Advances in Urethane Composites:
Resins With Tunable Reaction Times

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Abstract

The VITROX® isocyanate-based resin system is a novel development that provides a unique combination of high thermal stability and toughness in a resin system that is easy to process and to cure. The mixed resin system exhibits a low viscosity, which at the end of a tunable induction period of up to several hours at room temperature, the resin 'snap-cures'. The new resin chemistry can be formulated to yield a wide range of glass transition temperatures (up to 250 °C) while achieving the combination of high toughness in a high Tg system. Additionally, the novel resins exhibit excellent inherent fire, smoke density, and smoke toxicity (FST) performance without the use of added fire retardants. The benefits of the unique processing parameters, cure conditions, and high physical properties lead to opportunities in a number of composite processes including pultrusion, RTM, resin infusion and filament winding.

Introduction

High-performance lightweight composites are routinely produced with state-of-the-art resin, fiber, and processing methods; they are generally however, only commercially viable in applications where the performance requirements justify the higher cost of these materials. This cost issue has limited composite usage to lower volume military and commercial aerospace applications, high-end sports equipment, and high performance passenger vehicles.

State-of-the-art composites are cost prohibitive for high volume industries because part production is not scalable to high volumes as a result of constraints in cycle time and processing method. For these reasons, structural composite applications for mainstream automotive production have not yet been realized. Common aerospace grade epoxy resins require cure cycle times of 30 minutes or more which are well above the transportation industry's goal of five minute or less cycle times.

Polyurethanes are a promising alternative to traditional epoxy-based matrix systems as they offer the potential for fast cycle times, high toughness, and exceptional durability.[1] Polyurethanes are currently used in pultrusion applications where the polyurethane matrix has enabled new part design and production.[2] In other composite processes such as RTM and VARTM, polyurethanes are traditionally limited to the production of smaller composite parts due to the short pot-life of the mixed resin. After mixing, the urethane system begins to react and the viscosity increases, hindering the infusion of the resin into larger parts.

These viscosity and pot-life limitations of PU resins have been overcome through a major breakthrough in novel catalysis chemistry. This dual catalyst system extends the pot-life of mixed resins up to several hours at room temperature with a tunable induction period and a snap-cure profile at elevated temperatures.

In particular this chemistry offers the following advantages:

- Lower resin viscosity compared to epoxy resins which facilitates composite part production.
- A very long pot-life compared to commercial urethane-based resins.
- A reduction in cycle time which is achieved by a snap-cure mechanism.
- High mechanical property performance, particularly fracture toughness in high Tg resins.
- Materials with good thermal stability, excellent fire performance without added flame retardants and low smoke density & toxicity according to NF P52-901 standard.

Experimental

Rheological tests were carried out on a Dynamic Stress Rheometer using disposable parallel plates with a 25-mm diameter. To measure the onset of cure as evident by a rapid rise in viscosity, the instrument was run in a dynamic (oscillating) stress mode with a peak stress of 4 Pa, a frequency of 1 rad/sec and a 1 mm gap separation. However, due to the low initial viscosity of these materials, it was necessary to revert to steady state (non-oscillating) tests to accurately determine the viscosity of the uncured material. All components were mixed together in a high speed mixer for 30 seconds before being placed in the rheometer.

The reaction exotherm experiments were conducted by measuring the temperature of the mixed resin system versus time. The resin system was mixed in a high speed

mixer for 30 seconds before 100 g was placed into insulated container. The rapid rise in temperature indicates the onset of the curing reactions.

In order to perform full property testing on this system, it was necessary to find a way to produce void and bubble free samples by preventing out-gassing during the preparation of the neat resin plaques and the carbon fiber composites. The following scheme was developed. First the system components were degassed individually before being combined and further degassed after mixing in another container (the long room temperature pot-life of these samples makes this possible). The mixed components were transferred to a heated mold (with or without the carbon fiber) at 200-300 g/min. For the carbon fiber samples the total injection time was 12 minutes and the samples were cured 180°C for 2 hours or as indicated.

