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Modeling and Simulation of a Ternary System for Macromolecular Microsphere Composite Hydrogels

Guanghua Ji, Yuqi Yang* and Hui Zhang

Laboratory of Mathematics and Complex Systems (Ministry of Education), School of Mathematical Sciences, Beijing Normal University, Beijing 100875, P.R. China.

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Abstract. In this paper, we study a ternary system for macromolecular microsphere composite (MMC) hydrogels. Assuming that the graft chains are distributed randomly around the macromolecular microspheres, a phase transition model was constructed. The stabilised-scalar auxiliary variable (S-SAV) approach is used to present a first-order energy stable scheme for solving the nonlinear system. Some numerical experiments are carried out to show the accuracy of the scheme, including the mass conservation of the volume fractions, the decrease in the modified energy, and the influence of different parameters.

AMS subject classifications: 65H10, 65M06, 65M22

Key words: MMC hydrogels, ternary system, unconditionally energy stable, S-SAV.

1. Introduction

The macromolecular microsphere composite (MMC) hydrogel, proposed by Huang *et al.* [25] in 2010, is a new type of hydrogel. Later on, various materials have been used to synthesise the MMC hydrogel in a similar way [21, 23, 40, 45, 66]. The formation process is described as follows: evenly add monomers to the irradiated macromolecular microsphere (MMS) emulsion, and heat the mixture. The monomers will chemically graft onto the surface of the MMSs and grow into grafted polymer chains. It is possible for a polymer chain to graft onto another MMS or another polymer chain, so the MMSs can be joined by polymer chains. If the length of the polymer chain becomes larger than the distance between two MMSs, the chain entangles. The mixture finally transforms into a solid gel, the microstructure of which is shown in Fig. 1. Because of the chemical grafting and the entangled polymer chains, the MMC hydrogel has a well-defined network structure and very high mechanical strength [26, 46]. This led to wide application of MMC hydrogels in biomedical and industrial areas [21, 23, 25, 40, 66]. However, here we mainly focus on the method for simulating the phase transition of MMC hydrogels.

*Corresponding author. *Email addresses:* ghji@bnu.edu.cn (G. Ji), 201721130050@mail.bnu.edu.cn (Y. Yang), hzhang@bnu.edu.cn (H. Zhang)

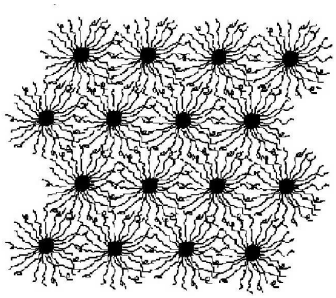

Figure 1: The microstructure of the MMC hydrogel.

The time-dependent Ginzburg-Landau (TDGL) mesoscale simulation method is based on the Cahn-Hilliard-Cook nonlinear diffusion equation and is used in the modelling of the phase transition of the polymer blends [19]. The method connects the rate of change of one or more spatiotemporal order parameters in time with the derivatives of a free energy, which is a functional of these order parameters. In particular, for incompressible binary polymer blends, the following equation is used:

$$\frac{\partial \phi(\mathbf{x},t)}{\partial t} = \nabla \cdot D \nabla \frac{\delta F[\phi(\mathbf{x},t)]}{\delta \phi(\mathbf{x},t)},$$

where ϕ is the spatiotemporal order parameter, D the mobility, and

$$F[\phi] = \int d\mathbf{r} \Big\{ f[\phi] + \kappa(\phi) |\nabla \phi|^2 \Big\}$$

the Ginzburg-Landau type free energy with the variable interface coefficient $\kappa(\phi)$ and the Flory-Huggins free energy of mixing $f[\phi]$.

In recent years, the TDGL method has been used to simulate the phase transitions of MMC hydrogels in binary systems. Zhai *et al.* [61] introduced a reticular free energy to describe the network structure of MMC hydrogels, derived a binary MMC-TDGL equation, and used a spectral method for its solution. Li *et al.* [29,30] solved the binary MMC-TDGL equation by a semi-implicit difference scheme and employed a finite difference method in combination with a convex splitting technique for the energy functional. Xu *et al.* [51] presented a stabilised semi-implicit scheme for the binary MMC-TDGL equation. Yang [53] employed the invariant energy quadratisation (IEQ) method to the phase field model for homopolymer blends (PF-HB). Thus the TDGL method is suitable for simulating the phase transition of MMC hydrogels in a binary system. Nevertheless, there are only a few works investigating the corresponding methods for ternary systems.

In binary systems, an important assumption is that the number of graft chains around an MMS is proportional to the perimeter [29, 30, 51, 61]. That is, the volume fraction of the polymer chains is proportional to the volume fraction of the MMSs. We can view MMSs and polymer chains as one component and water as the other.