

# Network Formation in Styrene/Vinyl-Ester Systems: Low Temperature Cure

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Vinyl-ester (VE) resins are one of the most widely used matrix resins for high performance thermosetting composite materials. The applications of these materials include construction of parts for automobiles and bridges. VE resins are comprised of two monomers, namely, vinyl-ester and styrene. The two monomers react via free radical chain growth copolymerization to form a network polymer. The development of the network significantly affects the physical, chemical and mechanical properties of the polymer, consequently affecting the behavior of the composite. Therefore, an understanding of the network formation in VE resins is important to the development of structure-property relationships for these materials. Furthermore, it will also aid in the selection of appropriate processing conditions for VE based composites.

Vital clues regarding the structure of the network have been obtained from cure kinetics studies. FTIR spectroscopy has been used to monitor the individual fractional conversion rates of styrene and VE double bonds. The final conversions of the two monomers have been found to be much lower than 100 %, with the final conversion of styrene always exceeding the final conversion of VE double bonds. The monomer reactivity ratios have been evaluated from the initial conversion rate data of the two monomers. Their values suggest that alternating copolymerization is favored in the initial stages of reaction. Four main factors affecting the cure kinetics of VE resins are identified, namely, chemical reactivity of the monomers towards the free radicals, diffusion effects, phase separation and microgel formation. It is the interplay of these factors that determines the kinetics of cure.

Information regarding the onset of network formation has been obtained by studying the pre-gel stage of cure of VE resins. Viscosity rise, kinetics and the size distribution of the polymeric material formed during the pre-gel stage, are the parameters that have been monitored. A strong correlation is found to exist between viscosity rise and the intensity weighted average diameter obtained from dynamic light scattering experiments. It is widely accepted that classic Flory-Stockmayer gelation model does not hold for highly cross-linking chain addition systems like styrene-VE. Instead, a microgel based gelation model has been proposed by various researchers. This existing gelation model, that is based on the linking of microgels, has been reviewed and it is found that this model also does not adequately represent the physical phenomenon during gelation for most free radical systems including styrene-VE systems. Much larger values of gel-point conversion, than those experimentally obtained, would be needed to meet the requirements of this model. In this work, alternative gelation schemes, which are consistent with all the experimental results obtained, have been proposed.

Key words: - vinyl-ester, 'cure kinetics, FTIR spectroscopy, Pre-gel stage, Dynamic Light Scattering, Microgels, Gelation mechanism.