Processing and Performance of Recyclable Composites for Wind Turbine Blades

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ABSTRACT

End-of-life disposal of wind turbine blades poses environmental problems because the currently, blades are made from composites which are non-biodegradable and non-recyclable. To address this issue, Adesso has developed Cleavamine® curing agents for epoxy resins. The curing agents contain cleavable bonds in the molecules that can be cleaved under mild conditions, opening a pathway to recycling of epoxy composites. In the present study, epoxy resins were formulated using Cleavamine® curing agents, then charactered and analyzed. Protocals for VARTM processing (vacuum assisted resin transfer molding) were developed for the recyclable resin systems. Lastly, fiberglass-epoxy laminates were fabricated and subsequently subjected to matrix dissolution, and the properties of recovered fibers were evaluated. Results showed that void-free laminates could be produced using the recyclable epoxy resins, and the recovered glass fibers retain surface quality nearly identical to virgin fibers.

Keywords: recycling, processing, glass fiber, thermoset, vacuum assisted resin transfer molding (VARTM)

1 INTRODUCTION

Wind energy has grown rapidly as a renewable energy source. In 2015 alone, the U.S. wind industry installed wind turbines generating 8,595 MW, a 77 % increase over 2014 [1], and the market growth is expected to continue. According to the Global Wind Energy Council (GWEC), since the 1980s, wind turbine blades have increased eight-fold, surpassing 60 meters in length, to harvest more energy as a green solution to meet global energy demand [2]. The demand for larger blade sizes is being met by development of lighter structures, particularly those based on FRPs (fiber-reinforced thermoset polymers). The average lifespan of wind turbine blades is 20 - 25 years. With increased use of FRPs in the wind power industry, within the next 25 years, 225,000 tons per year of FRP-based rotor blades worldwide are projected to become eligible for recycling [3]. Thus, production of future wind turbine blades will require more efficient materials and processing, more reliable performance, and FRPs that are recyclable. The focus of this work is development of such FRPs, which offer major economic and environmental benefits.

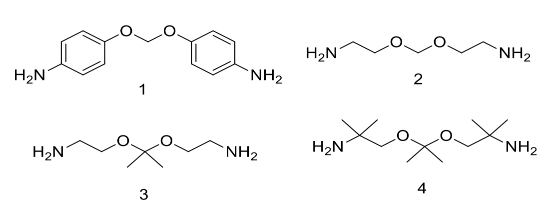
In this project, we address these goals by developing and demonstrating a recyclable epoxy resin based on patented Cleavamine® "cleavable" curing agents (Adesso) [4-6]. The cured resin can be chemically separated from fiber reinforcements and subsequently recycled under moderate pressure and temperature to yield small polymers. Thermochemical and thermomechanical properties of a prototype resin system are evaluated. Based on these properties, a VARTM process is demonstrated to produce lab-scale FRPs. Lastly, prototype laminates are separated using an aqueous-organic mixture and properties of reclaimed fibers are tested.

This work demonstrates an efficient and sustainable technology that provides a pathway to (a) optimizing in-process manufacturing of wind turbine blades, and (b) effective recycling wind turbine blades at end-of-life, as well as production waste.

2 EXPERIMENTATION

2.1 Resin Formulation

The resin selected (Recycloset® rAFV-2101S, Adesso) is a two-component, low-viscosity, recyclable epoxy system designed for VARTM processing. The Recycloset® technology is based on Adesso's patented Cleavamine® curing agents. By design, the curing agents contain acid-labile formyl, acetal or ketal bonds in the molecule. Fiber-reinforced composite parts produced from epoxy resins cured with a matched Cleavamine® curing agent can be dissolved in an aqueous-organic solvent mixture under appropriate (and mild) conditions, i.e., at atmospheric pressure and 100-150 °C.



Scheme 1: Cleavamine® curing agents used for Recycloset® rAFV-2101S

The acetal or ketal linkage in the middle of the curing agents can be cleaved by acid hydrolysis during the dissolution process to provide reclaimed resin product. In development of recyclable rAFV-2101S resin for RTM processes, the following Cleavamine® curing agents in Scheme 1 were selected to deliver suitable T_g, gel time, viscosity, and processing properties [4, 6].

2.2 Resin Characterization

Modulated differential scanning calorimetry (MDSC, TA Instruments Q2000) was used to analyze the reaction temperature, heat of reaction and the T_g of the resin. For each MDSC measurement, a ramp from -60 to 250 °C at a constant rate of 1.5 °C/min with ±0.5 °C/minute modulation was applied. After cure, a ramp from -60 to 250 °C at a constant rate of 10 °C/min with ±0.5 °C/minute temperature modulation was applied to the same sample. The T_g of the cured resin was obtained from the inflection point of the last reversible heat flow signal during the ramp.

