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Effects of Postcure Temperature Variation on Hygrothermal-Mechanical Properties of an Out-of-Autoclave Polymer Composite

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ABSTRACT: The effects of cure temperature variation on the properties of an out-of-autoclave polymer composite manufactured using Cycom 5320 8HS prepreg were investigated using different postcure temperatures of a two-stage cure cycle. In addition, the effects of adverse environmental conditions on the cure temperature variation were studied by conditioning the samples in an environmental chamber until they reached moisture equilibrium. The state of cure was obtained using a differential scanning calorimeter and dynamic mechanical analyzer. The mechanical properties were obtained using short-beam shear (SBS) and combined loading compression (CLC) test methods. The state of cure obtained showed increases in total heat of reaction, degree of cure, and glass transition temperature as the postcure temperature increased. The SBS and CLC strengths showed an increasing trend as postcure temperature increased. Good correlations were obtained between the material's cure temperatures, state of cure, and mechanical properties for room temperature dry and hot wet conditions. The study showed that the state of cure can be used to define, monitor, and verify the cure quality. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 3090–3097, 2013

KEYWORDS: composites; differential scanning calorimetry; mechanical properties

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INTRODUCTION

Out-of-autoclave (OOA) prepregs can reduce the cost of curing composites by producing parts that have high strength and low porosity similar to autoclave-cured parts.[1,2] Additionally, lowering cure temperature of the OOA composite can reduce cure temperature variations for larger parts, resulting in cost-effective curing equipment, tooling, and repair.

Previously, several researchers investigated the effects of curing variation on autoclave and OOA composites. For autoclave composites, the curing involves time, temperature, external pressure, and vacuum pressure where the external pressure and vacuum pressure variation are known to have significant effects on void content and mechanical properties of the final part.[3–6] The effects of cure temperature and state of cure variation were also studied by several researchers.[6–9] Lee and Springer[7] investigated the effects of curing on mechanical properties for a wide range of degree of cure ranging from 0.6 to 1 for Fiberite T300/976 graphite-epoxy composite. Koushyar et al.[6] and Alavi-Soltani et al.[8] studied the changes in short-beam shear strength for different isothermal cure cycles.

In the current practice, curing of polymer composites must precisely follow the cure specification to ensure structural integrity. The cure specification defines that the time-temperature data recorded by thermocouples must fall within a specified range as given by the prepreg manufacturer. As such, the quality of parts cured outside the time-temperature specification window is questioned and often rejected. Such time-temperature variation may be caused by invalid thermocouple readings, failure of heating equipment, or operation errors.[9] Previous studies have shown that materials rejected due to cure temperature variations may still have acceptable mechanical properties, because the variations in cure temperatures may not adversely affect these properties.[9–11] Accordingly, a good understanding of how cure temperature variation affects the state of cure and the mechanical properties is necessary for reducing rejected parts, resulting in cost-effective manufacturing of composite parts.

The performance of composite materials is very vulnerable to adverse environmental conditions such as high humidity and elevated temperature (i.e., hygrothermal condition).[12,13] When the composite part is exposed to humidity and elevated temperature, the absorbed water can attack resin-fiber interface, weakening the bond between them and softening the matrix, thus reducing the mechanical properties of the part.[12] Many applications require the composite part to operate in hot wet (HW) conditions and, hence the hygrothermal-mechanical properties are more imperative for design purposes. By applying a similar HW conditioning, the cure states and mechanical properties of

