

### Feature Project

### Effects of Resin Chemistry on Redox-Polymerization of Unsaturated Polyester Resins

By Huan Yang (Lee)

Three unsaturated polyester resins were synthesized based on maleic anhydride and different propylene glycols. Their number average molecular weights are similar, but the number of C=C bonds per molecule differs. Detailed properties of the materials and their corresponding resin codes are given in the table. For each resin, styrene was added to achieve a molar ratio of 2 between styrene and unsaturated polyester vinylene C=C bonds.

Isothermal polymerizations were conducted at 35, 45, 60, 75 and 90°C using a differential scanning calorimeter (DSC). The relationship between the final conversion and the curing temperature for the three resins can be clearly seen in Figure 1. The final conversions at different curing temperatures for UP-3 were unchanged, because the curing temperature is higher than the glass transition temperature of the cured resin. For UP-6 and UP-10, the polyester resin with a higher degree of unsaturation has a lower final conversion at the same temperature. This is because the crosslinking density in UP-10 is higher than in UP-6. For the resin with a higher degree of unsaturation, more unreacted C=C bonds are trapped inside the matrix when the resin vit-

trifies, resulting in a lower final conversion. By increasing the temperature, the final conversion of UP-10 is increased more significantly than in UP-6.

The DSC was also used to determine the glass transition temperature of the partially cured resins. In Figure 2, the glass transition temperatures of the partially cured samples are plotted as a function of the final conversion,  $a_p$ , at different temperatures. For both UP-6 and UP-10, the glass transition temperature of partially cured samples increases progressively with an increase in the final conversion. It can be seen that by increasing the final conversion, the glass transition temperature increases more significantly for the resin with a lower degree of unsaturation. A possible explanation is that for the resin with a higher degree of unsaturation, more C=C bonds are trapped inside the formed polymer. These trapped

C=C bonds may engage in an intra-molecular reaction, which does not contribute significantly to the increase of the glass transition temperature. On the other hand, for the resin with a lower degree of unsaturation, more C=C bonds may engage in the inter-molecular reaction, which would increase the glass transition temperature more efficiently.

An FTIR spectrometer was used to differentiate the rates of isothermal reactions of polyester and styrene carbon-carbon double bonds based on the spectral changes of different functional groups. Figure 3 shows the relative conversion of styrene vs. polyester C=C bonds at different temperatures. For UP-3, when the temperature varies between 35°C and 90°C, the three curves all fall around the diagonal line, indicating that the consumption ratio of ST C=C versus polyester C=C is 2 (i.e., azeotropic copolymerization). For UP-10, when the conversion of UP C=C bonds is less than 60%, the three relative conversion curves coincide with the alternating copolymerization curve. This indicates that the average consumption rate is one styrene C=C bond per one polyester C=C bond. For both UP-6 and UP-10, when the conversion of polyester C=C bonds is larger than 80%, the reactivity of polyester vinylene groups levels off due to the diffusion limitation effect, while the styrene reactivity remains relatively high at all temperatures.

	Monomers	$M_w/C=C$ (g/mol)	$M_n$ (g/mol)	$M_w$ (g/mol)	Molecular Weight Distribution (MWD)	N (average number of C=C/molecule)
UP-3	PPG-425 MA	505	1682	3577	2.13	3.1
UP-6	TPG MA	272	1517	6615	2.85	5.6
UP-10	PG MA	156	1600	N/A	N/A	10

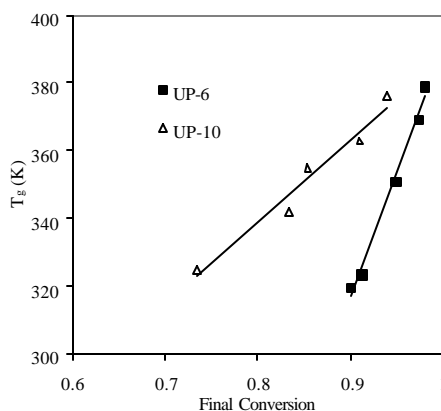
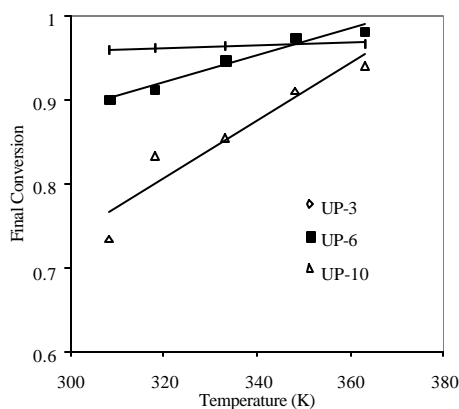


Fig. 1 (left): Final conversion as a function of curing temperature for various unsaturated polyester resins. Fig. 2 (right): Glass transition temperature ( $T_g$ ) as a function of final conversion.

