

Evaluation of Cure State of Vinylester Resins

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ABSTRACT: The objective of this investigation is to characterize the effect of time and moisture on the degree of cure of two room temperature (RT)-curable vinylester resins (VE), VE8084, and VE510A. Both resins were cured at RT for 24 h. Following the initial cure, some specimens were cured at RT over an extended period of time; others were immersed in seawater or a humidity chamber (85% RH) at 50°C, or post-cured (PC) at elevated temperatures. Dynamic-mechanic analysis (DMA) and differential scanning calorimetry techniques were performed to characterize the degree of cure. The degree of cure for 24 h RT-cured and seawater exposed specimens ranged from 83 to 86% for VE510A and from 86 to 93% for VE8084. After PC at elevated temperature, or exposure to 85% RH at 50°C, the degree of cure of both resins increased to about 99–100%. Analysis of the viscoelastic response of the resins by DMA revealed two heterogeneous transitions for partially cured VE resins and a single transition for fully cured resins. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000–000, 2012

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INTRODUCTION

Vinylester resins (VE) matrix composites are used extensively in primary and secondary US naval structures. VE resins offer great benefits in structural applications such as room temperature (RT) cure, low water absorption, excellent chemical resistance, thermal stability, mechanical strength, low weight, and low cost.¹ Moreover, its low viscosity allows processing by resin transfer molding and other inexpensive liquid molding techniques. Naval structures are typically exposed to water, which provides an opportunity for moisture absorption of the resin. Typically, the moisture saturation concentration for VE resins ranges from 0.3 to 2.5% depending on the type of resin, cure agents and mix ratios used, and the degree of cure of the VE resin.^{1–4} The absorption of water molecules inside the macromolecular network of a thermoset may cause swelling (expansional strains) and plasticization of the matrix^{5,6} leading to a reduction of the glass transition temperature, T_g .^{7,8}

VE resins cure by chemical cross-linking reactions between the VE oligomers and styrene, in which they are dissolved. Most VE resin formulations contain between 20 and 60% of styrene. The styrene reduces the resin viscosity, and during polymerization it reacts with the resin to form cross-links between the unsaturated points on adjacent vinyl ester molecules. The cross-linking reaction continues until all double bonds are consumed or until immobility of system prevents further contact between free radicals and double bonds.^{9–12}

VE resin systems cured at RT complete a substantial part of the cross-linking. However, RT may not be high enough to promote full conversion of the resin. The conversion plateaus as the diffusional limitations physically prevent unreacted species in the material from reacting. In this regime, the glass transition temperature (T_g) of the material continues to increase as it is very sensitive to slight changes in the degree of cure. To achieve complete cure, post-cure (PC) at elevated temperatures may be demanded. It is well documented that mechanical properties of neat resin and composite improve after PC when the cure state is complete.^{13–15} However, laminating resins used in marine construction and naval structures are unable to be PC at elevated temperatures due to their large size.

Incomplete cure not only leads to reduced properties, but also increases swelling and degrades the aging characteristics, such as, thermal stability and resistance to hydrolysis.¹⁶ Incompletely cured resin exposed to humid environments will experience the combined effects of moisture and completion of polymerization. The curing process of a thermoset resin transforms the resin into an infusible solid through the formation of a cross-linked network. The extent of cure is typically measured by the amount of heat released by the exothermic reaction between the resin and hardener.¹⁷ A number of investigators^{18–22} have used differential scanning calorimetry (DSC) measure the heat evolved during the cure reaction. DSC is the most commonly used technique to study the kinetics of cure reactions due to its

simplicity and the capability of detecting important thermal transition information without detailed knowledge of the chemistry. In addition, the glass transition temperature, T_g , of a thermosetting matrix is a strong function of the extent of cure.²³ Dynamic-mechanic analysis (DMA) has been found to be a very useful tool for such studies.

This article addresses the state of cure of RT cured VE resins exposed to water and humidity for extended times. DSC and DMA methods are used to characterize the degree of cure of two VE resins namely, VE510A and VE8084 resins. The VE510A and VE8084 resins are currently employed as matrix materials for naval composites structures reinforced with carbon fibers.²⁴

EXPERIMENTAL

Materials and Specimens

Two types of VE resins were used, namely, Derakane Vinylester 510A-40 (VE510A) and Derakane Vinylester 8084 (VE8084) provided by Ashland. The VE510A is derived from a brominated bisphenol-A resin and has good fire resistance but is relatively brittle, while the VE8084 includes rubber particles suspended in the resin to promote ductility. The VE510A was formulated with 1.0 parts per hundred resin weight (phr) of methylethylketone peroxide (MEKP), and 0.2 phr of cobalt naphthenate-6% (CoNap). The VE8084 was formulated with 1.5 phr of MEKP, 0.3 phr of CoNap 6%, and 0.05 phr of dimethylaniline.

To obtain solid neat resin specimens for DMA characterization, resin panels [$254 \times 254 \times 2.4$ (mm)] were manufactured by casting the resin between two glass plates (treated with release agent). After 24 h of RT cure, the panels were cut into DMA flexural test specimens (straightedge coupons) with dimensions 55 mm long by 10 mm wide and 2.4 mm thick. Some of the RT-cured specimens were put into a desiccator (0% humidity) for 1 week, while others were PC according to the specification for each resin. Cure and PC conditions for VE resins are indicated in Table I.