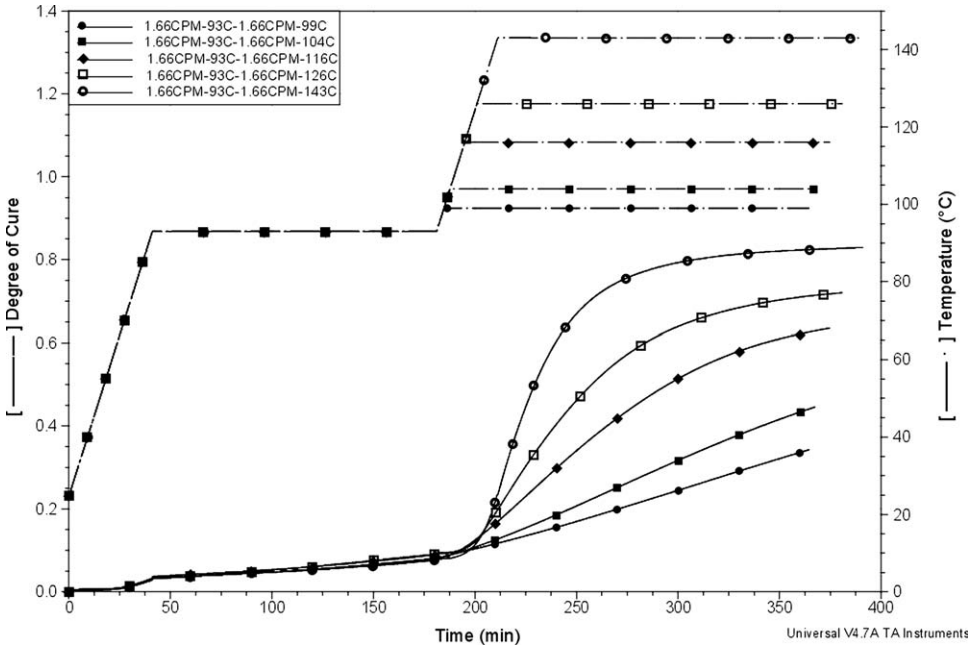

Figure 1. DOC during cure for different cure cycles.

the material with cure temperature variations can be obtained. The comparison of mechanical properties before and after hygrothermal conditioning can be used to predict the effects of humidity and elevated temperature on the composite laminate.

EXPERIMENTAL

Material and Cure Cycles

A commercial carbon fiber-epoxy prepreg, Cycom 5320 8HS, manufactured by Cytec Engineered Materials was used in this study. This out-of-autoclave prepreg is a toughened epoxy resin system reinforced by eight harness satin (8HS) carbon fiber and can be vacuum bag cured to produce autoclave quality parts with very low porosity.[2] Before curing, a minimum of 95 kPa at sea level vacuum was applied on 12-ply laminate for 16 h. All the panels were cured by applying the same initial ramp-up rate at 1.66°C/min to 93°C for 2 h, followed by ramp-up rate of 1.66°C/min to different postcure temperatures. Total of five panels for postcure temperatures at 99, 104, 116, 126, and 143°C were cured in this study (Figure 1).

Differential Scanning Calorimeter

Differential scanning calorimeter (DSC), a well-known thermal testing instrument to trace the aging of polymers, was used to obtain cure kinetics of 5320 8HS. The DSC was used to obtain heat of reaction, residual heat of reaction, degree of cure (DOC), and glass transition temperature of the samples. The uncured prepreg samples, which weighed between 10 and 15 mg, were encapsulated in Tzero^{TM} aluminum pans and were subsequently cured in the DSC. The heat of reaction of the samples during cure was measured with a TA Instrument Q2000 DSC. The DOC of the samples was calculated from the obtained heat of reaction.

Dynamic Mechanical Analyzer

Dynamic mechanical analyzer (DMA) was used to measure T_g of the cured composite samples. Five specimens of 4 mm × 25 mm for each cure were machined from 3-ply panels and tested using a TA Instruments DMA Q800 equipped with a three-point bending clamp according to ASTM D7028.[14] A constant force of 0.5 N, strain of 0.02%, frequency of 1 Hz, and dynamic scanning rate of 5°C/min were applied. T_g was defined as the inflection point of the sudden drop in storage modulus.

Sample Conditioning

To study the effects of hygrothermal conditioning on different cure cycles, the samples were conditioned before testing in accordance with ASTM D5229.[15] The HW samples were conditioned in an environmental test chamber Tenney T10RC. The samples were exposed to 85% RH at 71°C until the average moisture content of the traveler specimens changed by less than 0.02% for two consecutive readings within a span of 7 ± 0.5 days before testing.

Mechanical Testing

The mechanical properties of postcure temperature variation panels were obtained using both short-beam shear (SBS) and combined loading compression (CLC) test methods according to ASTM standards.[16,17] The SBS test method provides screening of the part quality while the CLC test method provides compressive properties such as compressive stress, compressive strain, modulus, and Poisson's ratio. The SBS and CLC tests were done on RTD samples at room temperature and HW samples at 82°C in a humidity-controlled test chamber.

