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14. ABSTRACT

We were recently informed by Dr. L.-S. Tan that the FC of the nitro acid can be performed in methanesulfonic acid with phosphorus pentoxide as a dehydrating agent (hereafter referred to as the MSA system). Since this FC reaction is performed upon the acid directly, there is no need to convert to the acid chloride, which obviates one step from the scheme. Upon learning this information we reproduced the reaction with the nitro acid and then quickly applied it to our imide first scheme. The result was a successful 3-step synthesis of monomer for PAEKI (See Scheme 3). Subsequent discussion with Dr. Tan revealed that they had also discovered this route (or similar) to monomer a few months earlier. (This occurrence motivated us to improve communications among collaborators.)

15. SUBJECT TERMS

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Hyperbranched Polymers for Resin Transfer Molding

Final Report
1 May 2006 through 31 October 2006

Grant No. FA9550-06-1-0274

Principal Investigator: Prof. Patrick T. Mather

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AFOSR/NL

PROGRESS REPORT

Hyperbranched Polymers for Resin Transfer Molding (FA9550-06-1-0274)

Prof. Patrick T. Mather,
Case Western Reserve University
Start Date: 1 March 2005

I. OBJECTIVE

The purpose of this proposal study new low viscosity thermoset additives – hyperbranched polymers (HBPs) – as processing aids and toughening additives for high performance resin transfer molding (RTM) resins. The proposed research project will culminate with a detailed understanding of the trends in performance properties with materials characteristics, including hyperbranched architecture, blend composition, and processing protocol.

II. APPROACH

The proposed research will involve intensive study of the impact of a family of high temperature hyperbranched polymers upon blending with state-of-art thermoset systems on: (i) processing characteristics, (ii) final thermal properties, (iii) fracture toughness, and (iv) bonding to graphite fiber. For all materials examined within a carefully designed test matrix, we will quantify the molecular architecture (incl. degree of branching, DOB) and examine their influence upon physical properties, stated above. More specifically, we will prepare reactive hyperbranched polymers with systematic control over chain architecture and study the cure behavior of the prepared reactive HBPs in two important composite matrix resins: AFR-RTM and PETI-330. We will also study and understand the influence of added HBPs on curing behavior, especially viscosity, and cured resin properties, including Tg, modulus, and fracture toughness. Next, we will determine the mechanism of toughening in HBP-modified systems in order to better know how to design the polymers for this improvement. Finally, we will study the modification to PETI-330 wetting and adhesion to graphite fiber resulting from HBP incorporation using the method of single fiber fragmentation.

III. SCIENTIFIC CHALLENGE

This proposal is quite aggressive, scientifically, presenting significant challenges in the elucidation of the mechanisms of viscosity reduction and toughening enhancement. Particularly challenging is the development of structure-property relationships in these complex hyperbranched polymers, where the architecture must be determined in a nonconventional way. Significant advances in experimental methods will be required which enable simultaneous observations of both structure and properties, particularly toughness.

IV. Technical Progress

The following is organized in the form of monthly reports that started in July (July, August, September, and October) that are sent to AFRL/MLB personnel on a continuing basis.

IV.A. July Report

Project Goal: Develop a quantitative understanding of how hyperbranched PE-PAEKI influences the processing and properties of high-performance RTM thermosets.

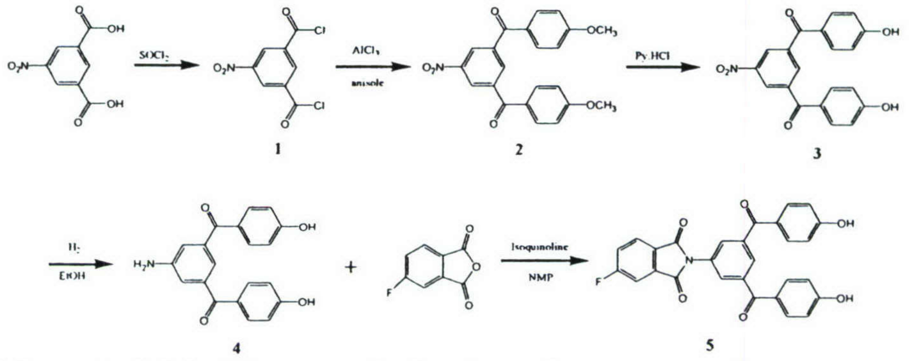
Short-Term Motivation:

1) Improvement of yield and time of monomer synthesis for PAEKI
2) Chemorheological Characterization of neat AFR-RTM (analysis of cure kinetics)

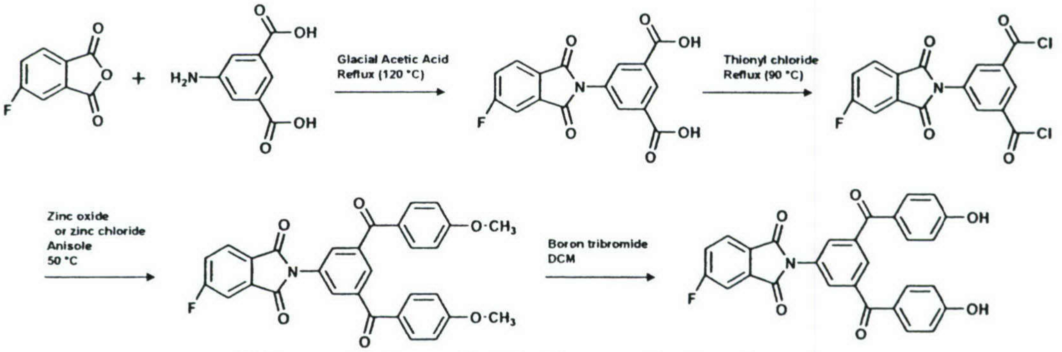
1) Previous Work:

Synthesis of monomer for PAEKI needs to be performed on a large scale (10g to 30g) and have a reasonably short production time and high yield in order to allow for sufficient testing of the final blend properties. In an effort to meet these goals, the monomer synthesis, previously a 5-step synthesis, was reduced to 4 steps by performing imidization first, thereby negating the need for hydrogenation (See Schemes 1 and 2). Imidization was accomplished by refluxing the aminoisophthalic acid with fluorophthalic anhydride in anhydrous glacial acetic acid (~140 °C) overnight to give 82% yield of pure white crystals.

By performing the imidization first, the reactivity of the reactant in the Friedel-Crafts reaction (hereafter referred to as the FC reaction) was changed requiring reaction conditions to be optimized. A variety of reaction temperatures and catalyst ratios were studied and the results quantified by the yield of the disubstituted (desired) product and the incompletely reacted monosubstituted product. Results are shown in Figure 1. A catalyst ratio of 5:1 $AlCl_3$:reactant at a temperature of 60 °C gave the best results from our set of experiments with a final yield of 42%, compared to 28% from the original scheme.



Scheme 1: Original 5-step synthetic scheme for monomer of PAEKI.



Scheme 2: 4-step imide-first synthetic scheme.

