TECHNICAL ADVANCES IN EPOXY TECHNOLOGY FOR WIND TURBINE BLADE COMPOSITE FABRICATION

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ABSTRACT

Epoxy composites offer high performance and proven reliability in many demanding applications including components for aerospace and wind turbine blades. While in operation, wind turbine blades are subjected to significant stresses from their movement, wind and other environmental factors such as temperature cycling, humidity and bird strikes. Failures of these composite blades have been attributed to fiber/matrix delamination and cracking. Significant technical advances have been made by Dow to fundamentally understand the critical resin formulation attributes needed for use in wind turbine blades and thereby provide solutions to address these failures by leveraging key novel technologies that have been developed within Dow for its Epoxy Systems.

1. INTRODUCTION

The wind industry has quickly established itself as one of the largest composite applications of the world. As wind energy grows there is a trend to fabricate bigger and better blades. Bigger blades are needed because the power collected by a wind turbine increases with the square of the radius of the swept area. Better materials are needed because the wind industry demands longer lasting blades. The requirements today are already stringent. The Germanischer Lloyd Guideline for the certification of wind turbines [1] calls for a design life of 20 years with full load of 3000 hours/year.

Comparing this to the automotive industry, 20 years at a speed of 20 rpm translates to an equivalent total mileage of around 350000 km for a car (assuming an average tire size), thus beating today's automobile lifetime requirements by far. Not to mention that this must be fulfilled night and day, sometimes under extreme climate conditions (Temperature Conditions: -40 to +50 °C with 7000 temperature changes/year). So it is not surprising that reliability of blades becomes a significant and important factor for the industry.

In addition to the "longer lasting" trend in this industry there is a need for faster production of these blades. With the growing demand in wind electricity, manufacturers are pushing

productivity to increase throughput. By 2020, based on the current scenario, one new blade will need to be made every 3 minutes to satisfy the demand. This huge output will only be possible when manufacturing cycles are optimized to bring maximum efficiency.

Both factors, reliability and productivity, will generate the decrease in cost per kWh which the industry needs to be competitive with other sources of energy. So in essence it is about resolving the conflict between short and long lasting; i.e., shorten the cycle time but keep the quality high to enable the longer life time of the blade composite.

1.1 Defining Resin Requirements in Infused Fiber Reinforced Wind Turbine Blades

Figure 1 summarizes the attributes of the resin formulations needed in fiber reinforced wind turbine blade composites made by infusion processes. This figure is used as a guide for determining the suitability of various technologies, for example a toughening technology, for use in wind turbine blade applications.
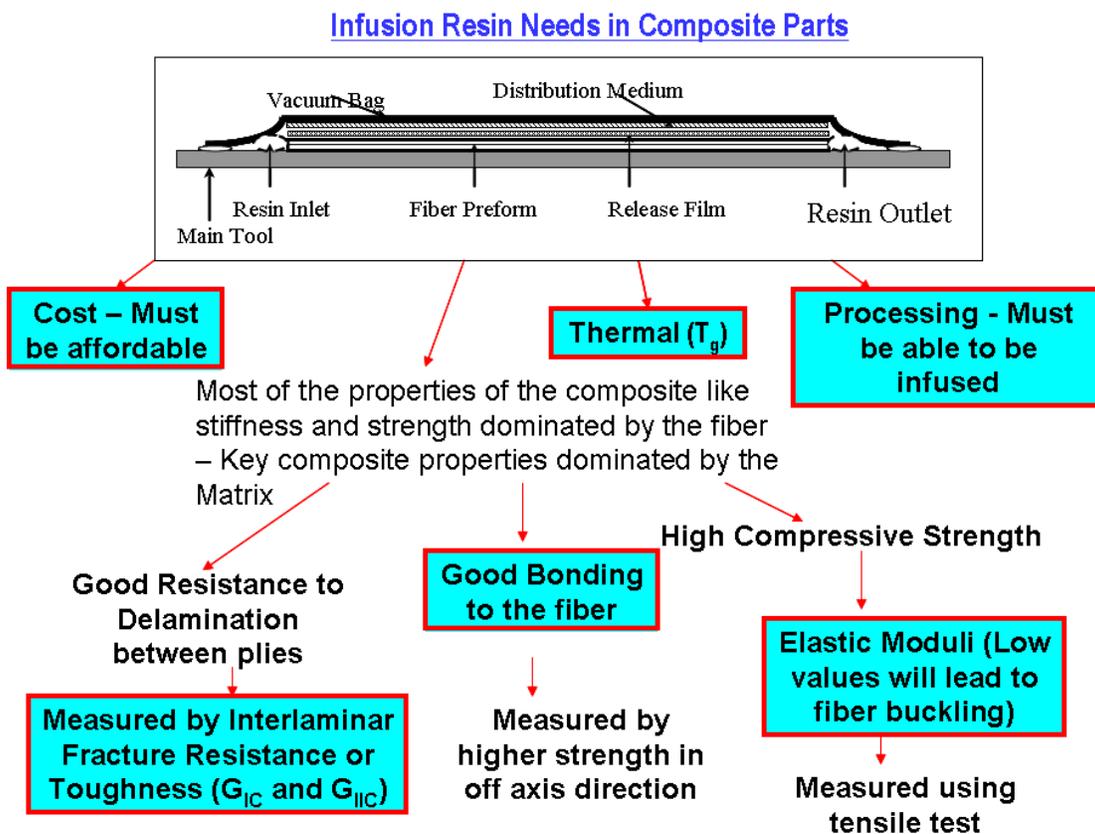
Figure 1. Summary of infusion resin needs in wind turbine blade composites.

