

# Curing Kinetics of Vinyl-Ester Resin

Russell P. Brill

A Fourier transform infrared (FTIR) spectroscopy technique was developed to investigate the isothermal curing kinetics of commercial vinyl-ester resins comprised of vinyl-ester monomer (dimethacrylate of DGEBA epoxy) and styrene. This technique enables a more complete evaluation of the copolymerization reaction of vinyl-ester/styrene systems by monitoring the depletion of vinyl-ester and styrene double bonds independently. For this work, Dow Derakane 441-400 vinyl-ester resin with Witco USP-245 initiator was cured at elevated isothermal reaction temperatures.

First, the effects of reaction temperature and reactant composition on the curing kinetics were studied in the bulk resin phase. The results indicate that the rate of fractional conversion of styrene double bonds is initially less than that of vinyl-ester vinyl groups. However, styrene monomer continues to react after conversion of vinyl-ester double bonds has ceased. In addition, the overall extent of conversion was found to increase with increasing isothermal cure temperature, and it was observed that higher styrene concentration enhances final conversion of vinyl-ester double bonds but not styrene double bonds. Increasing styrene monomer concentration also resulted in lowering the apparent activation energy for the reaction of vinyl groups from both monomers as characterized by an empirical autocatalytic model used to fit the conversion results for styrene and vinyl-ester double bonds independently. The results of this work demonstrate that reaction temperature and resin composition significantly affect the cure behavior of vinyl-ester resins and provide insight into the development of the resulting network structure.

Second, the influence of an interface on the curing kinetics was examined. Experiments were conducted using FTIR spectroscopy to monitor the reaction of vinyl-ester resin at the surface of a crystal treated with and without a silane coupling agent having vinylbenzyl and mine functional groups. The rate of conversion of both vinyl-ester (VE) and styrene (ST) double bonds near an unsized internal reflection element as obtained by FTIR-ATR was found to be similar to that obtained for bulk VE cure investigated by FTIR spectroscopy in transmission. However, the final extent of conversion was greater for ST and lower for VE near the interface as compared to the bulk. On the other hand, the cure behavior at the interface sized with styryl mine silane coupling agent (Dow Corning 2-6032) contrasted sharply with the unsized system. In this case, rapid consumption of ST double bonds in relation to the VE double bonds was observed. Perhaps due to a combination of altered copolymerization behavior and molecular mobility constraints, the final conversion of VE double bonds was found to be as low as 20% in most cases. It is proposed that a layer of homopolymerized ST is formed at the interface as a result of this behavior. The major implication derived from results of this work is that the composition of the VE-ST polymers found at interfaces in composite systems can be significantly influenced by the presence of silane-based sizing layers and that the potential exists for controlling these structures based on the selection of sizing material.