RESULTS AND DISCUSSION

Degree of Cure

In thermosetting composites, the DOC and the glass transition temperature (T_g) have a strong interrelationship: T_g proportionally increases with DOC.[18–20] Heat of reaction for different stages of different postcure temperatures and its final DOC are reported in Table I, and their corresponding DOC during cure is presented in Figure 1. For all cure cycles, insignificant changes

Table I. Heat of Reaction for Different Cure Stages and Final Degree of Cure Obtained from DSC

Postcure temp (°C)	$H_{ramp,1}$ (J/g)	$H_{iso,1}$ (J/g)	$H_{ramp,2}$ (J/g)	$H_{iso,2}$ (J/g)	H_{res} (J/g)	H_t (J/g)	α
99	5.2	9.1	0.6	46.4	117.7	61.3	0.34
104	5.2	9.2	0.9	63.9	98.4	79.2	0.45
116	5.3	9.4	2.7	87.4	60.2	104.8	0.64
126	4.6	10.7	5.6	100.1	47.0	121.0	0.72
143	5.0	8.6	27.9	106.1	30.4	147.6	0.83

in enthalpy, $H_{ramp,1}$ and $H_{iso,1}$, are observed during the initial ramp up and intermediate cure stage. The enthalpy increases quickly during the second ramp up ($H_{ramp,2}$) and postcure isothermal stage ($H_{iso,2}$), indicating rapid curing due to increase in cure temperature. Figure 1 plots DOC during cure (left *y*-axis) and different postcure temperatures (right *y*-axis) with respect to curing time. Figure 1 also shows that, once the DOC reaches ~0.7, the rate of change of DOC tends to be slower, indicating diffusion-controlled curing reactions. The point at which the cure kinetics changes from kinetic to diffusion-controlled is also known as vitrification. As can be seen, the postcure temperature variation strongly affects the final degree of cure. For higher postcure temperature at 126 and 143°C, the material has reached its vitrification.

Moisture Absorption

Through-thickness moisture conditioning for cure cycles with postcure temperature variation was performed at elevated temperature to investigate the hygrothermal effects on the state of cure and mechanical properties. Figure 2 presents the percentage of weight gain for different postcure temperatures over conditioning time. A rapid increase in weight gain is observed for all cure postcure temperatures during the initial periods of exposure. Then the rate of absorption is slower indicating that the moisture uptake is reaching equilibrium. It also indicates that higher postcure temperatures were less vulnerable to moisture absorption while lower postcure temperature specimens absorbed more moisture. This observation on moisture absorption behavior of the OOA composite is similar to the previous study by Tang and Springer[21] for degree of cure ranging from 0.6 to 0.9 for Fiberite 976 resin material. The changes in moisture content absorbed for different postcure temperatures could be related to the state of cure of the material, which shows that material with lower state of cure is more influenced by moisture.

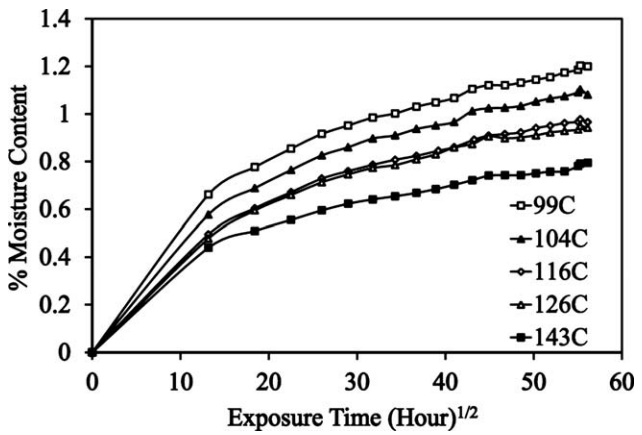

Figure 2. Moisture absorption for different cure cycles.

Glass Transition Temperature

T_g for different postcure temperatures was obtained by dynamic temperature scanning of 5°C/min from 25 to 216°C on the samples using a DMA. The T_g was obtained by determining the inflection of G' curve. Figure 3 shows the measured RTD and HW T_g for different postcure temperatures. Although the T_g for both RTD and HW specimens increased as the postcure temperature increased, the HW T_g showed less increase compared to the RTD T_g. It can also be seen that for postcure temperature at 126 and 143°C, the HW T_g is lower than the RTD T_g. However, for postcure temperatures ranging from 99 to 104°C, the HW T_g has no significant variation and is greater than the RTD T_g. This shows that hygrothermal conditioning has definite influence on the state of cure of the material. As such, for lower postcure temperatures from 99 to 104°C, HW conditioning enhanced the state of cure and that the obtained T_g was affected predominantly by the conditioning environment.

