HIGHER TG RECYCLABLE HIGH PRESSURE RESIN TRANSFER MOLDING (HP-RTM) EPOXY PROPERTIES AND HOW THEY COMPARE TO A COMMERCIAL SYSTEM

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Abstract

Implementation of composites in automotive manufacturing is driven by cost reduction. High Pressure Resin Transfer Molding (HP-RTM) allows part manufacturing cycle time to be on the order of minutes. Thermoset materials used in HP-RTM are not recyclable, which leads to artificially high production costs due to the lack of a suitable means to reincorporate waste in the value chain. Connora has developed a series of new epoxy curing agents called Recyclamines®. Use of these curing agents enables manufacturing of recyclable thermoset products. In the present work, Connora’s higher Tg curing agents were coupled with Hexion’s commercial epoxy resin to produce epoxy/carbon plaques. Mechanical properties of the resulting plaques were compared with epoxy/carbon plaques produced using Hexion’s commercial epoxy resin and curing agent. Mechanical properties of both systems were found to be similar at room temperature conditions.

Background

Application of composite materials in various technologies in the automotive industry has recently been on the rise. One such application is HP-RTM, which delivers two or more components (e.g., resin and curing agent) from separate tanks to the mixing head where they are mixed and injected into the mold under high pressure to create a thermoset. The mold usually contains a fiber fabric or a preform made from a fiber fabric. As the liquid thermoset material is injected into the mold and infused into the fiber fabric, a matrix develops resulting from the reaction between resin and curing agent. Efficient mixing and fast injection enables the use of elevated temperature molds, facilitating part production times in mere minutes. Short cycle times in conjunction with elevated physical performance makes HP-RTM-produced parts particularly attractive for the automotive industry. One major disadvantage of HP-RTM is sustainability, however, as neither the thermoset materials nor the carbon fiber reinforcement are reusable.

Connora Technologies has pioneered the development of recyclable, amine-based curing agents for epoxy resin to facilitate the creation of recyclable thermoset products and composites. Connora’s recyclable amine technology has a cleavage point in the center of the molecule, which under a specific set of conditions, breaks all cross-links in the epoxy matrix. Thus, cleavage of this bond effectively converts the epoxy thermoset matrix into a thermoplastic material. Figure 1 displays this reaction scheme. Replacement of recyclable amines for conventional amine curing agents allows for the recycling and/or repurposing of both matrix and the fiber fabric in post-manufacturing waste and end-of-life streams.

