The Effect of Marine Environment on a Vinyl Ester Resin and Its Highly Filled Particulate Quartz Composites

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ABSTRACT: The accelerated effects of immersion in seawater at 60°C, in comparison to distilled water, on a vinyl ester resin and on its highly quartz particles filled system were studied. The studied resin was cured at room temperature for 48 h and postcured at 100°C for 12 h, and the filled system contained 93 wt % quartz particles of a wide size distribution, either as received or silane-treated. The immersion in water results mainly in further curing and some extraction of low molecular substances, as reflected by the flexural mechanical properties and the DSC thermograms. The silane coupling agent treatment of the filler significantly improves the composite properties and its resistance to the water environment. No practical difference was observed in any of the studied systems between the effects of sea and distilled water, as tested by the immersion in boiling water for 48 h. Weatherometer conditions, cycles of ultraviolet radiation at 60°C and water condensate at 50°C, for up to 1000 h, also cause postcuring effects, without extractables' leaching effects. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 2229−2234, 1998

Key words: vinyl ester; polymer; composite; filler; water; marine

INTRODUCTION

Vinyl ester resins are being used in glass-reinforced thermosetting composites for marine applications due to their good combination of properties, including chemical resistance, especially long-term resistance to moisture, mechanical, and thermal properties, combined with rapid curing and ease of processing.[1] In recent years, considerable attention has been paid to the problem of moisture absorption by such materials as epoxies, polyesters, and vinyl esters, in their neat or reinforced forms[2−5]; almost nothing has been reported on the effect of immersion of vinyl esters in seawater. Moreover, the difference between the effects of plain water and seawater on the chemical and physical aging of plastic systems has not yet been elucidated. In composite systems, in addition to the matrix structure, the reinforcement and the matrix−reinforcement interface may also be affected by the sorbed water. Moreover, defects at the matrix−reinforcement interface may contribute to the level of moisture effects in composites.[6]

In the present article, the effect of seawater on some properties of neat and filled vinyl ester is compared with that of distilled water and of ultraviolet (UV)−water cycles.

EXPERIMENTAL

The vinyl ester (VE) resin used was a Derakane 411-45 (Dow Chemicals) containing 45% styrene.

Room temperature curing was done using methyl ethyl ketone peroxide (MEKP, Fluka) and a 6–8% cobalt naphthenate (CoNap) solution (Fluka).

For neat resin sample preparation, a mixture containing VE, 2 phr MEKP, and 0.3 phr CoNap was cast in a glass mold with an aluminum spacer. The room temperature reaction was completed in 2 days (as discussed below), yielding 3-mm-thick plaques. Postcuring was accomplished by annealing at 100°C for 12 h. A highly filled (93% wt) particulate composite was prepared by mixing quartz particles of a wide size distribution with the above catalyzed vinyl formulation and molding while under vacuum and vibrations, yielding 8-mm-thick plaques. ASTM D 790-71 samples for flexure testing and ASTM D 638-72 samples for tensile testing were machined.

Samples were exposed to the following 3 types of accelerated environmental conditions:

1. Seawater (synthetic, according to ASTM D 1141-90) at 60°C, up to 6 months;
2. Boiling, either seawater or distilled water, for 48 h;
3. Accelerated Weathering Tester (QUV), equipped with UVB-313 UV lamps.

Samples were exposed for up to 1000 h to cycles of 8 h at 60°C with UV irradiation and 4 h at 50°C with water condensing on the samples' surface.

All samples were dried at ambient conditions for 2 weeks prior to testing. Mechanical testing was performed using an Instron 5568 at a crosshead speed of 1.3, 3, and 1 mm/min for 3-point bending of the unfilled and filled samples and for the tensile testing, respectively.

Seawater weight gain, at 60°C, was followed for up to 200 days, by a weekly sampling, rinsing with distilled water, drying the surface, and weighing. Thermal analysis of the neat resin samples, before and after exposure, was performed to determine the resin's cure level and glass transition temperature, T_g, using a TA3000 DSC (Mettler) at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

The level of curing at room temperature of the resin used in the present study was determined by differential scanning calorimetry (DSC). The residual heat of curing, reflecting the fraction of uncured resin, and the peak residual curing temperature as function of the room temperature cur-
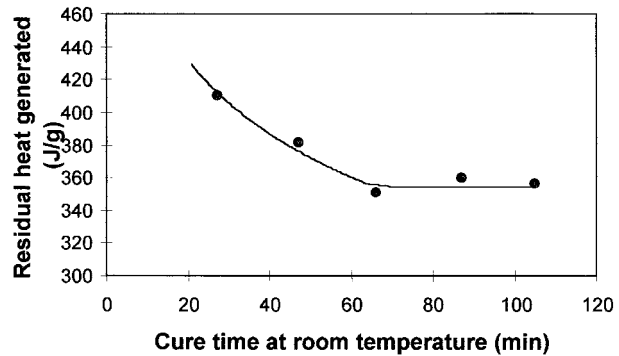

