

ABSTRACT

Water absorption in hydrogels and other biological materials is important to understand for such applications as tissue engineering, wound dressing, and implanted medical devices. In this application note a thermal analysis method used to evaluate moisture absorption and content of different forms of water in polymers using TA Instruments' Q Series™ DSC with Advanced Tzero™ Technology is described. An amphiphilic co-network is used to demonstrate the analysis procedure.

INTRODUCTION

The states of water in a polymer give valuable information on the absorption, diffusion and permeation properties of hydrophilic materials. The mechanical and physical properties of hydrophilic materials can change significantly upon water absorption due to the modification of the polymer chain structure. Differential scanning calorimetry (DSC) is commonly used tool to conduct such studies. Nuclear magnetic resonance spectroscopy (NMR)¹ and Infrared spectroscopy² are also performed to give more complete information. Due to phase transition behavior and molecular mobility^{3,4} during the interaction between water and polymer molecules, three forms of water are classified: (i) non-freezable water, (ii) freezable bound water and (iii) free water. Nonfreezable bound water is closely associated with a polymer matrix and does not show a phase transition by calorimetric analysis. Freezable bound water is the fraction bound to the matrix less closely and shows a melting and crystallization temperature remarkably different from bulk water. Free water shows similar melting/crystallization temperatures as bulk water. Besides the difference in the phase transition detected by DSC, wide angle X-ray diffraction analysis reveals that the basic difference is that bound water forms cubic ice and free water formed hexagonal ice upon crystallization.⁵ Moreover, a study conducted by Yoshida showed bound water forms metastable ice when crystallized by slow cooling but forms amorphous ice when quenched.⁶

All considered, melting, crystallization and glass transition (T_g) temperatures of water in hydrogels can reflect the state of the water-polymer interaction. In an amorphous polymer system,^{7,8} water that is absorbed into a polymer matrix can act as an effective plasticizer that increases polymer chain mobility and reduces the T_g . The glass transition depression behavior of hydrogels can be separated into four regions.⁹ Several mathematical models^{10,11} have been proposed to predict T_g of compatible blends of amorphous substances. This note demonstrates a simple but precise analysis on a model polymer network system.

EXPERIMENTAL

The polymer studied is an amphiphilic network containing various compositions of Polycaprolactone, PCL, and Polyethylene oxide, PEO. A range of compositions of amphiphilic polymers were dried under vacuum at room temperature overnight after synthesis. Samples were cut and weighed before and after immersing into deionized water for 24 h. Weight measurements were performed using three pieces of sample for each composition.

Hydrated amphiphilic polymer blends was sealed in a Tzero hermetic pans prior to analysis. Thermogravimetric analysis (TGA) was conducted prior with samples sealed in the hermetic pan to confirm no moisture leakage from the pan. The DSC temperature upper limit is set to 100 °C (according to prior TGA testing) in order to prevent any moisture leakage into the test chamber. DSC was performed on all compositions to investigate the transition temperatures and contents of different water states. The same heating and cooling rate were 10 °C/min for all runs.

RESULT AND DISCUSSION

DSC Analysis

First, dry sample DSC was conducted as a control group. In Figure 1, pure PCL and PEO networks exhibited sharp and single melting and crystallization transitions. However, phase separation was observed with 50%, 70%, and 80% PCL in the network system.

Upon hydration, the PEO phase becomes amorphous and all signs of melting or recrystallization disappear from the DSC traces. As displayed in Figure 2, melting and crystallization transitions both shift to lower temperatures for all compositions. At low PCL content, the crystallization peak disappears. Noticeably, a water crystallization peak in the cooling trace at ~20 °C gradually grows with decreasing PCL content indicating the hydrophilicity is increasing. Besides the water crystallization, hydrogels containing more than 50 wt% PCL are able to maintain the PCL crystallization peaks as well in the cooling cycle. The disappearance of PCL crystallization peaks indicate hydrogels with less than 50% PCL cannot crystallize or possibly merge with the water crystallization peak below room temperature.

