



Co-continuous polymer systems: A numerical investigation



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ABSTRACT

A finite volume based implementation of the binary Cahn–Hilliard equation was implemented using an open source library, OpenFOAM. This was used to investigate the development of droplet and co-continuous binary polymer microstructures. It was shown that the initial concentrations of each phase define the final form of the resultant microstructure, either droplet, transition or co-continuous. Furthermore, the mechanical deformation response of the representative microstructures were investigated under both uniaxial and triaxial loading conditions. The elastic response of these microstructures were then compared to a classic representative microstructure based on a face centred cubic arrangement of spheres with similar volume fractions of each phase. It was found that the numerically predicted composite Young's modulus closely followed the upper Hashin–Shtrikman bound for both co-continuous and classical structures, while significant deviations from analytical composite theory were noted for the calculated values of Poisson's ratio. The yield behaviour of the composite microstructures was also found to vary between the co-continuous microstructures and the representative microstructure, with a more gradual onset of plastic deformation noted for the co-continuous structures. The modelling approach presented allows for the future investigation of binary composite systems with tuneable material properties.

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1. Introduction

Structural adhesives are increasingly used for bonding components within critical load bearing engineering structures such as aerospace and automotive. Typically these adhesives are based on epoxy polymers. Epoxies are inherently brittle due to their homogeneous microstructure and highly cross linked nature. Thus, there has been much research focused on improving the fracture toughness of epoxy polymers by incorporating a second minority phase at the nano-scale. These modifiers fall into one of two main categories: inorganic additives, e.g. silica [1,2], glass [3], alumina [4], nano-clays [5] and carbon nanotubes [6,7] or organic, usually rubber particles. Rubbery additives can be either core–shell rubber particles [8–10] or can form during curing via reaction induced phase separation mechanisms [11,12]. The primary energy dissipation mechanisms for rubber toughened epoxies are known to be both plastic void growth and shear band development [13]. It has also been shown that a combination of the above additives to create a hybrid material can provide synergistic toughening effects, e.g. carbon nanotubes and silica nanoparticles [14] or rubber with silica nanoparticles [15–17].

Kinloch et al. [12] and Brooker et al. [18] have studied the morphology and fracture toughness of thermoplastic toughened epoxy polymers. They noted a change in morphology from a spherical-particulate morphology in an epoxy rich continuous phase at low concentrations of thermoplastic phase. The morphology changed to a co-continuous structure as the percentage of thermoplastic toughener was increased. Finally at very high concentrations of thermoplastic phase, a phase-inverted structure was observed where the epoxy was dispersed as spherical particulates in a continuous thermoplastic phase. The fracture toughness was found to increase with increasing thermoplastic content, although this was not attributed to the change in morphology but rather as a function of the percentage of the thermoplastic phase in the polymer blend.

More recently, significant advances [19] in polymer synthesis has allowed researchers and manufacturers the ability to create specific copolymers. There are many possible combinations of block copolymers (BCP), and amphiphilic BCPs are of particular interest for toughening epoxy polymers. The BCP modified epoxies have been shown to have a lower viscosity than conventional rubber modified epoxies [20] which make them attractive for resin infusion processes. Several researchers have already shown that these BCPs can form complex nanostructures via self-assembly [21,22] or reaction-induced phase separation [23] to significantly increase the mechanical and fracture performance of epoxy polymers. Some of these hierarchical substructures include spherical

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micelles, vesicles and worm-like micelles [24]. Of particular interest in this work is the formation of a co-continuous, or bicontinuous gyroid, structure [25]. Co-continuous structures are structures which contain two or more interpenetrating and self-supporting phases. These types of structures have been observed for thermo-plastic modified epoxies but the energy dissipation mechanisms for such a complex structure were not fully understood [12,26,27]. Most of the early work on BCP modified epoxies has been primarily focused on experimentally observing the morphology and resulting mechanical properties. The study of the toughening mechanisms and mechanics of deformation of the microstructure is required in order to fully understand the structure/property relations.

Furthermore, such complex designed binary ordered structures can provide outstanding combinations of material properties including stiffness, toughness and strength that would otherwise not be possible in a homogeneous material and have been the subject of intensive research efforts over the last number of years. Wang et al. [28] studied the energy dissipation in binary composite systems with the phase interface closely approximating a triply periodic minimal surface. Similarly, work by Lee et al. [29] has shown that the energy dissipated per unit volume in a voided epoxy nanostructure can be significantly enhanced for a system of lower relative density by close control of the nano-frame geometry. Torquato [30] has studied the developed of optimised co-continuous structures with targeted properties such as minimal thermal expansion. It is therefore clear that understanding the underlying physics of phase separation and the subsequent influence of the morphology on the mechanical properties of the composite blend, is key to guiding the future design of improved materials for structural applications.

In this work, we use the well-known Cahn–Hilliard equation to describe the temporal evolution of a binary phase field of two mixed polymers and subsequently investigate the mechanical response of the evolved microstructures under different loading conditions.

