Phase field interface modelling of phase separation for microporous structure fabrication

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INTRODUCTION: We have developed microporous non-volatile emulsion thermosets (MiNET), a new class of composite resins made from epoxies and nanoparticles, a liquid porogen, and a small amount of surfactant. These ingredients form an intermediate between a conventional emulsion and a Pickering emulsion to create a bicontinuous network of oil and epoxy composite. The oil phase can then be removed to leave the porous network.

The microporous structure fabrication is modelled here to simulate phase separation using a phase field method with a diffuse interface. Phase separation occurs when a homogeneous one-phase state (binary system) separates into the two-phase region ($T<T_C$). Rather tracking sharp interface during motion, diffuse (finite thickness) interface can be modelled without any prior assumption of their shape-distribution and represents continuous change in fluid properties from one phase to another phase.

Here we show the implementation of a phase field model of a binary mixture (Oil and epoxy) under a different wall contact angle and surface tension in 2D with goal to study 3D structure in detail.

COMPUTATIONAL METHODS: The phase field model implemented by using the moving interface[1] of COMSOL Multiphysics® Mathematics module. The components are represented by a dimensionless phase field function(ϕ) and are considered pure when ϕ=±1. The separation of the two immiscible phases is modelled by the Cahn-Hilliard equation *(1a,b)* and subjected to wall contact angle θ_w *(1c)* and non-penetrating *(1d)* boundary conditions[2]. The quantity λ is the mixing energy density (N), and ε is a capillary width that scales with the interface thickness (m).

$$\frac{\partial \phi}{\partial t} = \nabla \cdot \frac{\gamma\lambda}{\varepsilon^2}\nabla\psi \, ; \quad \psi = -\nabla \cdot \varepsilon^2 \nabla\phi + (\phi^2 - 1)\phi \quad (1a,b)$$

$$n \cdot \varepsilon^2 \nabla\phi = \varepsilon^2 \tan(\pi/2 - \theta_w)|\nabla\phi - (n\cdot\nabla\phi)n| \quad (1c)$$

$$n \cdot \frac{\gamma\lambda}{\varepsilon^2}\nabla\psi = 0 \; (1d) \quad \text{where } \gamma(\text{mobility}) = \chi\varepsilon^2, \lambda = \frac{3\varepsilon\sigma}{\sqrt{8}}$$

MiNET components mixing volume ratio calculated from weight ratio using densities with ~53% of overall reserved volume for nano-particles (400nm). Using this volume ratio, Single particle (0.5μm square with 0.2 μm dia. circle) and double particle (0.7μm square with 0.2μm dia. single center circle and quarter part at each corner) models are established with periodic boundary conditions on top-bottom and left-right side. The initial mixture is created by putting ϕ equal to a random number with 0.4 mean (Oil/epoxy=2.33 volume fraction ratio) and a 0.1 range.

RESULTS: Transient analysis performed using implicit solver for [0,0.1,20]ms in addition to adaptive mesh refinement to reduce calculation time.

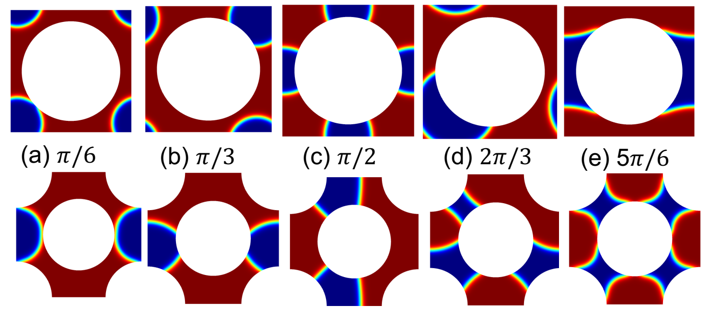

Figure 1. Phase field variable distribution at different $\theta_w$for single particle (Top row) and double particle (bottom row) model (at σ=1 N/m)

σ (N/m)	0.1	0.5	1	1.5	2	5	10
Time	50ms	10ms	1.5ms	0.7ms	0.5ms	0.15ms	0.1ms

Table 1. Time required for steady phase separation at different σ (at θ_w=90°)

Based on phase variable plots in Fig 1, Oil(red)-Epoxy(blue) phase is well separated, and particle(center) is connected to boundary using epoxy strips. Bicontinuous network observed at higher θ_w (2-double particle model) while spinodal of epoxy observed at lower θ_w in both models. Steady phase separation time in table 2 presents lower calculation time with quick phase distribution and finer structures at higher sigma value. To simulate actual mixture in 3D (with particle spherical cavity), 1 and 2 particle models shown in Fig 2. The nano-particles are linked vertically in (a) and diagonally in (b) via epoxy phase (blue) and formulates porous MiNET phase when oil will be removed.

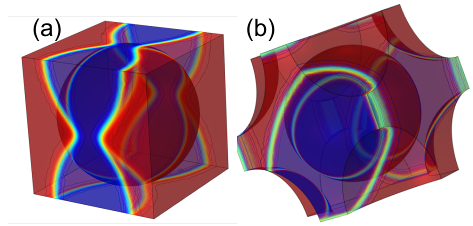

Figure 2. 3D phase separation for (a)single and (b)double particle model (σ=1N/m, θ_w=90°)

CONCLUSIONS: Phase field interface method was considered to model the phase separation at micro scale in 2D. Oil-epoxy phases demonstrates spinodal behavior at lower contact angle and quick distribution of phases observed at higher surface tension. In future, The 3D model will allow us to predict the limits of materials and particle sizes that will form the MiNET phase.

REFERENCES:

1. COMSOL Multiphysics® Application Library: Phase separation
2. P. Zhang, Periodic Phase Separation: A Numerical Study via a Modified Cahn- Hilliard Equation, M.Sc. thesis, Dept. of Mathematics, Simon Fraser University, Canada, 2006.