CAPCE

Thrust Area Update:

Thermoset Polymers and Composite Manufacturing

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Feature Project

Design of Curing Agents for Low Temperature Molding of Vinyl Ester Resins

By Ling Li (Lee)

An important requirement for room temperature cure is designing and controlling the mold filling and curing time without external heating. Curing agents like inhibitors or retarders prevent premature gel and provide a sufficiently long time to complete mold filling. However, the addition of inhibitors or retarders to achieve a longer gel time causes a low curing rate and long cycle time. The low curing rate also prevents the accumulation of reaction exotherm, which in turn may lead to low resin conversion. A proper design of the resin system is the typical solution to this problem, which requires a good understanding of the interactions between different curing agents.

2,4-P is often used with polyester and vinyl ester (VE) resins to adjust curing rate and gelation in low temperature composite manufacturing. As a chelating ligand, it can interact with metal ions and affect the reduction and oxidation reaction between initiators and promoters. The influence of 2,4-P on the reaction kinetics of a VE resin (VER-350 from Dow Chemical) was carried out at 35°C with 1.5% CHP, 0.3% CoNap in DSC. Results in Fig. 1 show that 2,4-P is an effective agent to slow down co-polymerization between vinyl ester and styrene C=C bonds, indicating that 2,4-P functions as a retarder.

Fig. 1 Effect of 2,4-P on the reaction rate profiles of VER-350 at 35°C

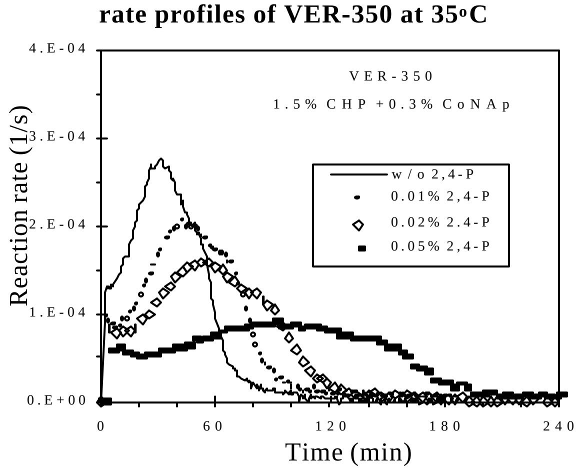
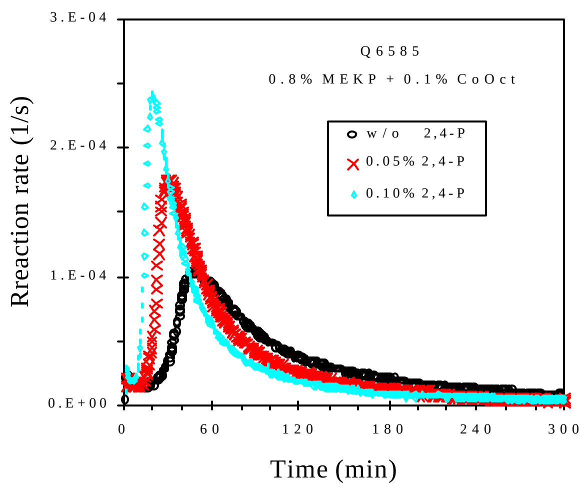


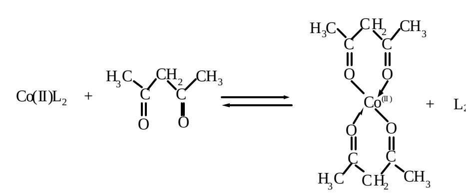
Fig. 2 Effect of 2,4-P on the reaction rate profiles of Q6585 at 35°C



The effect of 2,4-P on the reaction kinetics and rheological change of unsaturated polyester (UP) resins was also investigated at 35°C with the use of 0.8% MEKP and 0.1% CoOct in a UP resin (Q6585 from Ashland Chemical), shown in Figure 2. One can see that the addition of 2,4-P in Q6585 results in a consistent increase in the reaction rate and hence a shorter gel time, indicating 2,4-P acts as a co-promoter for Q6585 instead of a retarder. Similar results were obtained when another UP resin from CCP (UP551) was cured in the presence of 2,4-P.

Comparing VE with UP resins, a critical difference found between them is the acidity. The pH value of different resins measured in 10% methanol solution shows that both UP551 and Q6585 resins have a pH value of about 4. On the other hand, the pH value of VER-350 is 6.4. A variation of pH may result in the alternation of redox potentials of either or both components in the redox system, consequently affecting the total reaction rate. In the less acidic system, the addition of 2,4-P leads to a substitution of ligands associated with cobalt ions, forming a relatively stable cobalt compound as compared with CoNap or CoOct (Scheme 1). Thus, 2,4-P acts as a retarder. When 2,4-P is added to UP resins, the high acidity of the resin systems tends to degrade the formed metal chelate ring, forming more active metal ions that may enhance the activity of decomposing the initiators. The net effect is an increase in the rate of co-polymerization.

The acceleration effect of 2,4-P was also observed when it was added in a VE resin (VER-780). VER-780 is an epoxy-based VE, with a chemical structure similar to VER-350, except that it is acid functional and with a pH value of 2.9. Results measured by DSC and RDA show that the reaction rate increased and the gel time decreased with the addition of 2,4-P. From this result, one may conclude that the function of 2,4-P is altered from a retarder to a co-promoter when increasing the acidity of VE resins. We are currently developing a new curing agent system to achieve a long mold filling time but a short cure time (i.e. retardation in the beginning, but acceleration at the later time) for room temperature composite manufacturing.



