Glass-Transition Temperature Based on Dynamic Mechanical Thermal Analysis Techniques as an Indicator of the Adhesive Performance of Vinyl Ester Resin

Benjamin Herzog,[1] Douglas J. Gardner,[2] Roberto Lopez-Anido,[3] Barry Goodell[2]

[1]*APA—The Engineered Wood Association, Tacoma, Washington 98466*
[2]*Wood Science and Technology and Advanced Engineered Wood Composites Center, University of Maine, Orono, Maine 04469*
[3]*Department of Civil and Environmental Engineering and Advanced Engineered Wood Composites Center, University of Maine, Orono, Maine 04469*

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ABSTRACT: Vinyl ester resins are being used extensively as matrices in fiber-reinforced polymer composite materials, but their use as a structural adhesive has been limited. Initial studies investigating the durability of a vinyl ester as a wood adhesive showed unsatisfactory performance in comparison with other adhesives. In this work, the glass-transition temperatures (T_g's) of a vinyl ester and a E-glass/vinyl ester composite material, fabricated by the Composites Pressure Resin Infusion System, were determined with dynamic mechanical thermal analysis. The results indicated that the resin cured under ambient conditions had a much lower T_g (~60°C) than the postcured material (~107°C). This suggested undercuring, that is, incomplete crosslinking, of the resin when it was cured at room temperature. E-glass/vinyl ester samples, however, showed virtually no difference in T_g between room-temperature-cured and postcured samples. The exact reasons for this are not currently known but are thought to be both mechanical and chemical in nature. On the basis of the findings presented in this article, it can be concluded that if this vinyl ester resin is to be used as a structural adhesive, postcuring or formulation to ensure a high degree of crosslinking under ambient conditions is necessary. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 2221–2229, 2005

Key words: adhesives; composites; glass transition; thermosets

INTRODUCTION

Vinyl ester resins are being used extensively as matrices in fiber-reinforced polymer (FRP) composite structures.[1] Vinyl esters exhibit many desirable qualities, including mechanical properties comparable to those of epoxy resins,[2] excellent chemical resistance and tensile strength,[3] low viscosity (enabling room-temperature infusion), and cost competitiveness.[1]

There are three general fabrication options used in the reinforcement of materials with an FRP composite: adhesive bonding of prefabricated sheets, wet lay-up of fabric, and resin infusion. In both wet lay-up and variations of the resin infusion processes, the resin serves a double function as an adhesive for the FRP–material interface and as a matrix for the fabric reinforcement.[4] The characteristics of vinyl ester as a matrix for FRP composites have been well documented.[5–12] The role of vinyl ester as an adhesive, however, has received less attention.[3,13,14]

Hygrothermal cycling tests (ASTM D 2559) designed to investigate and characterize the durability of both FRP–wood and wood–wood bonds with vinyl ester resin as an adhesive were recently performed.[15] As part of these tests, bonded samples were repeatedly saturated with water, subjected to steam (100°C), and dried (65.5°C); this resulted in significant swelling and shrinking of the wood material. In both cases, the performances of these bond lines were unsatisfactory in comparison with those of an epoxy adhesive and a phenol resorcinol formaldehyde resin, in that greater interface delamination rates were observed with the vinyl ester resin. In an attempt to explain the relatively poor performance of the vinyl ester resin, a determination of the glass-transition temperature (T_g) of the resin was made with dynamic mechanical thermal analysis (DMTA).

Correspondence to: D. J. Gardner (douglas.gardner@umit.maine.edu).

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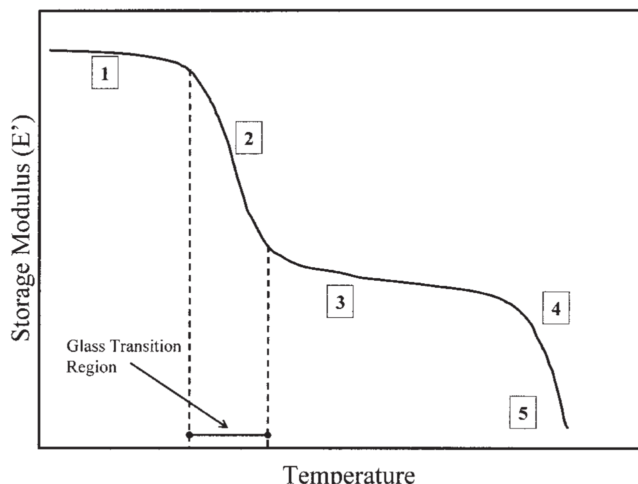

