RECYCLABLE HIGH PRESSURE RESIN TRANSFER (HP-RTM) MOLDING EPOXY SYSTEMS AND THEIR COMPOSITE PROPERTIES

S. Pastine[1], I. Swentek[2**], M. Nasrullah[1], S. Kosinski[1], R. Banatao[1], V. Ugresic[2], F. Henning[3]*

[1]Connora Technologies Inc., 1488 Zephyr Avenue, Hayward, CA USA 94544

[*]Phone: +1 (415) 315-9524 Email: stefan@connoratech.com

[2]Fraunhofer Project Centre, 2544 Advanced Ave, London, Ontario, Canada N6M 0E1

[**]Phone: +1 (519) 661-2111 Email: iswente@uwo.ca

[3]Department of Polymer Engineering, Fraunhofer Institute for Chemical Technology ICT, Germany

Abstract

The wide-scale adoption of composites for automotive applications will be contingent on effective cost-reduction strategies. The advent High Pressure Resin Transfer Molding (HP-RTM) has helped move the thermoset composite industry towards this goal, enabling cycle times of minutes. However, the cost of composites remains artificially high due to the fact that thermosets are not recyclable. The efficient recycling and reintegration of composite waste can further reduce the cost of composites by at least 7.5%, depending on the amount of manufacturing waste generated. Connora Technologies is solving the recycling problem for the industry by reengineering thermoset plastics. Connora has developed a series of high performance epoxy curing agents, called Recyclamines®, enabling the manufacture of inherently recyclable thermoset composites. These recyclable epoxy systems are first processed with carbon fiber laminates to generate baseline performance. The epoxy is recycled and the carbon fiber directly re-cast to demonstrate an efficient reuse of the material. From the mechanical characterization, there was no statistical drop in aligned fiber properties of the recycled laminate, while the perpendicular properties saw a slight decrease (10%) in tensile strength attributed to a reduced fiber spatial uniformity.

Introduction

Connora is commercializing a series of amine-based epoxy hardeners which have the unique property of being recyclable. Their epoxy systems are suitable for a variety of processes including infusion, filament winding and resin transfer molding. Of interest to the automotive industry is a low-cycle time process such as high pressure resin transfer molding (HPRTM) which is the subject of this paper.

These recyclable epoxy systems address both manufacturing waste and the end-of-life issue which typically plagues thermosetting polymers and their composites. Connora claims additional benefit is possible from their proprietary low-energy, inexpensive recycling process in that both epoxy and fiber components can be recovered separately. The fiber can be recovered in its original architecture without degradation or loss of fiber length. The recycled epoxy is collected as a thermoplastic material akin to a stiff polyamide but with exceptional adhesive properties. A pictorial view of this recyclable material is presented in Figure 1.

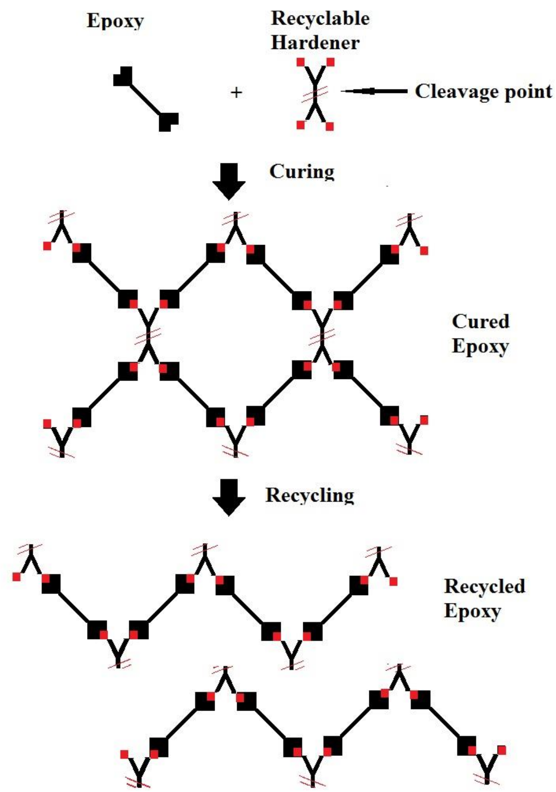

Figure 1 – A Programmed Epoxy Thermoset Conversion into its Thermoplastic Counterpart [].

