# Characterization of the chemical structure of vinyl ester resin in a climate chamber under different conditions of degradation

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## ARTICLE INFO

## ABSTRACT

Due to the good strength and similar toughness of epoxy resins, vinyl ester resins are widely used as thermoset adhesives in structural adhesive joints and as composites for different industrial applications. However, vinyl ester adhesives are difficult to cure completely under environmental conditions, even after long periods of time because of gel formation slows the necessary diffusion of the catalyst across the polymer network.

Several studies have used weathering chambers to investigate the degradation mechanisms of vinyl ester adhesives. However, a review of the scientific literature revealed both a wide variety of aging processes and several ambiguities between the recorded experimental results.

In this work, post-cured vinyl ester resins at different aging cycles were aged under high temperature and relative humidity, and the changes in their structure, mechanical and adhesion properties were studied. Chemical and structural changes were observed in the vinyl ester resins after aging in a climatic chamber.

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## 1. Introduction

Vinyl ester (VE) resins are thermosetting polymers that combine the good chemical, mechanical and thermal properties of epoxy resins with the rapid cure of unsaturated polyester resins [1]. VE resins have high chemical and hydrolytic resistances, good toughness, a high modulus and good thermal and electrical insulation properties [2–4]. Furthermore, VE resins exhibit higher toughness and shrink less with curing as compared to unsaturated polyester resins, which have a relatively similar chemical structure [5–7]. For these reasons, VE resins are widely used as thermoset adhesives in structural adhesive joints and composites in automotive, aeronautical and naval industries, among others [5,8,9]. However, one limitation of the VE adhesive is the difficulty with which a complete cure can be achieved under environmental conditions, even after extended periods of time [10,11]. This difficulty is due to the slow diffusion of the catalyst across the polymer network after gel formation is produced [12]. Without a complete cure, the VE resins

have incomplete crosslinking, which has been shown to be detrimental to their performance [11–15].

Cook et al. [16] studied the curing kinetics of dimethacrylate-based VE resins using scanning and isothermal differential scanning calorimetry (DSC), gel time studies and dynamic mechanical thermal analysis (DMTA). Physical aging appeared to occur during the isothermal polymerization of the samples when they were cured below the glass transition temperature (Tg) of the completely cured polymer, and additional curing was shown in during DMTA experiment. Ziaee and Palmese [17] studied the relationships among the cure temperatures, the chemical kinetics, the microstructures, and the mechanical performances of VE resins. They showed that the initial cure temperature significantly affected the mechanical behavior of VE resins. In particular, post-cured samples that were initially cured isothermally at 30 °C had significantly higher values of strength and fracture toughness than samples cured isothermally at 90 °C. Alía et al. [18] studied the influence of the post-curing temperature on the structure, properties and adhesion of VE adhesives, and concluded that the degree of cross-linking depended on the post-curing temperature; curing completed when post-curing above 100 °C, a temperature close to the Tg of the completely cross-linked polymer (115 °C). To fully

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**Table 1**
Properties of the vinyl ester resin [24].

| Tensile strength (MPa) | 80 |
|---|---|
| Elongation-at-break (%) | 5 |
| Viscosity at 25 °C (mPa s) | 520—620 |
| Pot life at 25 °C (min) | 14—24 |

cross-link the VE resin, a temperature of 140 °C was necessary. Jofre et al. [19] studied the interactions between the surface groups on graphite nanoplatelets (GN) and the C=O and OH moieties of the VE monomer, and their influence on both the crosslinking of VE resins cured at 25 °C and on the thermal, viscoelastic and mechanical properties of VE—GN composites.

Marouani et al. [20] studied the aging resistance of carbon fiber/epoxy (carbon/EP) and carbon fiber/VE composites under different accelerated aging conditions (thermal, hygrometric, chemical, thermochemical, hydrothermal, and freezing—thawing cycles) over 18 months. They found that the mechanical properties of the composite materials changed over time, especially when subjected to variable charge for long periods of time. Other authors [21,22] found similar evidence and recognized the importance of developing tests to accelerate the degradation process to better understand the deterioration of a joint's mechanical resistance under different environmental conditions.

Several studies have used weathering chambers to investigate the degradation mechanisms of VE adhesives [23,24]. For example, Mezghani [23] exposed glass fiber-reinforced VE pipes (GFRP) to outdoor conditions for 60 months. The effect of the outdoor exposure on the Tg, and the crosslinking index was discussed. The Tg rapidly increased with the exposure time up to 12 months and then slightly decreased after longer exposure times. Additionally, similar trends were observed in the degree of crosslinking.

However, a review of the scientific literature reveals a wide variety of aging processes and several ambiguities between the recorded experimental results. This situation can be explained by

the absence of standardized characterization procedures and different aging tests, which lead to contradictory results. Even so, the amount of available information on VE resin degradation is much more limited [20,23—25], and to the best of our knowledge, the physicochemical characterization of the changes produced in the VE upon degradation under different curing conditions have not yet been studied. Therefore, in this work different aging processes under high temperatures and relative humidity were carried out in VE resins that were post-cured at different temperatures (60, 100 and 140 °C), and the resulting changes in their structure, mechanical and adhesive properties were studied.

## 2. Experimental procedure

### 2.1. Materials

Two-component VE resin, Dion® 9100 (Reichhold, Durham, NC, USA), was used [26]. Some properties of the VE resin are given in Table 1. DION® 9100 series are bisphenol-epoxy vinyl ester resins. Fig. 1 shows the chemical structure of the VE resin monomer. The average number of Bisphenol-A groups (n) in the dimethacrylate backbone is around 0.56.

Vinyl ester is dissolved in a monomer, or reactive diluent, usually styrene, the result is a low viscosity liquid having a solids content of 36—39%. Vinyl-ester monomer contains two vinyl end groups that allow cross-linked structure to form during the reaction. The styrene is not only a solvent, but actively takes part in the cure reaction to form a crosslinked vinyl ester polymer, while reaction of the styrene extends the structure (Fig. 2).

The two components of VE resin were mixed in a glass container and stirred by hand for 5 min to obtain a homogeneous mixture. The mixture was allowed cure for 24 h at room temperature. Post-curing was carried out by placing these specimens in an oven (Selecta 2000208, Barcelona, Spain) at 60, 100 and 140 °C for 1 h.