Figure 1 Five regions of polymer viscoelastic behavior:[24] (1) glassy region, (2) glass-transition region, (3) rubbery region, (4) rubbery flow region, and (5) liquid flow region.

DMTA is an extremely versatile thermal analysis method, and no other single test method provides more information about the physical properties of a sample in a single test.[16] DMTA supplies an oscillating force, causing a sinusoidal stress to be applied to a sample, which generates a sinusoidal strain. By the measurement of the magnitude of the deformation at the peak of the sine wave and the lag between the stress and strain waves, properties such as the modulus, viscosity, and damping can be calculated.[17] When this is performed through a range of temperatures, the changes in the flexural modulus of engineering resins as a function of temperature can be monitored, and this allows the identification of T_g and the melting point and the determination of the effects of these changes on load-bearing characteristics.[18]

T_g is important both as a measure of the degree of cure and for establishing a maximal temperature for use, that is, a material operational limit.[19] When T_g of a polymer is exceeded, certain mechanical properties may be compromised severely. In addition, it is well understood that an increase in the moisture content will lower T_g of thermosetting polymers.[20,21] Therefore, the work presented here was used to test the hypothesis that layered materials bonded with vinyl ester subjected to water saturation and temperatures greater than T_g of the resin during the hygrothermal testing would perform unsatisfactorily because the behavior of the polymer would be compromised.

The first objective of this research was to calculate the differences in T_g to qualitatively compare the degree of cure of room-temperature-cured and post-cured vinyl ester resin. A greater understanding of these properties may aid in the engineering design of vinyl ester resin as both an adhesive and as a matrix in FRP composite materials. The second objective was to determine the appropriate calculation method of T_g—the onset of the change in the slope of the storage modulus (E') curve, the maximum loss modulus (E''), or the maximum loss tangent (tan δ)—for engineering design and comparison with DMTA.

BACKGROUND AND LITERATURE REVIEW

Determination of T_g by DMTA

Even though DMTA is used extensively in T_g calculation, uncertainties still exist regarding the proper methods of accurate determination. The procedures described in several standards and recommendations can result in significantly different values of the same data, as discussed in detail by Wolfurm et al.[22] This is due, in part, to the fact that T_g is a single temperature that represents a range over which the glass transition takes place.[23] The five regions of viscoelastic behavior typical of a thermoset polymer[24] are presented in Figure 1. The glass-transition range is characterized by a sharp decrease in the elastic modulus of the polymer and is dependent on the state of the polymer and its thermal history.[25]

In an effort to simplify the determination of T_g, it is commonly defined as the maximum of the damping ratio, E''/E' (tan δ), or the maximum of E''. Several researchers, however, have found that a more accurate determination can be derived from the onset of the change in the slope of the E' curve.[22,26–28] A comparison of these calculation techniques is shown in Figure 2. If T_g is used for engineering design, that is, the determination of maximal end-use temperatures, we believe that a conservative estimate of T_g is warranted. Therefore, in this work, one method of T_g calculation was based on the temperature at which mechanical properties began to be compromised, that is, the onset

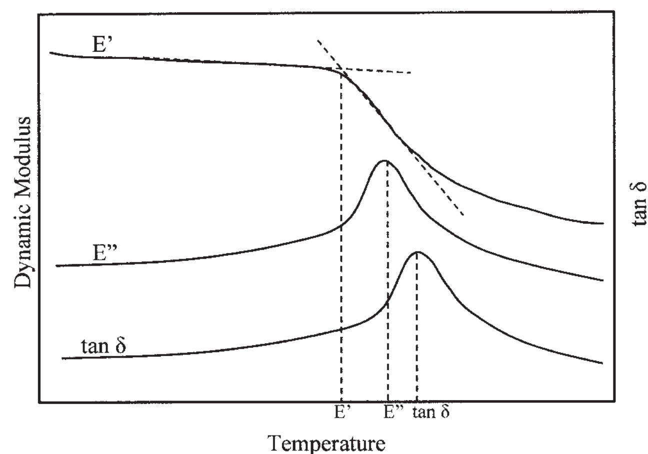

Figure 2 T_g determined by the onset of the E' change, the maximum of E'', and the maximum of tan δ. Clearly, the methods can produce different values for the same set of data.