In cases where a large quantity of resin formulation is used to make composite parts like in the wind blade, even small savings in total system cost per pound can be large. System costs include not only raw materials but processing and maintenance/repair costs as well.

For infusion processes it is important to have a low enough viscosity during processing because it is critical for ensuring thorough wetting of the fibers (carbon, glass, etc.). Insufficient fiber wetting can often lead to dry spots which cause premature part failure. In addition, having formulations with long resin pot life and increased gel times is also required for the same reason.

Following the infusion step, the composites are generally heat cured to create the final blade part which is capable of withstanding the stresses likely to be seen by it in actual use. In addition, the glass transition temperature, T_g, of the resin matrix limits the thermal stability of these parts so T_g is also important.

With respect to the mechanical properties of composite parts most of the properties [such as tensile strength, tensile modulus, etc.] are fiber dominated. However, there are a few properties that could be highly influenced by changes in the matrix resin such as the following:

- Good delamination resistance between the plies is dependent on the fracture toughness of the resin matrix. Mode I and Mode II interlaminar fracture resistance, or toughness, is a popular test to quantify delamination resistance in composites. For unfilled cured resin plaques compact tension (CT) or the single edge notch bend (SENB) test geometry can be used to measure the Mode I plane-strain fracture toughness.

- Compressive strength of a fiber composite is highly dependent on the elastic modulus of the matrix resin system in addition to fiber matrix adhesion. Low resin modulus values can lead to fiber buckling. This can be determined through a simple dog bone tensile test.

- It is well known that matrix resins have to efficiently transfer the stresses between the fibers for the composite to be able to meet its high strength requirements. For efficient stress transfer between the fibers it is important to have good fiber matrix adhesion. A simple test that indicates the level of fiber matrix adhesion is an off-axis strength-based test (a unidirectional fiber reinforced composite tested in the transverse direction). There are also more complicated tests to measure fiber matrix adhesion like the fiber pull out test. When evaluating an infusion resin system, compression tests on unidirectional fiber reinforced composites to determine their compression strength are very popular in the industry to have an idea of the resin modulus and also the fiber matrix adhesion.

- Finally, all of these mechanical and thermal properties described above have to be retained during temperature and humidity variations so it is also important to look at their residual properties after hot wet aging (or in other words their weatherability).

2. EXPERIMENTATION

2.1 Materials

The toughened epoxy infusion system consisted of a liquid epoxy resin (diglycidyl ether of bisphenol A, DGEBA), an epoxy-functional reactive diluent, a mixture of different amine curing agents to attain the appropriate reactivity, and one of Dow's amphiphilic block copolymer toughening agents designed for intermediate T_g composite applications added at 5 wt% loading.

The untoughened formulation had all the above mentioned ingredients minus the toughening agent.

2.2 Neat Resin Plaque Preparation and Composite Panel Fabrication

An aluminum mold (14 inch by 12 inch) lined with DuoFoil® was used to prepare a 3.2 mm thick neat resin plaque. Approximately 325 grams of resin formulation was blended at room temperature and degassed in a vacuum chamber until all foaming had subsided. The system was then poured into the mold at room temperature. The mold was immediately placed in a forced air convection oven and cured at 70°C for 7 hours. It was then cooled to ambient temperature in the oven, with the oven fan running continuously. The plaque was removed from the mold and visually inspected for inclusions, bubbles and defects. The plaque was then machined into the appropriate test specimens for measuring fracture toughness, tensile properties, flexure properties and T_g.

Glass fiber composites were fabricated using the Vacuum Assisted Resin Transfer Molding (VARTM) process. The glass fiber used was Knytex® DBM1708 which has a +/-45° fabric with a random mat (RM). The lay up employed was $[(RM/-45/+45)/(-45/+45/RM)]_3$ resulting in the laminate having an average thickness of 4.9 mm and a fiber volume fraction of about 40%. The same amphiphilic block copolymer toughening agent employed for the unfilled system study was used for fabricating the toughened composites. The toughening agent was added at 5 wt% of the epoxy resin matrix. The composite panels were cured at 90°C for 24 hours.

2.3 Differential Scanning Calorimetry (DSC)

Samples (10-20 mg) were cut from plaques with a razor blade and placed into open aluminum pans. A lid was placed on the pans then sealed by crimping the top to the bottom. A dynamic temperature scan was run under nitrogen from room temperature to 200°C at 10°C/min using a TA Model Q100 DSC instrument. The glass transition temperatures, T_{g1} and T_{g2}, from the 1st and 2nd scan, respectively, were recorded.