Single lap-shear of stainless steel-VE joints were prepared to measure adhesion. Stainless steel test pieces [27] (C<1%, Mn < 0.9%,
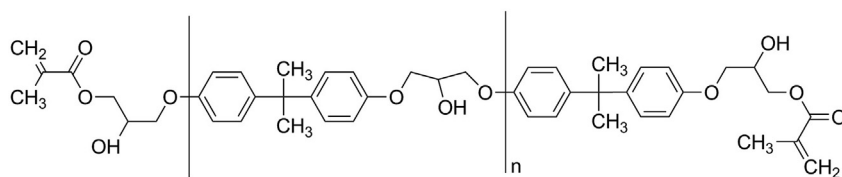


**Fig. 1.** Chemical structure of the vinyl ester resin monomer.
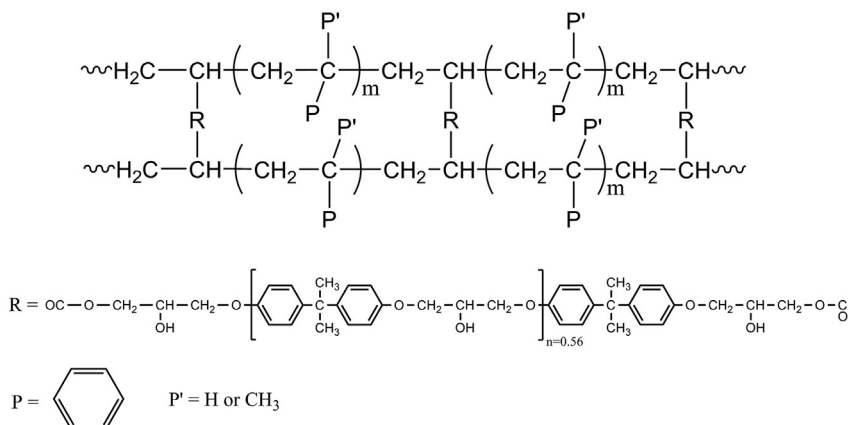


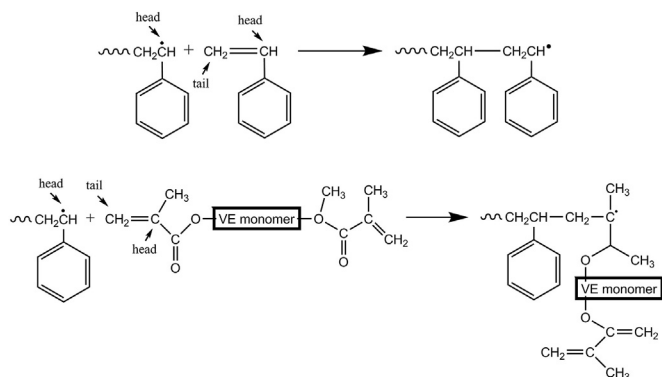**Fig. 2.** The structure of the vinyl ester/reactive diluent network.

**Fig. 3.** Free-radical polymerization mechanism of vinyl ester polymer.

temperature was varied between −25 °C and 200 °C and a heating rate of 5 °C/min was used.

*Optical microscopy.* The surface morphology of the VE resin after post-curing was analyzed with a Laborlux 12 ME ST optical microscope (Leitz GmbH & Co. Oberkochen, Germany) and a 5x/0.09 lens.

*Stress-strain tests.* The mechanical properties of the VE resin were determined by stress-strain tests using dumbbell specimens in accordance with ISO 37-2 standards. A universal testing machine (IBTH3630, IberTest, Madrid, Spain) provided with a 200 N load cell was used and the mechanical properties were measured according to ISO R527-1-966 standards [28]. The pulling rate used was 2 mm/min.

*Adhesion measurement.* Single lap-shear tests in stainless steel/VE resin joints were carried out in a TN-MD universal testing machine (Hoytom S.L., Bilbao, Spain) provided with a 200 kN load cell and using a pulling rate of 2 mm/min. The locus of failure of the joints was assessed by visual inspection.

Si<0.5%, P<0.1%, S<0.1%) of dimensions $150 \times 30 \times 1$ mm were used. Before joint formation, the surface of the stainless steel was wiped with MEK (methyl ethyl ketone) and later roughened manually with Scotch-Brite® aluminum wool (3M, St. Paul, MI, USA). Immediately after the two components were mixed, approximately 10 μl of VE resin was applied to a roughened stainless steel test sample and adhered to another stainless steel test sample. A pressure of 800 Pa was applied to the joints for 24 h. These adhesive joints were post-cured at different temperatures for 1 h. After cooling down to room temperature, the adhesive joints were tested.

## 3. Results and discussion

VE monomer reacts through a free-radical polymerization mechanism using methyl ethyl ketone (MEKP) as the initiator. The free radical polymerization differs from step-growth one because of it proceeds only in head-to-tail regio-selectivity during chain growth (Fig. 3). On the other hand, the ester groups of vinyl ester are susceptible to water degradation by hydrolysis during aging and this process is accelerated and catalyzed by the presence of acids or bases (Fig. 4).

Fig. 5 shows the ATR-IR spectra of VE resin cured at 25 °C and post-cured at 60 and 140 °C, both before and after aging at 80 °C for different times. The VE resin shows the absorbance O-H stretching band at 3336 cm$^{-1}$, C=C stretching at 1635 cm$^{-1}$, C-H out-of plane bending at 940 cm$^{-1}$, aromatic ring stretching at 1581 cm$^{-1}$, aromatic C-H bond bending of the vinyl group at 828 cm$^{-1}$, C=O stretching at 1712 and 1038 cm$^{-1}$, styrene bending at 765 cm$^{-1}$, C-O-C stretching at 1233 cm$^{-1}$ and C-O-C and C−CO−O stretching at 1160 cm$^{-1}$ [3,5]. After post-curing, the relative intensity of the bands due to styrene (765 cm$^{-1}$) and double C=C bond (828 and 940 cm$^{-1}$) both decrease, as crosslinking is produced in the C=C bonds [15].

After ageing, there is a change in the intensity of the bands at 3336 cm$^{-1}$ (O-H st), 1714 -1603 cm$^{-1}$ (C=O st) and 700-612 cm$^{-1}$ (O-H δ oop). The broad absorption band between 3400 and 3500 cm$^{-1}$ widens after aging, indicating the existence of O−H groups linked by hydrogen bridges or to other groups linked to molecular water through hydrogen bonds. This is confirmed by the increase in the wavenumber frequency of the 700-612 cm$^{-1}$ band due to the formation of hydrogen bonds.

When VE resin cured at 25 °C is aged at 80 °C, two structural changes are produced: (i) a post-curing caused by the temperature above the Tg of the uncomplete cured VE resin, as shown elsewhere [18]; and (ii) the hydrolytic degradation of the ester groups by moisture (Fig. 4). The post-cure at 60 °C of the VE resin cured at 25 °C also produces additional post-curing and hydrolytic degradation because of the aging temperature is above the post-curing

### 2.2. Aging conditions

Both VE samples (non-postcured and post-cured at 60, 100 and 140 °C for 1 h) and the adhesive joints were aged in weathering chamber Dycometal CCK/CM (Barcelona, Spain). The aging conditions were 80 °C at 95% relative humidity for 3, 7 or 14 days.

### 2.3. Experimental techniques

*Infrared spectroscopy (IR spectroscopy).* Changes in the chemical structure of the VE resin were studied by IR spectroscopy using the attenuated multiple total reflectance mode (ATR); a diamond prism was used. The IR beam used a 45° incidence angle and 60 scans were averaged with a resolution of 4 cm$^{-1}$.

*Differential scanning calorimetry (DSC).* The degree of cure and post-cure, and the Tg of the VE resin were determined using TA Q100 DSC equipment (TA Instruments, New Castle, DE, USA). Temperature was varied between −50 °C and 200 °C under a nitrogen atmosphere (flow rate: 50 ml/min) and two consecutive heating runs were carried out using a 10 °C/min heating rate. The residual cure enthalpy was obtained from the first heating run, and the Tg values were determined from the second heating run.