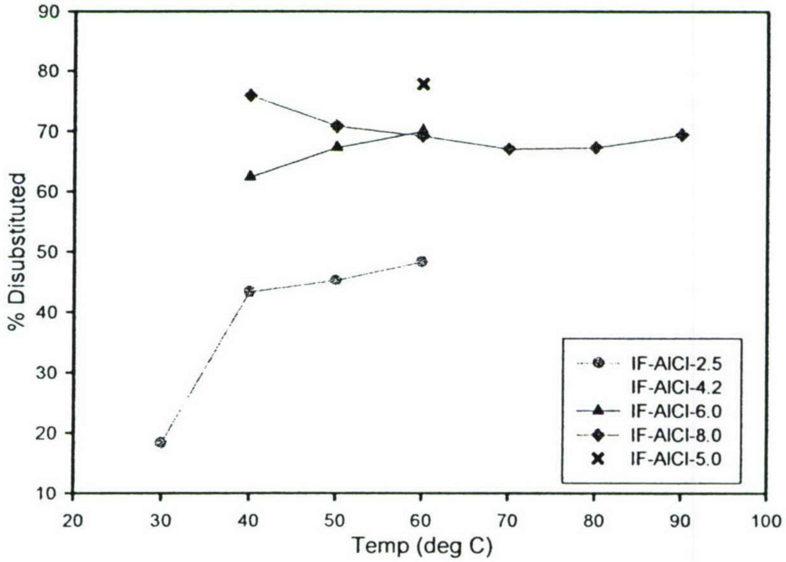
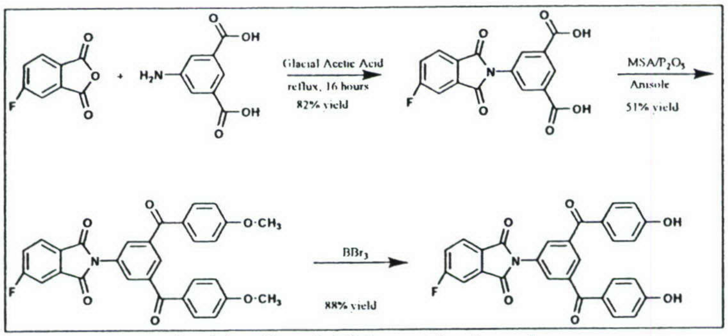


Figure 1: Effect of catalyst ratio and temperature on conversion (quantified by NMR as the ratio of disubstituted molecules to the monosubstituted molecules).

Results and Discussion:

We were recently informed by Dr. L.-S. Tan that the FC of the nitro acid can be performed in methanesulfonic acid with phosphorus pentoxide as a dehydrating agent (hereafter referred to as the MSA system). Since this FC reaction is performed upon the acid directly, there is no need to convert to the acid chloride, which obviates one step from the scheme. Upon learning this information we reproduced the reaction with the nitro acid and then quickly applied it to our imide first scheme. The result was a successful 3-step synthesis of monomer for PAEKI (See Scheme 3). Subsequent discussion with Dr. Tan revealed that they had also discovered this route (or similar) to monomer a few months earlier. (This occurrence motivated us to improve communications among collaborators.)



Scheme 3: 3-step imide-first MSA synthetic scheme.

While initial results were good, a few different temperatures were tested to see the effect on final yield. In total, the temperatures tested were (40, 50, 60, and 70) °C. The value of 60 °C gave the best results (52% yield) and will be used for larger scale reactions for monomer synthesis.

We attempted a method of demethylation that requires milder conditions than the original method, which involved a reflux with pyridine hydrochloride at 220 °C. We chose demethylation with boron tribromide in dichloromethane and proceeded to determine the necessary reaction conditions and workup. Since the methoxy reactant is soluble in the dichloromethane, but the hydroxy product is not, the reaction proceeds by precipitation. A series of reactions were performed to determine the reaction conditions that give good yields. The final result was nearly pure monomer (>95%) in 88% yield.

The final result of these monomer synthesis modifications is a total yield of ~37% in 3 steps in comparison to the original 5 step method that resulted in ~12% yield. This improvement will greatly increase our ability to perform characterization on our blend systems, especially those sent to AFOSR for the actual RTM process.

2) Chemorheological Characterization of neat AFR-RTM (analysis of cure kinetics)

Results and Discussion:

In order to compare the effect of hyperbranched phenylethynyl-terminated PAEKI (hereafter referred to as PEPAEKI) on it's blends with AFR-RTM, we first needed to study the neat AFR-RTM resin. Our preliminary results include tracking the rise of Tg with cure (by DSC) and analysis of cure by chemorheology.

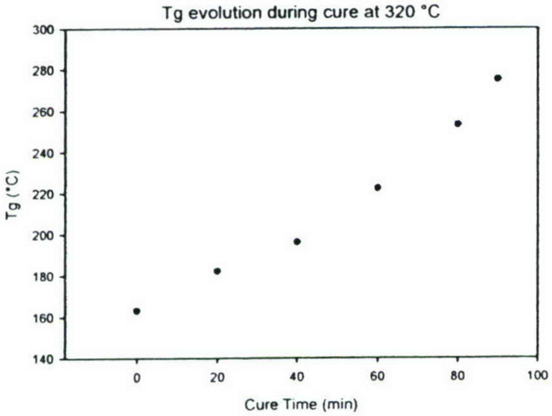


Figure 2: Effect of cure time on Tg of neat AFR-RTM at 320 °C.

The rise of Tg is a cure indicator and is also significant in relation to chain mobility and the ability of reactive phenylethynyl groups to reach each other for further curing. For this reason, we tracked Tg of neat AFR-RTM undergoing cure at 320 °C as seen in Figure 2.

Additionally, we have performed both isothermal and non-isothermal rheological experiments at temperatures between 250 °C and 371 °C. For isothermal experiments, we perform frequency sweeps (typically in a stress controlled mode). These results will allow us to determine important characteristics of the cure such as the time to gelation, which can be defined as the point where tanδ becomes independent of frequency (in the low frequency range). This gel point will help us quantify any effect that PE-PAEKI has on the gelation time. We are still working with our experimental procedure in order to get clean, analyzable data. Once completed, we will be able to quickly move on to comparison with blends with PE-PAEKI.

Non-isothermal experiments have been performed in order to characterize such features as the temperature at minimum viscosity. Previously, blends of allyl-terminated PAEKI showed both an increase in the temperature of minimum viscosity as well as the breadth of the transition, delaying that cure process and increasing the processing window. Figure 3 below shows a recent non-isothermal experiment where AFR-RTM was ramped from 288 °C to 371 °C at a rate of 4 °C/min. The properties were measured under a 1 Hz oscillatory shear with a controlled stress of 5 Pa.

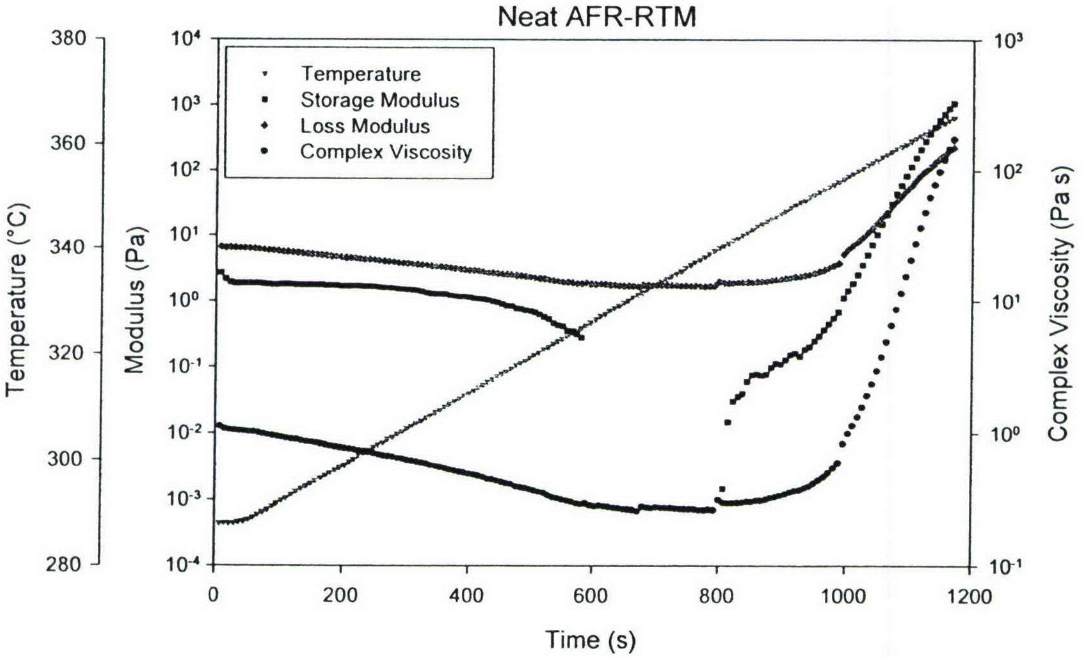


Figure 3: Non-isothermal chemorheology of neat AFR-RTM

Future Work:

1) Synthesize PEPAEKI from recently synthesized monomer
    a. Ensure completion of end-capping and removal of unreacted end-capper.
2) Prepare blends of 2% and 5% by weight of PEPAEKI in AFR-RTM for analysis.