2.4 Tensile Testing

Quasi-static tensile tests were run on Type I dog-bone specimens in accordance with ASTM D-638. The specimens were cut into rectangular strips on a circular wet saw and then brought to dog-bone geometry using a TensilKut® router. In an attempt to minimize scatter in the data caused by defects, the edges were wet-sanded using a series of graded grit sand papers (360 and 600 grit was typically employed and, if necessary, 800 and 1200 grit was used). Samples were then gripped using sandpaper as tabs on an Instron electro-mechanical test frame leaving a gage section of 2 inches. The samples were tested in replicates of 5 at a prescribed displacement rate of 2.5 mm/minute. A 2 inch extensometer was used to measure strain. Load, stroke, and strain signals were recorded using a computer controlled data acquisition system. These were used to calculate the tensile modulus, tensile strength, tensile strain at break, and tensile strain at yield. All tests were performed at standard room temperature conditions.

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2.5 Fracture Toughness Testing

Samples were tested for Mode I fracture toughness using the CT specimen geometry in accordance with ASTM D 5045-93. Samples were water jet cut to appropriate dimensions. Water jet cutting was used to avoid cracking and leaving the test specimens with almost no residual stress. A starter crack was very carefully introduced by gently tapping a razor blade cooled with dry ice into the chevron notch in the specimen. Specimens were loaded on an electro-mechanical Instron 5566 test frame by means of a clamp and dowel pin and loaded at a constant displacement rate. Load and stroke data were recorded during the test using a computer controlled data acquisition system. About 5-8 specimens were tested for each sample plaque.

2.6 Rheology

Parallel plate rheometry using the ARES rheometer was used to track and compare the viscosity increase as a function of time for a toughened and untoughned formulation subjected to similar temperature profiles. Standard 40 mm plates were used and the sample, inserted between the plates was subjected to a constant frequency of 1 Hz. The samples were exposed to the following temperature profile: 40°C for 1 hour followed by a heat ramp to 70°C at 0.25°C/min.

2.7 Fatigue

Fatigue tests were performed using an Instron servo-hydraulic testing machine on rectangular coupon geometries, 25 mm (1 inch) wide and 203 mm (8 inches) long. No additional tab material was applied to the test coupons. The tests were run under sine-wave, load control, constant amplitude using an R value (minimum stress/max stress) of 0.1. The frequency was varied approximately inversely with maximum load to maintain a constant load rate. Frequencies were in the 1 to 3.5 Hz range to avoid significant heating; surface temperatures were monitored for selected tests, and fatigue specimens were surface cooled with fans. The fatigue samples were tested in replicates of 3.

3. RESULTS

3.1 Toughness improvements for wind blades

Epoxy thermosets are commonly used and are best known for their high T_g, creep resistance, corrosion resistance and high stiffness. However, the above benefits may be offset by increased brittleness which can limit where they are used unless some modification to improve toughness is made.

In principal, this could be done using a number of different types of toughening agents such as liquid rubbers [2-5], core-shell particles [6-8], glass bead filled [9-11] and thermoplastic modified epoxies [12-14], as well as combinations of the above [15]. While all are capable of toughening epoxy thermosets, they either sacrifice other key performance attributes (mechanical properties like modulus and thermal properties like T_g) or results in formulations that are difficult to process (usually because of high viscosities). This has led to a continued interest in developing new toughening agents/technologies that give a better balance of improved toughness without tradeoffs to other key performance properties and ease of processibility. Target applications include composites, adhesives, marine and protective coatings and fusion-bonded epoxy powder coatings for rebar, and oil & natural gas pipe lines.

Typical failures that occur in composite laminates after a fatigue test are micro cracks and fiber de-bonding, as visible in Figure 2, a photomicrograph taken of a hand laminate after fatigue testing.

Figure 2. Defects in laminate after fatigue stress (16 x magnification).

These defects can be effectively addressed by using toughening technology. Very early on plasticizers were used to modify material brittleness. However plasticizers can hurt mechanical and chemical strength. Furthermore they are not bound into the resin matrix and can migrate over time which inevitably changes the material properties. Especially with wind blades this may be an unwanted scenario as the long life time requires having unchanged material properties over two decades. When plasticizers are not wanted then one can build toughness effect into the backbone of the resin matrix; i.e., loosen the thermoset network structure. Although now being built into the matrix, the detrimental effect stays the same: Normally the glass transition temperature (T_g) is decreased significantly as the result of the loose network structure. Only with the advent of rubber material, like for example carboxy terminated butadiene nitrile rubbers (CTBN), was true toughness achieved with the retention of T_g over improved cracking properties. However, the use of CTBN increases the viscosity of the epoxy resin quite substantially which is undesirable for resin infusion technology. Later efforts in core shell rubber toughening address this unwanted viscosity increase but still not to the extent that it appears suitable for infusion because of the pre-dispersed particles.