Rheometer was used to measure the rheological properties of Recycloset® rAFV-2101S. For each rheological measurement, an isothermal dwell of 120 min was applied to the resin samples. Resin viscosity profiles at various cure temperatures were recorded and ananlyzed. Mechanical properties of Recycloset® rAFV-2101S were also measured, including tensile strength and modulus, bending strength and modulus, and elongation at break. The standard used for mechanical testing was Testing Standard: GB/T 2567-2008 [7].

2.3 Composite Fabcrication

Figure 1 shows the schematic diagram of the VARTM setup. Glass fiber sheets of 216 × 216 mm^2 were cut and stacked to form two-layer reinforcement. Infusion was performed on a flat tool surface to avoid resin flow bleed/race-tracking and air leakage during the process. The tool surface was cleaned and treated with a mold release agent to facilitate laminate removal after cure. The prepared plies were placed on the tool, creating a preform. A peel ply was placed over the preform, facilitating separation of the consumables from the part and creating a smoothe surface finish. To ensure even resin distribution through the preform, a spiral slit hose was used at the inlet of the cavity, cut to a length of 230 mm and placed at the edge of the fiber sheets. Distribution media were laid over the peel ply to enhance resin flow. The spiral, foam piece, and the inlet pipe were the major inlet components. The vacuum bag was cut to cover the entire preform, and was positioned to minimize air pockets and wrinkles, which could adversely affect resin flow. Bag edges were sealed using tacky tape. Evacuation was carried out using a vacuum pump under (-1) bar. Resin and hardener were mixed homogeneously before injection.

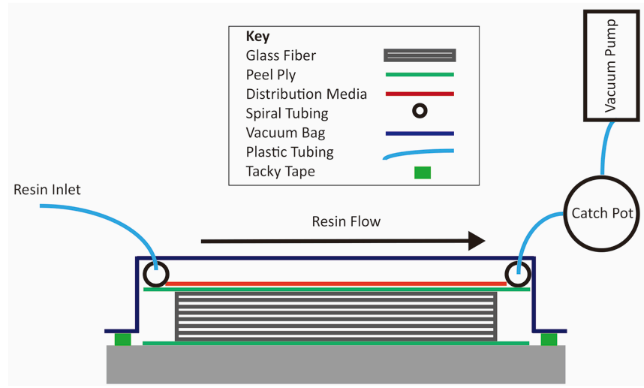


Figure 1: Schematic diagram of simple VARTM setup for a part made on a flat mold surface.

Figure 2 depicts different stages in the process. Once inlet and vent tubes were positioned, the vacuum bag assembly was sealed and closed and the inlet was clamped, vacuum was applied. This stage was referred to "pre-filling" (Figure 5(a)). After pre-filling, the inlet was opened and the resin infiltrated and filled the prefom. During the "filling stage" (Figure 5(b)), pressure inside the cavity varied with position and time. Within the impregnated portion of the preform, the resin pressure varied from vacuum at the flow front, to atmospheric pressure at the inlet. Once the preform was completely filled, either the inlet was clamped or inlet and vent port directly connected to equilibrate resin pressure within the laminate. The "post-filling" stage (Figure 5(c)) involved removal of excess resin, and allowed resin pressure and laminate thickness to equilibrate within the assembly. As excess resin bled through the vent, fibre volume fraction increased, and resin impregnated unsaturated fibre tows or macro- pores.

Vacuum was applied until complete gelation was achieved (2.5 hours). After gelation, the vacuum pump was switched off and the laminate was heated to 80 ºC at 2 ºC/min and held for 8 hours to achieve complete cure.

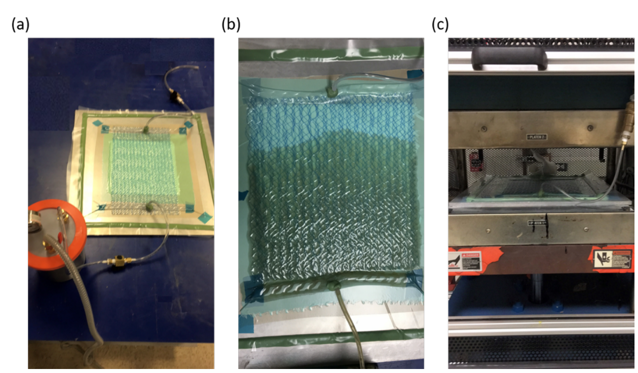


Figure 2: Three stages in the VARTM infusion process : (a) Pre-filling (b) Filling (c) Post-filling stage.