Cure State Characterization

DSC monitors the rate of heat generation during the cure reaction as a function of time. Incomplete cure of a thermosetting resin can be inferred by the presence of a residual exotherm in a DSC scan of the resin. The intensity of the residual exotherm can be measured to quantify the degree of cure as will be detailed in this section. This method applies to a polymer that is highly cross-linked but not 100% cured, such as the vinylester systems considered.

A Q10 series DSC apparatus from TA instrument was used to determine the degree of cure of VE resins. It is quite possible that styrene will evaporate during DSC testing, which may affect the degree of cure. To prevent styrene evaporation, the DSC

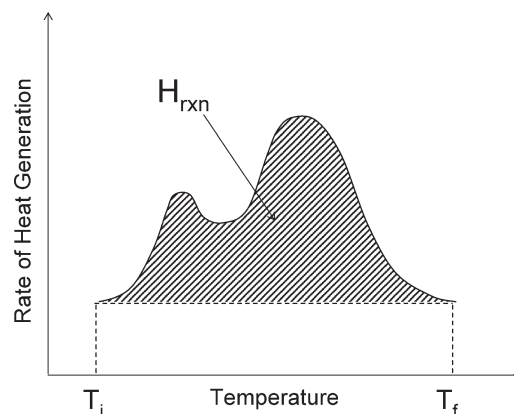


Figure 1. Schematic representation of the rate of heat generation during dynamic heating of a uncured or partially cured thermoset polymer in a DSC.

samples were placed in hermetically sealed crucibles. To measure the total heat of reaction of each resin, the uncured resin and catalyst were mixed and 5 mg of the mix was immediately put into the DSC pan. The resin was cooled to -10°C and slowly ramped to 300°C at a constant rate of $10^{\circ}\text{C}/\text{min}$. For determination of the degree of cure of the RT-cured and PC resin samples after different elapse times and environmental exposures, about 5 mg of each resin sample was placed in the hermetically

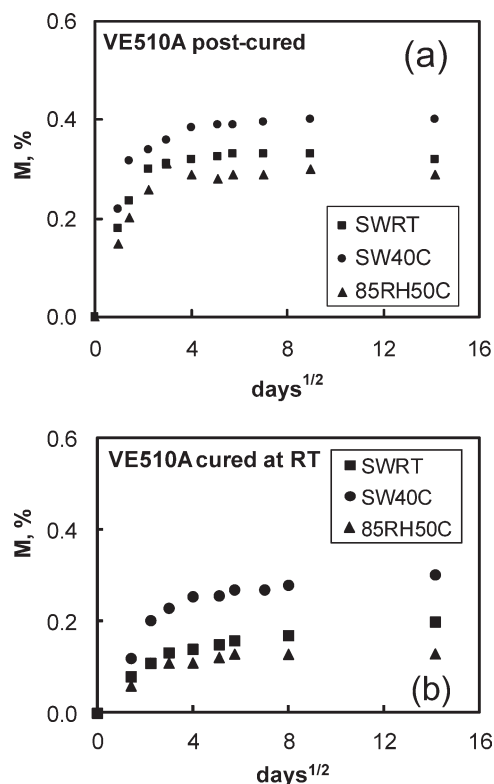


Figure 2. Moisture content as function of the square root of time for different exposure conditions of VE510A resin specimens. (a) PC and (b) RT-cured.

Table I. Cure Conditions for VE510A and VE8084

Resin	Cure	PC
VE8084	24 h; RT	2 h; 99°C
VE510A	24 h; RT	2 h; 120°C

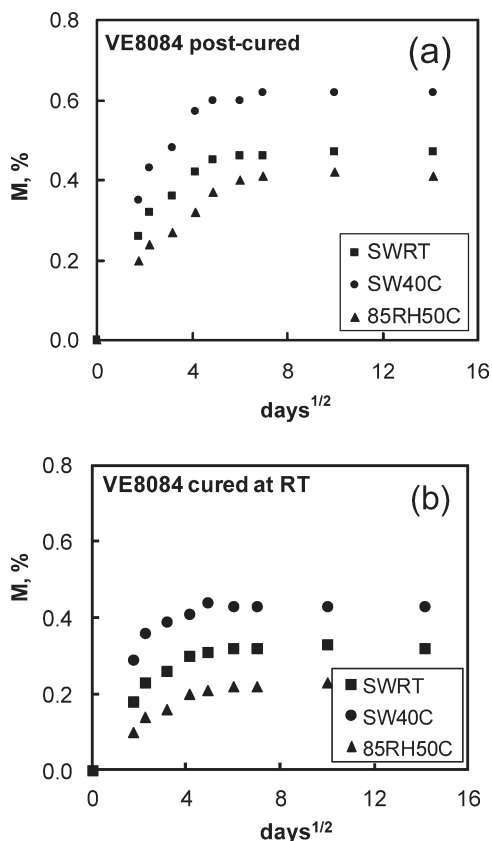


Figure 3. Moisture content as function of the square root of time for different exposure conditions of VE8084 resin specimens. (a) PC and (b) RT-cured.

sealed DSC crucible, then heated from RT to 300°C to determine the total residual heat of reaction.