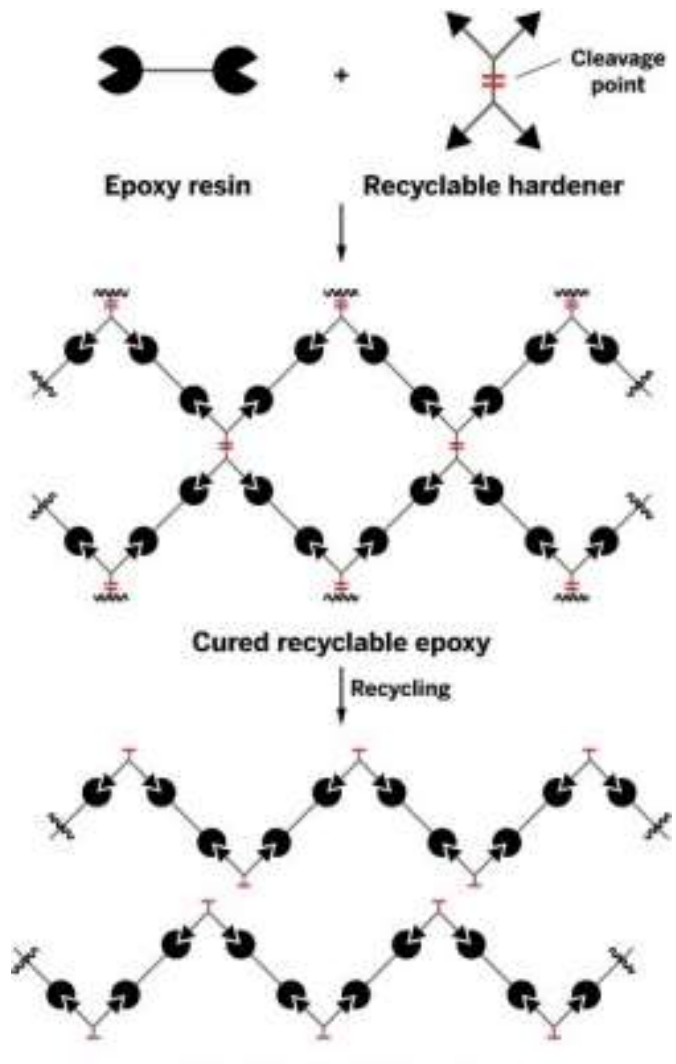

Figure 1: Schematic representation of recyclable epoxy technology

Previous research on the subject of HP-RTM manufacturing [1] focused on reuse of the fabric by reimpregnation with resin after the original resin matrix had been recycled. The new composite manufactured from recycled fabric had very similar properties to the initial composite manufactured from a virgin carbon fabric. In this research, panels (900x550 mm^2) were manufactured using Hexion commercial resin in combination with Connora's newly developed higher Tg hardener system. Mechanical properties of the resulting panels were tested and compared with properties of panels manufactured with Hexion's commercial Resin and Hardener system.

Materials

Hexion's Epikote 6000 resin with either Connora's Recyclamine 3182 or Recyclamine 3382 were loaded into the HP-RTM machine and injected into the mold. SGL supplied the unidirectional and multidirectional carbon fiber preforms placed in the mold. SGL preforms were also injected with Hexion's Epikote 6150 resin and Hexion's Epikure 6150 hardener. Molding was assisted by Hexion's Heloxy 112 internal mold release.

Equipment

The trial was performed by Fraunhofer Project Center (FPC) in London, Ontario. Krauss Maffei Rimstar 8/4/8 HP-RTM and Dieffenbacher CompresPlus 2500 ton servohydraulic press were used in the trial. Both are represented in Figure 2. A rectangular 900x550 mm2 mold was installed in the press. This mold was specifically designed to address the needs of the automotive industry by sizing it appropriately for real automotive parts. The mold is equipped with a center gate injection port, pressure sensors and two vacuum ports located at the horizontal edges. The mold design allows for part production of varying thickness. A thickness of 2.0 mm for unidirectional parts and 2.2 mm for multidirectional parts (±45o orientation) were selected for the current trial.

Figure 2: FPC equipment- press and HP-RTM

Panel Manufacturing

The HP-RTM apparatus operates in the following manner: 1) Resin components are first loaded into separate tanks; 2) The components are then delivered by pumps to the mix head, which mixes the materials and injects the mixture into the mold; 3) Prior to injection, vacuum ports are opened and a vacuum is generated inside the mold, the ports are closed one second before injection ; 4) During injection the press applies a force on the mold called "injection force" and after injection, it applies another force called "curing force." The HP-RTM's and Press's settings are presented in Table 1.

Table 1 – Trial process parameters that held constant

Constant process settings			
Press/tool parameters	Injection Pressure	1500 kN	
	Cure Pressure	4500 kN	
HPRTM parameters	Fiber Volume Fraction	50%	
	Mixing Head Pressure	120 Bar	
Resin parameters	Mixing Ratio by Weight	Recyclamine 3182	Recyclamine 3382
		100:24.5:1	100:23.2:1
	Resin Temperature	60°C	
	Hardener Temperature	30 $^{\circ}$C	
	IMR Temperature	35 $^{\circ}$C	

Analyzing Methods

Tensile tests were conducted on MTS load frame, model C45.105E. The testing displacement rate was set to 2 mm/min. The strain data was recorded using video extensometer. Tensile testing in 0° was performed according to DIN EN 2561 standard, wherein the load frame is equipped with 100 kN load cell, model MTS LPS.105. Tensile testing in 90° was performed according to DIN EN 2597, wherein the testing displacement rate is set to 2 mm/min. Flexural tests were performed using the 3-point bending method according to ASTM D7264/D7264M-07 standard, using a 10 kN load cell model MTS LPS.104 for the measurements. A 2 mm/min displacement rate was chosen for the tests. Compression tests were performed according to ASTM D3410/D3410M-03 standards with a displacement rate of 1.5 mm/min. The strain data was recorded using video extensometer. The frame was equipped with 100 kN load cell for the tests. The interlaminar shear strength (ILLS) tests were performed using the EN ISO 14130 standard. The displacement rate was set to 2 mm/min and the load measurements were taken using a 10 kN load cell. Tensile and compression tests were performed on the UD panels. Flexure and ILSS tests were performed on the multidirectional panels ($\pm 45^{o}$ tests).

Results and Discussions

Connora's Recyclamine hardeners in combination with Hexion's Epikote 6000 resin were easy to process. A typical manufactured panel is shown in Figure 6. The measured gel times of Hexion's Epikote 6000/Recyclamine 3382 and Hexion's Epikote 6000/Recyclamine 3182 were quite fast at 140 ^{o}C and 130 ^{o}C, and are summarized in Table 2. Hexion's Epikote 6150/Epikure 6150 commercial system gel time at 140 ^{o}C was taken from the material's TDS.

