Shrinkage, Viscoelasticity, and Stress Development in Curing Coatings
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Stress Development in Curing Coatings

Curing instead of or in addition to drying is used to reduce solvent use and speed up solidification. Curing is also a way to attain novel properties and sometimes this is done by trapping metastable coating microstructure. Shrinkage accompanies not only drying but also the polymerization and cross-linking that solidify a coating. Beyond a certain degree of cure, an appreciable elastic modulus appears, and the coating can support significant elastic stress. Thereafter, because a coating adhering to its substrate cannot shrink in its own plane, the difference between the shrunken stress-free state and the current incompletely shrunken state is shrinkage strain. The shrinkage strain leads to shrinkage stress, which in turn can lead to defects in the coating. The goal of this research is to optimize the cure process to maximize conversion and minimize stress or to optimize the balance between the two.

Microheterogeneity and Evolving Viscoelasticity

Polymerization reactions are usually diffusion controlled at high conversions and this leads to generation of microheterogeneities in the network. Wen's kinetic gelation network modeling is used to approximate the free-radical polymerization and cross-linking by which networks grow and develop microheterogeneities. As the coating cures, it changes from a viscous liquid to either a viscoelastic or an elastic solid. The

microscopic structure of a linearly viscoelastic coating is mechanically equivalent to a network of springs and dashpots, the springs representing elastic deformation and the dashpots representing viscous-like changes in the stress-free state.

Theoretical models of growing networks of springs and dashpots are used here to simulate curing coatings in which elastic and viscous modulii change continually. The liquid monomer is represented mechanically by a network of dashpots. As chemical bonds of polymerization form in the network, the dashpots are replaced by springs and the nodes that form the end-point of each new bond are made to come closer along the line joining their center to represent the shrinkage that accompanies curing (Figure 1).
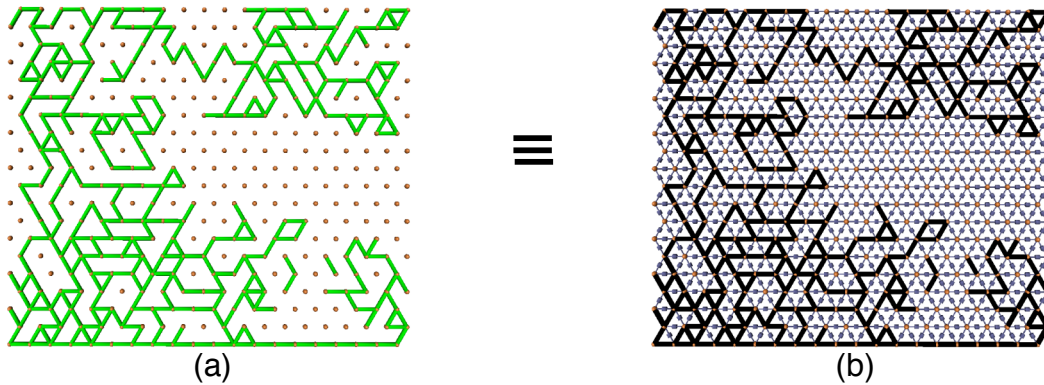

(a)   (b)

Figure 1. Figure (a) shows the network structure growth, the nodes representing monomer or initiator sites and the lines representing bond formation. Figure (b) shows a network of springs (represented by thick lines) and dashpots, with springs placed between monomer sites that have formed bonds.

The load displacement equation of the entire network is expressed as

$$\underline{\underline{K}}\underline{d} + \underline{\underline{V}}\frac{d\underline{d}}{dt} = \underline{p} \qquad (1)$$

where $\underline{\underline{K}}$ and $\underline{\underline{V}}$ are the stiffness and viscosity matrices of the network, $\underline{d}$ corresponds to the displacement of all the nodes, and $\underline{p}$ corresponds to externally imposed loads on the nodes. This differential algebraic equation system is solved numerically by using DASSL. The most interesting result of solving the equation system is the effect of inhomogeneous reaction on stress development

Results and Discussion

A goal of this study is to look at the effect of heterogeneities on the evolving viscoelasticity and stress development in the coating. In order to exaggerate the effect of inhomogeneous reaction and "gel formation" or "heterogeneities", the coating is divided into subregions and bonds are forbidden to form across their boundaries. When the mechanical relaxation time is decreased to 0.05, without changing the reaction time, the reaction in isolated clusters results in lower stress at higher conversion as compared to random cure (Figure 2). Also, the final stress is lower with more number of clusters or smaller size of clusters. The smaller clusters allow enhanced stress relaxation of the coating because they are connected to more number of dashpots per every bond in the cluster. It is important to note that if the cure is stopped at any time, the average stress in the coating relaxes to zero because the bonds do not percolate the network.