2.4 Chemical Recycling

Laminates were cut to 120 × 20 mm coupons and recycled using a chemical process - acid digestion - to separate glass fibers from the composites. The acid digestion solution consisted of 100 mL glacial acetic acid (Sigma-Aldrich) as solvent, and 10 mL hydrogen peroxide solution (30% (w/w) in H_2O, Sigma-Aldrich) as oxidant. A three-neck round-bottom flask (1 L) filled with acid digestion solution, and a composite coupon was refluxed at 110 °C. Additional hydrogen peroxide solution (30%, 5 mL) was added to the flask every hour. Recovered glass fibers were rinsed in water and acetone until no residues was observed. Fibers were oven dried prior to analysis.

2.5 Recovered Fiber Characterization

Recovered glass fiber sufaces were evaluated by scanning electron microscopy (SEM, JSM 6610). Fibers were sputter-coated with gold and mounted onto a stub with conductive tape. Accelerating voltage of 20 kV was used.

3 RESULTS

3.1 Resin Properties

Table 1 shows that the T_g of cured Recycloset® rAFV-2101S is 84 ^oC, which is comparable to the T_g of most commercially available non-recyclable resins designed for VARTM processing (70 to 85 ^oC) [8-10]. Table 2 shows that the mechanical properties of cured Recycloset® rAFV-2101S, including tensile strength and modulus, bending strength and modulus, and elongation at break. Data show that those values are also comparable to the commercial resins [8-10], indicating that Recycloset® rAFV-2101S is a suitable alternative for wind turbind blade manufacturing.

A : B（part by weight）	100 : 29
A Epoxy resin viscosity（cps@25±1°C）	800 ~ 860
B Harder viscosity（cps@25±1°C）	15 ~ 20
Mixed Viscosity（cps@25±1°C）	280 ~ 300
Gel time（min@25±1°C，100g）	330 ~ 360
T_g（°C@cure cycle: 80°C×8h）	80~85

Table 1: Resin rheological thermal properties

	Recycloset® rAFV-2101S	Commercial resins
Tensile strength (MPa)	70 ~ 75	60 ~ 80
Tensile modulus (GPa)	2.7 ~ 2.9	2.7 ~ 3.6
Bending strength (MPa)	115 ~ 125	90 ~ 122
Bending modulus (GPa)	2.6 ~ 2.8	2.7 ~ 3.2
Elongation at break (%)	4.0 ~ 4.5	3.3 ~ 16

Table 2: Mechanical properties (Cure cycle: 80 °C × 8h)

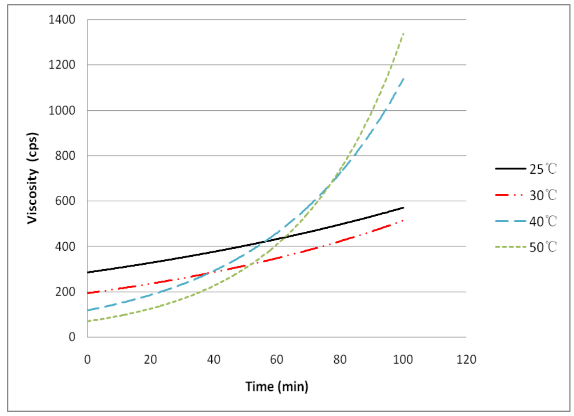


Figure 3: Viscosity vs time curve at different temperature for Recycloset® rAFV-2101S

Room temperature viscosity is one improtant criterion for VARTM resin systems, as it affects the injection process. Figure 3 shows the viscosity profile as a function of dwell temperature and time. Data show that as dwell time increases, the viscosity of the resin increases for all dwell temperature. We also observe that as dwell temperature increases, initial viscosity decreases, but the gelation time for the resin is shorter due to the faster reaction rate.

3.2 Composite Characterization

Void contents were measured by image analysis of polished sections. Samples 50 mm long were cut from the center of the part. Cross-sections were polishedat grits of 150, 240, 400, 600, 1200, 2400 and 4000. Images of polished sections were acquired using a digital microscope (Keyence® VHX-6000) at 150X. For void content analysis, images were converted to gray-scale, and voids were manually selected and filled to distinguish from solid phases. Image analysis software (ImageJ®) was used to “threshold” each image into a binary map of void (black) and solid (white) pixels, and to analyze the resulting areal void ratio.

The Figure 4 shows a cross-section of the laminate produced by VARTM. The void content is less than 0.7% with consistent fiber-resin adhesive contact. Therefore, a nearly void-free flat laminate can be produced by VARTM using the selected resin system. Also, the fiber mass ratio of reinforcement and matrix was 0.64±0.02 in this study.