(a)
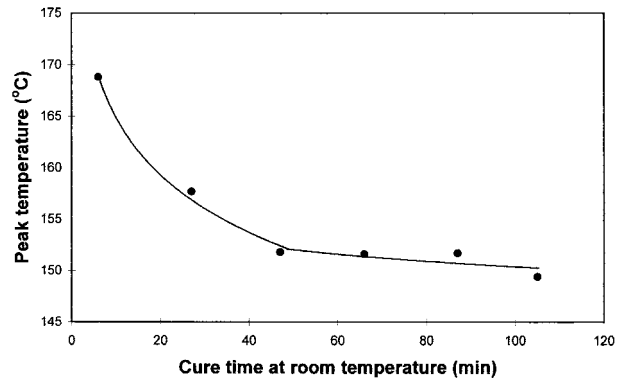
(b)

Figure 1 The residual curing heat (a) and residual curing peak temperature (b) as a function of ambient temperature curing time of VE resin.

ing time are depicted in Figure 1. Both the residual heat and peak temperature decrease rapidly with curing time during the first (approximately) 40 min (gel time was approximately 30 min). Longer curing times resulted in a lower rate of change of the residual curing heat (declined to a value of 80 J/g, after 48-h room temperature curing) and almost no further change in peak temperature. Postcuring (100°C/12 h), following 48 h room temperature curing, reduced the residual curing heat to 25 J/g. Hence, the room temperature curing kinetics of the neat VE resin is significantly changed, that is, dramatically slowed down, after gelation; the second-order reaction kinetics and its parameters, as reported by Han and Lem[7] actually describe the reaction prior to gelation. Moreover, the level of room temperature cure (residual heat/ultimate curing heat) after 1 and 48 h was found 22 and 83%, respectively, and 89% after postcuring.

The weight gain of the presently studied VE systems upon immersion in seawater, at 60°C, up
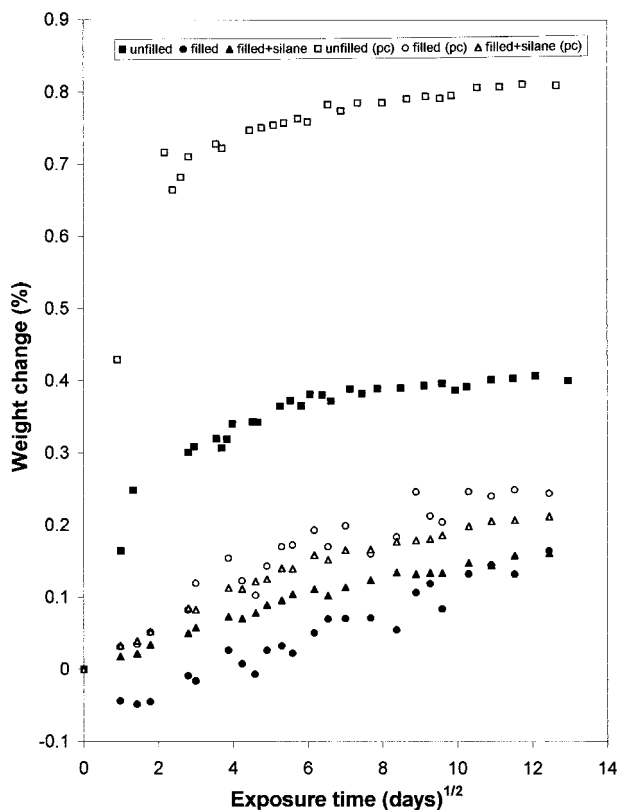
Figure 2 Weight change, relative to initial weight, of VE systems upon immersion in seawater at 60°C.

to about 200 days, is presented in Figure 2 as relative weight change versus the square root of immersion time. The neat VE resin samples gained weight mostly during the first 5 immersion days and leveled off only after 50 days. As expected, the filled samples' water gain is much lower than that of the neat resin (it is much higher on a VE basis due to the presence of matrix–filler interfaces); however, the water absorption process in the filled samples continues without leveling off even after 200 days of immersion. A similar behavior has been reported for fiber-glass-reinforced polyester.[8–10] The ultimate water absorption values obtained for the neat resin are similar to those reported in the literature for similar VE systems.[5,11] There is no significant difference between the level of absorption of distilled or seawater. Using energy dispersive X-ray spectrometry (EDS), no seawater salts were traced within the instrument's sensitivity limits (> 0.5%) in the fracture surfaces of the exposed samples. No reports on comparable, quartz-filled VE systems are available for comparison purposes.