Dow's toughening technology [16-18] is based on amphiphilic block copolymers. It forms a second phase only in the cured epoxy as depicted in Figure 3. This rubbery second phase allows the cured system to absorb more energy before cracking occurs. The key to doing this effectively is the control of the particle size, polydispersity and interfacial strength of the second phase; it is not enough to simply form a second phase in the cured system. The size, shape and interaction of that second phase with the host matrix is very important.
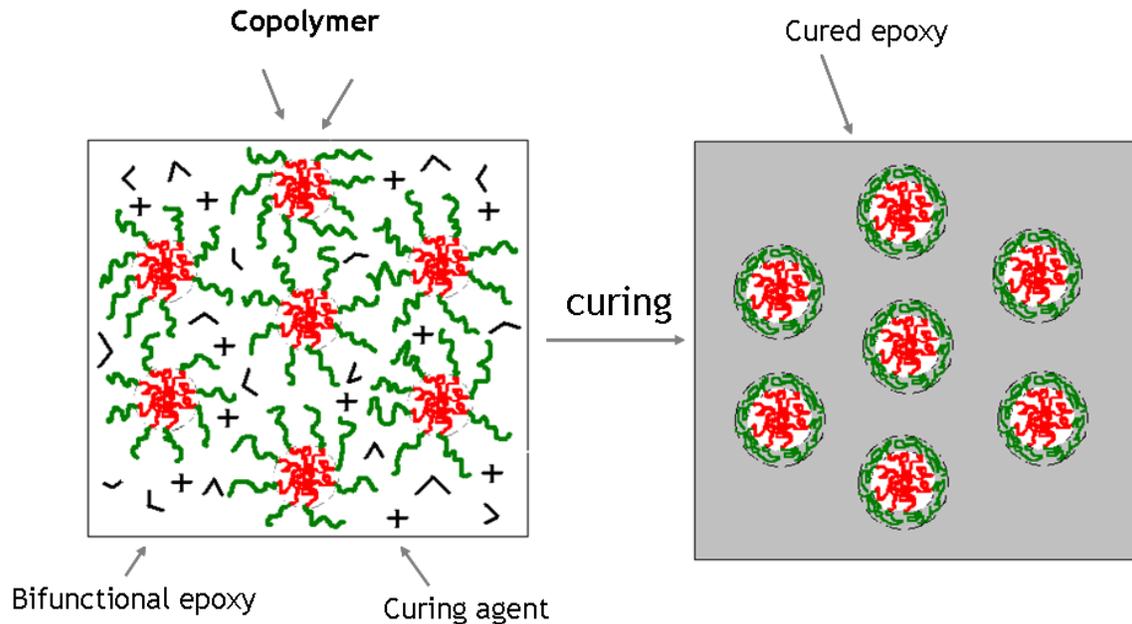
Figure 3. Formation of the second phase during curing.

One block is "epoxy-phobic" (will not mix with the epoxy matrix), and one is "epoxy-philic" (mixes easily in the epoxy matrix). When this block copolymer is added to the system, the epoxy-phobic block collapses on itself to form the second phase, while the epoxy-philic block surrounds the epoxy-phobic block and stabilizes it suspended in the host matrix. The advantage of this self assembly is that it takes less material to achieve the desired toughness. Consequently, the modified and unmodified sample will have the same stiffness. The modified or toughened system has an improved elongation and increased area under the stress/strain curve. By definition, the area under the stress strain curve is the toughness.

In an effort to determine the toughening mechanisms taking place an amphiphilic block copolymer toughener at 5 wt% was incorporated into a liquid epoxy resin formulation and self-assembled into well-dispersed nanometer scale spherical micelles with a size of about 15 nm. The toughening mechanisms were investigated [19-22], and it was found that the 15 nm size block copolymer micelles could cavitate to induce matrix shear banding, which mainly accounted for the observed remarkable toughening effect. This has been depicted in Figure 4. Other mechanisms, such as crack tip blunting, also play a role in the toughening.

The T_g stays unaffected since the toughening agent forms a second phase. Figure 5 plots fracture toughness versus T_g for a system that has been toughened using an amphiphilic block copolymer and one that has been flexibilized instead of toughening. It is seen that the block copolymer improves fracture toughness without compromising on T_g.

(a) initiation of a starting crack

(b) formation of a block copolymer cavitation zone at the crack tip when the specimen is loaded

(c) expansion of the cavitation zone and initiation of a matrix shear banding zone at the crack tip when the hydrostatic stress is relieved by the cavitation

(d) crack propagates when the shear strain energy builds up to a critical value, with a damage zone surrounding the crack