Constituent Contents

Porosity and variation in material constituent affect the properties of composite.[3–622–24] To evaluate the quality of the cured panels for different postcure temperatures, the constituent content must be known before conducting mechanical testing to ensure uniformity for all the panels. In this study, material

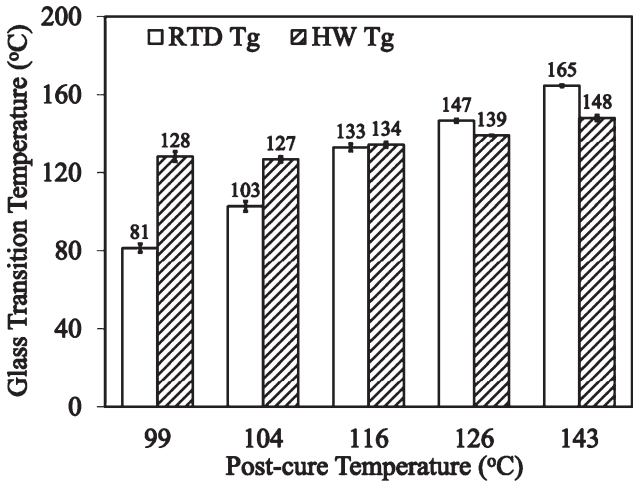

Figure 3. Glass transition temperature obtained for RTD and HW samples for different cure cycles.

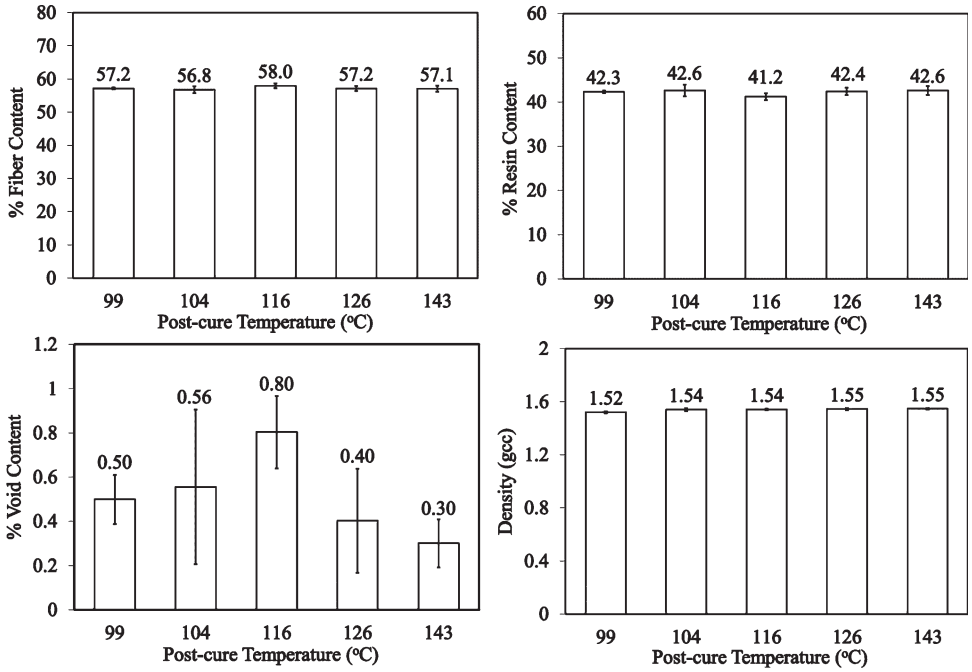

Figure 4. (a) Fiber volume content, (b) resin volume content, (c) void content, and (d) density for different cured panels.

constituent contents are determined by acid digestion method, which can be performed according to ASTM D3171 Method I Procedure B.[25] Figure 4 shows the average fiber volume fraction, resin volume fraction, void content, and cured panel density for panels cured with different postcure temperatures. The porosity for all the panels was found to be acceptable (within 2% of void content) as determined by the void content test. The resin density of 1.31 g/cm^3 and fiber density of 1.77g/cm^3 were used for void content calculation. The low-void content of the cured panels indicates that fabrication process was performed properly. However, a slight increase in laminate density as postcure temperature increases can be attributed to the difference in the state of cure of the panels.

Short-Beam Shear Test Results

SBS test method use shear as dominant load according to ASTM D2344.[16] However, because the internal stresses are complex, the SBS strength is widely used for comparison, quality control, and process specification purposes rather than defining any mechanical properties. Previous studies by Koushyar et al.[6] and Alavi-Soltani et al.[8] showed an increasing trend in the SBS strength as the material's state of cure increased.

Average values for the RTD and HW SBS strengths (along with standard deviations) are shown in Figure 5. Both RTD and HW SBS strengths show an increasing trend as postcure temperature increases. Similar to the T_g test results, the HW SBS strength shows less increase in strength compared to the RTD SBS strength as the postcure temperature increases. Also, the SBS HW strength is greater than the RTD SBS strength for lower postcure temperature at 99 and 104°C while it is less than the RTD SBS strength for higher postcure temperatures (116–143°C). This indicates that, during the time to reach moisture equilibrium in the conditioning chamber, the samples for postcure temperatures from 99 to 104°C underwent further curing, which led to an increase in their HW SBS strength compared to the RTD SBS strength. For higher temperatures (116–143°C), the decrease in the HW SBS strength relative to the RTD SBS strength shows the detrimental effects of moisture and elevated temperatures on the mechanical properties of the cured laminate.