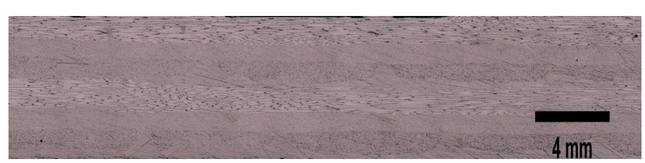


Figure 4: Polished cross-sections showing void contents

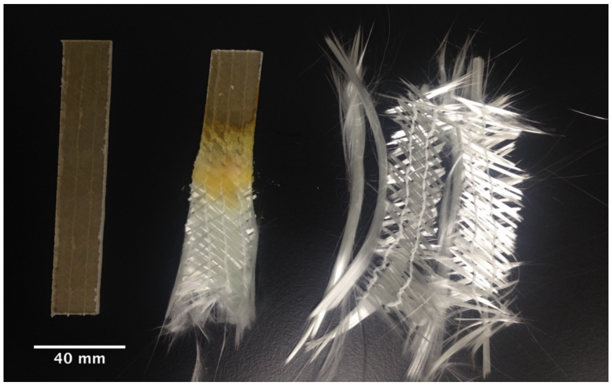


Figure 5: Recovered glass fibers after recycling

3.3 Composite Recycling

The recycling time of the laminate is defined as the time required for the matrix to fully dissolve, and allow clean glass fiber bundles to be separated (determined visually). Figure 5 shows that complete dissolution of the the matrix can be achieved via acid digestion, and clean glass fibers are recovered. The recycling time for a 120 × 20 × 2 mm composite coupon is ~ 2 hours.

3.4 Recovered Fiber Surface Quality

After recycling, the quality of recovered glass fibers is evaluated. The first criterion for recovered fiber quality is surface quality. SEM examination is used to detect resin residue on fiber surfaces. Figure 6 shows the surfaces of virgin glass fibers and glass fibers recovered by acid digestion. The recovered fiber surface quality is nearly identical to the surface quality of virgin glass fibers, and no significant defects or residues are evident. The diameters of recovered fibers are slightly less than those of virgin fibers due to removal of the sizing during acid digestion.

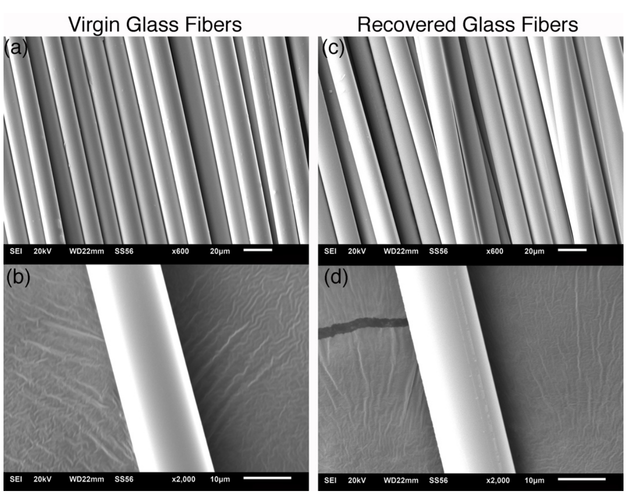


Figure 6: Recovered fiber surfaces: a) and b) virgin glass fibers; c) and d) recovered glass fibers from acid digestion

4 CONCLUSIONS

We investigated the possibility of using recyclable epoxy resin in VARTM processing. The thermal, rheological and mehcanical properties of the recyclable resin were compareble to commercial thermoset VARTM resins. Void-free laminates with fiber-resin adhesion can be produced by VARTM and recycled using low-cost chemicals at low temperature and atmospheric pressure. The recoverd glass fibers retain near-virgin surface quality.

By developing recyclable epoxies that are suitable for wind blades and can be readily recycled, clean fibers (glass and carbon) can be recovered from the blades. In addition, resin components can be recovered from the chemical feedstock after additional treatment. Thus most of the economic value of the materials can be recovered with modest investment. Widespread adoption in production of future wind blades could create a large supply of recovered fibers, potentially reduce fiber price, and pose new challenges. In particular, markets would have to develop to absorb the recovered fibers and put them to use in products.

5 ACKNOWLEDGEMENTS

Support from the M.C. Gill Composites Center is gratefully acknowledged. SEM images were acquired at the Center for Electron Microscopy and Microanalysis at the University of Southern California. Curing agent and formulation research were supported by Adesso Advanced Materials.

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