The extent of cure is calculated by:

$$(\%)\text{Conversion} = \left(\frac{H_{\text{rxn}} - H_r}{H_{\text{rxn}}} \right) \times 100 \quad (1)$$

where H_r is the residual heat of cure measured during the heating ramp of a specimen cured at RT after various elapsed times and environmental exposure: 24 h at RT, 300 days at RT, 100 days of exposure to seawater at RT, 100 days of exposure to 85% RH at 50°C, and PC. H_{rxn} is the total heat of reaction of the initially uncured (liquid) resin, determined from the area under the cure peak shown in Figure 1. This procedure was applied to the uncured resin and partially cured resins. Three replicate specimens were used for each condition.

Table II. Moisture Saturation Content for RT-Cured and PC VE510A and VE8084

	VE510A		VE8084	
	RT-cured	PC	RT-cured	PC
SWRT	0.21 ± 0.01	0.32 ± 0.03	0.32 ± 0.03	0.47 ± 0.04
SW40C	0.30 ± 0.02	0.40 ± 0.01	0.43 ± 0.03	0.62 ± 0.01
85RH50C	0.11 ± 0.01	0.29 ± 0.01	0.23 ± 0.02	0.41 ± 0.01

DMA tests were conducted on dry and moisture saturated specimens (cured and PC) using a dynamic-mechanical analyzer, Q800 from TA, set up for three-point flexure loading. The measurements were carried out at a fixed frequency (1 Hz) over a temperature range from -5°C to well above T_g (200°C) at a heating rate of 5°C/min. The flexure specimens were 55 mm long by 10 mm wide and 2.4 mm thick. At least three replicate specimens were tested. The T_g of the polymer was defined as the maximum peak in the loss tangent ($\tan \delta$) curve.

Environmental Exposure

DMA specimens were used to measure the moisture absorption. The dry reference is considered as RT cured specimens kept at least 1 week in the desiccator or specimens subjected to elevated temperatures during PC. Selected RT-cured and PC specimens were immersed in seawater at RT, seawater at 40°C, and in a humidity chamber controlled at 50°C and 85% relative humidity (RH). Ten replicate specimens were used for each environment. The weight change was periodically monitored. Each time a specimen was removed from an immersion tank, it was carefully dried with a paper towel. Then, weight measurement was done using a Sartorius precision balance accurate within ± 0.1 mg. The moisture content, M , (in percent) is calculating using

$$M\% = \frac{W_t - W_o}{W_o} \times 100 \quad (2)$$

where W_t is the measured weight of the specimen at time t and W_o is the specimen initial dry weight.

RESULTS AND DISCUSSION

Water Absorption

Weight gain of the neat VE8084 and VE510A resin specimens was monitored over 200 days. The moisture content was calculated using eq. (2). Figures 2 and 3 illustrate moisture absorption curves for the RT-cured and PC resins, immersed in seawater at RT (SWRT), seawater at 40°C (SW40C), and exposed to humid air at 85% RH at 50°C (85RH50C) versus square root of time.

The moisture content initially increased rapidly upon exposure to seawater or humid air for all temperatures and resins systems and approaches equilibrium (saturation) after longer exposure times. Higher slopes of the initially linear part of the moisture absorption curves are observed at higher exposure temperatures indicating a higher rate of moisture transport.²⁵

Table II list the saturation moisture contents of resins. The RT-cured and PC VE8084 resin shows overall larger moisture contents than VE510A. For both resins under all exposure

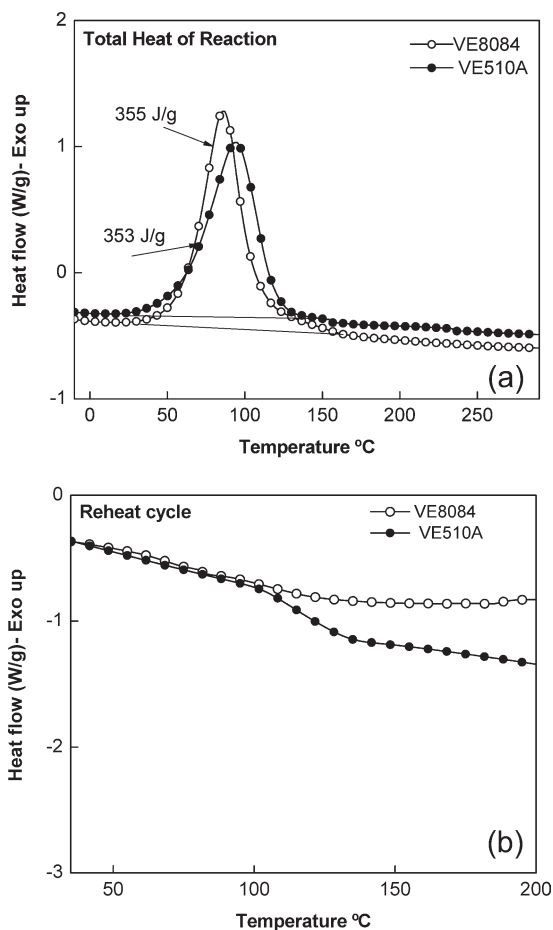


Figure 4. (a) Typical heat flow curves for the VE resins used to calculate the total heat of reaction. (b) Reheat cycle for the cured VE resins.