Interestingly, in all the presently studied systems, neat and filled, postcuring at 100°C resulted in both higher rate of water absorption and higher ultimate water gain. It is suggested that this unexpected phenomenon is caused by the formation of defects, resulting due to the residual styrene at the end of the 2 days of room temperature curing. These defects do not seem to adversely affect the mechanical behavior, as discussed below. Ghorbel and Valentin[11] have studied VE–glass laminates and reported that postcured (11 h at 80°C) laminates absorb water at a lower rate than the just cured ones; however, significant damage was observed in the postcured samples already after short immersion times in water.

The water weight gain data in the entire studied time interval (up to 200 days) for the neat resin, whether postcured or not, fit Fick's law[12] well [eq. (1)], and fit even better its modified version [eq. (2)], suggested by Springer,[13] as follows.

$$M = M_n[1 - 8/\pi^2 \exp[Dt\pi^2/h^2]] \qquad (1)$$

$$M = M_n\{1 - \exp[-7.3(Dt/h^2)^{0.75}]\} \qquad (2)$$

where M is the weight gain, M_n is the ultimate weight gain, D is the diffusion coefficient, t is the exposure time, and h is the sample thickness. The ability to describe the absorption process by a Fickian diffusion indicates that the cast samples are practically free of defects, at least those affecting water diffusion, and that the amount of water extractables is insignificant. The water uptake by the filled systems is not a Fickian process due to the presence of a filler and matrix–filler interfaces.[14,15] The water diffusion coefficient in the VE resins was calculated based on eq. (1), and the weight gain data for the initial exposure times (M is a linear function of $t^{0.5}$). The calculated D values, $3.20\ 10^6$ and $6.22\ 10^6$ cm^2/s for the cured and postcured VE resin, respectively, are in quite good agreement with literature values for similar systems.[3,14]

The combination of physical and chemical changes, which may occur during the immersion of VE resins in water, is expected to be reflected in the resins T_g. It has already been shown[11] that water acts as a plasticizer, exponentially reducing the T_g with immersion time. However, to study the permanent aging effects, the immersed samples were presently dried prior to their thermal analysis. The T_g of the just cured VE resin is rather low (60°C) due to the low degree of curing and the residual styrene. After immersion in wa-

ter at 60°C, the T_g (dry samples) sharply increases to 103.6 and 105.6°C after 15 and 30 days, respectively. Further exposure resulted in a slow decrease in the T_g, reaching 97.8°C after 6 months of immersion (Fig. 3). At the same time, the T_g of the dry, postcured resin was not affected by the water treatment and maintained its value of 113°C. Having, at present, no data available on the dependence of T_g on the degree of VE cure, it is impossible to separate between the physical and chemical changes taking place during the water treatment. However, the fact that the T_g of the postcured samples was not affected by the water treatment, assuming that the fully cured resin only undergoes physical changes, which are reversible upon drying, may indicate that most, if not all, observed changes in T_g of the just cured resin are due to chemical changes. They probably include effects of postcuring, occurring slowly at the immersion temperature (60°C), and of reduction of water extractables content, both increasing T_g. The small and slow reduction in T_g upon long exposure time could probably stem from some low levels of hydrolysis or from increasing amount of residual water molecules in the dried resin.