Past work with this material has examined how the cleavage functions in the presence of fibers and the effect on the post-recycled fiber performance [1]. The initial results suggest that a layer of resin remains bonded to the fiber since the amine cleavage site is not present in the fiber sizing. This residual resin sheath acts to strengthen the fiber, slightly improving its properties, with individual fiber strength increasing over 10%. However, the concern with individual fiber testing is that it is not reflective of large-scale composites.

To demonstrate for the first time, the cradle-to-cradle recycling of a thermoset composite, full industrial-scale trials were conducted. A series of panels were fabricated using Connora's Recyclamine 101 hardener together with Entropy Resin's SuperSap 300 resin. Carbon fiber preforms sized for epoxy, with the fiber in a unidirectional orientation, were supplied by SGL. Together, using the HPRTM process, recyclable carbon fiber/epoxy composite panels were manufactured. These half square meter panels were recycled in their as-molded state while preserving the fiber architecture. The dry recycled fiber was then re-molded with the same epoxy system on the same processing equipment and directly compared to virgin molded panels. The focus of this work is toward reuse of the carbon fiber, by means of the enabling recyclable epoxy, since carbon fiber is presently the more expensive product.

A comparative picture of two preforms, one recycled and one virgin, is shown in Figure 2 just prior to molding using HPRTM. The recycled fiber is evident from the outer fraying edges and visible stitching undulation. Since the panels were transported to and from Connora's headquarters for recycling, some of the damage is expected as a result of the shipping and handling. The molded panels using the pictured fiber are shown in Figure 3. The differences in the recycled and virgin fiber preforms are nearly undetectable in the molded panels.

Figure 2 – Recycled and virgin fiber preforms just prior to resin infusion

Figure 3 – Comparison recycled to virgin fiber molded panels; panel orientation matches that of Figure 2.

Experimental Studies

Composite panel manufacturing

For this work, the high pressure resin transfer molding equipment was used as located at the Fraunhofer Project Center (FPC) in London, Ontario. There, the facility is equipped with a KraussMaffei Rimstar 8/4/8 HPRTM and a Dieffenbacher CompresPlus 2500 ton servo-hydraulic press as in Figure 4.

Figure 4 – HPRTM and press equipment at FPC

A flat mold of dimensions 900 x 550 mm was used to produce the composite panels. This tool was designed to provide a comparative sized part to many automotive applications, but is suitable for development toward any composite application. The tool has a center fan-gate injection port and two vacuum ports located near the last-to-fill areas. Though this mold can be configured for a range of thicknesses, it was set to a nominal 2.2 mm cavity which would yield at least a 50% fiber volume fraction using the provided preforms. This thickness also matched the required thickness for the range of mechanical characterization tests to be performed.

A first series of panels were manufactured using just the Recyclamine 101 and SuperSap 300. These panels were shipped to Connora to remove the cured epoxy and then shipped back to FPC. Once the epoxy was recycled and removed from the fiber, the then recycled fiber was re-manufactured in a second series of panels, the focus of this paper.

The second round of manufacturing also employed Hexion’s Heloxy 112 as an internal mold release (IMR). This was added not because the panels had trouble in demolding, but to demonstrate the property comparison as close to what industry would expect in full production. An external mold release (EMR), Frekote 770-NC, was also used as a part of this trial. A panel with the recycled fiber was molded back-to-back with a panel using a virgin preform to minimize any differences in the manufacturing configuration. These panels were selected from the middle of a trial run with the epoxy, once a stable production process was reached. The manufactured panels were then sectioned and tested as-is, with no post-cure, within 2 weeks from the date of manufacture.

A common set of fabrication criteria was used to generate the initial and subsequent series of composite materials as in

Table 1. The injection molding variant (HP-IRTM) was used exclusively for this work with resin flow primarily in the x-y plane. The fiber preforms were oriented in the mold so that the unidirectional fiber alignment was parallel to the resin flow direction.

Table 1 – Trial process parameters held constant

	Constant process settings
Press/tool parameters	Mold temperature on cavity surface: 125 °C, 1500 kN press force during injection step, 4500 kN press force during cure step
HPRTM parameters	Fiber volume fraction 50%, Vacuum time: 60 s, Curing time: 300 s, Resin injection rate: 70 g/s, Resin injection amount: 800 g, Mixture ratio 100:21.5:1 (resin:hardener:IMR)
Resin parameters	Mixing head pressure: 120 bar, Resin temperature 60 °C, Hardener temperature 30°C, Internal mold release temperature 35 °C

The process is completed in 4 steps: fiber placement, resin injection, resin cure, and demold. A stack of pre-cut fiber was manually transferred to the hot mold. The mold was closed to 1500 kN and the vacuum ports opened for to evacuate any air from the cavity. After the 60 s vacuum step, the vacuum ports were closed and 800 g of resin was injected at a rate of 70 g/s for a total injection time of 11.4 s. Once the mixhead valve closed after injection, the press force was raised to 4500kN for the duration of the 300 s cure. Multiple panels were produced for each material combination to ensure reproducibility of the full process.