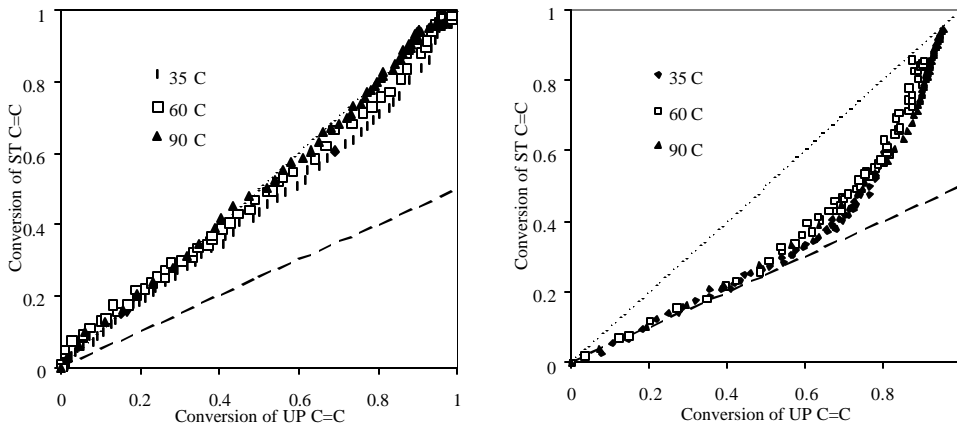


Fig. 3: Relative conversions of styrene vinyl vs. unsaturated polyester vinylene groups at different temperatures for (left) UP-3 and (right) UP-10 (0.8 wt.% MEKP, 0.1 wt.% Co).

Poor fiber wetting and voids are major concerns in all composite molding processes (e.g. prepreg/autoclave curing, SMC molding, resin transfer molding, pultrusion). Our results show that large voids outside fiber tows can be removed mechanically during mixing and mold filling. Smaller cylindrical-shaped voids inside the fiber tows are difficult to remove because of the fiber ring structure. Their removal depends largely on gas diffusion. Experimental analysis and theoretical modeling are being carried out to better understand the mechanism of void removal and how the fiber architecture and resin properties affect void removal.

### Shrinkage Control and Styrene Residue of Unsaturated Polyester and Vinylester Resin Systems Cured at Low Temperatures

by Xia Cao (Lee)

In low temperature composite manufacturing processes, improving shrinkage control and reducing residual styrene are the major concerns. Our recent study showed that a chelating agent, 2,4-Pentandione, can function as a retarder or a promoter for both vinylester and unsaturated polyester resins, depending on the acidity of the resin system used. It was also found that the thermal history (temperature gradient and peak temperature) of the resin system is crucial to the final volume shrinkage of cured resins. We are currently investigating how to control the resin acidity by introducing external acid during molding, in order to minimize the part shrinkage and residual styrene in low temperature resin systems. Effects of curing agent concentration and resin flow during mold filling will be studied. We will also investigate the effect of photocure on composite molding.

### The Friction Mechanism and Blister Formation in Pultrusion

By Shoujie Li, Zhongman Ding and Liqun Xu (Lee)

An experimental pultrusion simulator was developed in our lab to measure the frictional force between resin-impregnated fiber reinforcements and the mold surface. The resin

can be either liquid or partially cured to the gel state. The measured friction coefficient was found to increase significantly when the resin was in the gel state. More experiments are being carried out to investigate the effect of resin type and conversion, filler type and content, fiber type and content, and internal mold release agent on the friction coefficient. Modeling and analysis based on these experimental data will be conducted thereafter. This measurement method can be applied to other composite molding processes as well. Blister formation during high-speed pultrusion is also investigated by conducting kinetic analysis of vinylester resins and by heat transfer simulation.

### Molding Force, Fiber Wetting and Void Removal in Composite Processing

By Lisa Abrams and Shoujie Li (Castro, Lee)

Sheet Molding Compound (SMC) is widely used for truck body parts. Due to their large size, the molding forces are substantial. A model has been developed relating the instantaneous force needed to close the press, to the press closing speed and instantaneous gap between the molded surfaces. A simple method has been developed to measure the material resistance to extension and the hydrodynamic friction coefficient. Experimental study showed how the resistance to extension and friction coefficient are related to SMC paste rheology. More work is being done to further examine the effects of glass length, filler quantity and type, and quantity of filler and glass on the compression force.

### In-Mold Coating of Thermoplastic Substrates

By Xu Chen, Konstantin Zuyev and Mauricio Cabrera-Rios (Castro)

Kinetics and rheological equations have been developed for a new class of coatings being developed by Omnova Solutions, Inc. as a top coat for thermoplastic substrates. The simplified model for predicting pressures was experimentally tested and a model developed to predict cure time for the coating. A method is being tested to predict fill patterns and packing pressure as the coating is injected. Artificial neural network models are being developed to optimize the injection gate location and cure times of IMC in thermoplastics.

### Chemorheology of Pre-Preg Resins and its Influence on Composite Processing

By Gang Zhou and Liqun Xu (Lee)

The viscoelasticity and reaction kinetics of epoxy and rubber-modified epoxy resins used in pre-pregs were measured. Both shear viscosity and normal stress were measured by the Rheometrics RMS800. Reaction profiles were measured by DSC. Their effects on fiber movement during pre-preg molding are being investigated.

- continued on page 8 -