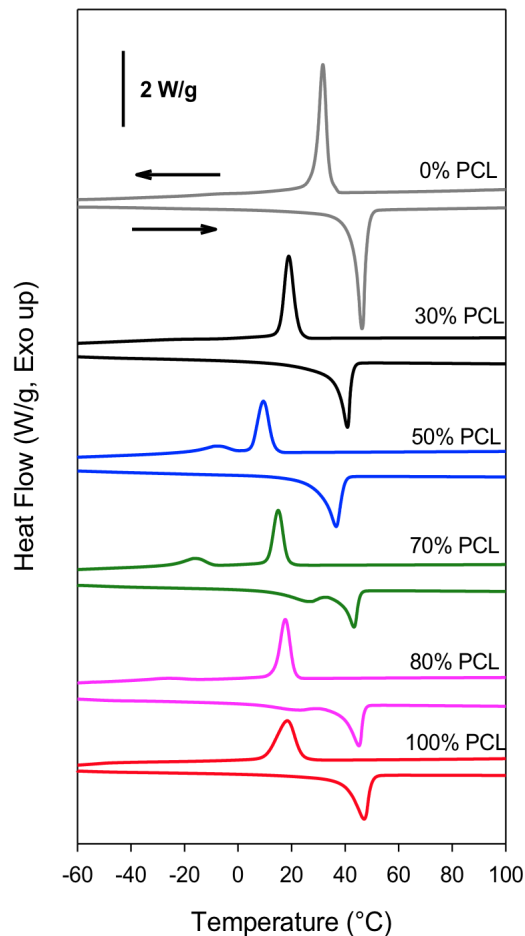


Figure 1: DSC thermograms of different compositions of dry amphiphilic networks.

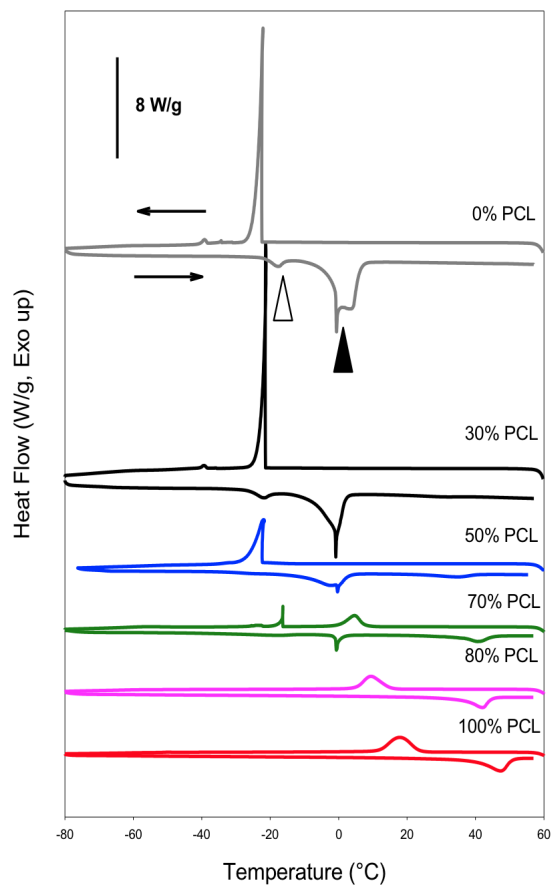


Figure 2: DSC thermograms of a water saturated sample. Heating and cooling rate were both 10°C/min. (Δ and ▲ indicate freezeable water and free water melting peak.)

Although two distinct water melting peaks around 0 °C and -20 °C are observed, only one sharp water crystallization peak appears in the cooling trace. According to the classification of three forms of water in the polymer, free water melts at 0°C and a water melting peak at -20°C is attributed to freezeable bound water. T_m of freezeable bound water is usually lower than bulk water due to hydrogen bonding, but changes slightly or remains constant with different polymer/ water mixtures². In some cases, a cold crystallization peak appears on the heating cycle for an intermediate water concentration range.^{6,12} That is mainly due to some water molecules unable to crystallize completely, yielding a higher fraction of water molecules that are non-freezable under the experimental condition.

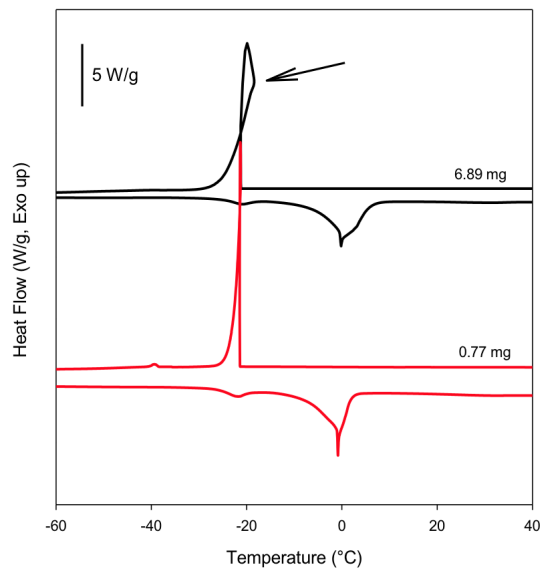


Figure 3: DSC thermograms of high water uptake sample with different sampling weight. (Arrow indicates the crystallization loop.)

With decreasing PCL content in the system, water crystallization around -20°C shows a significant artifact in the form of a large "loop" in the cooling trace, attributed to the large exotherm of water crystallization. To ameliorate this problem, one can lower the cooling rate or decrease the sample weight. Figure 3 demonstrates the latter approach to removing the loop.