*Thermal gravimetric analysis (TGA).* The thermal stability of the VE resin and changes in its structure were evaluated using TA Q500 TGA equipment (TA Instruments, New Castle DE, USA). A 10−15 mg sample was placed in a platinum crucible under a nitrogen atmosphere (flow rate: 100 ml/min) and the temperature was ramped up to 800 °C at a rate of 10 °C/min. At the end of the experiment, the nitrogen atmosphere was replaced by oxygen (flow rate: 60 ml/min) at 800 °C for 15 min to remove the carbon residue and determine whether inorganic fillers existed in the VE resin.

*Dynamic mechanical thermal analysis (DMTA).* The viscoelastic properties of the VE resin were studied using TA Q800 DMA equipment (TA Instruments, New Castle, DE, USA). A 3-point bending geometry was used. Experiments were carried out using a 1 Hz frequency and 20 mm amplitude of oscillation. The
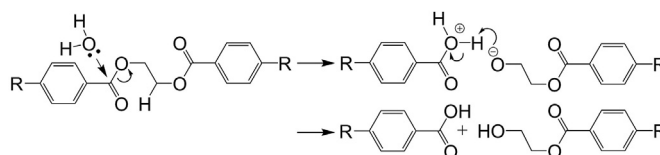


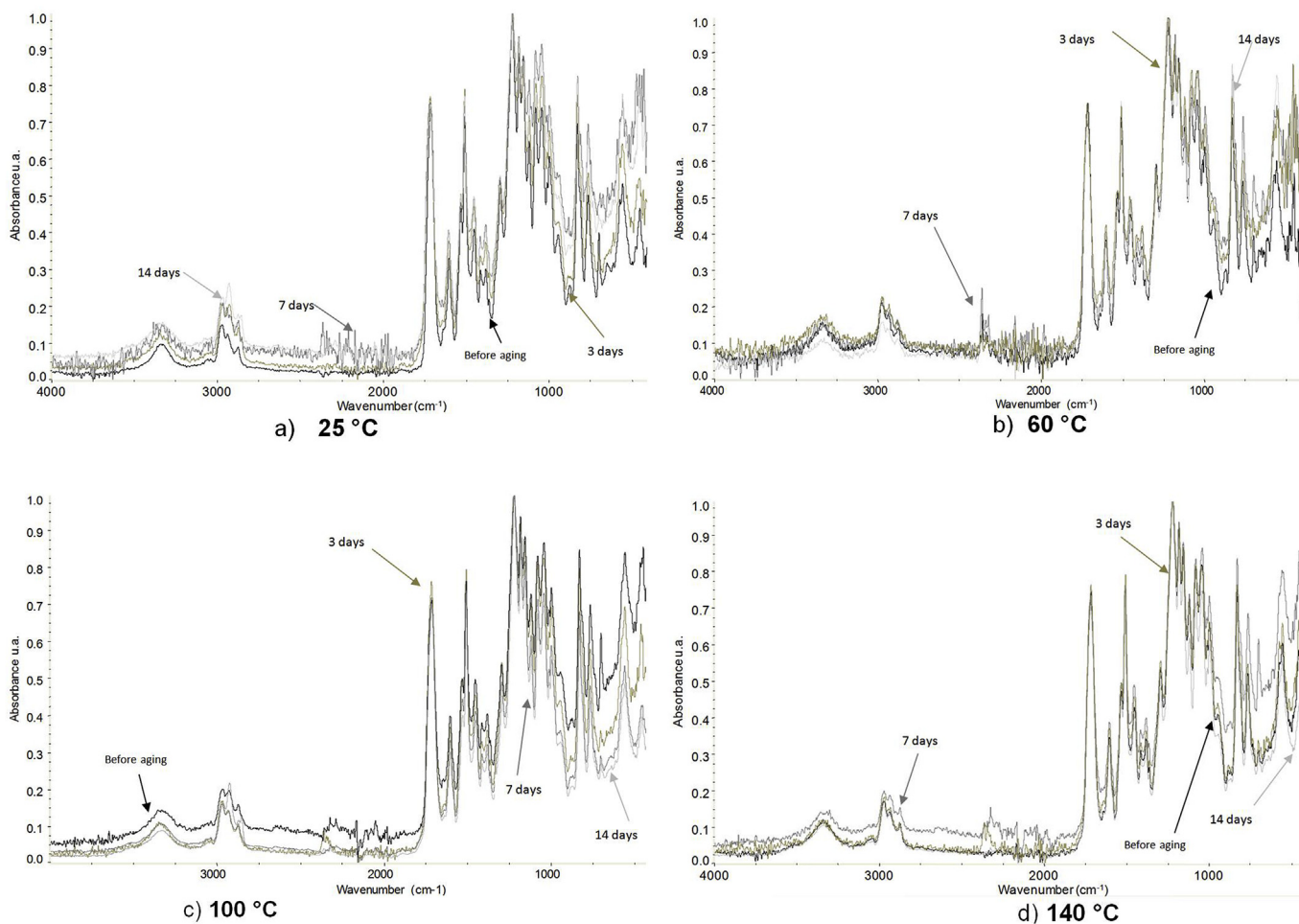**Fig. 4.** Degradation of vinyl ester by hydrolysis during aging.

**Fig. 5.** ATR-IR spectra of the VE resin cured at 25 °C (a) and postcured at 60 °C (b), 100 °C (c) and 140 °C (d) after being aged at 80 °C for 3, 7 and 14 days.

temperature; however, the aging of the VE resin post-cured at 100 and 140 °C does not change the chemical structure of VE resin as the aging is produced above the post-curing temperature. The extent of post-curing can be observed in the ATR-IR spectra by the decrease of the intensities of the bands at 828 and 940 cm-1 due to C=C double bonds of unreacted end-chain ester groups in VE polymer [17,18]. On the other hand, the intensity of C-O-C band of the ester group at 1233 cm-1 decreases upon aging because of the scission of ester group by hydrolytic degradation [29].

Fig. 6 shows the ATR-IR spectra in the region of 750—1750 cm-1 for VE resin cured at 25 °C and postcured at 60 and 140 °C during 1 h before and after aging at 80 °C and 95% R.H. during 7 days. The aging of the VE resin cured at 25 °C causes the reduction of the intensities of the bands of C=O and C-O-C of the ester group and the C=C band of the aromatic group near by the ester group. The aging of the VE resin postcured at 60 °C also shows the reduction of the intensities of the bands of C=O and C-O-C of the ester group, but the decrease in the intensity of the C=C band of the aromatic group is less noticeable. On the other hand, no changes are produced in the ATR-IR spectra of the VE resin post-cured at 140 °C because of complete curing is produced [18], and higher resistance against hydrolytic aging due to the more dense crosslinked structure is shown, which prevent the penetration of the moisture in the bulk by water diffusion across the polymeric network. Therefore, the higher is the postcuring temperature, the lower is the extent of hydrolytic aging of the VE polymer.