The DMA analysis on cured materials was conducted in oscillatory mode with a frequency of 1 Hz and a heating rate of 3°C/min in a torsion beam geometry. The Tg is described as the G' onset Tg, or the temperature at which the storage modulus G' begins to rapidly decrease with increasing temperature.

The tensile properties of the neat resins were evaluated in accordance to ASTM D638-03 and the composite samples using ASTM D3039. Mode I Interlaminar Fracture Toughness was conducted according to ASTM D5528 and the Interlaminar Shear Strength (ILSS) was based upon the ISO 14130 standard.

The Fire, Smoke, and Toxicity (FST) behavior was determined through two techniques. Fire Testing was conducted using NF P92-501 (1995) Exposure to Radiant Heat. Smoke and Toxicity performance was evaluated through NF F 16-101 Rolling Stock-Fire Behavior, Smoke Density NNFX 10-702-1 and 10-702-5, and Toxicity in accordance with NF X 70-100-1 and NF X 70-0200-2.

Results and Discussion

The unique rheological performance of long pot-life, tunable induction period, and snap-cure can be best illustrated through a 2^2 full factorial DOE based upon different levels of the two catalysts. Table 1 gives the experimental catalyst combinations and the sample identification used for all rheological experiments. All resin systems contained equal amounts of isocyanate and polyol. In each rheology experiment the novel materials were compared to a commercially available urethane resin system (PUR).

The pot-life of the resins was determined by measuring the temperature of the mixed resin as a function of time and by comparing the viscosity of the resins immediately after mixing and after a specified time period. Figure 1 shows the reaction exotherm plots for the novel resin systems A, B, and E and the commercial urethane resin. Immediately after mixing

there is a slow rise in temperature for all systems indicating that a reaction is occurring. The PUR system exhibits a slow temperature rise until approximately 20-22 minutes after mixing followed by a very rapid temperature rise as the material cures and solidifies. The shape of the curves for the novel systems is different than the PUR system. Samples A and B have an initial temperature rise that was significantly faster than the PUR. The exotherm curves for A and B are equal out to approximately 18 minutes after mixing. Sample A then exhibits a rapid temperature rise indicative of the curing of the resin while Sample B continues the slow temperature increase out to approximately 40 minutes whereafter the temperature begins to decrease. No rapid rise indicating curing of the resin is seen in Sample B. Sample E has a slower initial temperature rise and a lower maximum temperature than sample B and the rapid temperature rise was also absent in the reaction exotherm. Samples B and E have been specifically formulated to delay the onset of rapid cure to times in excess of two hours. The intial, modest temperature rise indicates that a reaction is occurring for both samples, however this reaction does not significantly increase negatively affect the pot-life of the system. After two hours the viscosity of both systems are still approximately 1000 mPas.

The rheological performance of the novel systems can also be compared to the PUR through measuring the viscosity as a function of temperature by heating the materials at 3°C/min in a rheometer (see Figure 2). The shape of the viscosity curves are determined by two competing processes: the decrease in viscosity that occurs as the resins are heated and the increase in viscosity as the materials begin to react. The PUR shows a slight decrease in viscosity at temperatures up to 65°C, but then the viscosity increases exponentially as the material cures. The novel systems have different shaped curves. Similar to the urethane system the novel materials' viscosity remains low as the temperature initially increases, however once a critical temperature is reached (this critical temperature is defined as the onset of cure or the kick-off temperature) the viscosity grows rapidly as the cure reaction becomes self accelerating and the material snap-cures. The critical temperature is formulation dependent; sample A has the lowest critical temperature (57°C) while sample E does not kick-off until 105°C. This ability to maintain a low viscosity for an extended time over a wide temperature range is a key advantage of these novel resin systems over conventional urethane systems.