of the glass-transition range, as determined by the onset of the change in the slope of E'. The specific procedure for calculation is described in the Experimental section. Also reported for comparative purposes are T_g values calculated by the maximum damping ratio. This value is used to represent the end of the transition period[29] and is included in this work to give an indication of the size of the transition range and also because this is the method commonly found in the literature.

T_g as a measure of the degree of cure

Previous work has shown that there is a unique relationship between the chemical conversion, that is, the extent of cure, of a thermoset and its T_g, independent of the cure temperature and thermal history, for many thermosetting systems.[19] Although a unique T_g–conversion relationship exists for most thermosetting systems, such a relationship cannot be assumed to exist for all systems.[19] In fact, Fink et al.[1] determined that because of the competing reactions involving styrene and vinyl ester, the relationship between T_g and the degree of cure is only direct for a specific cure temperature for this type of resin system. Therefore, the relationship between T_g and the degree of cure for a typical nonisothermal cure depends on the temperature history, and this greatly limits the use of T_g as a conversion measurement by restricting its application to isothermal conditions.[1]

EXPERIMENTAL

Sample fabrication

Samples of the catalyzed resin and FRP material were tested as part of this work. Derakane 8084 (Dow Chemical Co., Midland, MI), an elastomer-modified vinyl ester epoxy resin, was the polymer under study. Resin samples 3 mm thick were produced by the mixing of the resin with 0.30% cobalt naphthenate (6% active cobalt; Diversified Materials Co., La Mesa, CA), 0.20% dimethylaniline (100% active ingredient; Acros Organics, Fisher Scientific International, Geel, Belgium), and 2.00% cumol hydroperoxide (Trigonox 239, Akzo Nobel, Inc., Chicago, IL). The catalyzed resin was poured into a metal mold and allowed to cure at room temperature (22–26°C).

FRP samples were made by the infusion of five layers of E-glass unidirectional woven fabric (VEW 260, BTI-Saint Gobain, Brunswick, ME) with the aforementioned resin/promoter/accelerator/initiator system with the newly developed Composites Pressure Resin Infusion System method of composite fabrication.[30,31] After curing at room-temperature conditions, samples (ca. 3 mm × 6 mm × 34 mm, span/thickness ratio ~ 10 : 1) were cut from the panels and polished with 120- and 220-grit paper.

TABLE I
Description of the Curing History of the Tested Samples

Sample	Resin	FRP
a	Room-temperature cure	Room-temperature cure
b	Immediate retest of (a) samples	Immediate retest of (a) samples
c	Postcure of (b) samples: 99°C/2 h	Postcure of (b) samples: 80°C/6 h
pc	Postcure: 99°C/2 h	Postcure: 80°C/6 h

Experimental procedure

Samples were tested with a DMTA IV dynamic mechanical thermal analyzer (Rheometrics, Piscataway, NJ). Specimens were placed in the DMTA instrument and oscillated at a frequency of 1 Hz in a three-point-bending mode. The specimens were heated from 25 to 175°C at a rate of 5°C/min. The strain amplitude was maintained at 0.01%.

The samples were tested at various stages of cure (Table I). To directly investigate the effect of postcuring on T_g of a material, one-half of each material set, that is, the resin and FRP, underwent a total of three DMTA scans: following a room-temperature cure for several weeks (noted by subscript a), immediately following the initial DMTA scan (subscript b), and, finally, after being postcured (subscript c). The other half of each material set was scanned only once, after a postcure (subscript pc). The postcuring schedules were based on those used by the resin manufacturer in the company's published characterization of the resin and FRP material fabricated with the vinyl ester.[32] The resin material was postcured at 99°C for 2 h, whereas the FRP material was postcured at 80°C for 6 h. It is unclear why the manufacturer uses differing postcuring schedules for the resin and FRP material. However, by replicating these procedures, we could make a direct comparison between our derived results and the published values.