Hydrolytic attacks on specific chemical bonds, as indicated by the modifications in the ATR-IR spectra, are linked to the mechanisms of polymer degradation throughout the aging periods. In summary, as chain growth and crosslinking proceeds during post-curing, the radical's mobility decreases, the rate of monomer diffusion drops, and the reactive rate of chain growth decreases. Termination and chain transfer rates are also modified in complex ways. Some of the modifications depicted in Figs. 5 and 6 are consequently due to post-curing.
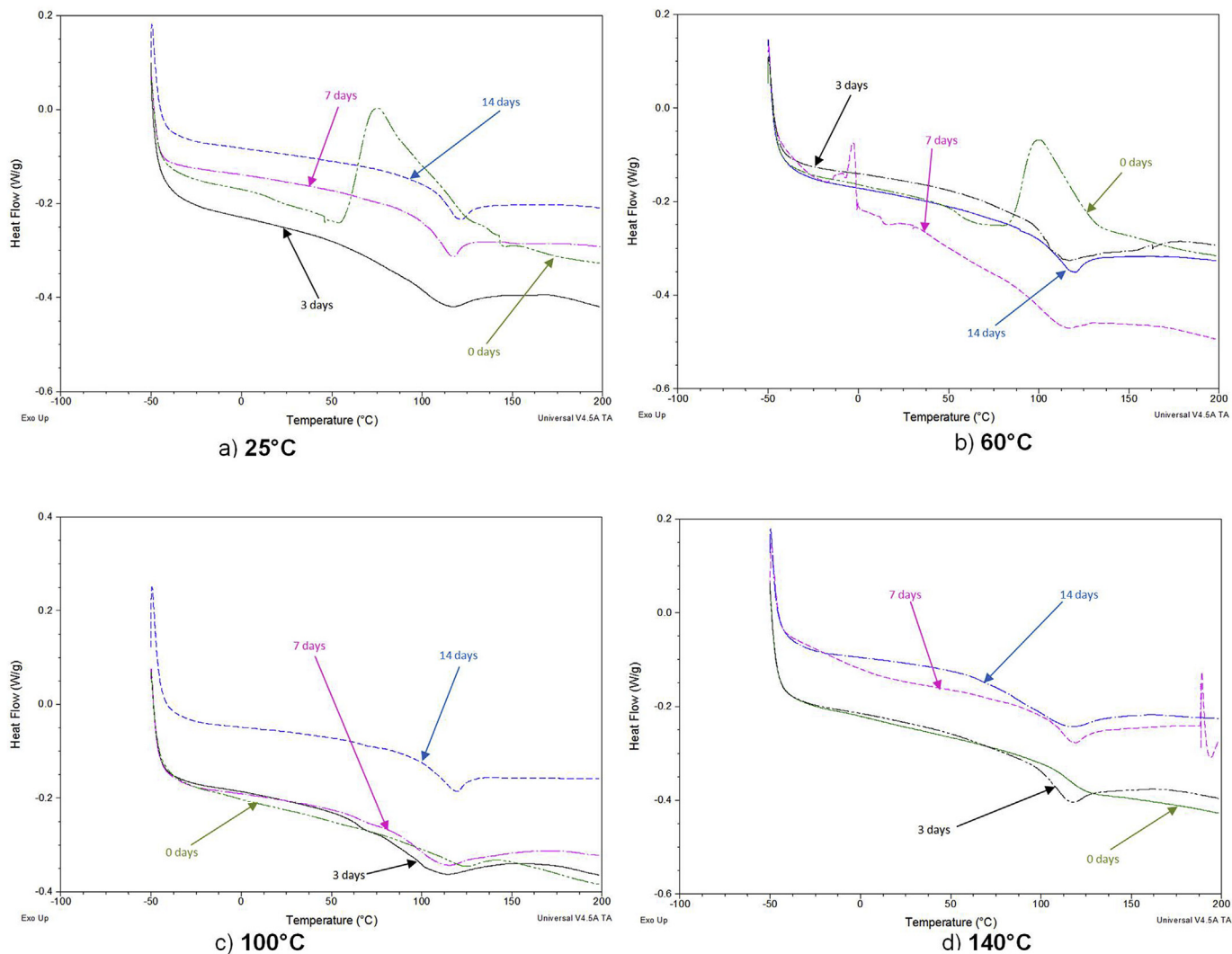
Fig. 7 shows the first DSC heating run of VE resins after three days of aging, each at different post-curing temperatures. Before aging, curing at 25 °C produces incomplete crosslinking, which presents as an exothermal reaction at 76 °C with a residual curing enthalpy of 68 J/g. From these DSC thermograms, it can be observed that by increasing the temperature (before aging in climatic chamber), additional curing of the VE resin occurs, as is evidenced by the existence of an exothermal process at higher temperatures and lower enthalpies as the post-curing temperature increases up to 100 °C. Curing at 140 °C shows one Tg at 115 °C that corresponds to the fully crosslinked VE resin. On the other hand, from the DSC thermogram at 25 °C, the exothermic peak evident before aging starts to disappear gradually as the aging time increases, and an endothermic peak appears. Exothermic processes completely disappear as the curing temperatures increase, showing that the curing reaction is complete.

The results after 3, 7 and 14 days of aging are shown in Table 2.
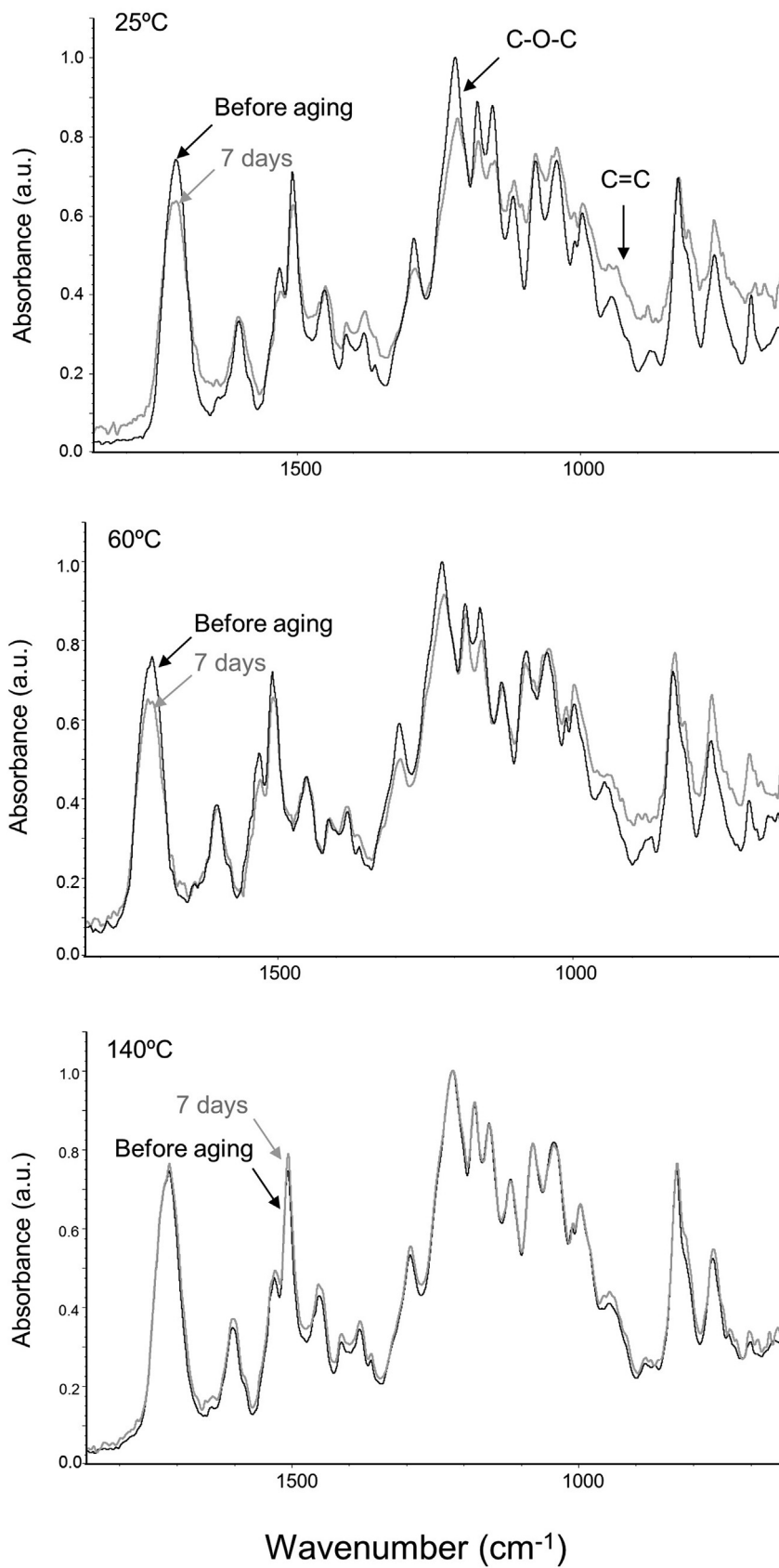
**Fig. 6.** ATR-IR spectra of VE samples cured at 25 °C and postcured at 60 and 140 °C for 1 h, before and after aging at 80 °C and 95% relative humidity during 7 days.