It is also desirable to understand the viscosity profile of the resin systems under conditions simulating RTM molding operations. In this case the viscosity was determined as a function of time under isothermal temperature conditions. The viscosity profiles at 80°C, as shown in Figure 3, further illustrate the snap-cure behavior of the novel resin systems. Immediately after mixing the viscosity of the PUR system increases by an order of

magnitude every two to three minutes as the system reacts. The novel materials do not have the immediate viscosity increase, rather they exhibit a low viscosity during an induction period followed by a very rapid viscosity increase. The length of the induction period was adjustable, with fast reacting systems A and C having induction periods of less than 2 to 3 minutes, to induction periods from 10 to 30 minutes for the slower reacting systems B, D, and E. It is important to note that once the induction period is over the systems snap-cure very rapidly. To achieve a viscosity of 10^6 Pas the PUR system took approximately 18 minutes. The novel materials, once the induction period is over, go from the 0.1 Pas to 10^6 Pas in less than 10 minutes.

Since the initial viscosity of the novel systems are very low and they remain nearly constant until the onset of snap-cure, the mold filling operations of infusion processes will be easier with these novel urethane systems relative to higher viscosity materials. The rapid conversion to a fully cured system enables fast demolding of a composite part. Since the onset of cure can be adjusted through proper resin formulation, the reaction time can be matched to a particular process leading to the lowest possible cycle times.

The thermal performance of the cured urethane system was compared to a conventional PUR resin and a standard epoxy resin. Figure 4 is a plot of the storage modulus G' of neat resin samples as a function of temperature. For the novel materials the storage modulus curve is relatively independent of temperature up to 200°C and exhibits a G' onset Tg of approximately 260°C and 220°C for novel resins 1 and 2. For comparison, the same test was conducted on the epoxy and urethane systems which had an G' onset Tg of 120°C and 140°C respectively.

Table 2 lists the mechanical property data of an epoxy resin and the two urethane formulations as measured on neat resin plaques and on carbon fiber composites. Novel resin 1 exhibits a tensile strength, an elongation at break, and a Young's modulus similar to the epoxy despite the significantly higher glass transition of the urethane. Novel resin 2 sacrifices modulus and tensile strength to achieve a higher strain-at-break while maintaining a high Tg.

The fracture toughness and fracture energy values are the most striking difference between the epoxy and the novel urethane systems. When tested on neat resin samples, the urethane systems have a G_{1C} values of 350 and 460 J/m2; significantly higher values than the 190 J/m2 of the epoxy. These values, in combination with the high Tg values of 260 and 240°C, demonstrate that the urethane resin systems can achieve a high Tg without sacrificing toughness.

Table 2 also lists mechanical property data for the carbon fiber composite samples including interlaminar shear strength (ILSS) measurements before and after exposure to various chemical solutions. The

tensile strength of the epoxy system is approximately 21% higher than the two urethane systems while the tensile modulus and interlaminar shear strength are essentially equivalent. As seen for the neat resin samples, the fracture energy G_{1C} of the urethane composite samples are nearly twice as high as that of the epoxy system.

The chemical resistance of the composite systems was tested by exposure to HCl and NaOH solutions and toluene. The ILSS before and after exposure are equivalent for all materials, indicating a strong interface between the resin and the carbon fiber. There is some difference in the weight change after the 7 day exposure tests: the epoxy system had a lower weight increase in the HCl solution but the urethane systems performed better in the NaOH solution and in boiling water. The effect of toluene on the weight change for the three systems was minimal.

The FST performance was determined on Urethane 1 by a third party laboratory. The highest rating of M1 was assigned after testing in the fire test NF P92-501 "Exposure to Radiant Heat". The smoke and toxicity classification was given the second highest rating of F1 with emission values of 0 mg/g of HCl, HBr, and HF and 2 mg/g of HCN. It should be noted that these fire and toxicity values were obtained on the neat resin system without the addition of external flame retardant additives.