T_g values computed with the onset of the change in the slope of the E' curve were obtained by the plotting of E' on a logarithmic scale as a function of temperature. T_g was then determined to be the intersection of two slopes from the E' curve. The first slope was selected at a temperature before the modulus drop step; the second slope was selected at the temperature indicating the middle point of the modulus drop.

DISCUSSION

T_g of the resin samples

The results of the resin testing show that an extended room-temperature-cured sample had two apparent T_g

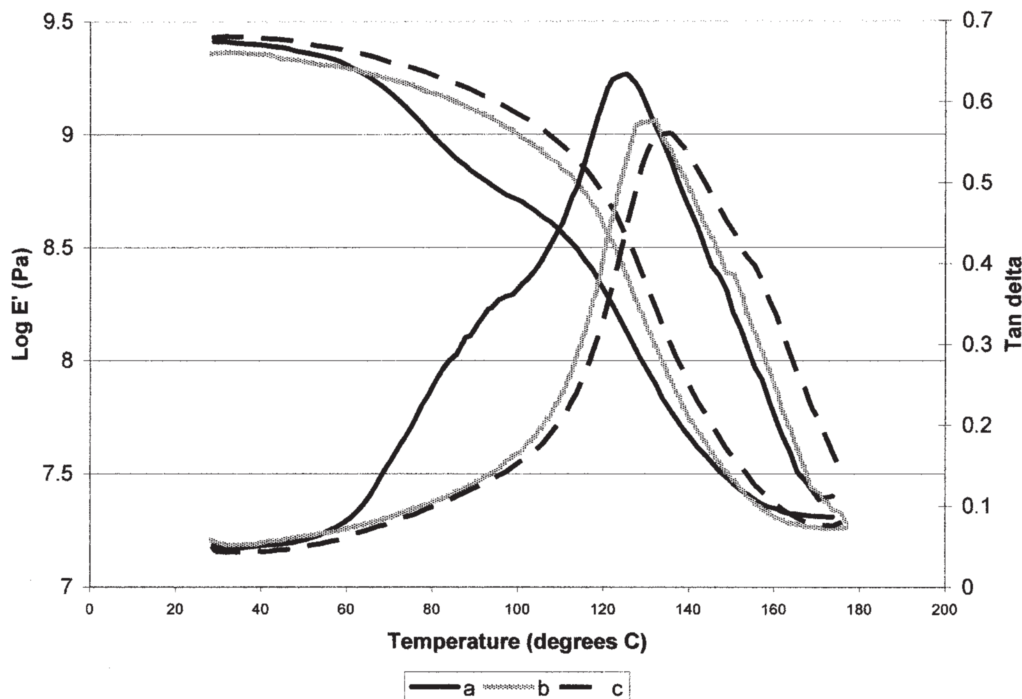

Figure 3 Typical results of resin samples a–c. The two T_g values apparent in the room-temperature-cured samples, as shown by the two changes in the slope of E', suggest that the resin was not fully cured at that time. The E' curves and the maximum tan δ peaks of the b and c curing regimens show that further curing, either through postcuring or DMTA cycling, increased T_g of the samples.

values, as shown by the two changes in the slope of the E' curve or the two peaks in the tan δ curve (Fig. 3). In interpreting these results, we decided that the conservative approach would be to calculate T_g on the basis of the lower temperature part of the transition. The average T_g values of these room-temperature-cured samples based on the onset of the E' curve (T_g–E') were approximately 60°C and 95°C when based on the initial peak of the tan δ peak (T_g–tan δ; Table II). After exposure to elevated temperatures, through DMTA analysis or through postcuring, T_g of the resin increased to 106–108 (T_g–E') and 131–133°C (T_g–tan δ; Fig. 4).