IV.B. August Report

Project Goal: Develop a quantitative understanding of how hyperbranched PE-PAEKI influences the processing and properties of high-performance RTM thermosets.

Short-Term Motivation:

1) Synthesis and Purification of PE-PAEKI in a one-pot polymerization/endcapping procedure.
2) Chemorheological Characterization of AFR-RTM (analysis of cure kinetics)

1) Synthesis and Purification of PE-PAEKI

Phenylethynyl endcapped PAEKI has been synthesized in a one pot, two step procedure. Initially, the monomer, potassium carbonate, and NMP are heated to 145 °C for a given time (typically 4 hours) followed by heating to 160 °C or 180 °C for a given time. Subsequently, a solution of endcapper in NMP is added to the reaction and reacted for another 3 hours. After this time, the polymer is precipitated over 5% aqueous HCl and purified. In order to remove unreacted endcapper, a toluene extraction was developed where the raw polymer (after initial precipitation and drying) is slurried in hot (~90 °C) toluene for 1 hour and then filtered and dried. This method has proven to be successful as best evidenced by the GPC results seen in Figure 4. The toluene extraction apparently not only removes the unreacted endcapper (seen at about 19.5 mL), but also some of the low molecular weight material (~17 to 19 mL).

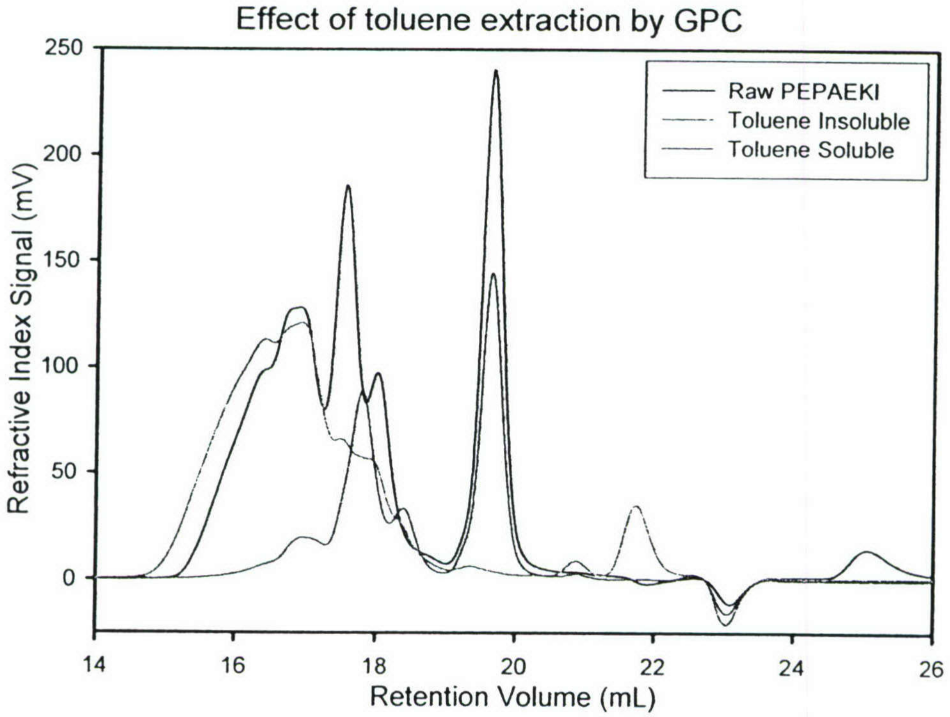


Figure 4. GPC fractionation of PEPAEKI before extraction, soluble, and insoluble fractions.

After extraction, we have confirmed by NMR that reacted endcapper is present in significant quantities although it is difficult to quantify the degree of endcapping with this method. The sample shown above had a second stage of polymerization at 160 °C for 3 hours before endcapping for an additional 3 hours at the same temperature. The calculated molecular weight was about Mw=7,500 g/mol. In an effort to increase molecular weight, a polymerization was performed with a second stage at 160 °C for 17 hours before endcapping. Under these conditions we achieved a polymer molecular weight of 33,000 g/mol. Currently, we are exploring the effect of increasing the second stage temperature to 180 °C on polymer properties.

2) Chemorheological Characterization of neat AFR-RTM (analysis of cure kinetics)

Sample preparation:

Samples for chemorheology were melt-degassed under vacuum at 260 °C for 4 hours in a foil cup. Significant foaming occurs during this procedure, but the final product is a transparent amber glass. A blend of 5-wt% PE-PAEKI in AFR-RTM was also prepared although its rheology is still in initial stages and results will be presented in the future. Currently, the blend is made by solution blending in THF. The transparent solution is evaporated and then melt degassed with the same procedure as the neat resin to yield a clear amber glass. The most recent PEPAEKI (33 kDa), however, appears to not be fully soluble in THF, yielding a turbid solution. Solution blending may still allow for homogenous mixing, however, since the heterogeneity is small enough that diffusion in the subsequent melt degassing step should form a homogenous film. Ideally, we intend to develop an entirely melt-mix method in order to circumvent the use of solvent, which will not be feasible for scale-up.

Chemorheology:

Our chemorheology focuses on two major techniques that reveal different aspects of the thermoset curing. While non-isothermal studies focus on the initial curing of the resin upon injection into a heated mold, isothermal studies can more accurately quantify the kinetics of the curing reaction and reveal subtle differences between various batches and blends. We are currently performing both types of studies, but here we will focus on isothermal studies of the neat AFR-RTM resin.

Figure 5 shows an example result for cure at 300 oC of neat AFR-RTM wherein we plot the time evolution of the shear storage and loss modulus and the complex viscosity for an oscillatory shear of 0.996 rad/sec. An arrow shows the gel point as determined by loss tangent frequency independence, which we now describe. An important quantity to measure in isothermal curing studies is the time to gelation. In order to measure this time we must first pick a definition of gelation. A commonly accepted definition is the point at which $\tan(\delta)$ becomes independent of frequency (within a low frequency range). This point can be obtained by performing sequential frequency sweeps on a material undergoing isothermal cure and finding the point at which the $\tan(\delta)$ curves converge on a plot of $\tan(\delta)$ versus time for various low frequencies.

For our experiments, samples were loaded between preheated, disposable parallel plate fixtures. Care was taken to minimize the time of loading and the drop in temperature from the open oven. Temperatures typically were stabilized to within 5 °C of the set temperature within 2 minutes of loading and were fully stabilized (accuracy 0.1 °C) within 10 minutes of loading. Cure time is referenced from the moment the sample first comes in contact with the preheated rheometer plate. At low viscosities, the loss tangent can be difficult to measure since the storage modulus for oligomeric resins is very low. In order to achieve good results, a stress amplitude of 50 Pa was chosen, which allows for accurate measurements of the loss tangent leading up to the gel point. After gelation, the data again becomes noisy because there is not enough stress to induce a measurable strain in the sample. An example of our data can be seen in Figure 2 for isothermal cure at 300 °C. In this experiment, the storage modulus became measurable (allowing accurate calculation of loss tangent) around 7,600 seconds of cure time. The gel point can be seen as the convergence of the curves at 11,600 seconds, after which the data again becomes noisy due to low strain values. Even through the noise, though, we can clearly see that the order of the curves has reversed.