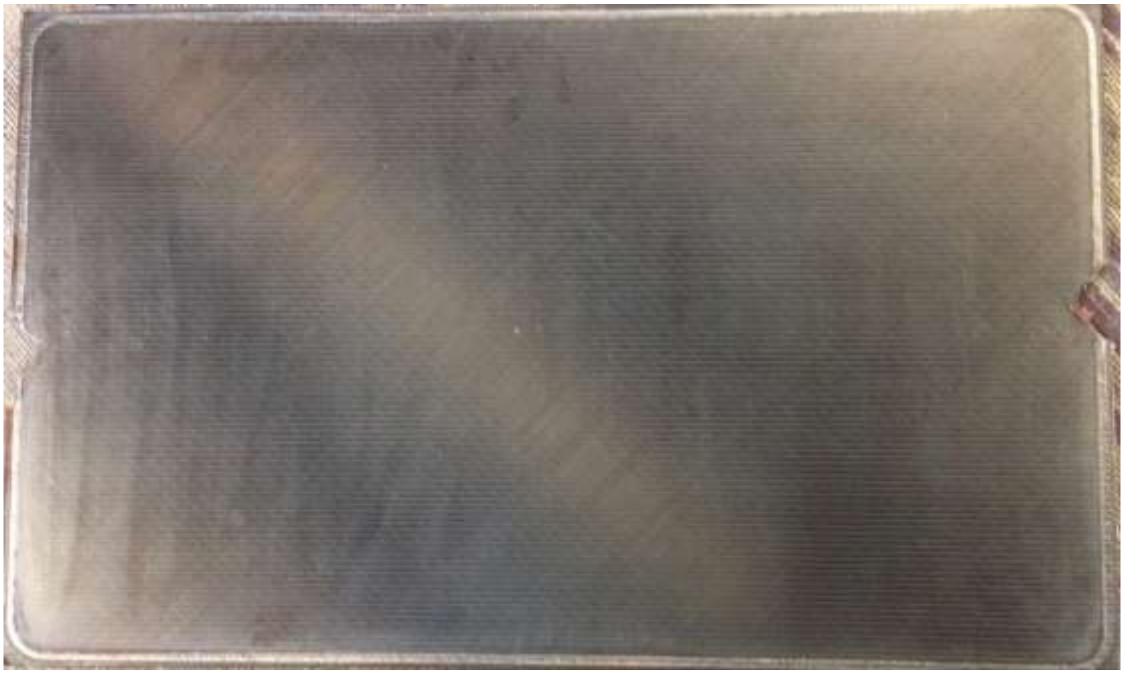

Figure 6: Panel manufactured at a trial using Hexion's Epikote 6000/Recyclamine 3182 system

Table 2: Gel time on hot press at 140°C

Gel times	
System	Gel Time [s]
Epikote 6150/Epikure 6150	90
Epikote 6000/Recyclamine 3382	36
Epikote 6000/Recyclamine 3182	27

Typically, a commercial HP-RTM system can be de-molded with a sufficient Tg at a cycle time three times the recorded gel time. Similarly, this guideline roughly applied to the Connora epoxy resin systems. Composites were fabricated at press temperatures of 120, 130, and 140 °C, with cure cycles ranging from 90 sec to 5 min. Table 3 provides the demold Tg and % cure measured for select panels using the Epikote 6000/Recyclamine 3182 system containing 1 PHR IMR. Tg and % cure values of the Recycalmine 3382 systems were found to be similar to 3182 system. As a reference, the Hexion control system yielded a demold Tg of 118 °C at 120 °C for 5 minutes.

Table 3: Tg Values and % cure of Recycalbe Carbon composites at different cure intervals

Epikote 6000/Recyclamine 3382/ Heloxy 112			
Mold temp	Cure time	Demold Tg	% Cure
120 °C	3 min	87.0 °C	96.0%
120 °C	4 min	97.7 °C	96.6%
120 °C	5 min	102.5 °C	97.6%
130 °C	3 min	103.4 °C	97.3%
130 °C	5 min	109.4 °C	98.7%
140 °C	2 min	106.7 °C	98.6%
140 °C	3 min	107.0 °C	98.2%
140 °C	5 min	110.5 °C	99.1%

For a comparison of mechanical properties, composite panels were selected with the respective cure conditions as show in Table 4.