The trend of two apparent T_g values associated with room-temperature-cured vinyl ester resin has been observed elsewhere[33–35] and suggests one of two things: the sample is being cured additionally during the DMTA scanning or the water in the sample makes precise measurements difficult. In the former case, an increase in the thermal energy would provide an undercured material sufficient molecular mobility to recommence the curing process.[33–35] In the latter case, drying would occur primarily at the outside surface during the temperature scan. The lower temperature slope change of the E' curve would reflect T_g of the wet interior, whereas the higher slope change would

TABLE II
T_g Values of Resin Samples

	Cure schedule							
	a		b		c		pc	
Sample	E'	tan δ	E'	tan δ	E'	tan δ	E'	tan δ
1	57	96.8	105	130.5	105	131.7	—	—
2	58	94.3	109	130.4	106	133.4	—	—
3	61	95.5	106	132.1	108	132.5	—	—
4	—	—	—	—	—	—	106	135.4
5	—	—	—	—	—	—	108	130.4
6	—	—	—	—	—	—	110	132.6
Average	59	95.5	107	131.02	106	132.5	108	132.8

T_g was measured using two methods: onset of E' change and maximum tan δ.

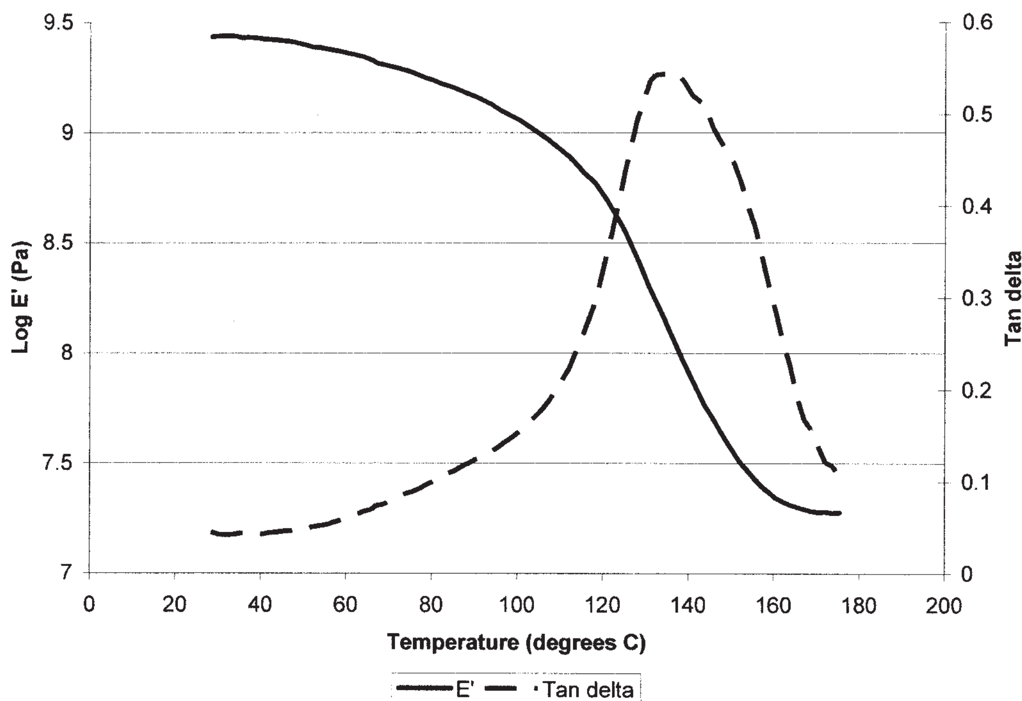

Figure 4 Typical results for the resin pc samples. The T_g values of these samples were consistent with those of samples b and c.

reflect T_g of the dry material.[36] In this study, because the samples were not artificially wetted or exposed to high humidity conditions for prolonged periods, it is assumed that the cause of the two slope changes was mainly the additional curing of the sample.