SCHEME 1. Substitution Effect of 2,4-Pentanedione (L: ligand, i.e., naphthenate or octoate).

Effects of Resin Chemistry on the Reaction Kinetics of Unsaturated Polyester and Vinylester Resins

By Huan Yang (Lee)

Unsaturated polyester and vinylester resins are the two major thermoset resins used in low temperature composite manufacturing processes, e.g. the Seemann Composite Resin Infusion Molding Process (SCRIMP). Understanding the reaction kinetics and network formation can be critical to SCRIMP. A series of well-defined model resins are being used to study the effect of resin chemistry on the reaction kinetics and rheological changes. The effects of styrene concentration and temperature on the cure kinetics of styrene/vinylester systems are under investigation. The glass transition temperature of polyester/vinylester resins cured at different temperatures is measured and used to monitor the final conversion change. A mechanistic kinetic model is proposed to simulate the reaction kinetics and the final conversions of the various resins in low temperature copolymerization. The results may shed light on resin modification and process innovation.

SMC Formation and Molding

By Shoujie Li, Travis Horstman, and Lisa Abrams (Lee and Castro)

Dry fibers in SMC can cause defects in molded parts. Experiments are being carried out to understand the relation between dry fibers and the quality of molded composites. When optimizing the SMC compression molding cycle, it is important to look at the filling stage. The shorter the filling time, the more reactive an SMC can be used and thus the shorter the cycle time. Being able to predict the press force needed to close the mold at a given speed is extremely important. We have developed a simple model that can be used to obtain the closing force. The longest part of the molding cycle during SMC compression molding is the curing stage. Thus it is extremely important to be able to predict its duration to estimate the cost of manufacturing a part. We have developed a series of charts that can be used to estimate the steady state cure time (and hence the manufacturing cost) for new parts. The long-term goal of our research is to develop a model to predict closing forces as a function of raw material parameters—paste rheology, glass length and concentration—without the need to make the SMC.

Tackifier Assisted SCRIMP for Aerospace Applications

By James Shih (Lee)

A high temperature, tackifier-assisted SCRIMP technique has been successfully developed in our laboratory. The composites molded by this method based on PR500 resin and PT500 tackifier show mechanical properties similar to the composites molded by RTM, and the fiber content can achieve 60% by volume. Experimental results show that G-prime sizing on the AS4 fiber surface functions like tackifier. It strongly improves the preform dimension control. Without the G-prime sizing, the tackifier should stay inside the fiber tows in order to maintain good dimension control. However, tackifier located inside the fiber tows tends to result in more microvoids there, which greatly reduces the composite interlaminar shear strength. PT500 tackifier does not affect the PR 500 composites as long as the void content remains the same. Our current research is focused on molding high temperature SCRIMP panels with various resins and tackifiers and comparing their properties with PR500/PT500 composites.

Shrinkage Control of Resins Cured at Low Temperatures

By Xia Cao (Lee)

When unsaturated polyester (UP) resins are cured at low temperature, poor shrinkage control and high residual styrene are the major concerns. Our recent study showed that when the degree of unsaturation (i.e. the number of C=C bonds per molecule) decreases, the shrinkage control efficiency of low profile additives (LPAs) also decreases. On the other hand, the final conversion of the resin increases. Further investigation found that the thermal history (temperature gradient in particular) of the system is critical to the final volume shrinkage of the cured resin. We are currently investigating the effect of temperature or the temperature ramping rate during molding on the final shrinkage and final resin conversion of low temperature resin systems. The effects of combining the UP and vinyl ester resins and changing the curing agent will also be studied. Our goal is to develop a low temperature resin system with good surface quality and low styrene residue.

Design of an Accelerated Outdoor Aging Simulator for Tire Rubber Compounds

By Bart J. LaCount (Castro)

Tire rubber compounds are subject to physical and chemical property changes due to aging. Currently the available standard tests involve only one or at most two influencing factors, making it difficult to accurately predict the aging resistance in real service. Research has been completed on the behavior due to thermal aging, dynamic ozone aging, an outdoor aging test, and a novel multiple factor test. This cyclic aging study consisted of four single-factor sub-tests designed to simulate the outdoor aging by artificial means. A prototype "service-simulating, accelerated aging chamber for tire rubber compounds" is proposed. This prototype chamber will include the different aging factors and will operate at a moderate temperature to avoid changing the aging mechanisms. It also will utilize a small specimen size to reduce the test time to weeks.

Solvent-less Prepregs for Electronic Applications

By Ranjeet Hogade, Lynnette Dehnke and Ming Li (Castro, Lee)

An isothermal lubricating model on injection pultrusion of electronic pre-pregs was developed and verified experimentally. Experiments were conducted using a Rheometrics RMS 800 and a pilot facility. The model offers an accurate prediction of the pulling force and the onset of back-leakage. When using a low viscosity fluid, when only one side of the die in injected, the lubricating layer on the opposite side needs higher injection rates to develop. This points to the need for injecting at both the top and bottom in the real process. The model is being used to study the technical feasibility of the process.

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