Chapter 4. Conclusions

Some important conclusions of this work can be summarized as follows:

1. The reactivity ratio of styrene with terminal methacrylates on vinyl ester oligomers was estimated to be r_s=0.36 and r_m=0.24. The azeotropic point for the vinyl ester-styrene resin having a backbone molecular weight of 690 g/mol occurs at approximately 26 weight percent 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. It was found that the predicted composition curves agree well with the experimental data even at high conversion levels.

2. Compared with the networks that are cured with step growth mechanisms, such as epoxy resins, gelation of vinyl ester resin systems in this work occurred in the relatively early stage of the reaction. The first gel could be detected as early as about 12 percent double bond conversion using Derakane 441-400 (120^{o}C). The analysis of sols and gels isolated during a reaction with a feed composition near the azeotropic point (Derakane 441-400) confirm that the composition of the gel remains nearly constant except for the very early and very late stages of the reaction.

3. The conversion of the cure reaction of vinyl ester resin increased as cure temperature increased. Nearly complete conversion can be approached between 120-140^{o}C for the BPO and t-BPT initiator system. A more dense material was obtained at higher cure temperature.

4. The glass transition temperature and crosslink density of vinyl ester-styrene network decreased as styrene concentration increased. Glass transition temperature and crosslink density follow the Fox and Loshaek relationship.

5. Solvent extraction and swelling experiments showed that the gel fraction for this system is 97-98%. The vinyl ester-styrene networks swell more in CH_2Cl_2 than in MEK. The vinyl ester-styrene network from higher molecular weight dimethacrylate (1000g/mol) has a higher swelling index than the vinyl ester-styrene network with low molecular weight (690 g/mol) dimethacrylate.

6. The shrinkage level of vinyl ester resins during cure increased from 4 to 9 volume percent as the styrene content increased from 20 weight percent to 60 weight percent. Shrinkage increases with the vinyl ester resins of lower molecular weight due to the formation of more dense networks.

7. The toughness of the vinyl ester resin increased with styrene content and became much higher when the chain length of vinyl ester oligomer was increased. For example, at 30 wt.% styrene, the K_{1c} value of a vinyl ester resin with vinyl ester oligomer molecular weight of 690g/mol is 0.73 $MN/m^{3/2}$ and that of vinyl ester resins with a vinyl ester oligomer molecular weight of 1000g/mol is 1.5 $MN/m^{3/2}$.

8. The viscosity of vinyl ester-styrene mixtures is inversely proportional to styrene contents and temperature. For the vinyl ester resins with vinyl ester oligomer M_n = 690 g/mol, when the $T-T_g$ is above 70°C, the desired low viscosity (2000 cP) for the processing can be achieved.

9. A low viscosity vinyl ester resin has been synthesized and confirmed by NMR and FTIR. The new resin has a structure in which the hydroxyl groups on the backbone are replaced by methyl groups. The neat resin can be directly processed to make a composite without styrene. The conversion of the neat resin is 90% at 160°C. The cured neat resin is a brittle material and the toughness is 0.53 $MN/m^{3/2}$. The toughness can be improved by mixing with styrene and high molecular weight vinyl ester resins.