**Fig. 7.** DSC thermograms resulting from the first heating run of VE resin cured at 25 °C (a) and postcured at 60 °C (b), 100 °C (c) and 140 °C (d) after being aged at 80 °C for 3, 7 and 14 days.

Tg values from the first DSC heating cycle increase as the curing time increases due to crosslinking and the consequent reduction of the chemical reaction enthalpy. This effect is evident before the polymer ages. However, after 3 days of aging, resins cured at 25 °C and post-cured at 60 °C shift to higher Tg values, but resins that were cured at temperatures above 60 °C shift to decreased Tg values. Enthalpies decrease for every curing temperature when compared to the non-aged condition. After curing at 100 °C, Tg value first degrades and then remains constant at 7 and 14 days. However, for a fully crosslinked polymer (i.e., at a 140 °C curing temperature), Tg value reduces as the aging time increases.

In Fig. 8, it is shown that Tg value increases as the curing temperature increases, due to the crosslinking of the non-aged polymer. However, when the polymer has been aged for periods ranging from 3-14 days, the crosslinking does not proceed further, as indicated by a limited Tg value for every curing temperature. In Table 2, the parameters of the post-cured VE resin obtained from the first heating run in DSC thermograms are shown.

The residual heats of reaction were found to decrease as the isothermal temperature increased. This is in agreement with previous results showing residual heat to be a closely linearly dependent function of post-curing temperature. This behavior appears to be reasonable since the degree of cure generally increases with increasing temperature. However, for no-post-cured VE resin, Tg

**Table 2**
Parameters of the post-cured VE resin obtained from the first heating run DSC thermograms.

| Post-curing temperature (°C) | Before aging | | | 3 days | | | 7 days | | | 14 days | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Tg (°C) | ΔHc (J/g) | Tc (°C) | Tg (°C) | ΔHc (J/g) | Tc (°C) | Tg (°C) | ΔHc (J/g) | Tc (°C) | Tg (°C) | ΔHc (J/g) | Tc (°C) |
| 25 | 17 | 68 | 76 | 88 | 5 | 112 | 62 | 4 | 116 | 65 | 6 | 119 |
| 60 | 55 | 34 | 101 | 75 | 7 | 113 | – | 4 | 111 | 63 | 7 | 117 |
| 100 | 73 | 3 | 120 | 65 | 6 | 111 | 65 | 4 | 108 | 66 | 4 | 117 |
| 140 | 115 | – | – | 83 | 6 | 115 | 71 | 4 | 117 | 67 | 7 | 111 |
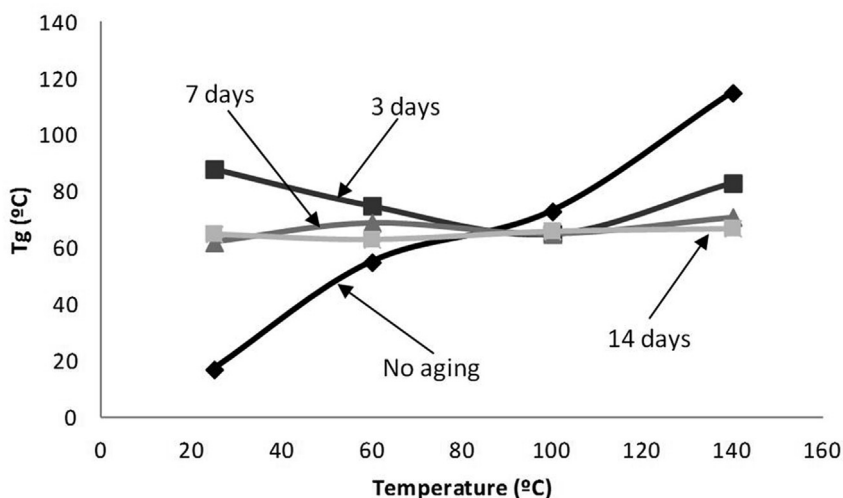
**Fig. 8.** Variation of the Tg values obtained from the first heating run DSC thermograms of VE resin cured at 25 °C and post-cured at different temperatures after being aged at 80 °C as a function of the post-cure temperature.

**Table 3**
Tg values obtained from the second heating run DSC thermograms of the VE resins post-cured and aged at different temperatures.

| Post-curing temperature (°C) | Tg (°C) | | | |
|---|---|---|---|---|
| | Before aging | After aging | | |
| | | 3 days | 7 days | 14 days |
| 25 | 110 | 108 | 106 | 113 |
| 60 | 117 | 110 | 108 | 110 |
| 100 | 118 | 101 | 105 | 111 |
| 140 | 117 | 109 | 114 | 107 |

value increases (17–88 °C) during the first 3 days of aging and then start decreasing. This can be interpreted as the result of a higher degree of cure and, at the same time, a minimum hydrolytic attack on the ester groups of the VE resin. For longer aging times, the absorbed water molecules increase the distance between the polymer segments resulting in an increase in chain mobility (or free volume) and thus a decrease in the Tg value. The same could be said for post-curing temperature of 60 °C, but changes is Tg value are

now much less important (55–63 °C).

Specimens post-cured at higher temperatures above that of aging conditions (80 °C) do not show an initial increment in Tg value. The maximum is obtained in dry condition, before aging, and then Tg value steadily decreases as the number of days in the weathering chamber increase. The residual heats of reaction are small, showing that curing was already completed after post-curing at 100 and 140 °C.