The flexure modulus of the postcured neat resin is 3500 MPa compared to 2500 MPa of the just cured resin. However, upon immersion in seawater, at 60°C, for 15 days, the latter's modulus increases, reaching the value of the postcured resin. During longer exposure times, up to 6 months, the modulus of both resin is practically identical, slowly increasing up to 4000 MPa. The behavior of the filled system is slightly different (see Fig. 4). The flexural modulus of the postcured system slowly decreases with immersion time, from 29 to 18 GPa in 6 months, while the modulus of the
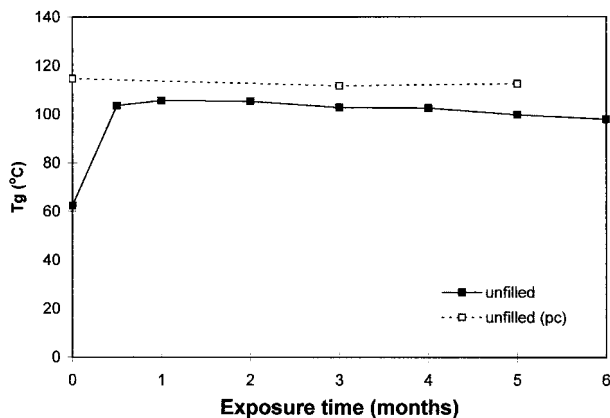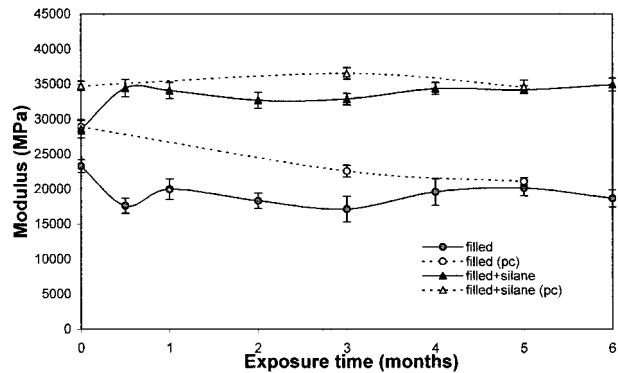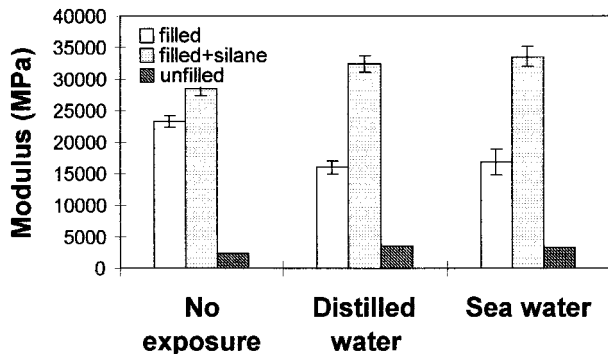

Figure 4 The flexural modulus of quartz-filled VE composites after immersion in seawater at 60°C.

just cured system first slightly decreases and then slowly increases, reaching, after 5 months, the value of the postcured system. Interestingly, when a silane treated quartz particles are used as the filler, the initial (prior to immersion) flexural modulus value of both, just cured and postcured systems, are significantly higher than those containing an untreated filler. Moreover, the modulus of the postcured system, containing the treated filler, is not affected by immersion in seawater, while the modulus of the just cured system slowly increases, reaching, after 5 months, the modulus value of the postcured system. As to the flexural strength, that of the neat resin is practically not affected by the immersion, while that of the filled systems dramatically decreases, from 48 to 16 MPa, during the first month of immersion. However, when a treated filler was used, the flexural strength gradually and slowly decreases, from 60 to 47 MPa, during the first 5 months. A significant difference between the fracture surface of the filled system containing silane-treated or untreated filler was observed. In the untreated filler system, the fracture occurs at the filler–matrix interface, and some filler particles have even been detached, leaving empty space. In the treated filler system, however, the fracture occurs both in the matrix and in the filler; many fractured particles are observed. This difference was observed in samples before and after 6 months of immersion. This silane treatment effect is in agreement with literature reports on other particulate[15] and fibrillar[16] reinforced systems.
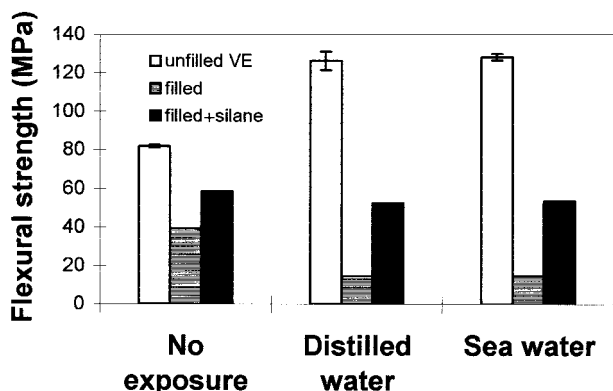
Comparison between the effect of seawater and distilled water on the VE resin was made by an accelerated test, namely, immersion in boiling water for 48 h. For demonstration purposes, the flexural modulus (Fig. 5) and flexural strength

Figure 3 The glass transition temperature of dried VE resin after immersion in seawater at 60°C.