Table 4: Cure conditions evaluated in the study

Carbon Composites evaluated in this study		
System	Mold temp	Cure time
Epikote 6150/Epikure 6150	120 °C	5 min
Epikote 6000/Recyclamine 3382	130 °C	3 min
Epikote 6000/Recyclamine 3182	140 °C	5 min

Samples were cut from produced panels with water jet and tested in a variety of tests: tension, flexure, compression and ILSS. Each test was performed on five samples from each panel. The comparison of mechanical properties from Hexion's commercial 6150 system, Connora's Recyclamine 3182/Hexion's 6000 Epikote resin system and Connora's Recyclamine 3382/Hexion's 6000 Epikote resin system obtained by mechanical tests is shown in Figures 7-10.

Figure 7 compares tensile properties of the composites prepared with each system. Properties were compared in both 0° and 90° orientation, where 90° orientation properties primarily represent those of the matrix, and 0° orientation primarily those of the fiber. While the strength properties are higher for the Recyclamine systems, modulus is higher for the Hexion 6150 commercial system in both directions. However, both systems exhibit similar tensile properties once standard deviation is accounted for.

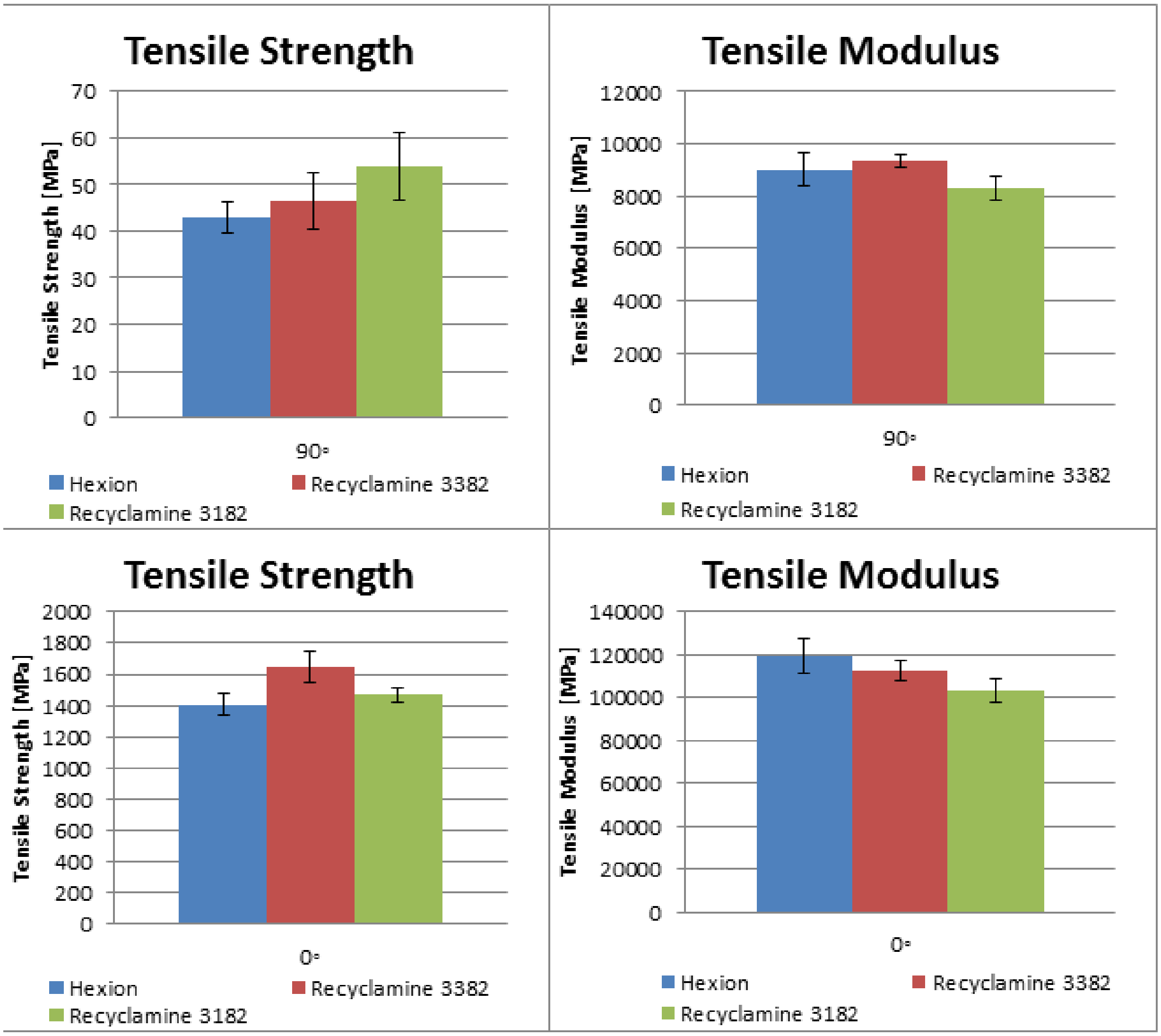

Figure 7: Tensile properties comparison between composites produced from three different systems in both 0° and 90° orientations.