The Tg values obtained from the second DSC heating run of the VE resin samples are shown in Table 3. After a second DSC heating cycle, the Tg value for every curing temperature decreases irrespectively of the aging time. Even so, in Fig. 9, it is shown that Tg value is approximately constant after a DSC heating run for each aging duration.

The structural changes in the VE resins that are post-cured at different temperatures can also be evidenced in the derivative TGA thermograms (Fig. 10). There are four thermal decompositions, irrespective of the post-curing temperature. However, the peaks are shifted as the aging time increases. As the post-curing temperature increases, the weight loss associated to each thermal
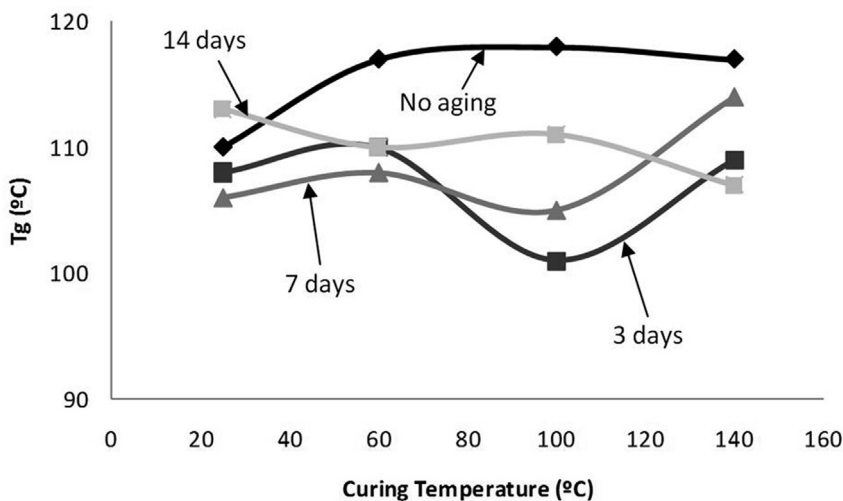


**Fig. 9.** Variation of the Tg values obtained from the second heating run DSC thermograms of VE resin cured at 25 °C and post-cured at different temperatures after being aged at 80 °C as a function of the post-cure temperature.
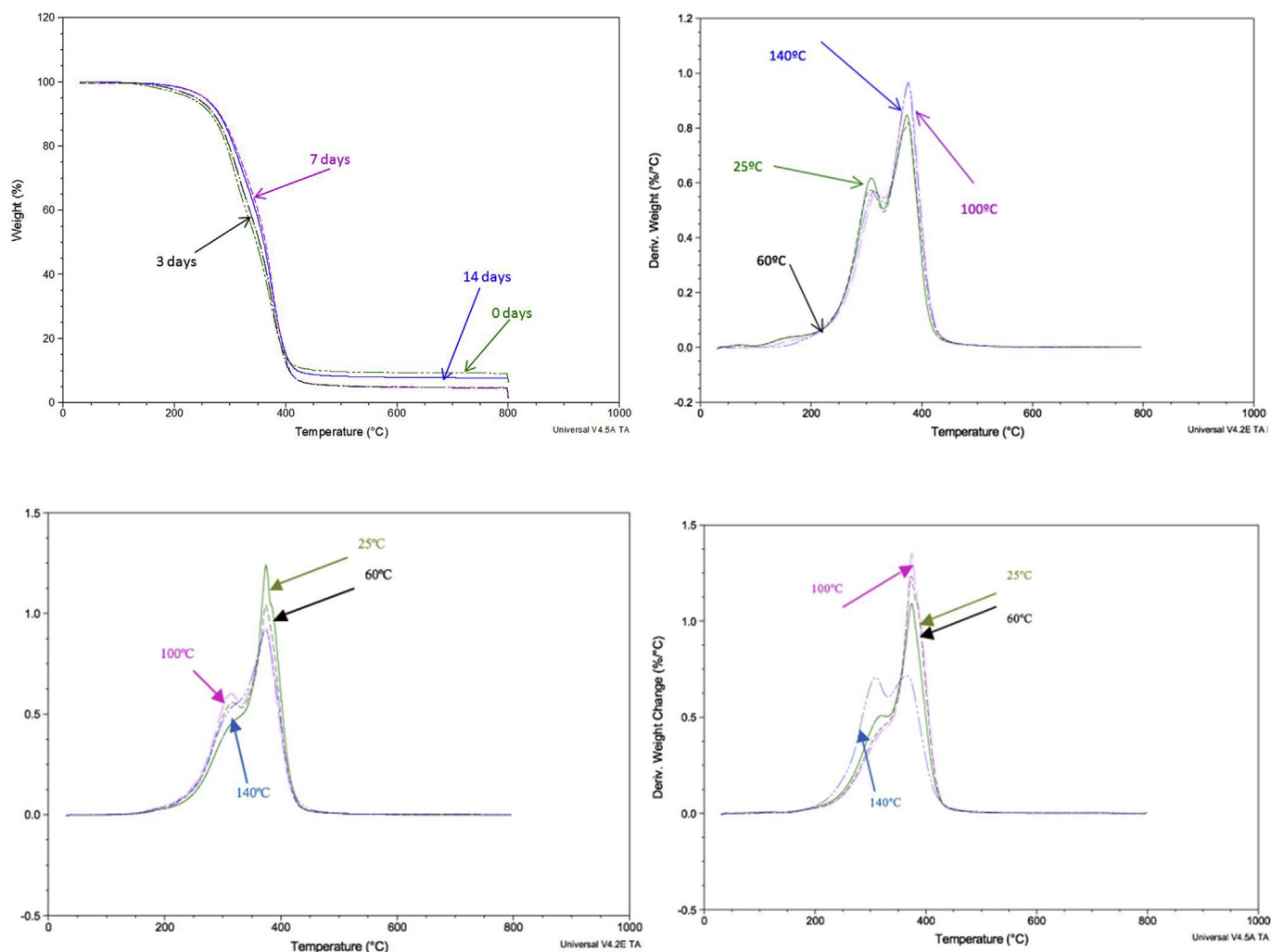
**Fig. 10.** Variation of the weight and the derivative of the weight as a function of the temperature of VE resin at different post-curing temperatures and aging times: (a) non post-cured VE resin; (b) after 3 days of aging; (c) after 7 days of aging; (d) after 14 days of aging.

decomposition decreases, and the weight variations can be associated to the unreacted styrene in the incompletely-cured VE resin. In Tables 4 and 5, some parameters from the TGA thermograms of the VE resin are shown at different curing temperatures. There is no influence of aging time on the four decompositions' temperatures. These are related to changes in the molecular structure that are unaffected by the hydrolytic processes during aging.

The effect of the post-curing temperature on the viscoelastic properties of the VE resin was studied using DMTA (Fig. 11). In Fig. 12, it is shown that increasing the curing temperature for specimens leads to variability in Tg value at several aging times (3, 7, 14 days and no aging), as indicated by DMTA. As the aging time in the climate chamber increases, Tg value decreases, as compared to the non-aged polymer (Table 6). The lowest point in the Tg value

occurs at 3 days of aging. However, after 7 and 14 days of aging, Tg remains almost constant at every curing temperature. The temperature levels out because water attacks the polymer chains mostly during the first few days, whereas there are no meaningful structural changes after one week in the climate chamber.