☐ Cavitation   ■ Shear Banding

Figure 4. Toughening mechanism in nano-sized amphiphilic block coplymers.
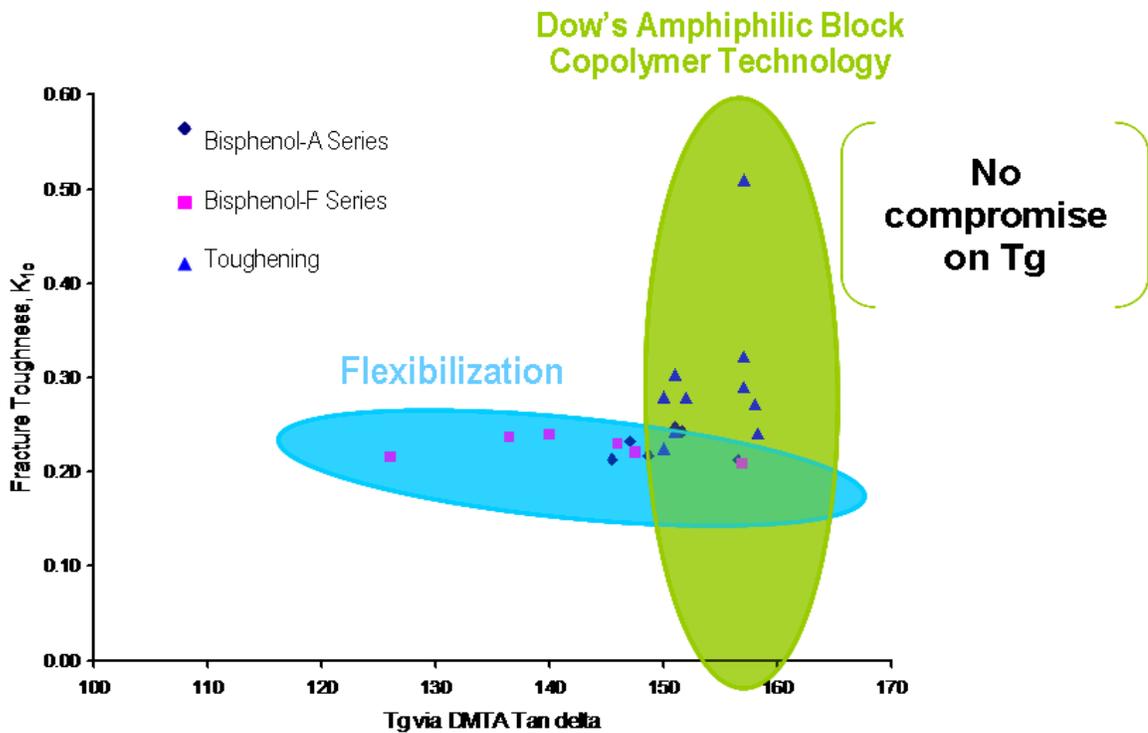
Figure 5. Toughness improvement without compromise in T_g.

It should be emphasized that Dow's block copolymer toughening technology is based on a completely miscible, low viscosity material that can be used very well in a resin infusion molding (RIM) process which is the major fabrication technique employed in the wind blade industry. Since the toughening agent material is transferred completely dissolved in the liquid matrix there will be no filtering effect as can be expected by conventional particle toughening. Figure 6 depicts the existence of second phase nanosized domains of the amphiphilic block copolymer between the glass fibers (white circles) in a composite illustrating the no filtering effect. Only on curing, the second phase will separate to give the toughness improvement; thus only after the material has been injected and cured. This is a very significant improvement in terms of meeting the need to increase productivity in wind blade manufacturing.
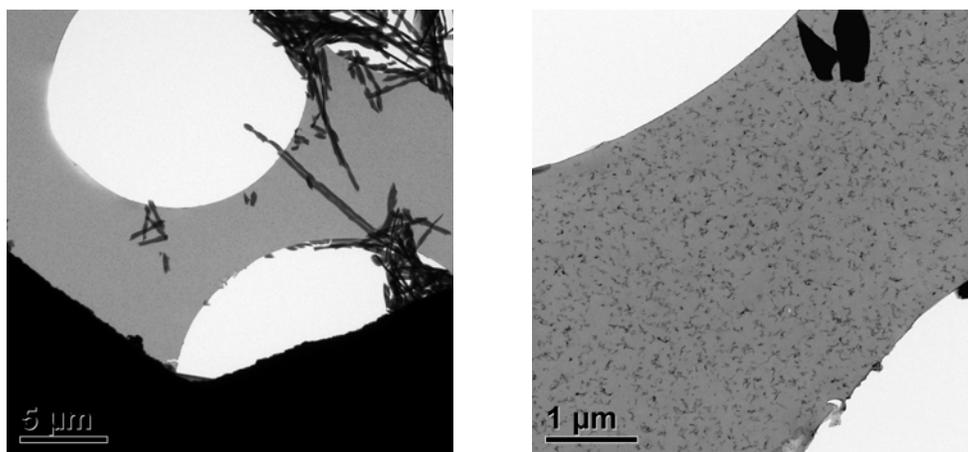
Figure 6. Existence of nanosized domains between the fibers illustrating no filtering effect.

The potential suitability of Dow's amphiphilic block copolymer toughening technology as a performance enhancer for epoxy systems in wind turbine blade applications will be explored below. This technology was designed to provide a balance of performance and processability in intermediate T_g fiber reinforced composites.