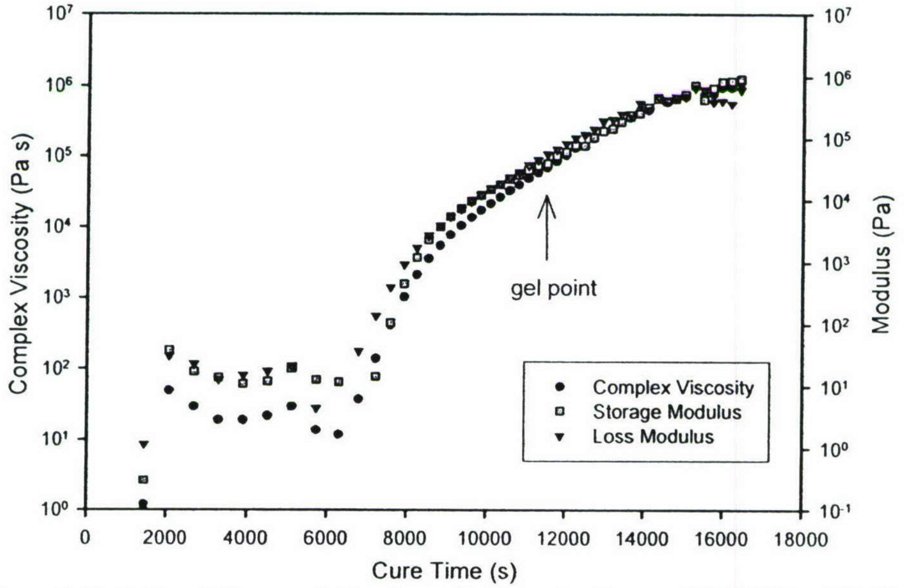


Figure 5. Evolution of shear moduli and complex viscosity for neat AFR-RTM at 300 °C.

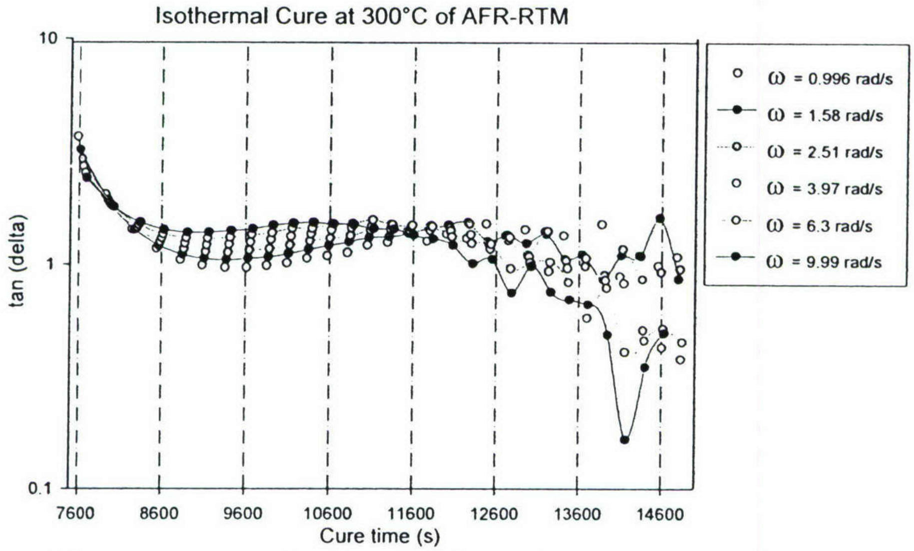


Figure 6. Loss tangent versus time for various frequencies during cure of AFR-RTM at 300 ₒC.

By measuring this gel point for various isothermal temperatures, we can construct a process diagram of gelation time versus temperature (Fig. 7) for this material. Additionally, we can fit this data to a model such as the Arrhenius model, commonly used for kinetics. The Arrhenius equation (Eqn. 1) relates a rate constant, *k*, to an activation energy, which is a material property that quantifies the amount of energy needed to reach a given state.

$$k = k_0 \cdot \exp\left[\frac{-E_a}{R \cdot T}\right] \qquad (1)$$

By replacing the rate constant with the inverse of time to gelation we adapt the equation to quantify the energy required to reach gelation in our materials. This activation energy can be extracted from the given data by replotting it on an Arrhenius plot as shown in Figure 8. For the neat AFR-RTM resin, we calculate an E_a value of 119.3 kJ/mol.

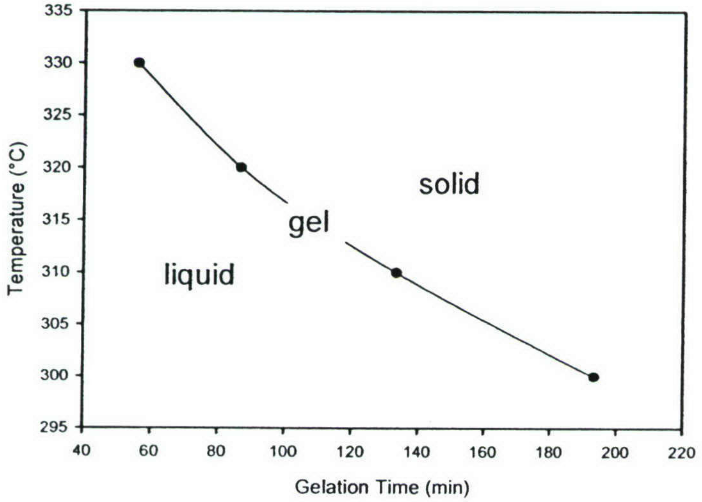


Figure 7. Process diagram showing the dependence of gel time on cure temperature.

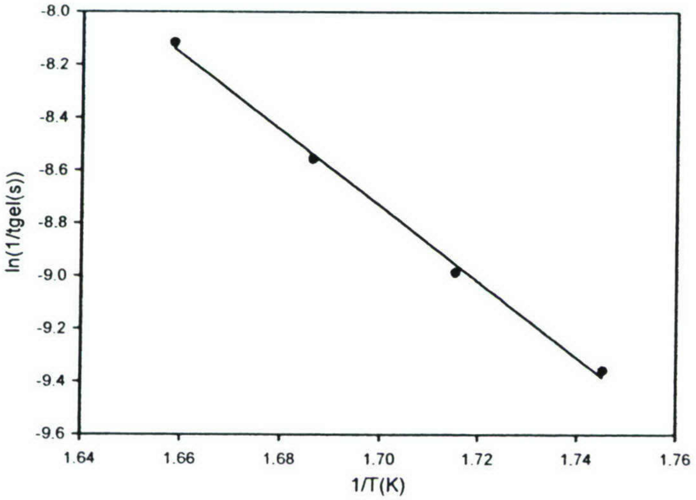


Figure 8. Arrhenius plot of gelation time for calculation of activation energy.