2. Cahn–Hilliard model

The Cahn–Hilliard equation was originally proposed in 1958 [31] to model phase separation phenomena in binary alloys. Since then, it has been applied to a wide number of other diverse uses including the evolution of arbitrary microstructures [32,33], tumour growth [34] and image in-painting [35]. The Cahn–Hilliard equation can be written as:

$$\frac{\partial c}{\partial t} = \nabla \cdot (M \nabla \mu) = M \Delta \mu \quad (1)$$

where c is the concentration of one phase in the mixture, t is time, M is defined as the mobility, and μ is the local chemical potential, more commonly defined as:

$$\mu = F'(c) - \gamma \Delta c \quad (2)$$

In Eq. (2), $F(c)$ represents the free energy density of a homogeneous material of concentration c , and γ is a constant related to the thickness of the interfacial regions between phases. The free energy, $F(c)$, is based on a Ginzburg–Landau functional of the form:

$$\epsilon(c) = \int_{\Omega} \left[F(c) + \frac{\gamma^2}{2} |\nabla c|^2 \right] dx \quad (3)$$

The first term on the right hand side of Eq. (3) represents the homogeneous free energy while the second term penalises large gradients. The free energy is generally deduced via the Flory–Huggins model [36]:

$$F(T, c) = RT[(1 - c) \ln(1 - c) + c \ln c] + \theta c(1 - c) \quad (4)$$

where θ is a variable representing the Flory–Huggins interaction parameter, and R and T are the universal gas constant and temperature respectively. From Landau theory, an alternative quartic approximation can be written as [36]:

$$F(c) = \alpha(c - \beta)^2(c - \gamma)^2 \quad (5)$$

where α , β and γ can take suitable values. In order to derive an easily implementable numerical solver for Eq. (1), we first define an order parameter ϕ which represents the concentration difference between phase A and B at any point in the domain of interest. Therefore, we have $\phi = c_A - c_B$ with $c_A + c_B = 1$. It is easy to observe that $\phi = 2c - 1$. Eq. (1) can then be rewritten as:

$$\frac{\partial \phi}{\partial t} = M \Delta [\phi^3 - \phi - \gamma \Delta \phi] \quad (6)$$

It can be seen in Fig. 1 that the new definition of $F(\phi) = \frac{1}{4}(\phi^2 - 1)^2$ is a double well potential with local minima at $\phi = \{-1, 1\}$ corresponding to the pure phases.

The initial concentration of each phase in the mixture determines the subsequent pattern evolution. Specifically, for near equal concentrations of phase, a co-continuous pattern emerges. However, in the case where one phase is present in the mixture in a much greater concentration than the other, a droplet pattern emerges. In this case, one phase can be considered as the matrix and the other as dispersed spherical inclusions.

Eq. (6) was implemented in foam-extend-3.0 [37,38]. FOAM is a fully 3-dimensional, finite volume, object oriented C++ library. It is primarily used to create numerical solvers for multi-physics problems. Originally developed for computational fluid mechanics, it has recently found application in other areas such as solid mechanics [39–42] including fracture mechanics [43–46], solidification problems [47] and fluid–structure interactions [48,49].

2.1. Two-dimensional cases

Using the model described, we can examine the evolution of the concentrations of two phases with a random perturbation in a two-dimensional system. First, we prescribe the concentration difference between each phase as an initial condition (the concentration difference as defined by Eq. (6) can take any value between -1 and 1). To initialise the random perturbation, we chose a Gaussian normal distribution about the mean concentration with a standard deviation of 0.1, i.e. 5% of the total range.

A unit square domain with equal sides of $100 \mu\text{m}$ with a cell size of side length $1 \mu\text{m}$ was used. A time step of 0.1 ms was used in all cases while the mobility, M , was set to $0.01 \text{ m}^2/\text{s}$, with γ (which controls the width of the interface region) equal to

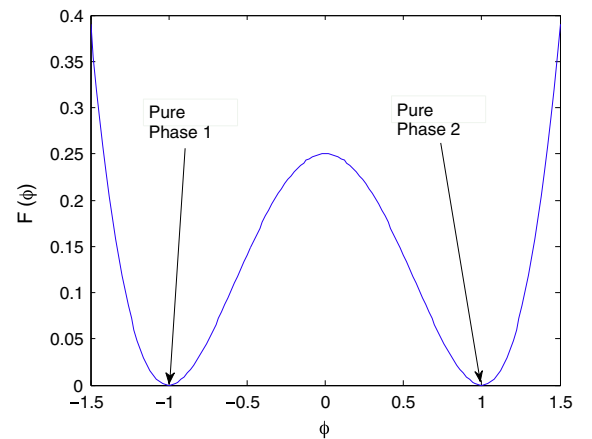


Fig. 1. The double well potential $F(\phi) = \frac{1}{4}(\phi^2 - 1)^2$.

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