3.1.1 Thermal & Mechanical Properties of the Unfilled Amine Cured System

A comparison of the thermal (T_g) and mechanical properties (tensile and fracture toughness) between the amine cured untoughened and toughened resin system is summarized in Table 1. The fracture toughness from the fracture-based test and the failure strain from the strength-based tests (tensile) for the toughened system were larger than that for the untoughened system. An approximately 200% increase in fracture toughness was observed for the toughened system. This means that the toughening agent will likely lead to improved delamination resistance of the composite. This is because good delamination resistance between the plies may be attributed to high fracture toughness of the neat resin matrix. Additionally, this observed toughness enhancement was achieved without compromising key thermal properties such as T_g and strength-based mechanical performance properties such as modulus. This was different from other typical toughening agents (e.g., thermoplastics or elastomers) which oftentimes adversely affect these properties.

Table 1. Comparison of the Mechanical and Thermal Properties between the Amine Cured Untoughened and Toughened Resin System.

Property	Untoughened System	Toughened System
DSC T_{g1} (^{o}C)	88	85
DSC T_{g2} (^{o}C)	99	97
Tensile Yield Strength, MPa	68 (stdev = 0.6)	63 (stdev = 1.0)
Tensile Modulus, GPa	3.5 (stdev = 0.2)	3.1 (stdev = 0.04)
Tensile Strain @ Yield, %	4.3 (stdev = 0)	4.3 (stdev = 0.4)
Tensile Strain @ Break, %	5.8 (stdev = 0.7)	8.5 (stdev = 0.3)
Fracture Toughness (MPa m^0.5)	0.96 (stdev = 0.07)	2.59 to 2.80

The compressive strength of fiber reinforced polymer composites is highly dependent on the elastic modulus of the matrix resin system. Lower modulus leads to fiber buckling in compression. This suggests a composite part toughened with Dow's amphiphilic block copolymer technology would maintain its compression strength provided fiber-matrix adhesion has not been altered. The tensile yield strength of the toughened systems was less than their untoughened counterparts. This was expected considering the mechanism by which a soft phase amphiphilic block copolymer toughens an epoxy thermoset, namely, by cavitation of the toughening agent followed by shear yielding of the epoxy matrix [20].

3.1.2   Viscosity of the Amine Cured System

The viscosity change for the unfilled amine-cured system formulations using a temperature profile similar to what is used during an infusion process during blade fabrication is shown in Figure 7. The initial viscosity of the two formulations at 40°C is the same. This would likely not be the case with most toughening agents such as CTBN or core-shell rubbers which very often increase formulation viscosity. For example, the viscosity of D.E.R.[TM] 383 is 10030 cps at 25°C while the viscosity of D.E.R.[TM] 383 with 5 wt% of a core-shell rubber is 13260 cps at 25°C. On the other hand a similar mixture containing Dow's amphiphilic block copolymer toughening agent at 5 wt% results in a viscosity of about 8400 cps at 25°C.

Figure 7 shows that during the temperature ramp up from 40°C to 70°C the viscosity of the toughened system (lower curve) increased more slowly than that of the untoughened system. This could be advantageous because it would allow more time for the matrix formulation to wet the glass fibers. This would be beneficial because insufficient fiber wetting could lead to dry spots which could cause premature failure of a composite. The source of the slower viscosity increase was likely due, in part, to a dilution of the reactive species. However, there was some

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precedent in the literature that indicated there could also be hydrogen bonding between the amine curing agents and the block copolymer that could also decrease the reaction rate [23].
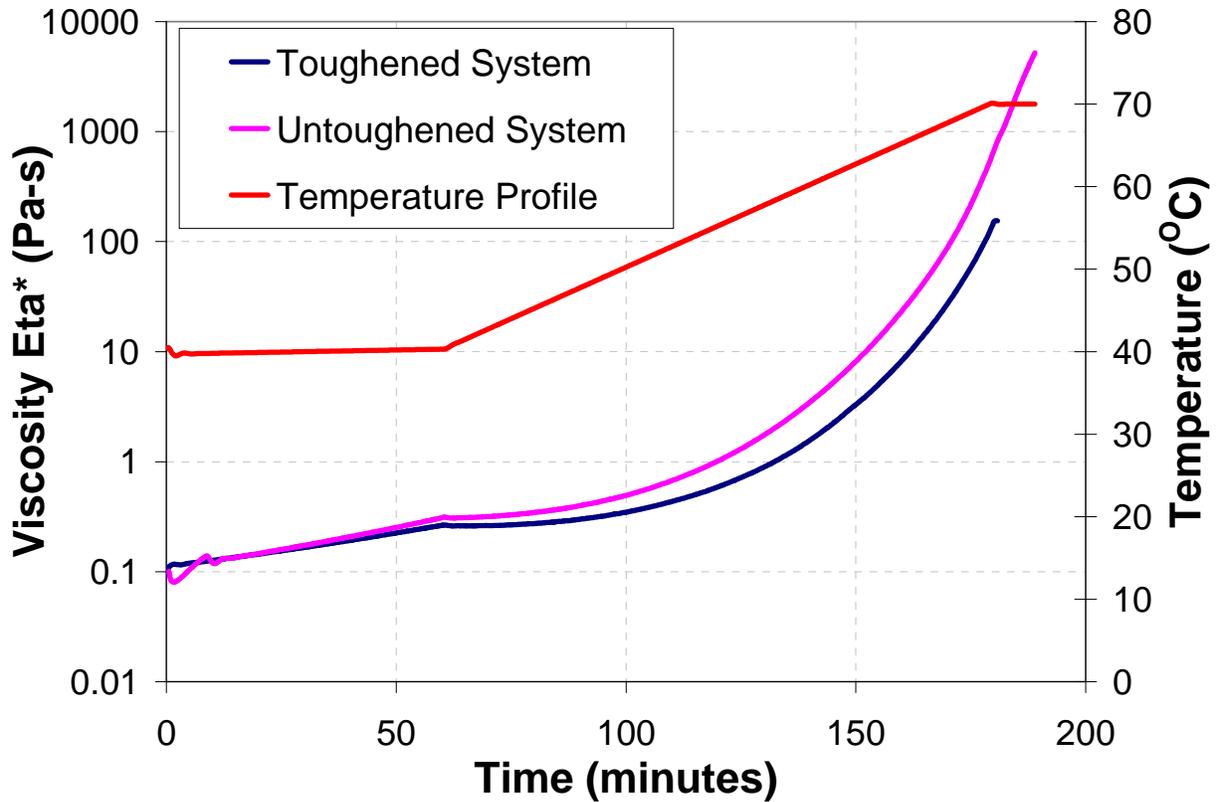
Figure 7. Comparison of the Viscosity Increase between a Amine Cured Untoughened and Toughened Formulation Resin System.