One problem that we have been investigating is that there tends to be an expansion of material out of the rheometer plates during cure. We recently determined that the cause of the expansion was due to large bubbles forming in the material during cure. This problem is seen even when testing immediately after a 4 hour degas under vacuum at 260 °C. Figure 9 displays the TGA of neat AFR-RTM resin after degassing. It is clear that mass loss is minimal up to the degassing temperature, but increases significantly at higher temperatures. If the mass loss were due to existing volatile compounds such as high boiling solvents, I would expect to see a significant range of temperature between that of the degas and the onset of weight loss due to the effect of vacuum during degassing. The rapid onset suggests that the weight loss is actually due to thermal degradation. Since bubbling is not seen in the resin transfer molded samples prepared at AFRL, it is possible that the pressure present during cure plays a significant role in suppressing bubble formation. We will continue to study the problem and attempt to ensure the accuracy of our rheological characterization. In the past, Anton Paar manufactured ovens for their rheometers capable of elevated pressure measurements; PTM will look into this.

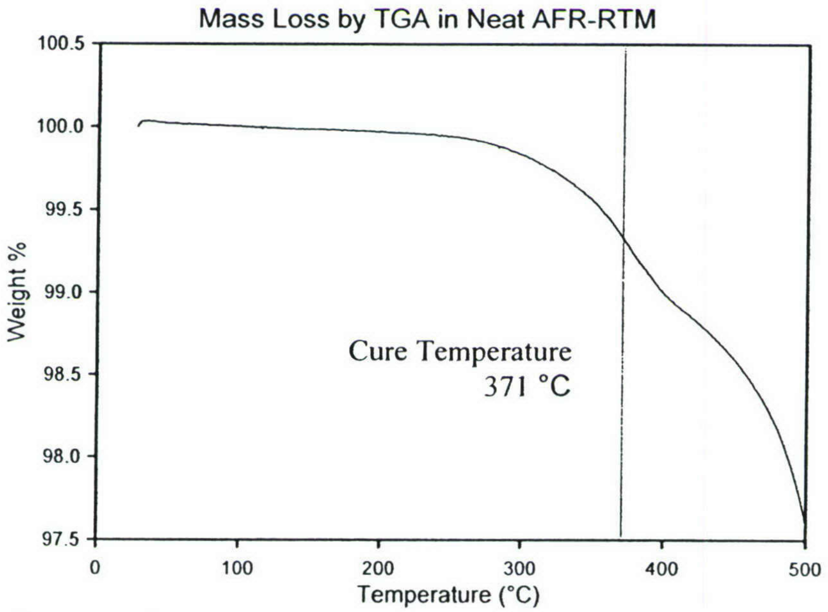


Figure 9. Weight Loss during a temperature ramp of 20 °C/min under nitrogen.

Future Work:

1) Develop method of sample prep and/or experimental to prevent or reduce the effect of bubble formation during cure.
2) Perform chemorheological analysis of blends of 2% and 5% by weight PEPAEKI in AFR-RTM.

IV.C. September Report

Project Goal: Develop a quantitative understanding of how hyperbranched PE-PAEKI influences the processing and properties of high-performance RTM thermosets.

Short-Term Motivation:

Chemorheological Characterization of AFR-RTM – The issue of gas evolution during cure.

1) Gas Evolution during Cure of AFR-RTM

In our efforts to monitor the kinetics of cure in the AFR-RTM resin, we have encountered the evolution of gas during cure at atmospheric pressure. Bubbles occur even when the resin is cured immediately after the degassing step. Bubbles formed from this gas in the resin make accurate rheological measurements using current fixtures unfeasible. Our recent efforts have been focused at preventing the evolution of this gas during our experiments. Our first approach was to purify the resin by a solvent precipitation step that should be able to remove residual high boiling solvents and possibly some impurities as well. AFR-RTM resin was precipitated from tetrahydrofuran into methanol with high yield (>98%) and then dried at 80 °C. Figure 10 demonstrates the effectiveness of this method in comparison to melt degassing.

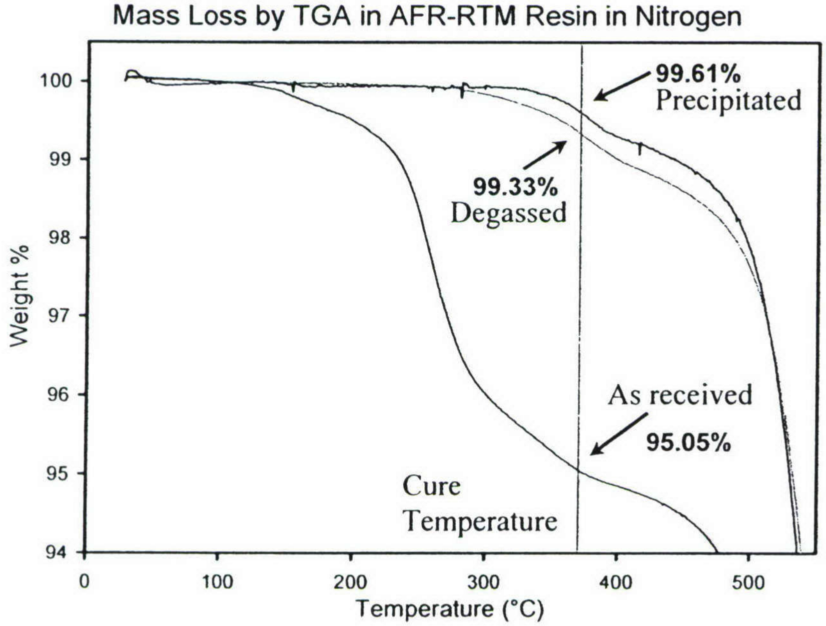


Figure 10. Comparison of AFR-RTM weight loss in nitrogen for various samples. Degassed sample was degassed under vacuum at 260 °C for 4 hours. Precipitated sample was precipitated from THF into methanol and dried under vacuum at 80 °C for 3 hours. As-received resin is included for comparison.

While the melt degassed sample begins losing weight just above the degassing temperature of 260 °C, the precipitated sample holds off weight loss until over 300 °C at this ramping rate of 20 /min. To compare more directly with cure conditions, an isothermal TGA experiment was performed in air on this precipitated sample after an additional melt degassing step of 4 hours at 260 °C under vacuum as shown in Figure 11.

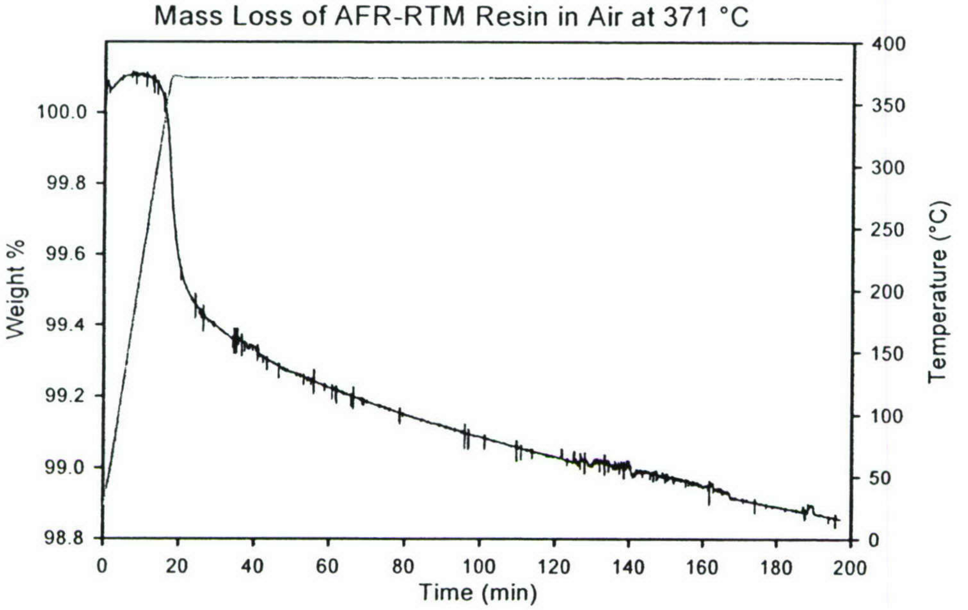


Figure 11. Cure simulation of AFR-RTM resin that has been precipitated from THF into methanol and then vacuum degassed for 4 hours at 260 °C. Ramping rate is 20 °C/min to 371 °C followed by a 3 hour isothermal.