In order to impart rigidity to the coating and to achieve good final mechanical properties, the isolated clusters have to be linked up laterally and to the substrate. Reaction in early stages is simulated in four isolated clusters and these clusters are linked up at different stages of cure (figure 3). It is clear that when the isolated clusters are linked together and to the substrate, later in the cure process, the stress is lower. This can be attributed to enhanced relaxation of the isolated clusters, and the decreased relaxation due to the formation of a stiff elastic backbone once the clusters are linked up laterally and to the substrate. One way of reducing stress in curing coatings is to cure in isolated clusters as long as is feasible, and then link the clusters up to form a dense coating.
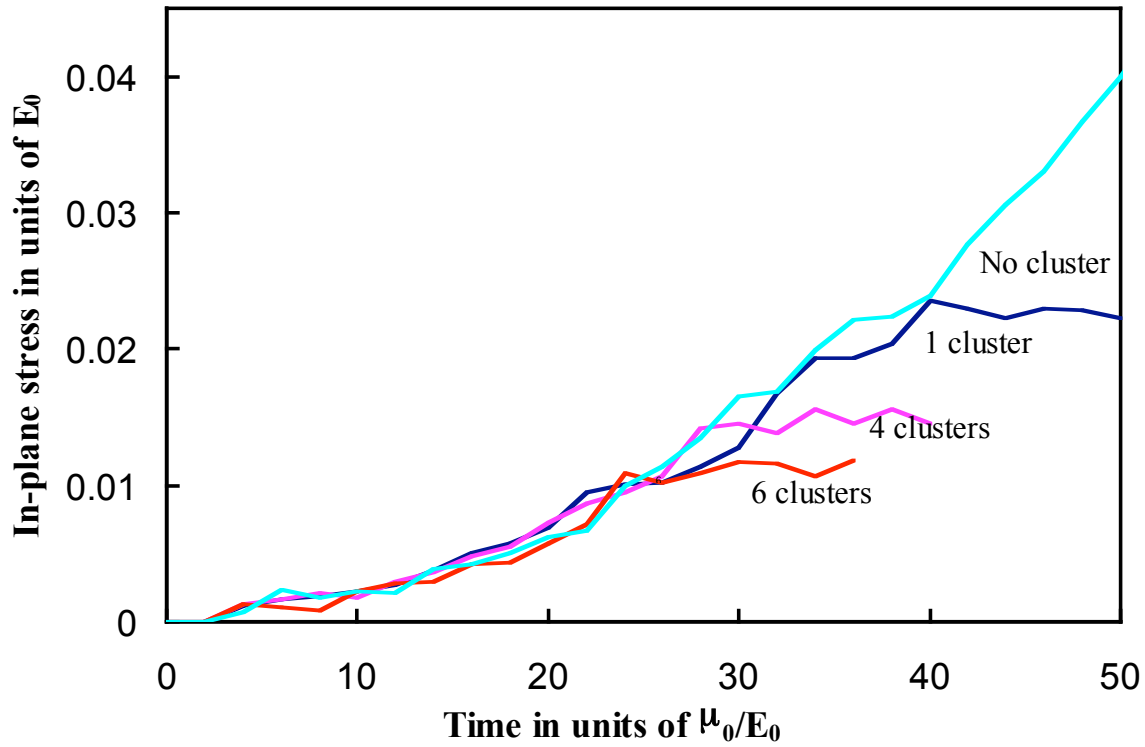
Figure 2. Effect of reaction in isolated clusters on average in-plane stress in the coating
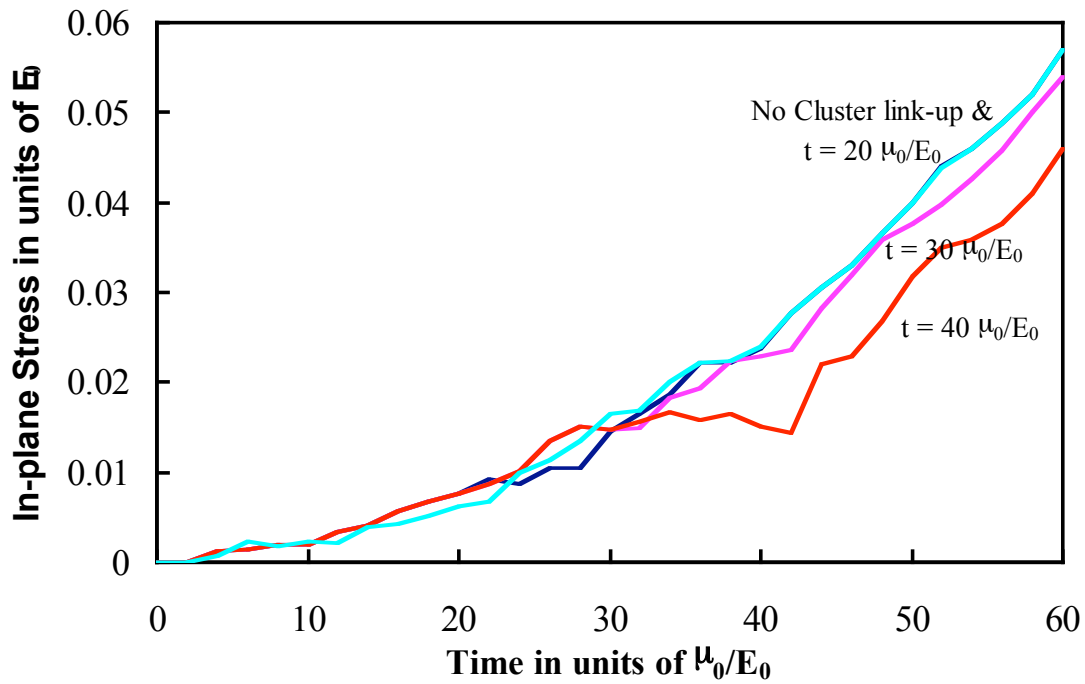

Figure 3. Effect of cluster link-up at different stages of cure on the average in-plane stress in the coating.