Combined Loading Compression Test Results

To determine the effects of environmental conditioning on compressive properties, the average HW and RTD CLC strengths (along with standard deviations) are shown in Figure 6 for different postcure temperatures. Both RTD and HW CLC strengths increase as postcure temperature increases. Similar to the T_g and SBS results, a decrease in compressive strength is observed for postcure temperature of 143°C after conditioning. For postcure temperatures ranging from 99 to 126°C, there is a

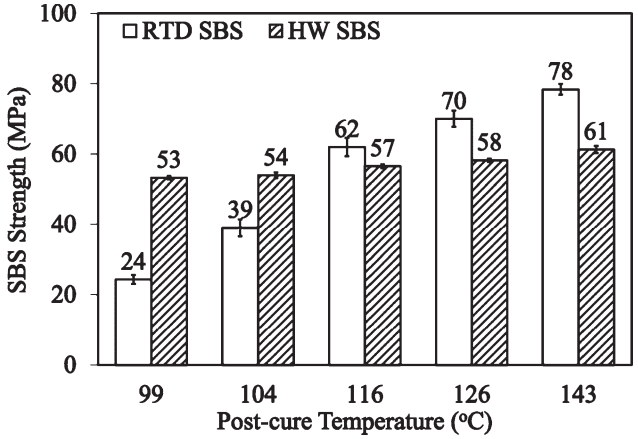

Figure 5. Comparison of RTD and HW SBS strength for different cure cycles.

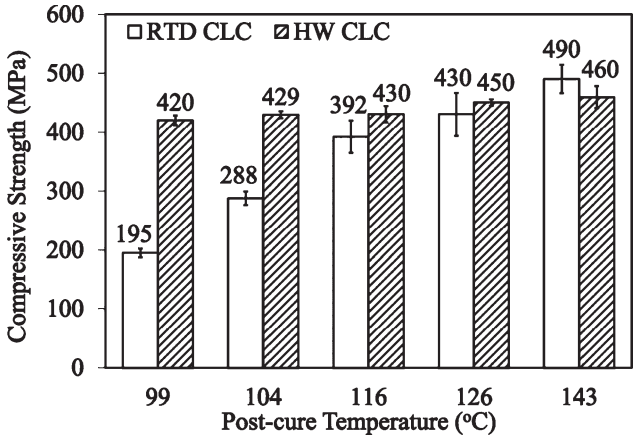

Figure 6. Compressive strength for different cure cycles.

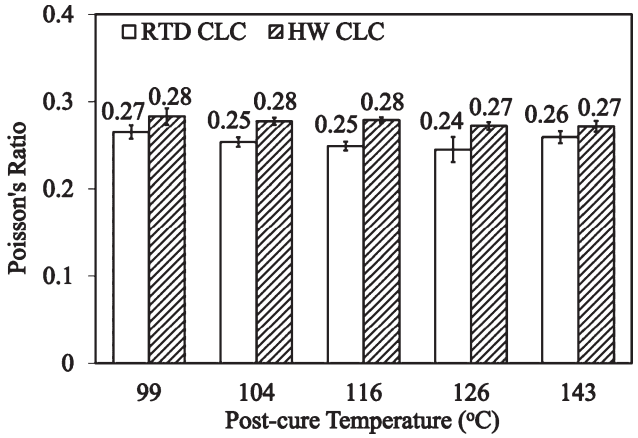

Figure 8. Poisson's ratio for different cure cycles.

noticeable increase in the CLC strength after hygrothermal conditioning. There is no significant difference in HW compressive strengths for panels cured at postcure temperatures ranging from 99 to 116°C.

The compressive modulus and Poisson's ratio for RTD and HW samples are shown in Figures 7 and 8, respectively. The modulus was obtained using the slope of the linear portion of the compressive stress–strain curve for each specimen. These figures show that the CLC modulus and Poisson's ratio do not vary significantly for different postcure temperatures. Previous studies also show similar observation for the compressive modulus.[8,21] On the other hand, hygrothermal conditioning shows no significant effect on the compressive modulus while it slightly increases the Poisson's ratio. As such, no particular trend is observed for the compressive modulus and the Poisson's ratio with postcure temperature variation.