conditions, PC specimens show higher levels of water absorption than the RT-cured specimens. The partially cured specimens have a greater concentration of unreacted chemical species

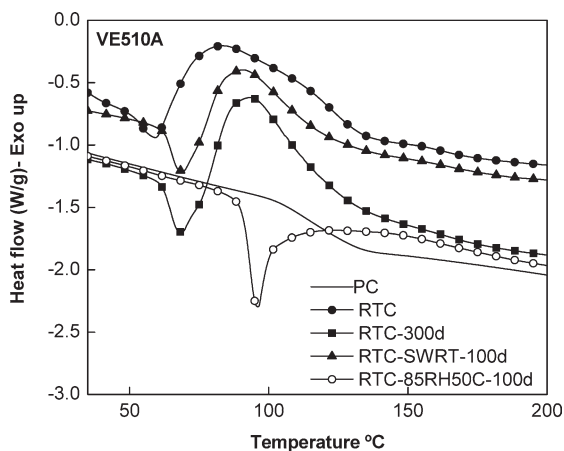


Figure 5. Typical heat flow curves for VE510A specimens after RT-cure for 24 h (RTC), RT-cured for 300 days (RTC-300 d), RT-cured exposed to SWRT 100 days (RTC-SWRT-100 d), RT-cured exposed to 85RH50C 100 days (RTC-85RH50C-100 d), and PC.

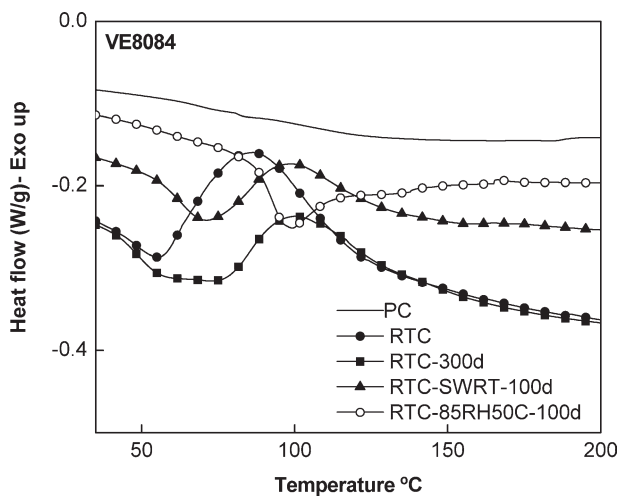


Figure 6. Typical heat flow curves for VE8084 specimens after RT-cure for 24 h (RTC), RT-cured for 300 days (RTC-300 d), RT-cured exposed to SWRT 100 days (RTC-SWRT-100 d), RT-cured exposed to 85RH50C 100 days (RTC-85RH50C-100 d), and PC.

within the VE resin. It is possible that unreacted species are released into the seawater resulting in a reduced net weight gain for the RT-cured specimens. Similar trends were reported by other authors^{26,27} where infrared spectroscopy has been used to trace the leaching of the unreacted species.

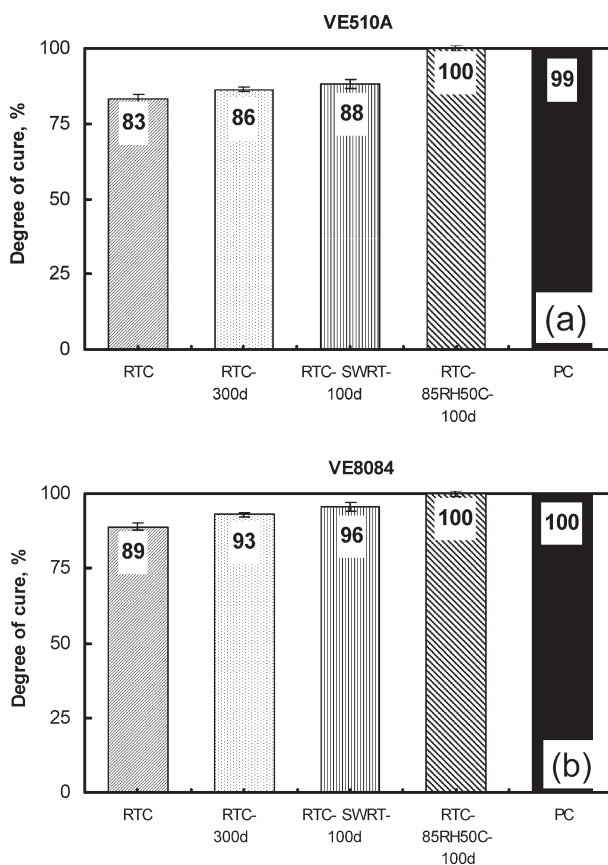


Figure 7. Degree of cure for VE resins. (a) VE510A and (b) VE8084.