T_g of the FRP samples

The T_g values associated with the FRP composite, regardless of the curing schedule, were higher than those of the resin samples (Table III). In addition, the difference in T_g between room-temperature-cured and additionally cured FRP was much smaller than it was for the resin material. For example, in the FRP sample set, this difference was generally less than 10°C. Conversely, the difference in the room-temperature-cured and additionally cured resins often approached 50°C. The differences in T_g between the FRP and resin materials may have been due to differences in the dynamic behavior, determined in part by the stiffness, mass, and damping properties of the materials. For example, because the fibers are stiffer and can carry more load than the matrix, the properties observed in samples loaded in three-point bending may not be appreciably sensitive to variations in the mechanical properties of the matrix.[26] Other possibilities for the differences in T_g may be a greater amount of curing or crosslinking found in the FRP material. For example, the heat transfer through the FRP may have

TABLE III
T_g Values of FRP Samples

	Cure schedule							
	a		b		c		pc	
Sample	E'	tan δ	E'	tan δ	E'	tan δ	E'	tan δ
1	111	127.3	120	128.9	116	132.3	—	—
2	114	126.0	117	131.2	119	134.2	—	—
3	111	125.4	120	132.2	120	130.9	—	—
4	—	—	—	—	—	—	114	129.2
5	—	—	—	—	—	—	115	126.0
6	—	—	—	—	—	—	113	129.2
Average	112	126.2	119	130.8	118	132.5	114	128.2

T_g was measured using two methods: onset of E' change and maximum tan δ.

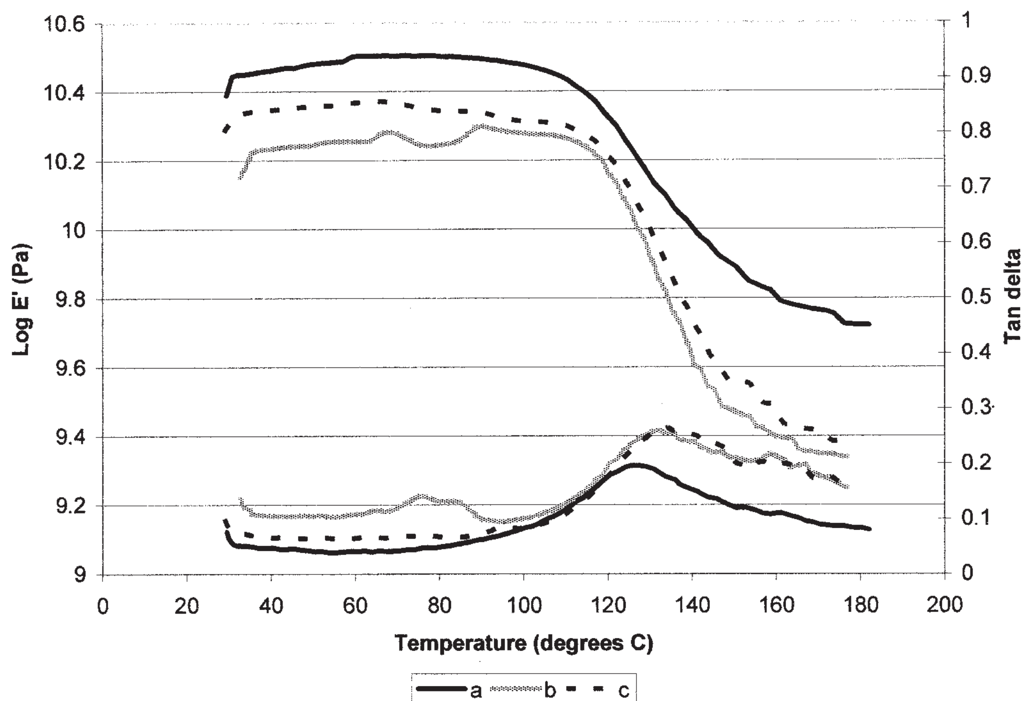

Figure 5 Typical results for FRP samples a–c. The differences in the T_g values based on the curing schedule were much smaller than those of the resin samples.

been different than that in the resin during the DMTA temperature ramp because of the fiber reinforcement acting as a thermal energy conduit. It also is possible that the surface chemistry of the fibers reacted in such a way with the resin to produce a higher exotherm and, therefore, a higher degree of crosslinking than that found in the resin alone.