CORRELATIONS

Correlation Between Degree of Cure and Glass Transition Temperature

Previous studies have shown that the final DOC and T_g are predominantly affected by curing temperatures.[8,20,26] According to DiBenedetto,[27] the DOC and T_g have a strong interrelationship: T_g increases proportionally with the DOC. Figure 9 shows the relationship between the DOC, T_g, and postcure temperatures. For the postcure temperatures ranging from 99 to 143°C, the value of DOC ranges from 0.35 to 0.83 while the value of T_g ranges from 81 to 170°C. As shown in Figure 9, the values for both DOC and T_g increase as the postcure temperature increases. Also, obtaining the relationship between the DOC and T_g is useful in predicting the DOC based on the T_g or vice versa.

Figure 10 shows the RTD T_g plot versus the final DOC for different postcure temperatures. The T_g-DOC relationship obtained in this study is slightly different than the one obtained in a previous study. Sabzevari et al.[26] showed experimental results for a nonlinear T_g-DOC relationship and DiBenedetto model for a wide range of DOC and T_g. However, the T_g-DOC relationship in Sabzevari's study for DOC ranging from 0.35 to 0.83 shows an almost linear fit, as also obtained in this study.

Correlation Between State of Cure and Moisture Absorption

As mentioned earlier, the moisture absorption increased the material's cure state for lower postcure temperatures while experimental results showed direct correlation between the state of cure and postcure temperature. Figure 11 shows that the percent of moisture content decreases proportionally with the state of cure ranging from 0.35 to 0.83.

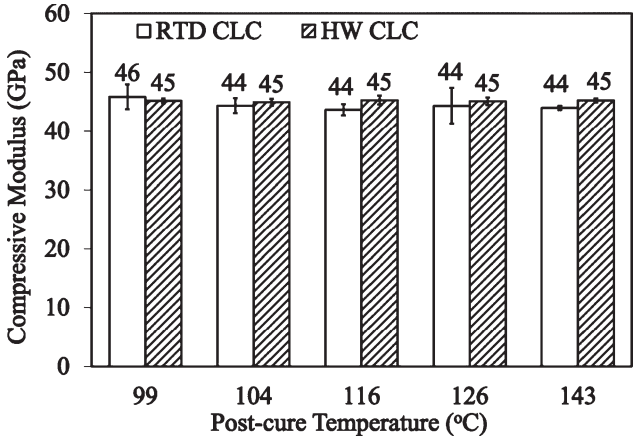

Figure 7. Compressive modulus for different cure cycles.

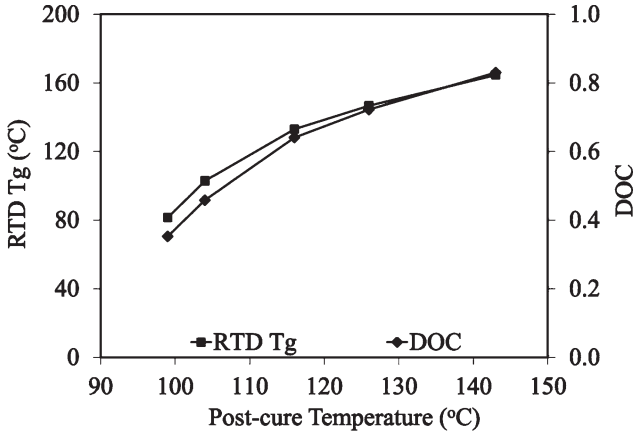

Figure 9. Relationship between DOC and T_g versus postcure temperatures.

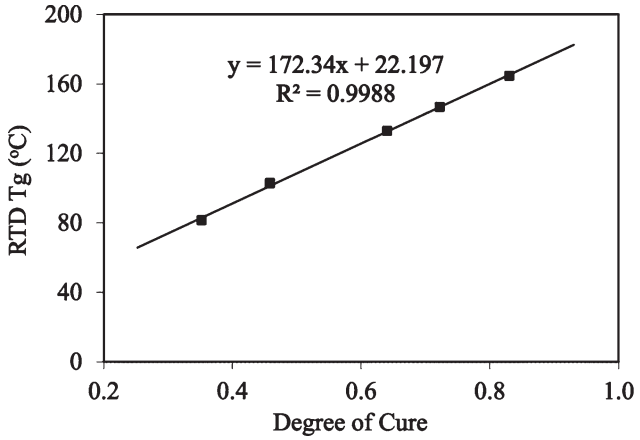

Figure 10. Linear correlation between T_g and DOC.