Materials characterization

Coupons were machined from a panel of each material using a small-diameter end mill to minimize surrounding damage. The samples were cut and tested within 2 weeks from manufacture at nominal ambient conditions of 22 ±2°C temperature and 50 ±5% relative humidity. A single sample series consisted of at least 6 tested coupons such that a statistical analysis could be performed. As the panels were manufactured using unidirectional fiber, samples were cut and tested in both the 0° and 90° orientations, again for each material.

The material volume fraction was measured following by ignition loss. 25 mm disks were cut at various panel locations and heated in a LECO TGA701 with a mass sensitivity of ±0.0001 g. The crucibles were all fitted with lids to contain all solid content. Nitrogen was used as the flood gas to minimize oxidation of the carbon fibers once the resin degraded at high temperature.

Tensile testing in the 0° orientation was conducted in accordance with DIN EN 2561. An MTS load frame, designation C45.105E, was equipped with a 100kN load cell, serial MTS LPS.105. The testing displacement rate was set to 2 mm/min and a 50 mm clip gauge extensometer, MTS 634.25F-54, was used to capture strain data. The 90° orientation samples were tested following DIN EN 2597 using the same load frame, but with a 10 kN load cell, MTS LPS.104.

Flexure testing was performed after DIN EN ISO 14125 for both fiber orientations using the 3-point bending method. The nominal sample dimensions were 15 mm width and 100 mm length. A support span was set to 80 mm with 5 mm radius rollers. A 10 kN load cell, MTS

LPS.104, was used to record force data at displacement rate of 5 mm/min.

Results and Discussion

Both the virgin and recycled fiber composites were manufactured with identical process settings. There was no change to the internal mold pressures observed during the production suggesting the recycled fiber had a similar permeability to the virgin preform. Thus the recycling process is thought to have fully removed the epoxy from the first molded parts.

Examination of Figure 2 indicates a relatively unharmed stack of fiber. It is also then thought possible to reuse continuous fiber composites several times without having to immediately down-cycle the material. By molding successively smaller parts, avoiding the outer fraying fibers, potentially several continuous fiber recycled components could be fabricated from a large first structural part. Grinding or chopping the recycled fiber is always possible to produce carbon SMC or as a feedstock to other processes such as injection molded short-fiber thermoplastic composites, but this severely limits the ability for the carbon fiber to participate as a structural element in all but the first use.

The mechanical testing is summarized in Table 2 below for both the virgin and recycled samples together with the standard deviations for each test. The fiber volume fractions ended being higher than the targeted 50% since the panels were molded thinner than the intended 2.22 mm. Oddly, the recycled fiber showed a higher fiber volume fraction than the virgin fiber, which is as yet unexplained, but possibly due to the slight differences in panel testing locations.

One issue which can arise during comparison is that most composite properties are based on the volume fraction of fiber. In panels with different volume fractions, a comparison between properties can be difficult to make. Thus it is common practice to normalize a set of properties with respect to a single fiber volume fraction. So long as the selected volume fraction is close to the actual value, the error associated with the normalization will be small. For the comparisons in this report, the properties were normalized to a 55% volume fraction according to Equation 1. All of the panel volume fractions are within 2% of the selected value, so the material property corrections are not excessive.