Conclusions

Unique urethane catalysis has recently been developed, eliminating the pot-life issues of traditional urethane resins and replacing the normal, gradual viscosity increase with a snap-cure reaction profile. This advance has greatly expanded the ability to use urethane chemistry for composite applications and resulted in the formulation of new resin systems that offer a number of material attributes and processing advantages:

- High Tg materials with high toughness (impact strength; strain at break; crack resistance; etc) compared to thermoset resins with equivalent Tg.
- Robust fire and smoke and toxicity (NF P92-501 standard) without fillers or other additives.
- Resistance to chemical and moisture exposure.
- A wide range of pot lives with a snap-cure reaction profile and short cycle times.

The unique chemical and physical properties of these urethane resins enable the production of composite using common thermoset composite processing operations. The result is new opportunities for a number of composite manufacturing processes such as RTM, filament winding, and pultrusion.

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2. Connolly M., King J.P., Shidaker T.A., Duncan A.C., "Processing and Characterization of Pultruded Polyurethane Composites", Proceedings of the 8th World Pultrusion Conference, European Pultruders Technical Association, March 2006.

Biographies:

David Bareis is a Market Development Manager for Urethane Composites in Huntsman Polyurethanes Business Development. For over 20 years at Hunstman David has been involved in the development and commercialization of polyurethane systems for automotive and composite applications.

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Michael Connolly, Ph.D. is Product Manager–Urethane Composites for Huntsman Polyurethanes in Auburn Hills, MI. Michael has been employed in polyurethane product development for 14 years at Huntsman and has 20 years experience in a range of polymer materials development roles. He received his doctoral degree in Polymer Science and Engineering from the University of Massachusetts-Amherst in 1989.

Table 1. Experimental Catalyst Combinations of the Novel Resin Systems.

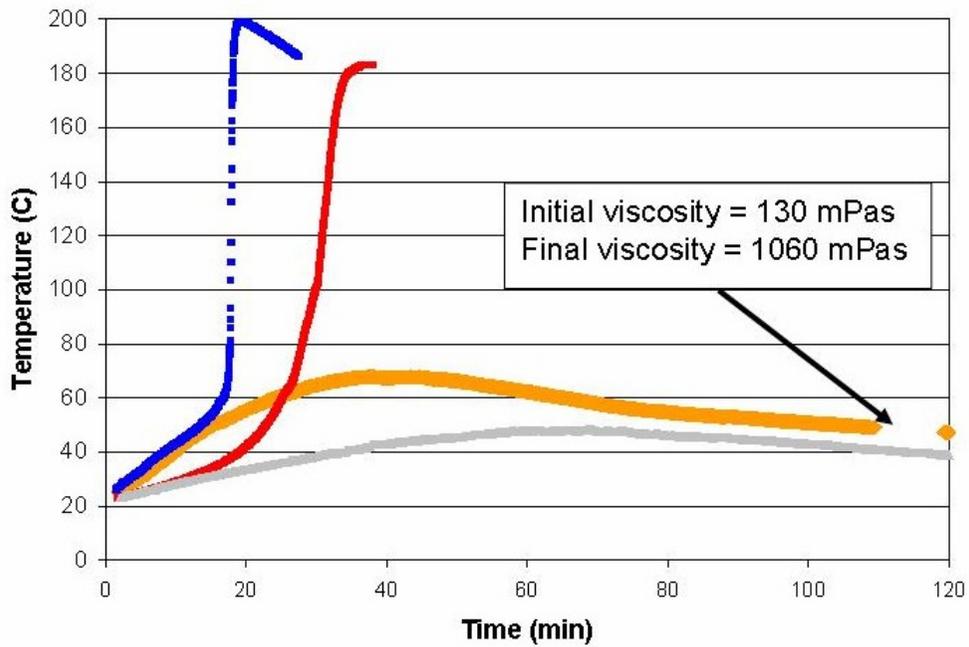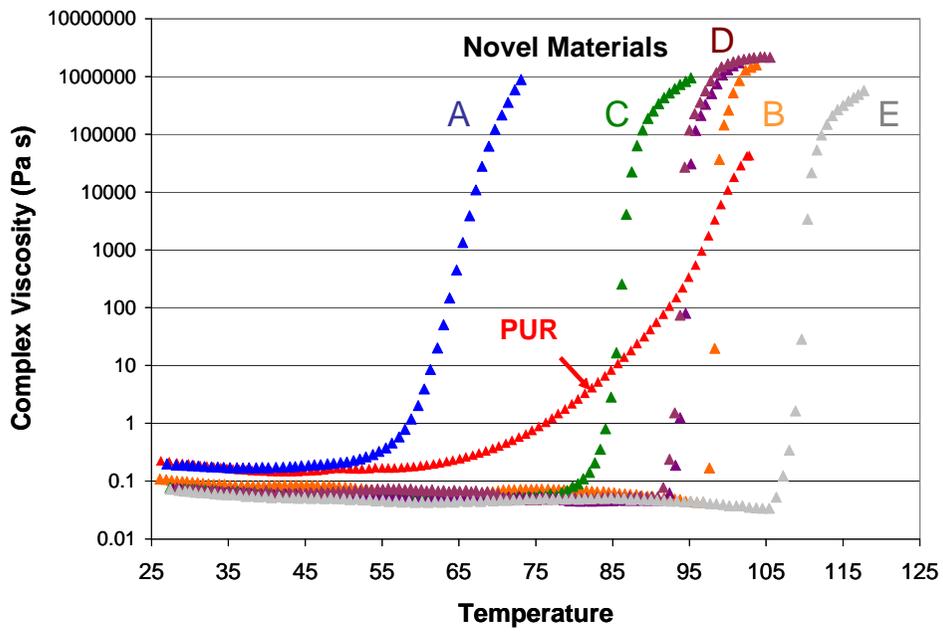| Sample ID	Catalyst A	Catalyst B
A	High	Low
B	High	High
C	Low	Low
D	Med	Med
E	Low	High

