

# Synthesis, Characterization and Properties of Vinyl Ester Matrix Resins

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## (ABSTRACT)

Vinyl ester oligomers diluted with styrene are important matrix resins for thermosetting polymer composites. A major objective of this work has been to study the chemistry and kinetics of the cure reactions of vinyl ester resins at elevated curing temperatures, which are consistent with typical composite processing conditions. The crosslinking reaction of vinyl ester resins was studied by FTIR and the loss of the carbon-carbon double bonds of the methacrylate ( $943\text{ cm}^{-1}$ ) and styrene ( $910\text{ cm}^{-1}$ ) were followed independently. A small background absorbance overlapping the absorbance at  $943\text{ cm}^{-1}$  was subtracted from all spectra collected as a function of reaction time to quantify conversions. Copolymerization reactivity ratios of styrene and terminal methacrylates on vinyl ester oligomers were calculated to be  $r_s = 0.36 \pm 0.05$  and  $r_m = 0.24 \pm 0.1$  from early conversion data obtained at  $140\text{ }^\circ\text{C}$  on a series of resins with systematically increasing levels of styrene. The composition data were analyzed using the integrated form of the copolymerization equation and assuming a terminal reactivity model to predict copolymer compositions throughout the reactions. These curves agreed well with the experimental data even at high conversion levels.

Another important part of this research was to study structure-property relationships of vinyl ester resins. Characteristics of vinyl ester resins and networks such as shrinkage, viscosity, crosslink density, glass transition temperature, gel swelling, and toughness have been studied. The shrinkage of vinyl ester resins during cure was calculated according to density measurements to be 4% - 10% depending on styrene content. It was found that the chain length of vinyl ester oligomers strongly affects the properties of the networks. For vinyl ester resins with longer lengths ( $M_n = 1000\text{ g/mol}$ ), crosslinked networks have higher fracture toughness values and lower  $T_g$ 's.

Finally, the synthesis, cure reactions and toughness of a new low viscosity vinyl ester resin were also investigated in this work. The new oligomer has a structure with which the hydroxyl groups on the backbone are replaced by methyl groups. They could be processed without a diluent. The cure reactions of the new resin were studied by FTIR, DSC and  $^{13}\text{C}$ -NMR.

*Dedicated to*

**My daughter Melissa**

*and*

**My husband Jianye Wen**

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