Figure 8 compares compression properties for composites produced using Connora's Recyclamines and Hexion's 6150 system. Results indicate compression properties of each composite compare similarly to tension properties shown in Figure 7. Namely, Hexion's 6150 system exhibits a better modulus while Connora's Recyclamines produce composites with higher strength. As is the case with tensile properties, all three systems perform similarly once standard deviation is accounted for.

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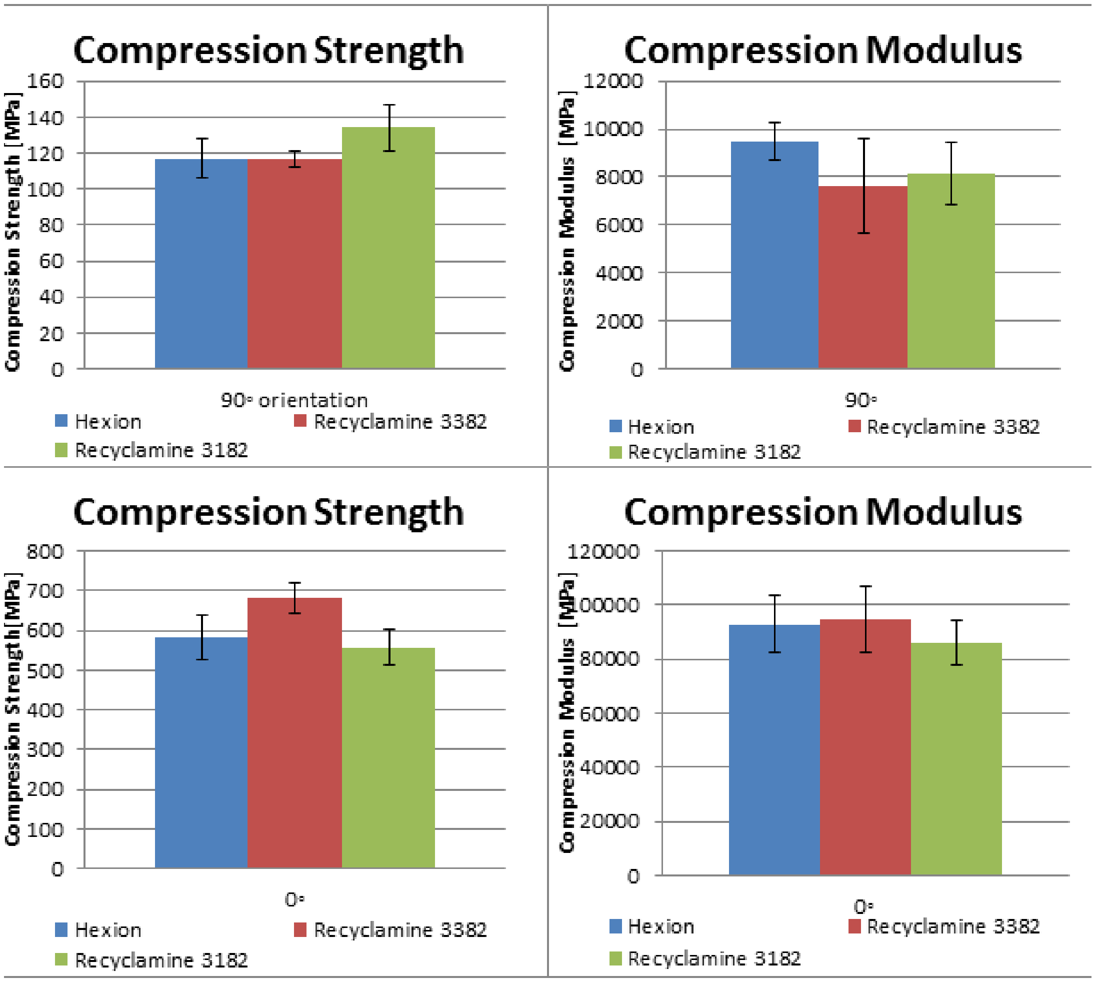


Figure 8: Compression properties comparison between composites produced from three different systems in both 0o and 90o orientations.

Figure 9 compares flexural properties of composites prepared with the three different resin systems using a preform with ±45° fiber orientation. The properties were measured and compared at both room and elevated temperature (80°C). Results in Figure 9 indicate the three systems exhibit similar flexural properties at room temperature. However, at elevated temperature the flexural properties of Hexion's 6150 system drop less than Connora's Recyclamine systems. This phenomenon is a result of the Hexion 6150 system's 10-15°C higher Tg than Connora's Recyclamine systems.