3.1.3 Fatigue of Glass Fiber Reinforced Composite Systems

To determine how improvements made at the unfilled plaque level for the toughened system translate into fatigue resistance at the composite level, composites fabricated from the toughened and untoughened systems were subjected to a regular fatigue protocol. Tensile fatigue results for the toughened and untoughened composite panels are presented in Figure 8. The data are presented in terms of normalized maximum tensile stress vs. log cycles to failure for R = 0.1. Failure during the fatigue tests was determined as complete separation of the test coupon. Fatigue results are represented with the power law model $S = A N^B$, where S is the normalized stress, N is cycles to failure, and A and B are constants. The number of cycles to failure for the toughened composite was more than twice the untoughened version at lower stress levels. While research in this area is still "work in progress", initial results are revealing that considerable improvements in composite fatigue resistance can be made when using block copolymer toughening for the wind application.
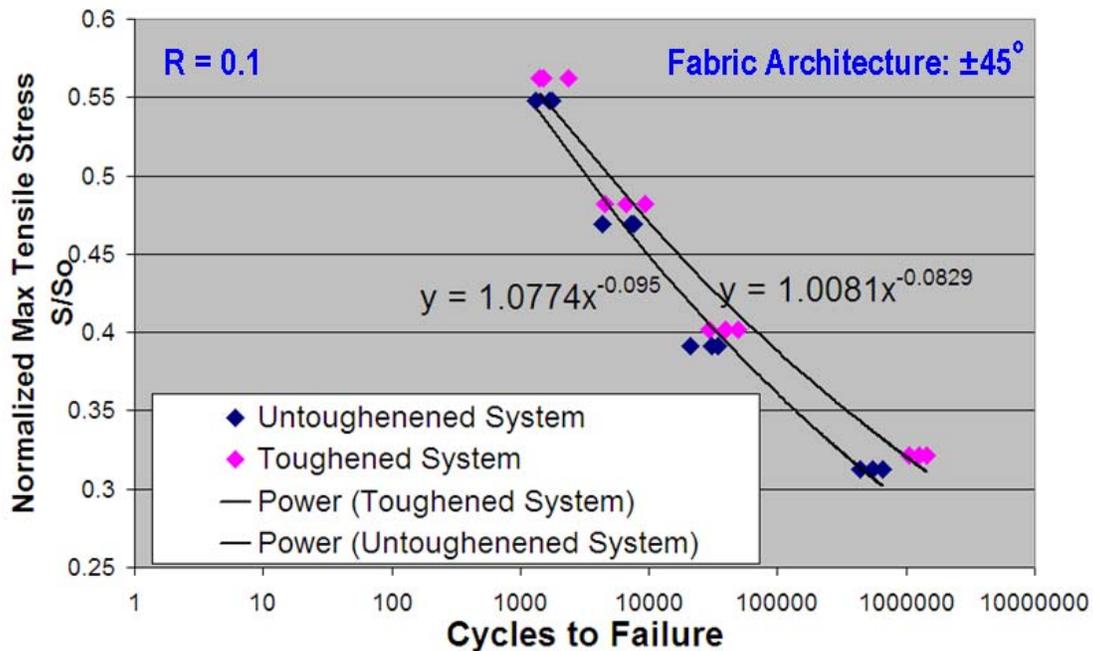
Figure 8. Tensile fatigue results for the toughened and untoughened composite panels.