Here we see that a weight loss of over 1% occurs during the 3 hour cure cycle. Similar results are seen in nitrogen. Even though 1% is small in terms of mass, it can attain a very significant volume upon conversion to a gas phase. While we have not yet determined the source of the gas, it is apparent that the RTM method, involving pressures of 100 psi, prevents its evolution as evidenced by the lack of voids observed in photomicrographs of AFR-RTM composite panels produced at AFRL.

We are exploring two possible solutions to the current challenge. First, we are considering different plate geometries for our rheometer that allow the venting of evolved gasses. Second, we are exploring alternative rheometers such as a piston-capillary type rheometer that allows characterization of liquids under pressurized conditions. At the same time, we plan to attempt cure in a pressurized reactor as a means of verifying these conclusions and preparing samples for mechanical testing.

Future Work:

1) Develop a method of rheological characterization that minimizes the effect of gas evolution by either pressure or venting.
2) Begin preparation of sample bars by cure in a pressurized oven.

IV.D. October Report

Project Goal: Develop a quantitative understanding of how hyperbranched PE-PAEKI influences the processing and properties of high-performance RTM thermosets.

Short-Term Motivation:

To obtain accurate rheological characterization of AFR-RTM and blends during cure, the problem of gas evolution during cure must be solved. Here we attempt two methods:

1) Ring-plate fixture design for rheometer.
2) Particle Tracking Microrheology

1) Ring-plate fixture design for rheometer

Large bubbles form during chemorheology between parallel plates because of the large volumes of material with no free surface for release of gases. In order to minimize the effect of bubbles, we attempted to design a rheometer fixture that would have a larger surface to volume ratio and shorter distances for bubbles to travel to reach a free surface. We took advantage of the fact that most of the signal (torque) in parallel plate fixtures is generated at the edges to design a top ring fixture that will be mated with a bottom plate. In our design, the ring generates 66% of the torque that would be obtained with a plate of the same diameter. The design forces large bubbles to escape from the measurement zone and thus reduces the total effect of the bubbles on the rheological calculations. Figure 12 displays our new fixture, which features a disposable ring with a more permanent bolt plate. The bolt plate includes vents maintain atmospheric pressure.

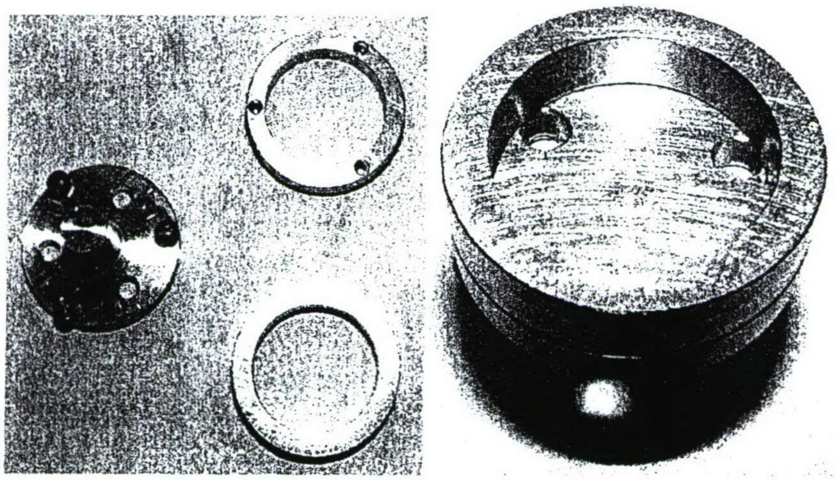


Figure 12. Picture of the new ring fixture fabricated at Case. Left shows the disassembled fixture consisting of a bolt plate and a disposable ring (top and bottom shown). Right shows the assembled ring fixture (upside down for viewing).

The new fixture was qualified by testing standard and well characterized materials before moving on to AFR-RTM resin. Initial testing shows that the ring design significantly reduced the accumulation of trapped bubbles but did not completely solve the problem. Figure 13 shows a sample cured at 320 °C for about 90 minutes. The resin had been dried at 260 °C (after a precipitation from THF into methanol) previously and was redried at 150 °C immediately prior to the experiment to remove absorbed water. The bubbles cover about 40% of the measurement surface.

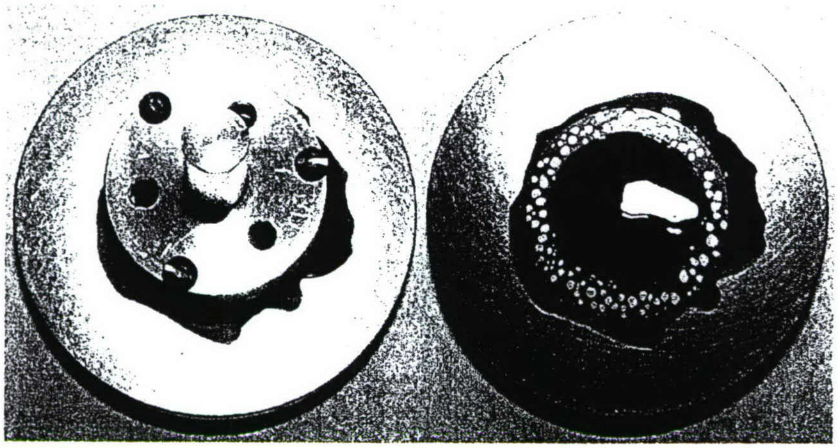


Figure 13. Picture of an AFR-RTM sample after cure at 320 °C for 90 minutes. Left shows the sample between the fixtures as it was cured. Right shows the sample after removal of the top ring fixture (no material adhered to the top ring).

This system should give more reproducible measurements for analysis such as time to gelation. It may also be possible to infer rheological properties such as viscosity by accounting for the reduced contact area, but we are researching a better method for this type of data in the form of particle tracking microrheology.

2) Particle Tacking Microrheology

There is a growing body of research that focuses on measuring rheological properties on micro-scale regions within a sample. This method has been developed to aid in characterization of material properties that are difficult to measure in bulk, either because samples are too small or there are complications maintaining the state of the sample in a traditional rheometer. One sub-category of microrheology focuses on the movement of micron-scale particles embedded in a material and the response of the particles to forces imposed on them. In the simplest setup, the forces are the Brownian forces associated with thermal energy. By tracking the motion of the particles, we can we can determine the rheological properties of the fluid in which they move.

Much of the equipment required for particle tracking microrheology (PTM) is already owned by the Mather group (high power microscope and hot-stage with video image-capture). Additionally, software has already been developed in other research groups to analyze images and calculate the motion of the particles. Additionally, from Figure 13, we can see that resin that was not covered during cure contains no bubbles. Additional experiments showed that no bubbles are ever formed in the uncovered resin, leading to the conclusion that gases can travel short distances through the resin without forming bubbles if they are able to reach a free surface. This led us to test the feasibility of studying AFR-RTM by an uncovered PTM.

Only a specific range of viscosities can be accommodated by PTM dependant on a variety of factors such as the size of the probe particle and the densities of the particle and the surrounding medium. Rough calculations show that using 1 μm particles with a density typical of inorganic crystalline compounds, our system falls well within the measurement range. Thus the movement of the particles should be measurable and the particles are not expected to sediment out of the material on the time frame of the experiment. Next we needed to verify that we could visualize a probe particle within the resin. Figure 14 shows images taken of uncovered AFR-RTM resin on a glass slide that had been blended with a fine zinc oxide powder at 250 °C.