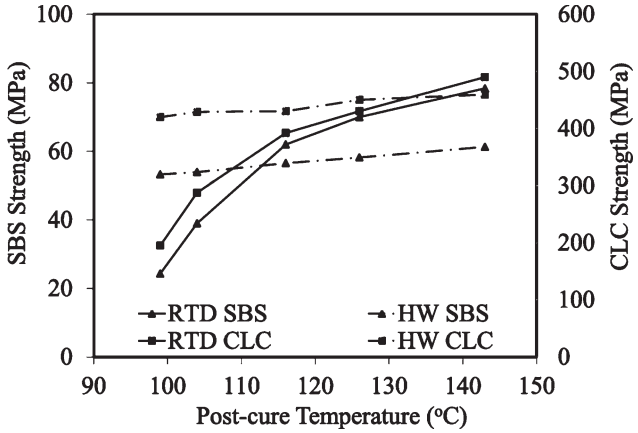

Figure 12. Relationship between SBS strength and compressive strength versus postcure temperatures.

Correlation Between Short-Beam Shear Strength and Compressive Strength

The SBS strength obtained in this study is a good way to screen the quality of the cure panels.[16] To see the relationship between the SBS strength and the compressive strength with respective to postcure temperatures, both strengths are plotted versus postcure temperatures in Figure 12. Because the results show similar increasing trend for SBS strength and compressive strength as postcure temperature increases, both strengths are believed to have a strong interrelationship.

An effort was made to correlate the compressive strength with the short-beam shear strength for RTD and HW specimens. Figures 13 and 14 show the relationship between compressive strengths and SBS strength for RTD and HW conditions, respectively. The graphs illustrate that SBS strength increased proportionally with the compressive strength; therefore, the SBS strength could also be used to represent the mechanical strengths. Because the SBS test method is simpler than other mechanical test methods, the correlation between the SBS strength and other mechanical strengths could be used for obtaining information about the mechanical strengths without conducting the particular mechanical test.

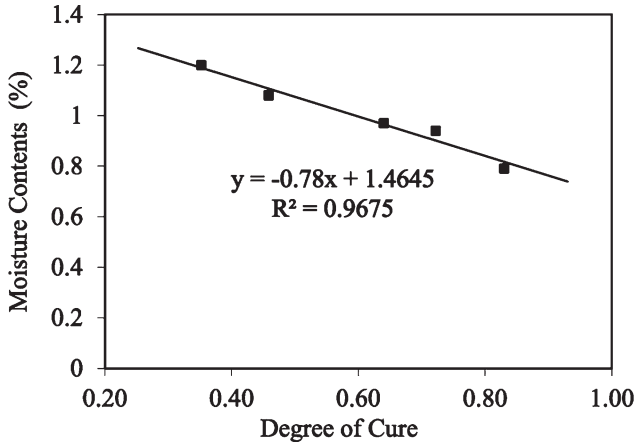

Figure 11. Linear correlation between moisture absorption and DOC.

Correlation Between Mechanical Properties and State of Cure

Evaluation of the correlation between cure temperatures, state of cure, and mechanical properties is important for quality control of composite structures. Using the test results, the state of cure and mechanical properties were compared among the various postcure temperatures. To investigate the correlation for different material properties for various postcure temperatures, all the properties were normalized using the maximum value of the corresponding property for all cure cycles.[8,9]

Figures 15 and 16 show the normalized SBS strengths and compressive strengths with respective to T_g for RTD and HW samples, respectively. As shown in these figures, all the strengths increase with the increase in state of cure. A linearly increasing trend shows that the material state can be used to predict mechanical properties for DOC ranging from 0.35 to 0.83. The study illustrates that as the state of cure is increasing, the SBS strengths and compressive strengths also increase proportionally. The quality of a polymer composite part due to cure time-temperature variation could be validated by ensuring the acceptable porosity contents and obtaining proper final state of cure for different cure cycles.

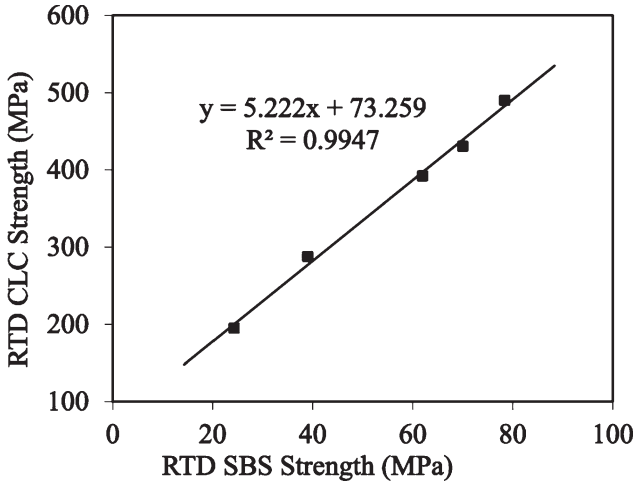

Figure 13. Linear correlation between CLC strength and SBS strength for RTD samples.