Figure 5 Comparison between the effect of immersion for 48 h in boiling sea and distilled water on the flexural modulus of filled and unfilled VE resin.

(Fig. 6) of the unfilled and filled resin before and after exposure to water are depicted. Unfortunately, no difference between the effect of the 2 types of water was observed, as also reported by Pollard et al.[4] The immersion in both sea and distilled water for 48 h at 100°C resulted in mainly a postcuring effect, similar to the effect of immersion in seawater for 15 days, at 60°C, as shown above.

Interestingly, the exposure of the VE systems to UV–water-condensate cycles also has a postcuring effect and mainly that. Exposure up to 1000 h causes the flexural modulus of both, just cured and postcured samples, to gradually increase the flexural strength of the postcured unfilled resin to gradually decrease, and that of the just cured was not affected. For the filled systems, the flexural strength of the untreated filler system gradually decreases, while that of the silane-treated filler system is not affected. The observed

Figure 6 Comparison between the effect of immersion for 48 h in boiling sea and distilled water on the flexural strength of filled and unfilled VE resin.
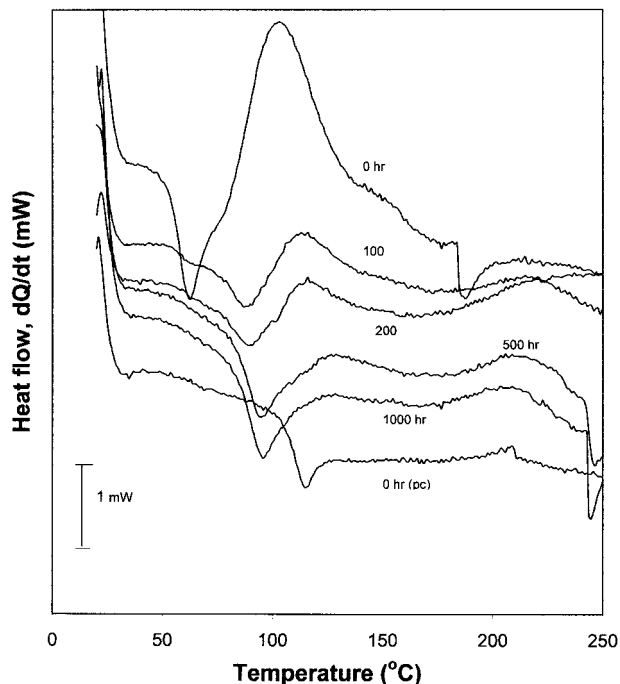
Figure 7 DSC thermograms of ambient temperature cured VE resin, as affected by exposure to cycles of UV irradiation and water condensate, at 50°C, and of a postcured (PC) resin.

postcuring effect under the weatherometer conditions, 50–60°C, is clearly depicted in the DSC thermograms (Fig. 7). The exotherm, due to the completion of the curing reaction (residual heat), decreases in size with exposure time, and the T_g shifts to higher values, both approaching the characteristics of the postcured resin. However, the exposure to UV–water-condensate is less effective than the immersion in water, as all changes in the prior are more gradual than those in the immersed samples. Hence, it seems that the UV radiation, for up to 1000 h, does not affect the VE resin; the environment temperature effect is similar to that in the water bath, and the water condensate are less effective in extracting low-molecular-weight substances than during immersion.

CONCLUSIONS

Accelerated marine environment tests of vinyl ester resin, cured at room temperature and postcured, neat or highly filled with quartz particles, lead to the following conclusions.

1. It seems that there is no difference between the effect of long-term immersion in distilled or seawater on the behavior of VE.

2. The weight change during immersion is due to both water absorption and extraction of low-molecular-weight molecules. The water absorption in the neat resin, whether post-cured or not, is a Fickian process. It is not the case in the filled systems.

3. Postcuring results in increased water gain, probably due to defect formation during post-curing, but less extractables in the resin.

4. Immersion in water at 60°C has a postcuring effect, mainly during the first 15 days, as reflected by the resin's residual heat of curing, T_g, and mechanical properties.

5. Exposure to UV–condensing water at 50°C up to 1000 h also has similar postcuring effects, though more gradual, on the various presently studied VE systems. The postcured systems exhibited high resistance to this type of environment, as reflected by the unchanged resin properties.

6. Silane treatment of the filler particles enhances the composites resistance to the marine environment due to the improved filler–matrix adhesion. This improved resistance, compared to composites with untreated filler, is reflected by the lower water gain, lower amount of extractables, and lower changes in flexural modulus and strength upon immersion in water.

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