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The Phase Transition Model for Heat-Shrinkable Thermo-Sensitive Hydrogels Based on Interaction Energy

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Abstract. A biphase mixture continuum mechanics model is derived for neutral heat-shrinkable thermo-sensitive hydrogels in this paper. The mixing free energy of the special mixture is recalculated based on the partition function of Bose system, and it evaluates the contribution of the hydrophilic, hydrophobic interaction and hydrogen bonding to the volume phase transition behaviors. The ideas of the Flory lattice theory and the UNIFAC group contribution method are employed to get the expression of the mixing free energy. Then we deduce a particular model by combining this mixing free energy with the conservation laws equations and constitutive relations of both phases to predict the volume transition behaviors of these special hydrogels.

AMS subject classifications: 76A05, 76T99, 35Q92, 92E10

Key words: Heat-shrinkable thermo-sensitive hydrogels, volume phase transition, free energy, Flory lattice theory, group contribution method, conservation law equations.

1 Introduction

Hydrogel is a kind of macromolecular materials which are constructed by swelled hydrophilic polymers and the absorbed water in the interspace of polymer networks. There are complex micro-structure [26], phase transition process [27] and large deformation [25]. An environmental stimuli-responsive hydrogel or the smart hydrogel is the hydrogel which would undergo discrete or continuous volume transformations in response to infinitesimal changes of the external environment, such as the pH of the solution, the electric field, the solvent composition, the temperature, the salt concentration or the light, etc [15]. The thermo-sensitive hydrogel is a kind of smart hydrogels. It can sense

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the variation of the external temperature and respond to it by imbibing or extruding fluid from the surroundings. For a thermo-sensitive hydrogel, there is a critical temperature in which it undergoes the volume phase transition. There are heat-shrinkable hydrogels and heat-swellable thermo-sensitive hydrogels. The former will lose its water and shrink when the temperature increases, and the latter will absorb water and swell with the rising of temperature. Here, we pay our attention on the heat-shrinkable hydrogel and call its critical temperature as its LCST (lower critical solution temperature). Poly(N-isopropylacrylamide) (PNIPAAm) is a particular kind of these hydrogels because its LCST is around $33^{\circ}C$ which is very close to the temperature of human body. At the temperature lower than $33^{\circ}C$, uncross-linked PNIPAAm can be dissolved in water and form a colorless and transparent liquid solution. When the temperature is increased beyond this temperature, the solution separates into two liquid phases with different concentrations of the polymers and the thicker part turns white and turbid [23]. This particular property makes it potential to be used as sensor or inductor or in drug control and release system.

It can be explained for the volume transition of the heat-shrinkable thermo-sensitive hydrogels as follows. This kind of hydrogels contain both hydrophilic amide groups and hydrophobic alkyl groups which interact with water molecules in the solution. When the temperature is lower than its LCST, the polymer is dissolved in water. And the interaction between the polymer and water is the hydrogen bonding interaction between amide groups and hydrones. At this time, the hydrones around the polymer chains are forming a highly ordered solvent shell connected by hydrogen bonds. With the rising of temperature, the hydrophobic effect is growing, and the solvent shell is broken. When the temperature rises to a certain value, water molecules will dissolve out from hydrogels and the phase transition behaviors happen [23].

The characteristics of volume phase transition of the smart hydrogels have drawn considerable attentions. In recent decades, people have got a lot of achievements in prediction of the phase transition behaviors of thermo-sensitive hydrogels by establishing mathematical models and molecular simulation ([14, 15] and references therein). The well-known mathematical models are the collective diffusion model [19], the hydrodynamic model [6,18], the continuum theory model [1,8,10,11], etc. The collective diffusion model was firstly proposed by Tanaka based on the assumption of the linear elasticity and the small deformation ignoring shear energy and the relative motion between the crosslinked polymer networks and the fluid in the hydrogels' swelling process [22]. This original theory was further improved by Wang et al. [21] and T.Yamaue et al. [24]. The most extensively used thermodynamic model was derived by Flory [6] in 1953 for description of the equilibrium volume transition of the hydrogels. The free energy of the hydrogels is assumed to be a sum of the mixing free energy due to the mixing process and the elastic free energy due to the swelling process and the ionic contributions. Then the chemical potentials of both phases and osmotic pressure acting on the hydrogel network can be derived according to their thermodynamical relationships with the free energy. In the continuum theory, both the solid phase and the liquid phase are assumed to be