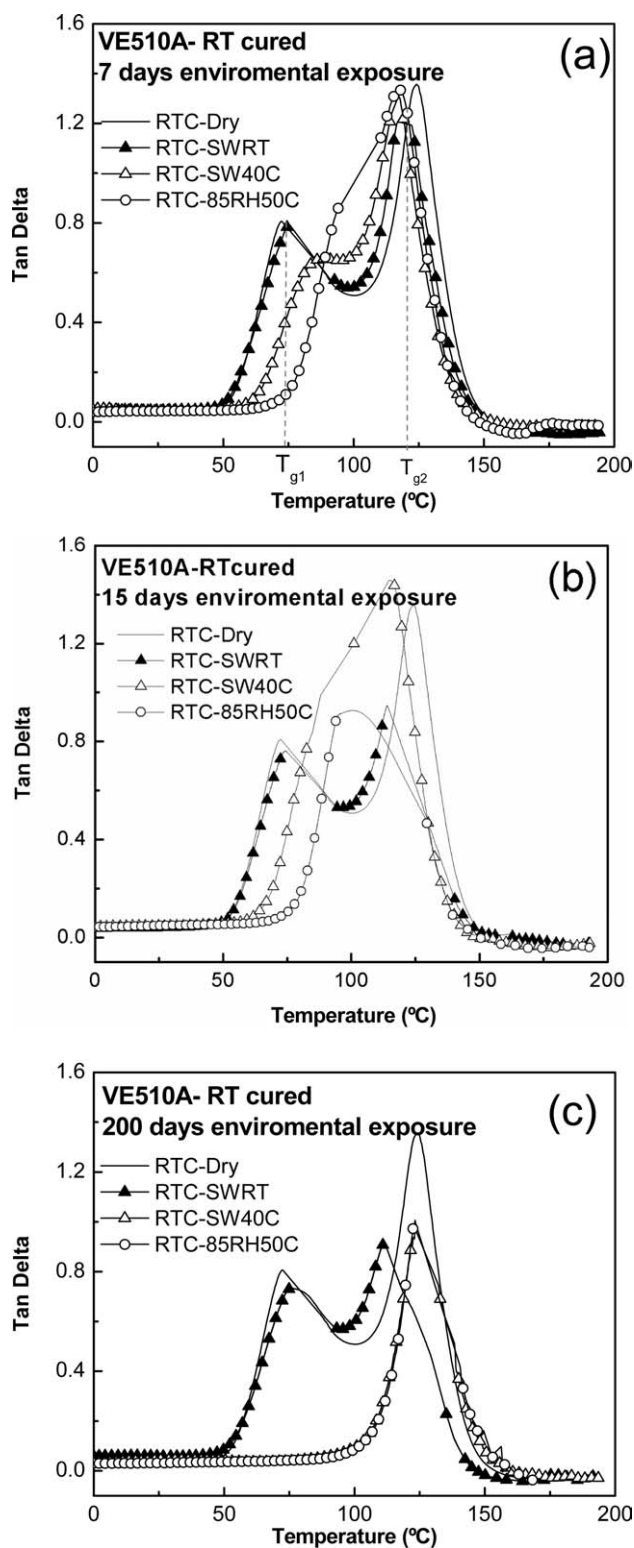


Figure 8. Loss tangent versus temperature for RT-cured VE510A specimens after (a) 7 days, (b) 15 days and, (c) 200 days of exposure.

Degree of Cure

DSC scans of the liquid resins are shown in Figure 4(a). The total heat of reaction is provided by the area under the exotherm peak obtained in the dynamic heating experiment, which

yields 353 ± 7 J/g and 355 ± 10 J/g for VE510A and VE8084, respectively. These results agree with the value of 360 J/g determined for VE resin by Suzuki et al.²⁸ A reheat cycle was