Figure 1. Reaction Temperature versus Time.
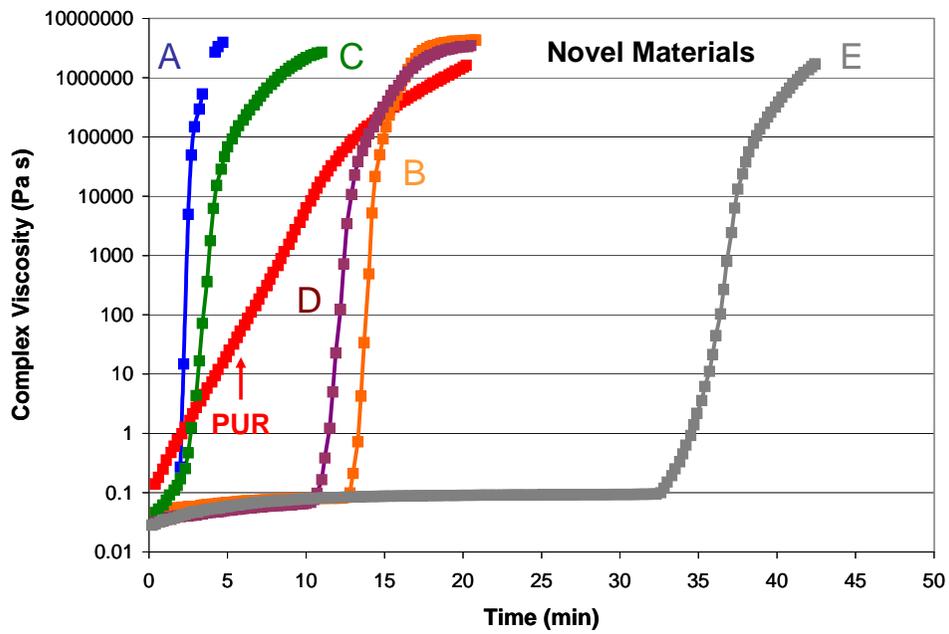
Figure 2. Viscosity Profiles During Heating.