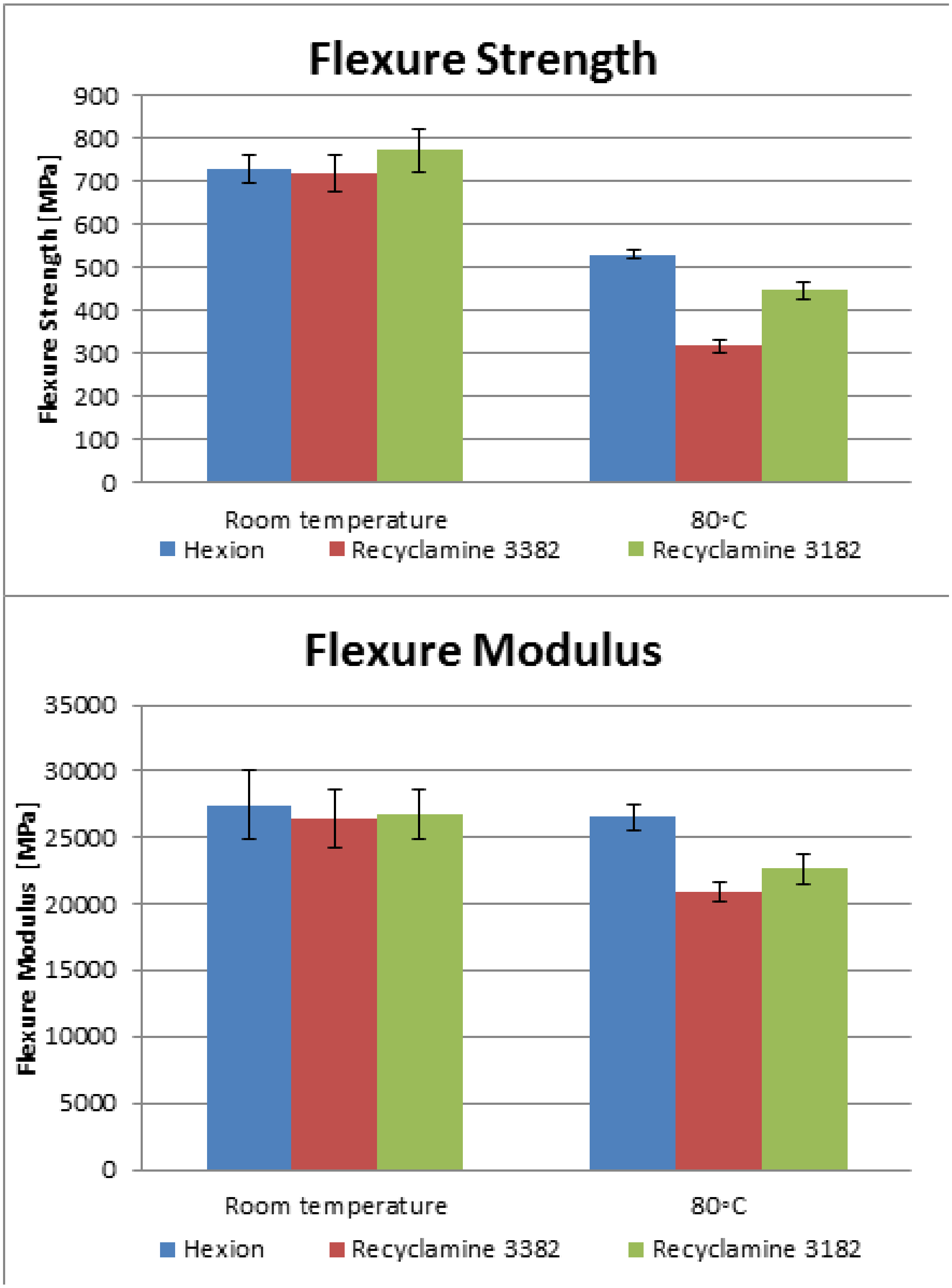


Figure 9: flexural properties comparison between composites produced from three different systems in ±45° panels at room and at elevated temperature (80°C)

Figure 10 compares the interlaminar shear strength (ILSS) of the three systems in samples with ±45º fiber orientation. Figure 10 shows room temperature ILSS properties are identical among the three composites. Once temperature is elevated to 80ºC the ILSS properties of all drop significantly. At 80 ºC, the Hexion system showed significantly higher ILSS properties than Connora's Recyclamine, also explained by the higher Tg of Hexion's commercial system.