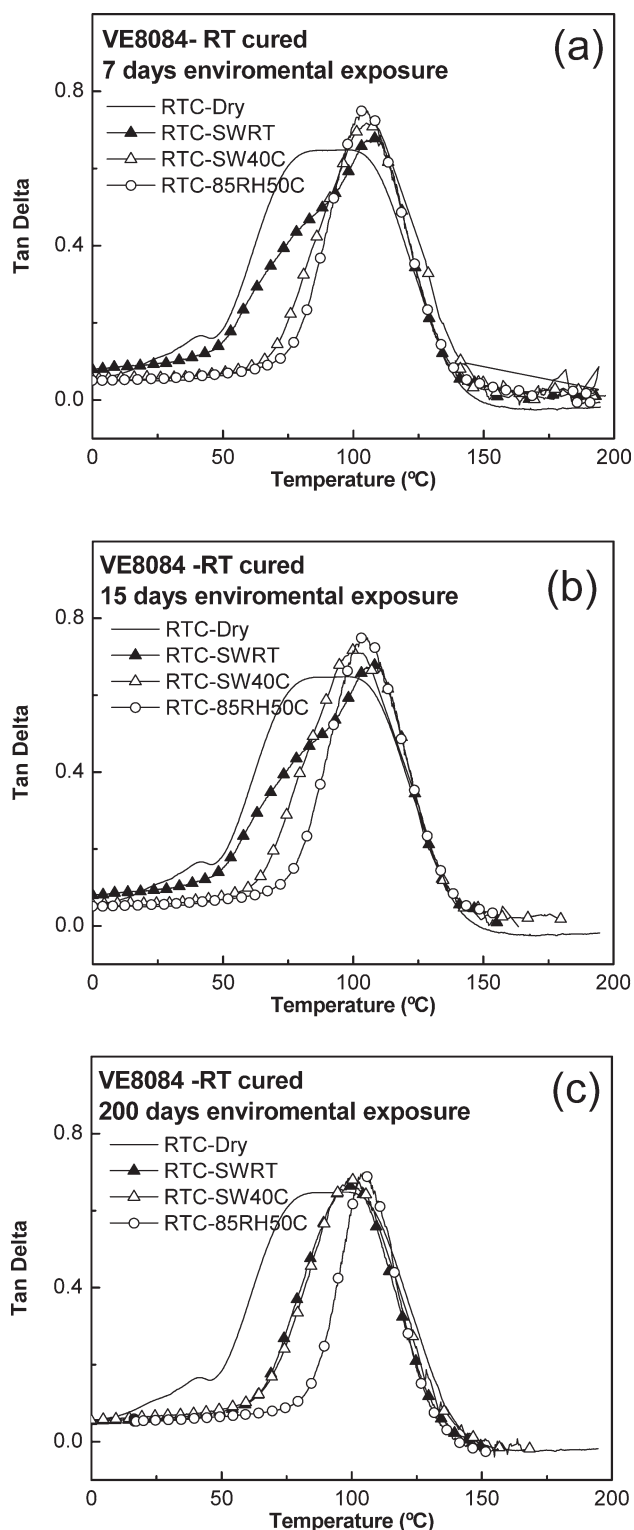


Figure 9. Loss tangent versus temperature for RT-cured VE8084 specimens after (a) 7 days, (b) 15 days and, (c) 200 days of exposure.

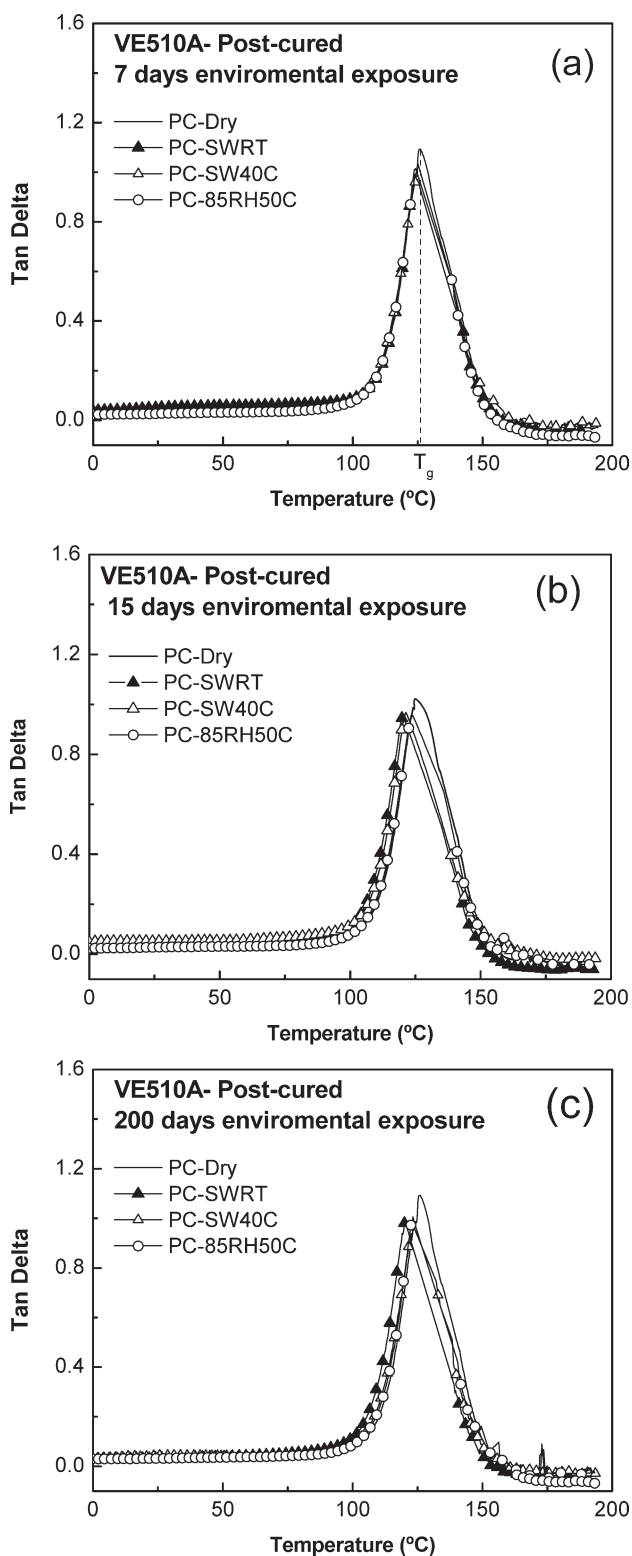


Figure 10. Loss tangent versus temperature for PC VE510A specimens after (a) 7 days, (b) 15 days and, (c) 200 days of exposure.

conducted on both specimens to confirm that VE resins did reach the full cure state. The reheat cycles shown in Figure 4(b) for the resins show that residual heats of reaction are negligible.