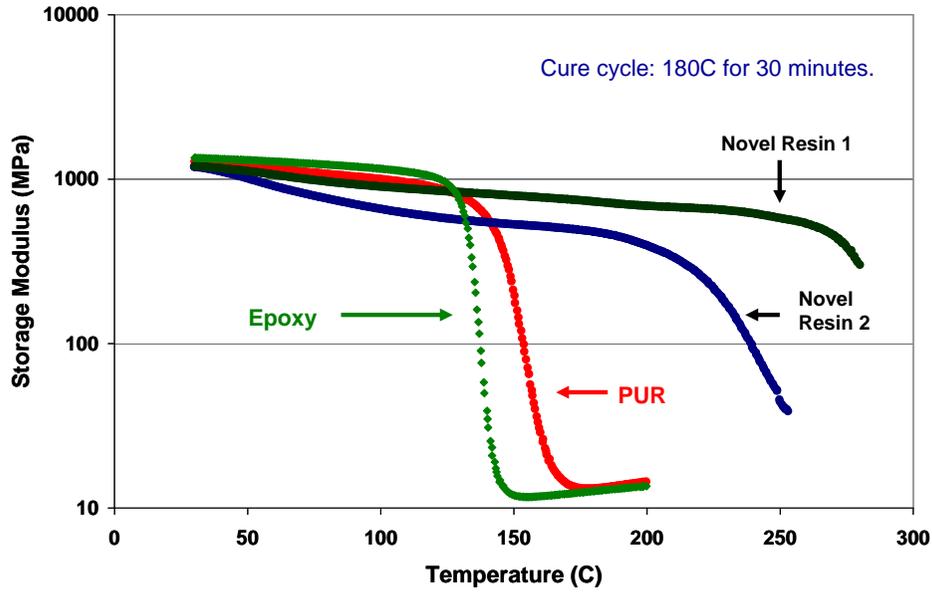**Figure 3. Viscosity Versus Time at 80C.**

Figure 4. DMA Plot of Storage Modulus vs. Temperature.

Table 2. Mechanical Properties of Neat Resins and Carbon Fiber Composites.

	Test	Property	Units	Epoxy Resin	Novel Resin 1	Novel Resin 2
Neat Resin	**Neat Resin Tensile**	Modulus	MPa	2200	2250	1450
		Strain to failure	%	5	6	10
		Strength	MPa	74	75	56
	Fracture Toughness	Fracture Energy (G_{IC})	J/m²	190	350	460
		Fracture Toughness (K_{IC})	MPa·m^{½}	0.63	0.88	0.81
	Viscosity	Initial viscosity (23°C)	(mPa s)	1200	70	80
	Thermal	Tg	°C	120	260	240
Composite [1]	**Composite Tensile Properties**	Fibre volume fraction (Vf)	%	55	55	54
		Modulus	GPa	44	44	42
		Strain to failure	%	1.8	1.4	1.5
		Strength	MPa	690	570	560
	Fracture Toughness	Mode-I Fracture Energy (G_{IC})	J/m²	186	340	450
	ILSS	Interlaminar Shear Stress (ILSS)	MPa	47	51	46
	Chemical Resistance	ILSS after 7 days in HCl solution	MPa	46	54	46
		ILSS after 7 days in NaOH solution	MPa	47	50	44
		ILSS after 7 days in Toluene	MPa	50	53	47
		% weight gain (7 days in HCl)	%	0.9	1.7	2.2
		% weight gain (7 days in NaOH)	%	3.1	1.9	2.4
		% weight gain (7 days in Toluene)	%	0.2	0.1	0.4
	Moisture uptake	% weight gain (3 days in boiling H_2O)	%	1.1	0.4	-