Water Content Analysis

It is noted that the separation of free water and freezable bound water is very difficult to observe in the cooling cycle as they crystallize continuously. The large loop of water exotherms is also considered inappropriate for calculation. Therefore, heating traces are chosen to analyze water content. Two similar methods are presented in this application note. The first method is calculated using the following equations:

$$W_s(\%) = \frac{m_w - m_d}{m_d} \times 100\% \quad (1)$$

$$W_{fs}(\%) = \frac{\Delta H_{hydrogel}}{\Delta H_{m,H_2O}^{\circ}} \times 100\% \quad (2)$$

$$W_{nfs}(\%) = W_s - W_{fs} \quad (3)$$

where m_d is the initial dry weight before submersion, and m_w is the weight after 24 h hydration, $\Delta H_{m,H_2O}^{\circ} = 333.5(\text{J/g})$, $\Delta H_{hydrogel}$ is the summation of all the melting enthalpy in the heating trace of wet DSC. W_s is the swelling ratio. W_{fs} and W_{nfs} represent freezable water and non-freezable water content in the hydrogel.

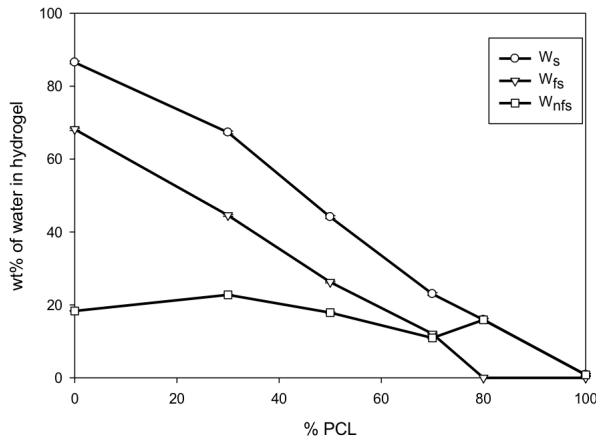


Figure 4: The distribution of different forms of water present in the hydrogels.

An alternative way to present the data is calculated in a similar manner as follows:

$$W_c(\%) = \frac{m_w - m_d}{m_d} \times 100\% \quad (4)$$

$$W_f(\%) = \frac{m_f}{m_d} \times 100\% = \frac{\Delta H_{hydrogel}}{\Delta H_{m,H_2O}^{\circ}} * (W_c + 1) \quad (5)$$

$$W_{nf}(\%) = W_c - W_f \quad (6)$$

Here, W_c is water uptake, m_f is freezing water weight in hydrogel. W_f and W_{nf} represent freezable water and non-freezable water content in amphiphilic polymers.

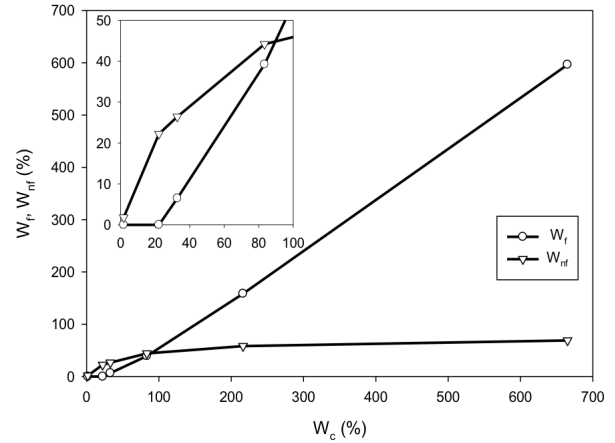


Figure 5: The relationship between amount of freezable water (W_f), non-freezable water (W_{nf}) and water uptake (W_c) in the polymer system. The inserted window shows detail with low W_c .

In Figure 4, it is evident that with increasing PCL content, the non-freezable water fraction did not vary that much except for pure PCL networks. The freezable water content decreases significantly with increasing PCL fraction, indicating it is strongly affected by the hydrophobicity of the polymer. Another alternate way to interpret the relationship among various forms of water is shown in Figure 5 where the independent variable examined is the total water content. Similar to our observations for Figure 4, at a low swelling ratio, most water molecules are present in a form that is non-freezable. This non-freezable fraction slowly increases with water uptake and reached the maximum value of 68%. The critical water content above which the freezable water appears is 22%. After reaching the critical value, freezable water content increases linearly with total water content. In our system, W_{nf} / W_f is higher for high PCL composition samples suggesting that interaction between polymer and water molecules is stronger and that the polar sites have larger hydration ability.²

Finally, to further discriminate free water and freezable bound water, simply replace $\Delta H_{hydrogel}$ with water melting enthalpy in the heating trace at 0°C and -20°C , respectively.

CONCLUSION

DSC characterization and analysis are demonstrated to understand the physical state of water within a hydrated

polymer is characterized by DSC. This application note also has features a broad appeal to thermal analysis in water-contacting polymeric materials to predict drug dissolution in the hydrogel and their release behavior and hydrolytic degradation/erosion process of the hydrogels.

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