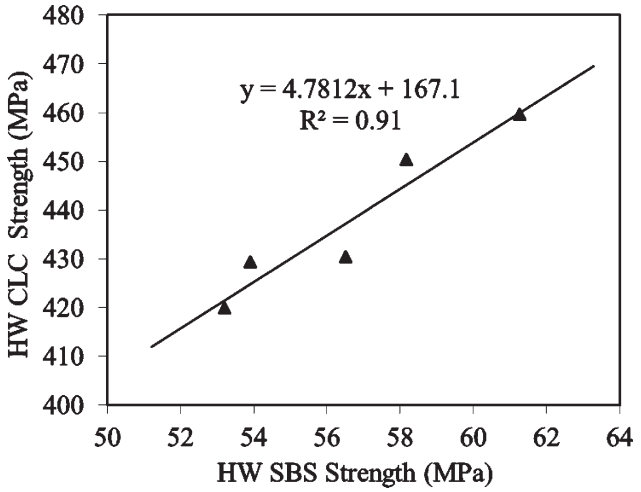

Figure 14. Linear correlation between CLC strength and SBS strength for HW samples.

CONCLUSIONS

The effects of postcure temperature variation and hygrothermal conditioning on different stages of curing for an out-of-autoclave polymer composite made from Cycom 5320 8HS were investigated. The effect of postcure temperatures was studied by varying the recommended two-stage cure cycle from 99 to 143°C. The effects of adverse environmental conditions on the cure temperature variation were studied by conditioning the samples in a conditioning chamber until they reached moisture equilibrium. The material cure state was obtained by using DSC and DMA. The mechanical properties were obtained using SBS and CLC test methods. It was observed that postcure temperature variation does not affect the porosity level, but it affects the moisture absorption of the laminate. Final DOC, T_g, SBS strength, and CLC strength gradually increased with increasing postcure temperature. Hygrothermal conditioning also showed that the moisture content was related to the postcure temperatures and state of cure of the material. The correlations showed that the final DOC, T_g, SBS strength, and CLC strength are well-correlated. Moreover, the SBS strength and CLC strength linearly changed with T_g, which suggests that the material state

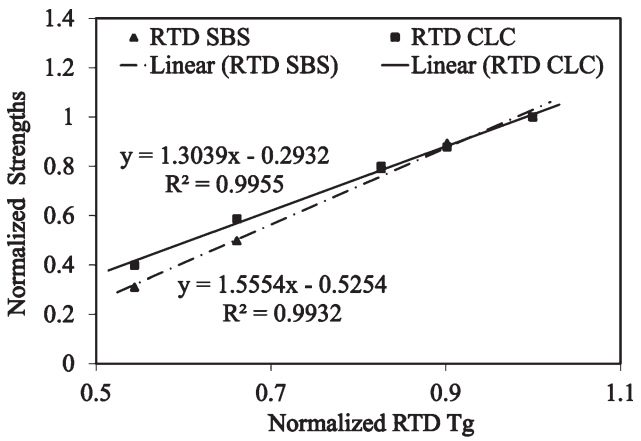

Figure 15. Linear correlation between mechanical strengths and state of cure for RTD samples.

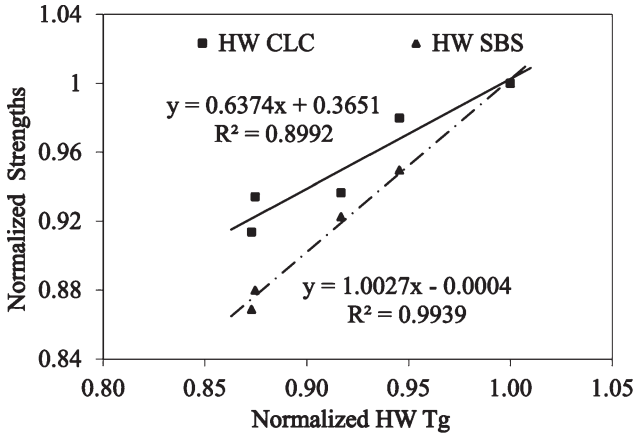

Figure 16. Linear correlation between mechanical strengths and state of cure for HW samples.

rather than the cure specification based on time-temperature can be used to predict mechanical properties. Thus, the state of cure can be used to define, monitor, and verify the cure quality.

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