The changes in VE resin surface morphology as a result of aging in a 60 °C environment are shown in Fig. 13. The VE resin shows a smooth topography before aging due to poor crosslinking and gelation, whereas the fully crosslinked resin shows clear domain separation and evidence of roughness after 14 days. After 7 days of immersion, a viscous white layer and small voids appear on the sample surfaces. When the aging time is increased, the white layer becomes thicker and an increase in both the number and size of the voids can be clearly observed. As was observed previously to the

**Table 4**
VE resin decomposition temperatures obtained from the TGA thermograms.

| Post-curing temperature (°C) | Before aging | | | | 3 days | | | | 7 days | | | | 14 days | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 25 | 60 | 100 | 140 | 25 | 60 | 100 | 140 | 25 | 60 | 100 | 140 | 25 | 60 | 100 | 140 |
| Temperature of decomposition (°C) | 68 | 78 | — | — | 185 | — | 240 | 237 | — | — | — | — | 195 | 210 | — | — |
| | 149 | 162 | 160 | 227 | 315 | 317 | 314 | 311 | 192 | 192 | 187 | 226 | 317 | 319 | 319 | 309 |
| | 308 | 307 | 319 | 313 | 377 | 378 | 374 | 370 | 319 | 316 | 315 | 317 | 374 | 374 | 374 | 365 |
| | 373 | 376 | 375 | 375 | — | 391 | — | — | 374 | 374 | 374 | 374 | — | 384 | 387 | — |

**Table 5**
Weight loss of VE resins obtained from TGA thermograms.

| Post-curing temperature (°C) | Before aging | | | | 3 days | | | | 7 days | | | | 14 days | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 25 | 60 | 100 | 140 | 25 | 60 | 100 | 140 | 25 | 60 | 100 | 140 | 25 | 60 | 100 | 140 |
| Weight loss (%) | 100 | 99 | – | – | 98 | – | 95 | 96 | – | – | – | – | 98 | 98 | – | – |
| | 99 | 98 | 98 | 97 | 71 | 79 | 68 | 68 | 98 | 98 | 99 | 97 | 74 | 78 | 79 | 68 |
| | 71 | 71 | 70 | 72 | 29 | 40 | 29 | 31 | 75 | 71 | 71 | 72 | 35 | 39 | 41 | 31 |
| | 31 | 28 | 31 | 31 | – | 27 | – | – | 40 | 32 | 31 | 31 | – | 28 | 24 | – |
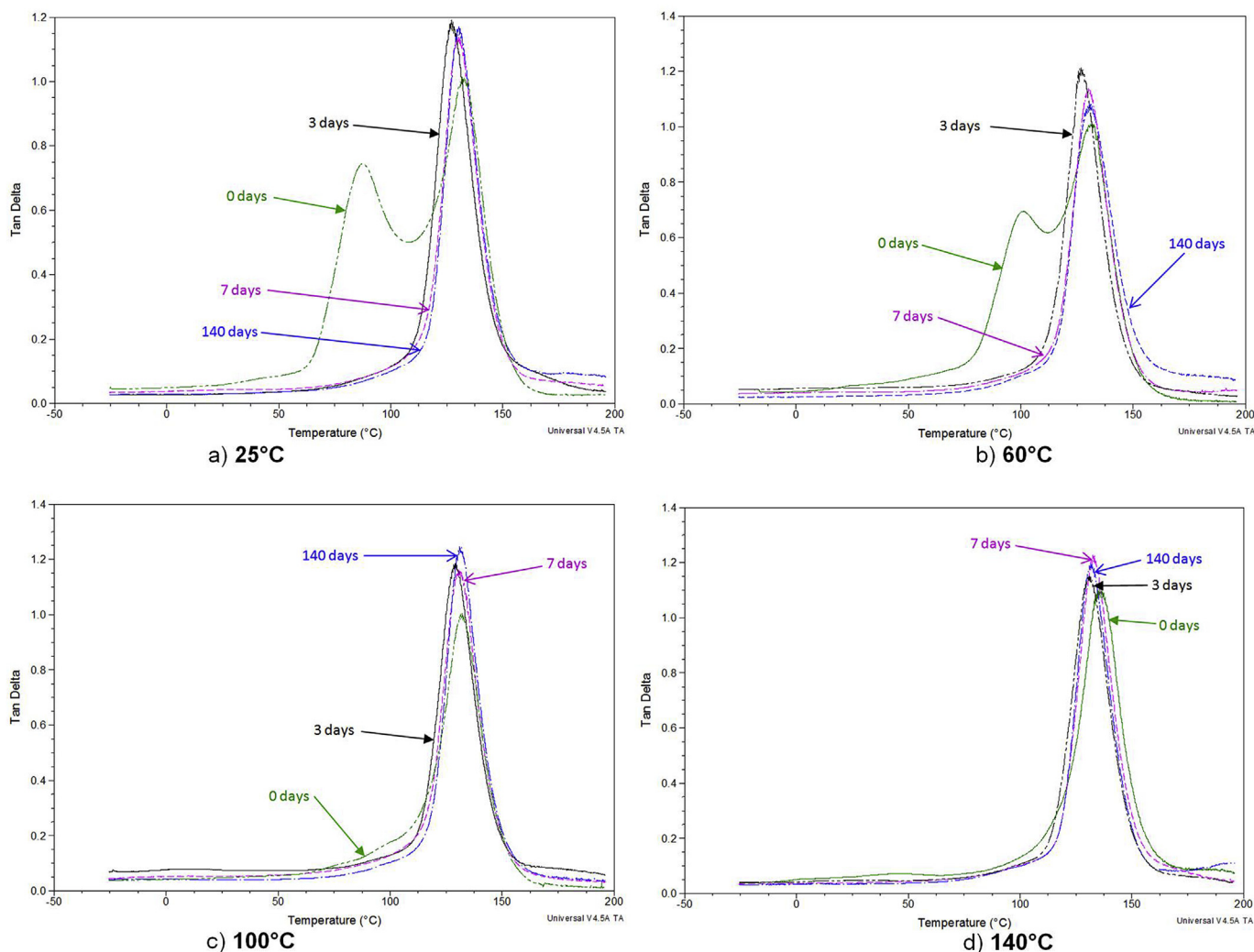


**Fig. 11.** Variation of the loss factor (tan δ) as a function of the temperature of the VE resin cured at 25 °C (a) and postcured at 60 °C (b), 100 °C (c) and 140 °C (d) after being aged at 80 °C for 3, 7 and 14 days.

aging, the surface is clear and smooth. Previous work [30—32] also reported similar changes in the aspect of several types of resins after water absorption. They observed the development of voids on the surface and inside the polymer, as well as simultaneous loss of resin in the process.