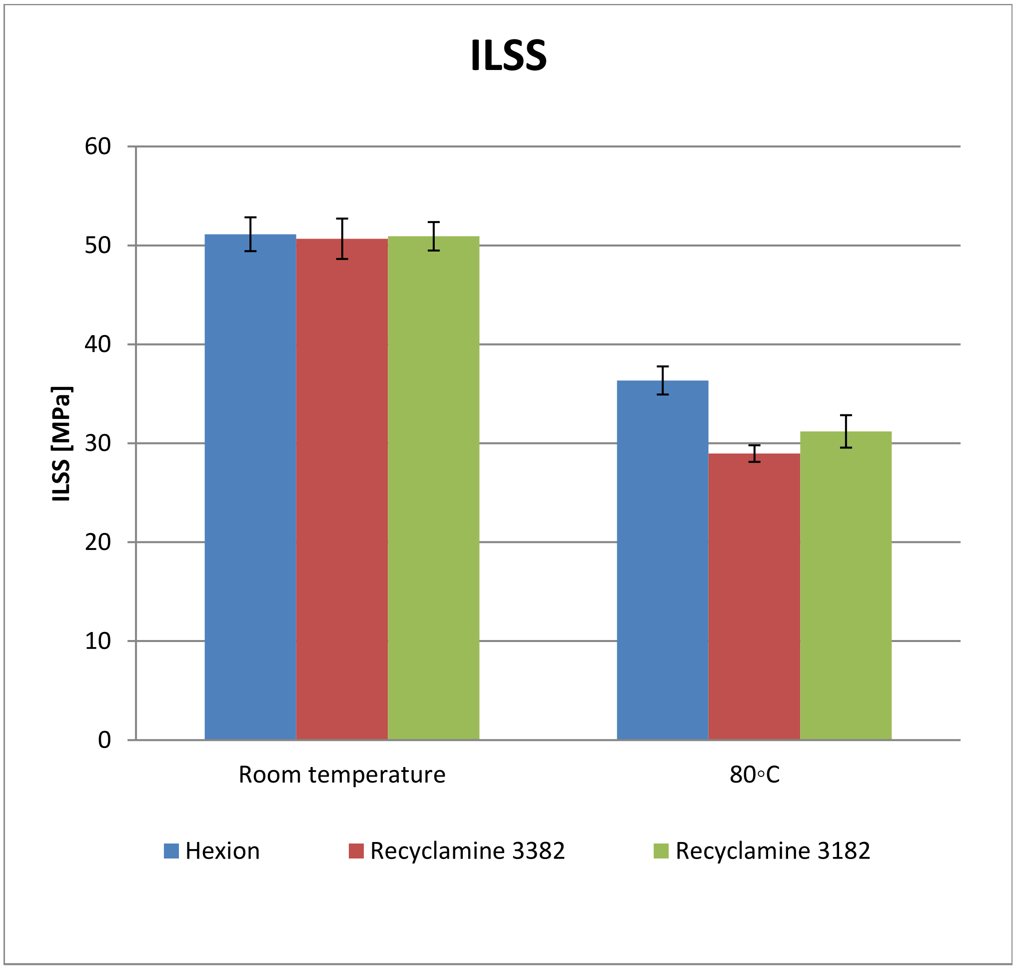
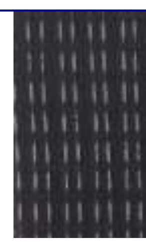


Figure 10: ILSS properties comparison between composites produced from three different systems in ±45º panels at room and at elevated temperature (80ºC)

A common misconception about recyclable epoxy technology is that its chemical resistance is inferior to that of conventional non-recyclable epoxy. This misconception was refuted by an additional test in which samples were subjected to preconditioning before testing. Five 90º tensile samples from each group were submerged in gasoline, 1% sulfuric acid and 5% acetic acid for a week. A visual comparison of samples before and after conditioning is displayed in Table 5. After conditioning, the samples were tested and the resulting properties compared with those obtained from as molded samples without preconditioning. Figure 11 reveals that all three systems respond similarly to preconditioning. All three precondition solutions reduce the composites' modulus and increase their strength. This result is explained by solvent absorption softening the composite.

Table 5 shows sulfuric acid treatment exposed the stitches in composites manufactured from all three systems by acid-etching the exterior epoxy layer. Acetic acid treatment exposed the stitches on the composite manufactured with Hexion's 6150 system but did not expose the stitching of composites manufactured with Recyclamine systems. Gasoline pretreatment did not aesthetically alter the samples. Figure 11 shows all three pretreatments exhibit reduced the modulus of composites produced from each of the three different systems and increased their strength. All three tested systems reacted similarly to the pretreatments.