Figure 14. Visualization of AFR-RTM resin with (left) and without (right) incorporated zinc oxide particles.

Here we can see that, while dust is present in the original resin, it is quite feasible to image the zinc oxide particles through an uncovered ~0.5mm thick resin sample at room temperature. This leads us to believe that PTM is a viable method for measurements up to the gel point of our material and we will be considering the implementation of this technique for our experiments.

Future Work:

1) Continue development of analysis by ring-plate and possibly microrheology techniques.
2) Develop techniques for characterization of final cured sample properties.

IV.E. November Report

Project Goal: Develop a quantitative understanding of how hyperbranched PE-PAEKI influences the processing and properties of high-performance RTM thermosets.

Short-Term Motivation:

To obtain accurate rheological characterization of AFR-RTM and blends during cure, the problem of gas evolution during cure must be solved. Here we attempt two methods:

1) Particle Tracking Microrheology
2) Cured Sample Bar Preparation

1) Particle Tracking Microrheology

Samples of AFR-RTM have been purified by solution filtration from THF so that less dust is present during optical rheological characterization. Filtered solutions were precipitated over methanol and powder blended with ZnO powder at various dilutions to yield samples with a workable concentration of probe particles for particle tracking microrheology. A mass loading of about 0.005% gives the roughly 100 particles needed in our field of view.

Pictures were first obtained with AFR-RTM/ZnO blends at room temperature in order to develop the image analysis needed to accurately identify and determine the position, with sub-pixel accuracy, of the ZnO particles. Figure 15 shows a blend of AFR-RTM with 0.008% loading of ZnO.

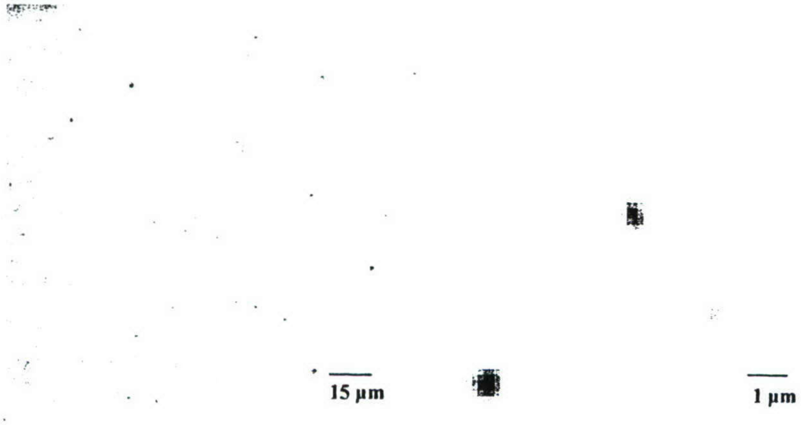


Figure 15. Optical microscopy of an AFR-RTM/ZnO blend at 0.008% mass loading. Left shows the full field of view. Right shows a zoom of one particle in the image to the left.

Accurate mapping of the Brownian motion of the probe particles will require measurement of position to subpixel accuracy. This accuracy can be achieved by fitting a Gaussian peak to the intensity of pixels that make up a given particle. As long as the diffraction of the particle is spread over enough pixels (10 to 20) then a careful fit can accurately determine the position of the peak to an accuracy of 0.1 pixels. While we are currently obtaining software designed for this purpose, we can perform simple line scans on individual particles in the x and y directions to yield their position. An example of this process is shown in Figure 2 for the pixel centered in Figure 1 (right).

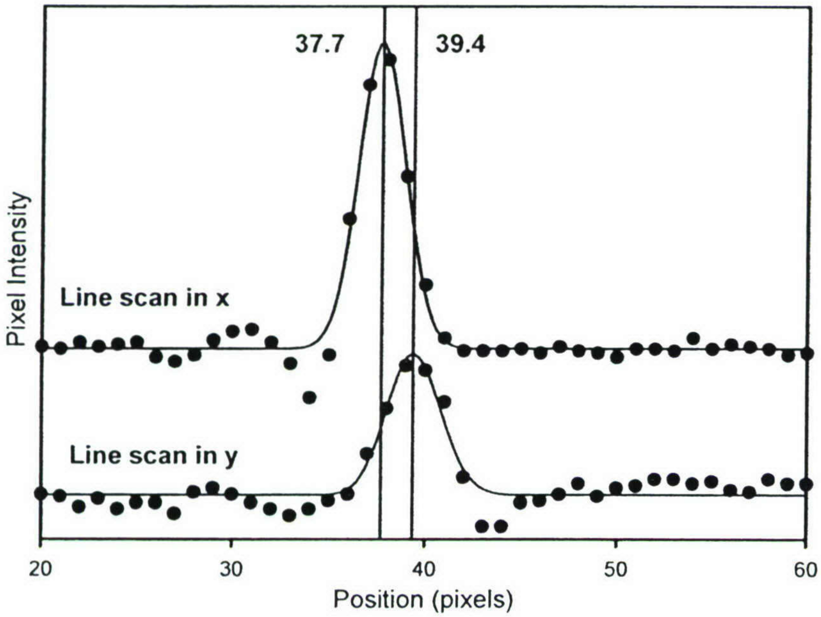


Figure 16. Line scans in the x and y directions of a particle indicating it's position to a sub-pixel accuracy.

Next, we need to confirm that we can measure the Brownian motion of probe particles within our matrix. As an initial test, we prepared samples of a commercially available DGEBA/DDS epoxy resin blended with the same ZnO particles. This resin was chosen because of its relatively lower cure temperature (~140 °C) and a similar viscosity to AFR-RTM at cure temperatures.

Two initial problems have presented themselves in the epoxy system that are currently being worked on. First, vibrations in the room have an effect on the image sequences in the form of jitter. While this could be corrected using appropriate image analysis, we will first attempt to remove the vibrations by moving our microscope to a vibration-dampening table. Second, there was a significant flow of the material before gelation that would significantly interfere with analysis. This flow likely comes from both the level of the microscope as well as the non-uniformities in the sample surface. Leveling of the microscope can be easily performed once it is on the vibration-dampening table. Additionally, we plan to correct for thickness variations by applying the sample to the slide with a flat edge. We may also need to alter the slide by etching a grid or using Teflon lines to confine the sample.

2) Cured Sample Bar Preparation

To prepare for analysis of final cured resin properties we are developing a cure schedule that will produce bubble-free sample bars with dimensions required for mechanical testing such as SENB fracture toughness, which requires 2.5 mm x 5 mm x 25 mm. The difficulty in producing these bars is in the prevention of bubbles. As has been shown in our previous results, AFR-RTM resin cured at atmospheric pressure produces a large number of bubbles in samples of significant thickness (greater than 1 mm). This problem is not present in samples cured under pressure such as those produced at AFRL with an RTM injection pressure of about 100 psi. Our primary approach to cure without bubbles is to initially cure the material at a lower temperature. Observation of the location and shape of bubbles within sample bars indicates that the resin is still liquid once all the bubbles have formed. This is apparent by the lack of bubbles near the very bottom of the bar and the teardrop shape of all bubbles in the center of the bar.

For this reason, we hypothesize that there is a critical degree of cure or viscosity above which bubbles will no longer form. Our goal then is to reach this degree of cure at a lower curing temperature before increasing to the final cure temperature. An initial experiment was performed to examine effect of curing sample bars at 370 °C, 320 °C, and 300 °C. Figure 17 shows reflective optical micrographs of the final, cured sample bars at each temperature. It is clear from the images that bubble formation is reduced drastically at lower cure temperatures. All three samples were cured for a period long enough to reach the gelation point based on our previous chemorheological results.