The FRP samples suggest that an increased T_g may be obtained, but not necessarily through the postcuring schedule used as part of this research. For example, the average T_g values of the room-temperature-cured samples (a) and the postcured samples (pc) were both approximately 112–114 (T_g–E') (Figs. 5 and 6). The samples that underwent the temperature scanning as part of DMTA showed an increase of approximately 5°C. Therefore, temperatures above 80°C may be needed for additional curing of FRP.

Comparison of the derived values and the published literature

The manufacturer of the vinyl ester resin (Dow Chemical) reported a T_g value of 115°C for Derakane 8084.[32] This was calculated with thermomechanical analysis (TMA) on samples cured at room temperature for 24 h and then postcured for 2 h at 99°C.

In an extensive study of the methods necessary to achieve complete cure of this resin, Dumant[33] used differential scanning calorimetry (DSC) and DMTA to calculate T_g values and the degree of cure under various postcuring schedules. It was determined that when the resin was postcured at 110°C for 5 h, T_g was approximately 115°C, and full cure had been achieved. At lower postcuring temperatures, both the resulting T_g and degree of cure were substantially decreased. Of particular note, samples cured at room temperature for 10 days had a T_g between 20 and 60°C and had only an 85% degree of cure. Dumant also investigated whether longer postcuring times would result in improvements in the degree of crosslinking, as evidenced by a higher T_g value. Resin samples were postcured for 1, 5, 10, and 24 h at 60°C. This temperature was chosen because it is the reported postcuring temperature used by a shipbuilding company related to the research focus. The results showed that there were decreases in the residual energy, corresponding to an increasing degree of cure, when the postcure time was increased. Even after a 24-h postcure, however, the resin was not fully cured (96.6% cure). It also was determined that when samples were postcured at 60°C, there were no differences in the degrees of cure based on the amount of the initiator used.

A summary of the T_g values found in the literature is shown in Table IV. Caution should be exercised when this table is used, however. Different test methods and oscillation frequencies can result in different T_g values. Therefore, the values found in Table IV

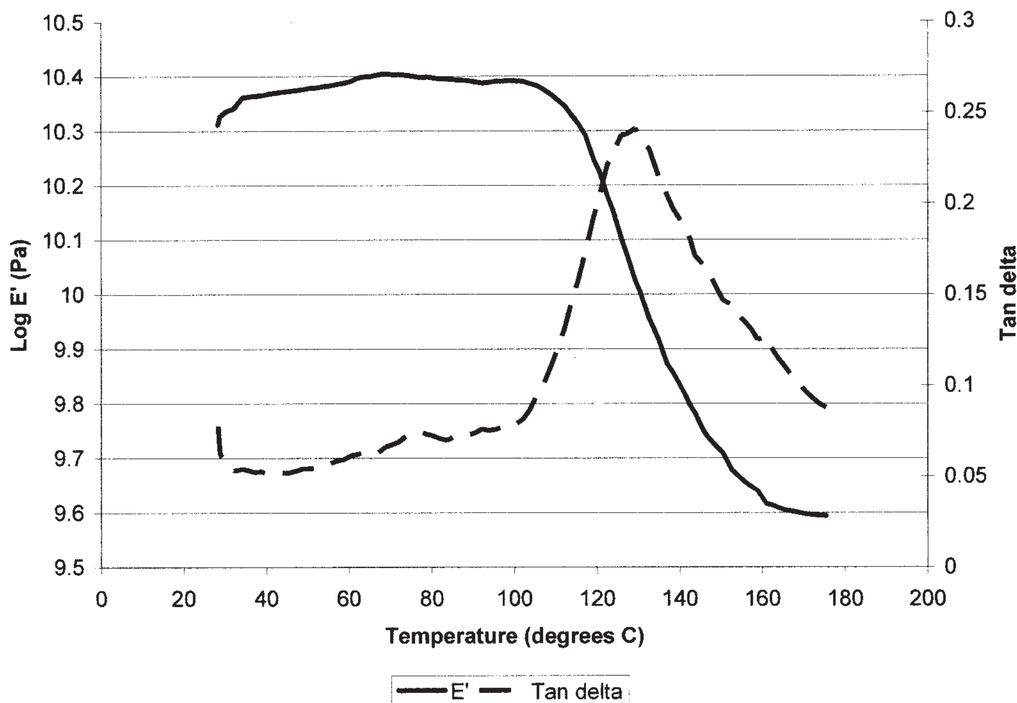

Figure 6 Typical results for the FRP pc samples. The T_g values of these samples were consistent with those of FRP samples b and c.

should be viewed qualitatively because values from different studies cannot be compared directly. The values calculated in this research, therefore, support the trends found by others. It can be concluded that room-temperature curing is inadequate to achieve a full cure of the resin system and that postcuring is necessary.