Table 5: Effect of gasoline and acids on composites

Glass Transition Temperature				
System	As Produced	Gasoline	Sulfuric Acid	Acetic Acid
Epikote 6150/Epikure 6150				
Epikote 6000/Recyclamine 3382				
Epikote 6000/Recyclamine 3182				

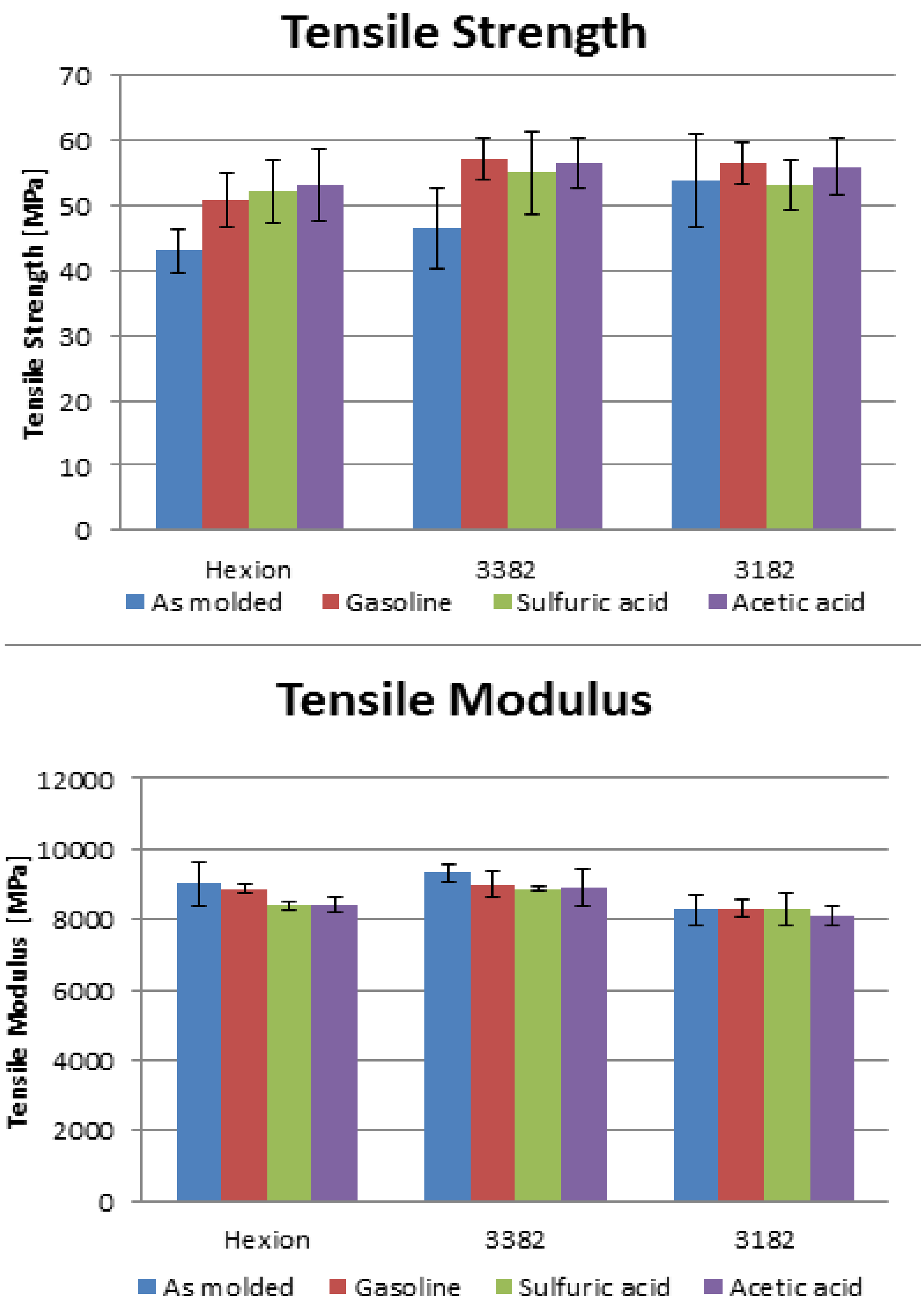


Figure 11: Effect of solvents conditioning on different systems properties

Summary and Next Steps

Connora's Recyclamine curing agents were easy to process in HP-RTM technology and the resulting composites exhibited comparable mechanical properties to Hexion's commercial resin system when tested at room temperature. At elevated temperature, Hexion's commercial system exhibited better results than Connora's Recyclamine systems presumably due to the slightly higher Tg of the Hexion system. Connora's Recyclamine system responded well to preconditioning with gasoline, sulfuric acid and acetic acid. All results presented in this study are averages and standard deviations of five samples for each test which. While five is the minimum number of tests to assess statistical significance, more tests are recommended for enhanced statistical analysis.

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