, but as the above results demonstrate, choosing the correct DSC greatly impacts the level of information obtained. The choice of instrument will highly depend on the nature of the sample and magnitude of the transition of interest. The sensitivity of the Nano DSC allows transitions to be detected at lower concentrations and heating rates. The data shows that gelatin gelation is kinetic in nature, as identified by the effect of both scan rate and concentration.

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