$$X_{normalized} = X_{test} \frac{v_{f_{selected}}}{v_{f_{actual}}} \tag{1}$$

Table 2 – Virgin and recycled CFRP mechanical results

Fiber orientation	Property		Unit	Virgin	Recycled
		Density	[g/cm^3]	1.49 ±0.01	1.50 ±0.01
		Fiber volume fraction	[%]	55.2 ±0.6	56.8 ±0.9
		Moisture	[%]	0.07 ±0.01	0.09 ±0.01
0° direction	Tensile	Modulus	[GPa]	97.9 ±7.1	102.4 ±16.2
		Strength	[GPa]	1.22 ±0.06	1.15 ±0.05
		Failure strain	[%]	1.10 ±0.08	1.14 ±0.22
	Flexure	Modulus	[GPa]	90.4 ±4.6	92.8 ±3.9
		Strength	[GPa]	1.52 ±0.09	1.47 ±0.06
		Failure strain	[%]	1.75 ±0.19	1.65 ±0.10
90° direction	Tensile	Modulus	[GPa]	7.50 ±0.41	7.63 ±0.39
		Strength	[MPa]	51.1 ±2.6	47.5 ±2.6
		Failure strain	[%]	0.73 ±0.03	0.64 ±0.06
	Flexure	Modulus	[GPa]	7.18 ±0.17	7.16 ±0.22
		Strength	[MPa]	92.5 ±2.4	78.0 ±4.1
		Failure strain	[%]	1.33 ±0.08	1.03 ±0.05

The raw data presents well with no large differences to past similar structural materials [2]. Here the modulus is a bit lower than other carbon fiber and epoxy composites, reflective of the fiber properties. The strength properties are otherwise excellent with good performance even in the 90° direction. The low standard deviations stem from the stable manufacturing process. While the tendency might be to suggest equivalent performance between the virgin and recycled fiber, the recycled fiber yielded a composite with higher fiber volume fraction.

The normalized composite material properties are thus presented in Table 3 along with a percent difference where there exists a statistical difference between the two values. A statistical difference is recognized when the standard deviations overlap by less than 30%.

Table 3 – Normalized properties for virgin and recycled panels

Property			Unit	Virgin	Recycled	Statistical Difference
0° direction	Tensile	Modulus	[GPa]	97.6	99.1	No
		Strength	[GPa]	1.22	1.11	No
		Failure strain	[%]	1.09	1.11	No
	Flexure	Modulus	[GPa]	90.1	89.8	No
		Strength	[MPa]	1.51	1.43	No
		Failure strain	[%]	1.75	1.60	No
90° direction	Tensile	Modulus	[GPa]	7.47	7.39	No
		Strength	[MPa]	51.0	46.0	9.7 % lower
		Failure strain	[%]	0.73	0.62	14.5% lower
	Flexure	Modulus	[GPa]	7.16	6.93	No
		Strength	[MPa]	92.2	75.5	18.2% lower
		Failure strain	[%]	1.33	1.00	25.2% lower

All the moduli values, whether tension, flexure, or compression are nominally the same suggesting that the fiber remained intact and aligned in the recycled panel. Further, in the 0 degree direction, where the fiber properties dominate, there was no difference in the strength or failure strain data as well. The main point of difference is with the panel strength specifically with respect to the strength in the 90 degree direction, where the resin properties are more predominant.

In both tension and flexure of the 90 degree samples, the strength is 10-20% lower with the recycled fiber likely as a result of some low-strength, resin-rich regions between the imperfectly packed fibers. This could also be an effect from the distortion to the fiber stitching. This lower strength also resulted in a lower recorded failure strain. It should be pointed out, however, that even though the data is nominally similar, the recycled panel data did have much higher coefficients of variation in the measured samples indicating a product with lower consistency.

Summary

As an industrial first, full-scale continuous carbon fiber composite panels were fabricated, recycled, and re-fabricated with the same carbon fiber. These panels were characterized to understand and compare the mechanical performance of the virgin and recycled fiber alike.

No significant difference was detected in the panel tensile properties. Some minimal decrease in flexure strength was recorded and is understood to reflect the loss of perfect fiber alignment as a result of the recycling process. The overall performance of the recycled fiber suggests minimal fiber damage.

The ability to recover fiber from a thermoset composite creates new pathways toward cost reduction and sustainable manufacturing for structural applications.

Acknowledgements

Steve Greydanus of Hexion was kind enough to donate Heloxy 112 internal mold release for the process trials and also provided guidance toward efficient HPRTM processing. This work was supported by the National Science Foundation, through an SBIR Phase I Grant: Award #1520527.

Bibliography

1. ***Pastine, S.J. (2013) Sustainable by design: introducing recyclable epoxy technology. Automotive composites conference and exhibition, ACCE 2013. Novi, Michigan. Conference proceedings.***
2. ***Swentek, I et al. (2015) Impact of HPRTM process parameters on mechanical properties using epoxy and polyurethane. Automotive composites conference and exhibition, ACCE 2015. Novi, Michigan. Conference proceedings.***