RT-cured and PC VE specimens were ramped at the same rate as the uncured resins from RT to 300°C in the DSC apparatus to determine the residual heat of reaction. Figures 5 and 6 show typical DSC scan curves for RT-cured VE510A and VE8084

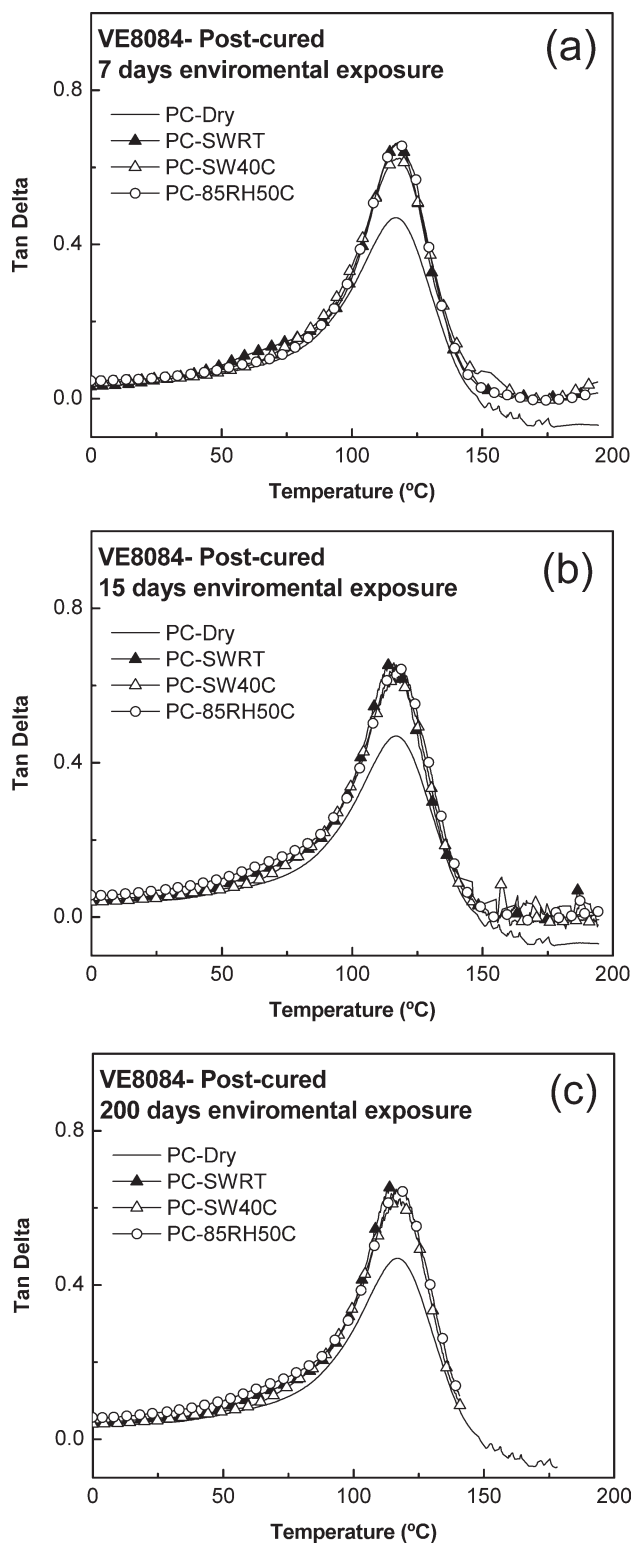


Figure 11. Loss tangent versus temperature for PC VE8084 specimens after (a) 7 days, (b) 15 days and, (c) 200 days of exposure.

Table III. Glass Transition Temperature for RT-Cured and PC Resins

	VE510A				VE8084		
	RT-cured		PC T_g		RT-cured		PC T_g
	T_{g1}	T_{g2}			T_{g1}	T_{g2}	
Dry	75.9	123	124	Dry	-	90	117
SWRT-7D	74.9	120	123	SWRT-7D	82	109	116
SWRT-15D	75.1	120	123	SWRT-14D	85	109	116
SWRT-200D	75.3	119	123	SWRT-200D	86	109	117
SW40C-7D	85	117	123	SW40C-7D	-	104	117
SW40C-15D	86.2	119	124	SW40C-14D	-	105	117
SW40C-200D	-	123	123	SW40C-200D	-	116	116
85RH50C-7D	95	118	123	85RH50C-7D	-	109	117
85RH50C-151D	-	118	123	85RH50C-14D	-	114	118
85RH50C-200D	-	123	122	85RH50C-200D	-	117	116

specimens after environmental exposure and PC. The absence of an exothermic peak in the DSC scans for PC specimens and specimens cured at RT and exposed to humid air at 85°C for 100 days (CRT-85RH50C-100 d) suggests that these specimens are completely cured. However, specimens RT-cured for 24 h (RTC), RT-cured for 300 days (RTC-300 d), and RT-cured exposed to SWRT for 100 days (RTC-SWRT-100 d) show an exothermic peak. This indicates that these specimens are not fully cured.