Similarities of vinyl esters and epoxies as structural adhesives

Like vinyl esters, epoxies have found widespread use as matrix materials for FRP composites and as adhesives. Also, similarly to vinyl ester, epoxy resins have been limited as wood structural adhesives because of creep issues and performance under wet conditions.[37,38] Because of the large size of many structural wood composites, such as glued–laminated beams, and the slow heat transfer through wood, curing generally is not conducted in an oven or autoclave, but instead a catalyzed resin is used to permit room-temperature curing. If these ambient conditions are not in excess of the T_g associated with a fully cured polymer, the system either gels or vitrifies before a complete cure is achieved. This is common in thin parts in which the heat produced in the exothermal curing reaction dissipates rapidly. With most room-temperature-curing epoxies, the resin does not go to complete reaction, and T_g of

TABLE IV
Summary of T_g and Degree of Cure Values by Postcuring Schedule and Method of Analysis Found in the Literature

Postcure schedule	T_g (°C)	Degree of cure (%)	Method of analysis	Source
10 days at RT	$20 < T < 60$	85	DSC	Dumant[33]
3 weeks RT	59 (96)	—	DMTA, E' (tan δ)	This work
5 h at 60°C	77	94	DSC	Dumant[33]
5 h at 85°C	101	99	DSC	Dumant[33]
2 h at 99°C	115	—	TMA	Dow Chemical Co.[32]
2 h at 99°C	108 (133)	—	DMTA, E' (tan δ)	This work
5 h at 110°C	115	100	DSC	Dumant[33]
After DMTA cycle	107 (131)	—	DMTA, E' (tan δ)	This work
After DMTA cycle; 2 h at 99°C	106 (133)	—	DMTA, E' (tan δ)	This work

RT = room temperature.

such epoxies is no more than 50–60°C.[39] Therefore, epoxies, as well as vinyl esters, need to be postcured to achieve a high degree of crosslinking.

CONCLUSIONS

On the basis of the research work presented in this article, the following conclusions can be drawn:

1. The vinyl ester resin tested in this work had a relatively low T_g (<60°C) and was not associated with a high degree of crosslinking when curing took place at ambient conditions.
2. Through additional curing techniques, via DMTA temperature ramping or traditional postcuring, T_g increased to approximately 106–108°C. This was in agreement with published values.
3. E-glass/vinyl ester samples showed virtually no difference in T_g with respect to the curing strategies. The exact reasons for this, as well as the cause of differences in T_g between room-temperature-cured FRP and resin materials, are not currently known but are thought to be both mechanical and chemical in nature.

The following practical recommendations are proposed:

1. The postcuring of vinyl ester resin is recommended when it is used either as a matrix material for FRP composites or as an adhesive. Postcuring will result in a higher degree of crosslinking, in comparison with room-temperature curing, thereby improving the mechanical properties, adhesive qualities, and durability performance of the resin. In addition, T_g of the polymer will increase, and this will result in a higher maximal end-use temperature.
2. If they are used as adhesives cured at ambient conditions, the thickness of the vinyl ester bond lines may be much less than that of the samples tested in this work. In that case, a lower exotherm presumably will be generated by the curing reaction. This may result in bond lines with an even lower T_g and degree of cure than found in this study.
3. Postcuring strategies need to be determined for large structural members, such as glued–laminated beams, if these materials include vinyl ester resin. Because the application of heat to large materials may not be feasible, the compatibility of other methods of curing compatible with flammable resins should be investigated. Alternatively, methods of increasing and prolonging the generated exotherm of the reaction may be explored.

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