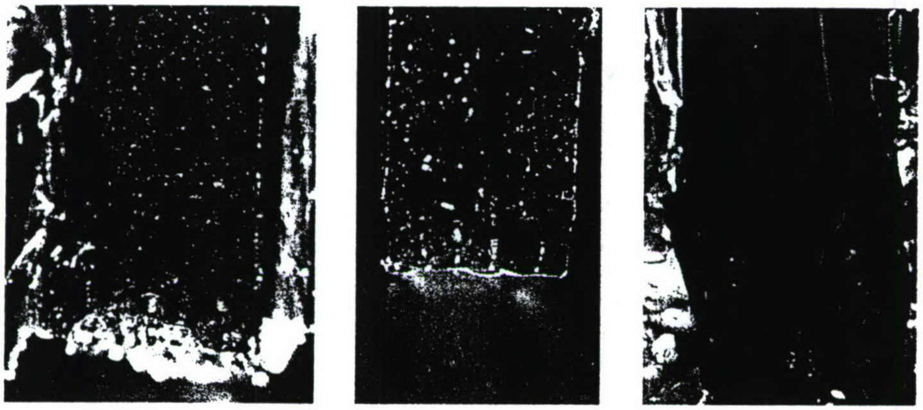


Figure 17. Cured sample bars of neat AFR-RTM resin. All samples were melt-degassed at 260 °C for 6 hours prior to curing. Samples were cured for 3 hours at 370 °C (left), 320 °C (middle), and 300 °C (right). Bar dimensions are roughly 5 mm wide by 3 mm thick.

We will continue this study with cure temperatures of 290 °C and 280 °C. Since these cure temperatures take a significant amount of time, we will also be attempting to perform a secondary degassing at 260 °C after a certain amount of pre-curing at 300 °C. This may allow us to create a shorter method to reach the gel point without formation of bubbles. Once a sample bar has been cured to the gel point, we should be able to ramp the temperature slowly to the final cure temperature of 371 °C to avoid formation of bubbles.

Future Work:

1) Advance sample preparation and image acquisition techniques for particle tracking microrheology to allow measurement of Brownian motion of probe particles.
2) Complete cure profile of AFR-RTM sample bars and begin mechanical testing (DMA and SENB fracture toughness).

V. Personnel Supported

a. Number of PI's and Co-PI's involved in the research project: **1**
PI: Prof. Patrick T. Mather

b. Number of Post Doc Supported in the last 12 months under AFOSR: **0**

c. Number of graduate students supported in the last 12 months: the equivalent of **1** graduate assistants. Timothy Marsh

d. Other researchers supported in the last 12 months by AFOSR: **1**
1 intern from France: Mr. Morgan Cante

VI. Publications

Publications by PI submitted, accepted, or appearing in the last 12 months period in refereed journals and referencing AFOSR support: **6**

H. Qin, P.T. Mather, J.-B. Baek, and L.-S. Tan, "Modification of bisphenol-A based bismaleimide resin (BPA-BMI) with an allyl-terminated hyperbranched polyimide (AT-PAEKI)," *Polymer* **47** (8) 2813-2821 (2006).

B.-S. Kim, P.T. Mather, "Amphiphilic Telechelics with Polyhedral Oligosilsesquioxane (POSS) Endgroups: Dilute Solution Viscometry," *Polymer* **47**, n17, 6202- 6207 (2006).

B.-S. Kim and PTM, "Amphiphilic Telechelics Incorporating Polyhedral Oligosilsesquioxane (POSS): 2. Microstructure and Rheology," in press *Macromolecules* (2006).

P.T. Mather, Byoung-Suhk Kim, Qing Ge, Changdeng Liu "Nonionic telechelic polymers incorporating polyhedral oligosilsesquioxane (POSS) and uses thereof," **US Patent 7,067,6060 B2**, Issued June 27, 2006. *Claims Allowed, October 2006*

David H. Wang, T. Marsh, P.T. Mather, L.-S. Tan, "Improved monomer synthesis for poly(arylene ether ketone imide)," *Polymer Preprints (American Chemical Society, Division of Polymer Chemistry)* **47**(2), 530-531 (2006).

Woojin Lee, Suolong Ni, Byoung-Suhk Kim, Sushil K. Satija, Patrick T. Mather, and Alan R. Esker, "Telechelic poly(ethylene oxide) amphiphiles with polyhedral oligomeric silsesquioxane (POSS endgroups at the air/water interface," *Polymer Preprints (American Chemical Society, Division of Polymer Chemistry)* **47**(2), 1214-1215 (2006).

VII. Interactions and Transitions

a. Participation and Presentations at Meetings

Invited Lectures (5)

Syracuse University, "Biodegradable Nanocomposites," Dept. Biomedical and Chemical Engineering, Syracuse University, November 3, 2006.

General Motors, Inc., "Shape Memory Polymers: Fundamentals to Applications," Warren, MI, September 12, 2006.

SPIE Great Lakes Photonics Symposium, Dayton Convention Center, Dayton OH, "Liquid Crystalline Polymers and Elastomers," June 16, 2006.

Bayer Corp., Leverkusen GERMANY, "New Directions with POSS-Based Materials," June 8, 2006.

MEDICAL POLYMERS 2006, "POSS-Based Polyurethanes: from Degradable Polymers to Hydrogels," Cologne, Germany, June 6, 2006.

Contributed Talks (2)

Cheryl J. Campo, Olivier Arnoult, and Patrick T. Mather, "Crystallization of Shape Memory Binary Blends Containing One Crystallizable Component," 78th Annual Meeting of the Society of Rheology, Portland, Maine, October, 2006.

Patrick T. Mather, Kyung-Min Lee, Changdeng Liu, and Charles Burstone, "Shape Memory Polymer Orthodontics," *SPE ANTEC* Medical Plastics Division, May 9, 2006.

b. Consultation and Advisory Functions with other Laboratories and Agencies

This project is a close collaboration with Dr. Loon-Seng Tan of AFRL/MLBP on hyperbranched polymers of direct use in this program. Numerous conversations and conferences at scientific meetings have been conducted toward designing of polymers for high toughness and Tg.

c. No transitions to practiced technology exist for this research as yet.

VIII. New Discoveries, Inventions or Patent Disclosures. None

IX. Awards and Honors received by the PI (lifetime received): **18**

Case Western Reserve University, Undergraduate Student Government Teaching Excellence Award	2006
Keynote Lecturer Applied Rheology Special Interest Group (ARSIG) SPE ANTEC 2005	2005
Rogers Corporation Award for Outstanding Teacher in Chemical Engineering	2003
SPE Medical Plastics Division, ANTEC 2002 Best Paper Award	2002
Member of AFOSR Star Team, "Lightweight Low-Cost Membrane Structures"	2002
School of Engineering Outstanding Junior Faculty Award, University of Connecticut	2001
NSF CAREER Award, "Orientational Dynamics in Flows of Thermotropic Polymers"	2001-2006
AFRL-Sponsored Assessment Team, "Applicability of Organic Matrix Composites to Cryogenic Rocket Propulsion applications,"	Spring 2001
Who's Who in Plastics and Polymers	1999
SPE Engineering Properties and Structure Division, ***Best Paper***, 55th ANTEC	1997
Member of AFOSR Star Team, "Inorganic Synthesis"	1997
USAF Palace Knight Fellowship	1992-1994

National Defense Science and Engineering Grad. Fellowship (A.R.O.)	1989-1992
University Scholars - Penn State Honors Curriculum	1986-1989
Tau Beta Pi	1988-present
Best Summer Research, Rohm and Haas Company	1988
Golden Key National Honor Society	1989-present
George Gleeson Scholarship for Undergraduate Research	1989-1990