The degree of cure for the two resins and exposure conditions was calculated from eq. (1). The results are displayed in Figure 7. The degrees of cure for the two resins cured at RT for 24 h are 83 and 88%. The degree of cure for the VE8084 resin is slightly higher than for VE510A for all exposure conditions. The small additional degree of cure for RT-cured resins due to exposure of RT for 300 days at reveals that the cure reaction progresses very slowly at RT. In addition, moisture exposure at RT for 100 days promotes PC and a slight increase in the degree of cure was observed as compared with the dry condition. However, conditioning at 85% RH and 50°C for 100 days leads to complete cure of both resins.

Dynamic-Mechanical Response

DMA tests were performed on RT-cured and PC VE510 and VE8084 specimens exposed to dry conditions and after 7, 15, and 200 days of exposure to different media (SWRT, SW40C, and 85RH50C). Figure 8 depicts $\tan \delta$ versus temperature for the RT-cured and PC VE510A resin specimens.

RT-cured specimens kept at dry (RTC-dry) conditions for 7 days display two $\tan \delta$ peaks [Figure 8(a)], one at around 75°C and the second at 123°C. The low temperature transition indicates the T_g of the uncured oligomer phase within the vitrified resin while the high temperature peak is characteristic for the fully cured part of the system.²⁹ Two transition peaks are observed also for SWRT exposure, while exposure to SW40C and 85RH50C shifts the low transition temperature to higher temperatures (85 and 95°C). The same trend was observed after 15 and 200 days of exposure [Figure 8(b, c)]. The transition at

lower temperature shift progressively with the exposure time to higher temperatures until a single peak is observed after 200 days of exposure to SW40C and 85RH50C. This single peak is the glass transition temperature of a fully cured resin. However, for SWRT exposure, no significant changes in the response curve were observed over the entire exposure time; the two transition peaks remain separated even at 200 days of exposure. This is a clear indication that cure was progressing mainly as result of the elevated temperature (40 and 50°C) rather than the exposure to moisture. Similar trends were observed for the VE8084 resin see Figure 9. For RT-cured VE8084 at dry condition a broad transition peak is observed (Figure 9), which probably is an overlap of two transition peaks (as observed for the VE510A resin, Figure 8). After longer exposure to seawater at RT [Figure 9(b, c)] the transition peak became narrower and shifts toward higher temperatures. After 15 days of exposure, Figure 9(b), only a shoulder at around 82°C is observed indicating the lower temperature transition. Over time, the broad peak is collapsing into a well-defined transition peak at 109°C. After moisture exposure at elevated temperatures, one transition peak is detected over the entire exposure time, which is an indication of a fully cured resin due to the initial elevated temperature exposure.

Figures 10 and 11 show $\tan \delta$ versus temperature for PC VE510A and VE8084 specimens after 7, 15, and 200 days of exposure to SWRT, SW40C, and 85RH50C. The PC specimens display one single transition temperature peak (T_g). This occurred at 123°C for VE510A and at 117°C for VE8084. The fully cured materials have a single T_g because at higher temperature, the molecular mobility increases and unreacted and partly reacted monomers/oligomers become mobile and rearrange themselves so that they come closer and react.³⁰ Additionally, only small influence of moisture on T_g is observed for PC specimens.

Table III summarizes the glass transition temperatures of the resins for various cure times and environmental exposures. The elapse time and environmental exposure to reach a target T_g will allow estimation of the time and conditioning to reach a fully cured state of the resin. For example, VE510A achieved a T_g of at least 118°C after at least 15 days of exposure to 85%

RH at 50°C. For the same time and exposure conditions, the glass transition temperature for VE8084 reached 114°C. Exposure to seawater at 40°C also promotes achievement of a fully cured state; however, this requires more than 15 days of such exposure.

Based on the results presented, it can be recommended that composite structures made from composite materials with a VE resin matrix, such as large naval vessel, that cannot be PC at elevated temperatures could be PC naturally at a reasonable rate if placed in warm region of the world.

CONCLUSIONS

In this study, the progression of cure of RT cured VE510A and VE8084 resins subjected to various environmental conditions was explored. Moisture absorption experiments revealed that VE8084 resin absorbs more moisture than the VE510 resin, and that the rate of moisture absorption increases with increasing exposure temperatures resulted in higher rates of moisture transport for both resins systems.

DSC measurements show that the VE resins become fully cured after elevated temperature PC. It was found also that exposure to humid air at 50°C and seawater at 40°C for more than 200 days resulted in complete cure of these resins. However, the moisture exposure itself does not appear to have a strong effect on the cure progress. Analysis of the evolution of the glass transition temperature by DMA supports this finding.

It was observed that after 200 days of seawater exposure at RT the VE510A resin still remains only partially cured, while the VE8084 resin reach or is very close to full cure state.

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