3.2 Push for Productivity

Current demands from the market circulate around process requirements like low exotherm, long pot life and fast cure response. In response to this Dow has been developing the new AIRSTONE™ 78-Infusion line which meets all the requirements for infusing large blades fabricated currently and longer ones that will be fabricated in the future. It however raises the need to have a relatively latent epoxy system that will have no significant increase in viscosity over the period of infusion. This requirement seems to contradict the need for a fast cure response which can ultimately reduce the cycle time more significantly than having faster infusion. Nevertheless, with the 78-Line Dow has managed to optimize the rate of reaction at different temperatures in such a way that the cure speed at higher temperatures exceeds that of conventional infusion systems. Ultimately a more homogeneous degree of cure can be achieved over the entire blade when the cure response is better as illustrated in Figure 9. Reaching earlier the target T_g at all sections of the blade will lead to shorter cure times. Ultimately Tg's in excess of 90°C are possible depending on curing conditions. With its infusion system Dow has contributed significantly to the industry's need to push productivity. AIRSTONE™ epoxy systems for wind blades have received approval from the industry's leading certification body, Germanischer Lloyd.

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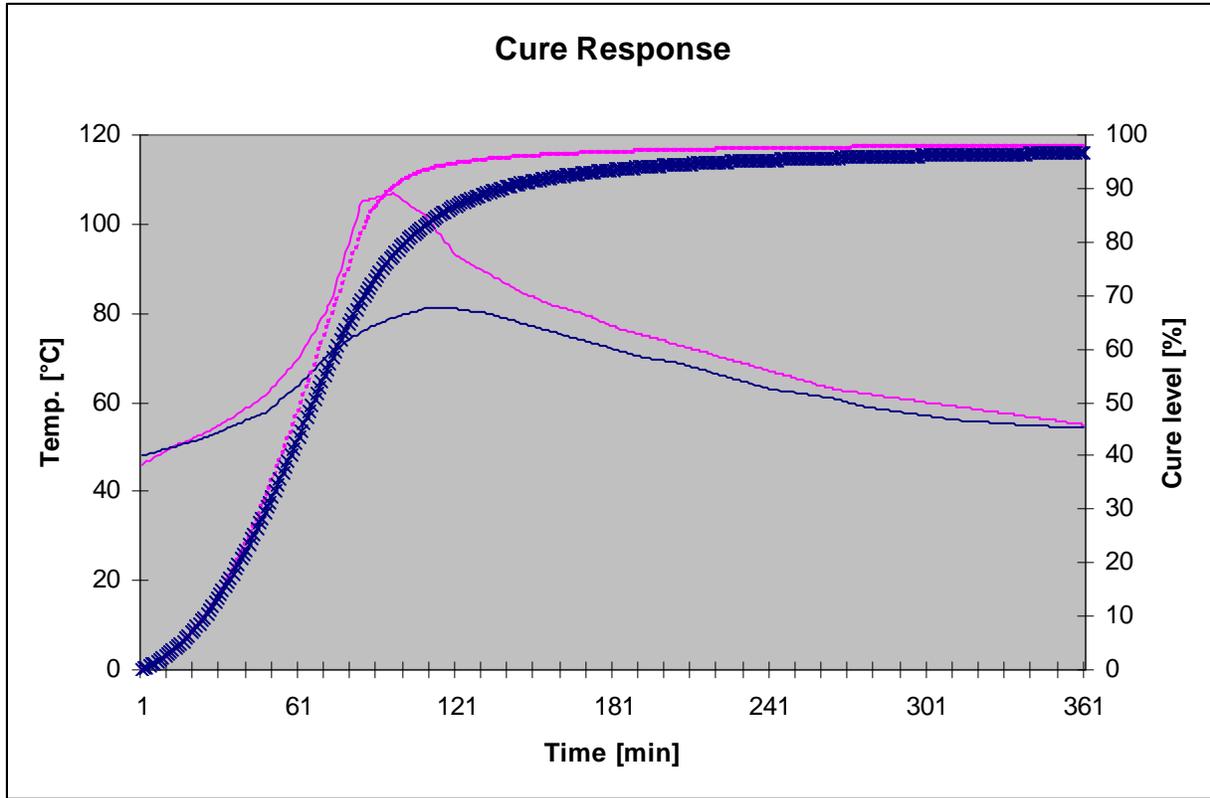
Figure 9. Cure degree over two different exothermic reactions.

4. CONCLUSIONS

This paper summarizes the significant technical advances that have been made by Dow to fundamentally understand the critical resin formulation attributes needed for use in wind turbine blades and thereby provide solutions to address failures/shortcomings in these blades by leveraging key novel technologies that have been developed within Dow for its Epoxy Systems. The potential suitability of Dow's amphiphilic block copolymer toughening technology as a performance enhancer for epoxy systems in wind turbine blade composite applications was evaluated. The use of this toughening technology was found to give a better balance of improved toughness and fatigue resistance without tradeoffs to other key performance properties and processibility. Dow with its new AIRSTONE™ infusion line has contributed significantly to the industry's need to push productivity.

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