The tensile strength values of the VE resins post-cured at different temperatures are given in Fig. 14. Notably, with the curing temperatures up to 100 °C (i.e., below the Tg value), the aging time does not affect the behavior of the resin. However, for temperatures above Tg, loss of strength occurs with increasing aging time. After 14 days of aging, the resins have a beneficial boost tensile strength, making their mechanical properties similar to unaged polymers. At room temperature, a greater loss of tensile strength also occurs

with increasing aging time. At temperatures of 60 °C, when the resin is not completely cured, aging increases the mechanical properties of the resin.

Fig. 15 shows the shear strength—temperature curve. In the tests carried out, the load/displacement curves were linear until failure. The type of failure is determined visually. The rupture of adhesive joints is essentially mixed. Similar behavior to simple lap joints is observed. The specimens at curing temperatures of 25, 60 and 100 °C produced higher shear strength values without degradation. However, for temperatures above the Tg (i.e., fully crosslinked), the degradation time is not significant with regard to the strength of the adhesive bonds. It is also noted that the lower resistance values are after three days of aging, and yet after 7 and 14 days in the
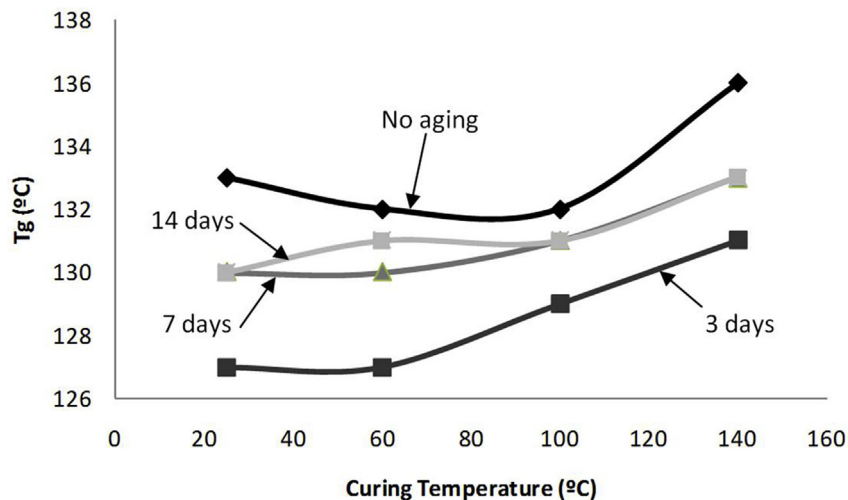
**Fig. 12.** Variation of the Tg values obtained from the DMTA plots of VE resin cured at 25 °C and post-cured at different temperatures after being aged at 80 °C as a function of the post-cure temperature.

**Table 6**
Tg obtained from the DMTA thermograms of VE resins that were both post-cured and aged at different temperatures.

| Post-curing temperature (°C) | Tg-Before aging (°C) | Tg-3 days aging (°C) | Tg-7 days aging (°C) | Tg-14 days aging (°C) |
|---|---|---|---|---|
| 25 | 133 | 127 | 130 | 130 |
| 60 | 132 | 127 | 130 | 131 |
| 100 | 132 | 129 | 131 | 131 |
| 140 | 136 | 131 | 133 | 133 |



a) Before aging

b) 3 days

c) 7 days
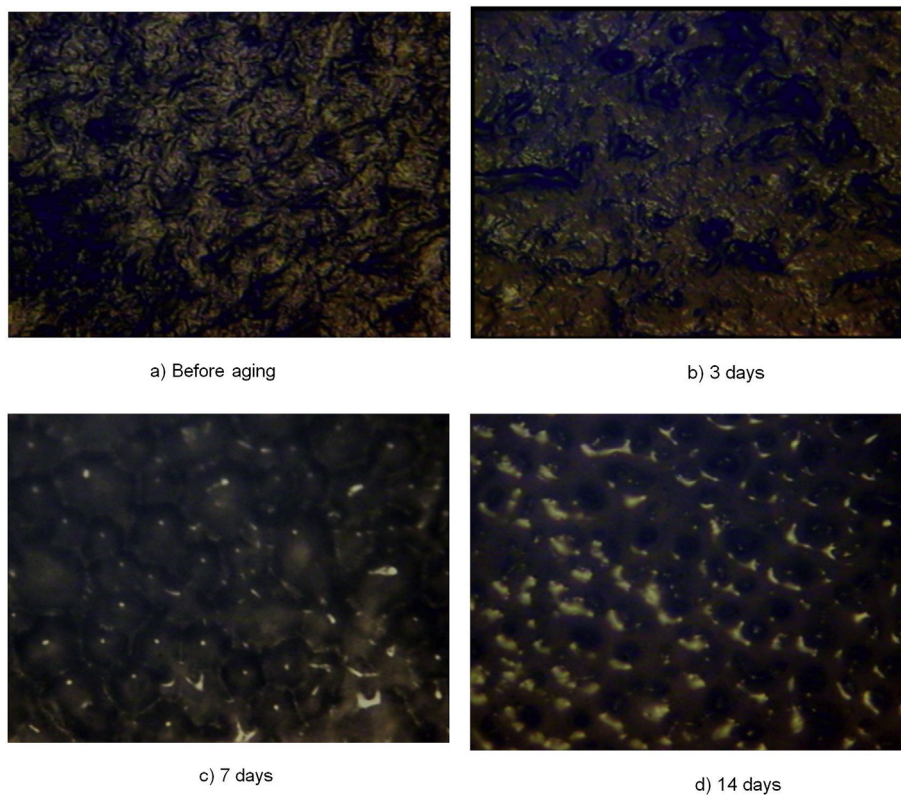
d) 14 days

**Fig. 13.** Optical micrographs of the VE resin surface postcured at 60 °C and aged at 80 °C for 3, 7 and 14 days. Magnification: 5X.
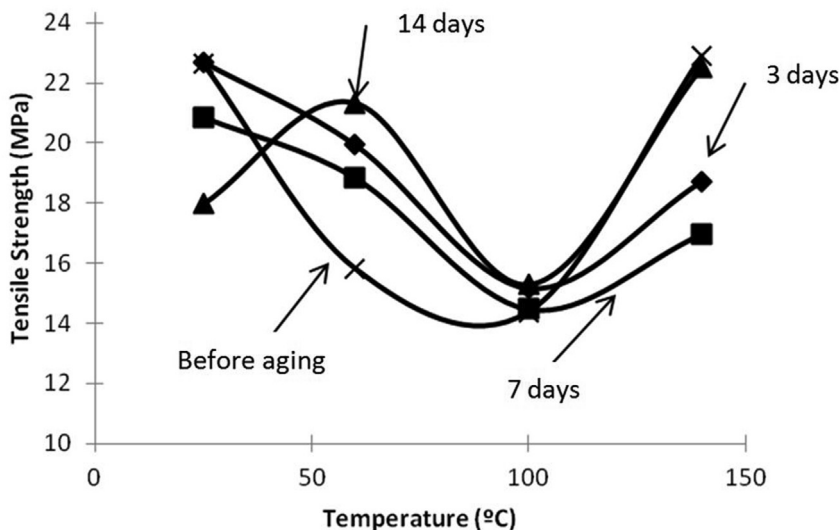
**Fig. 14.** Variation of the tensile strength values as a function of the post-curing temperature for VE resin post-cured at different temperatures and aged at 80 °C for 3, 7 and 14 days.
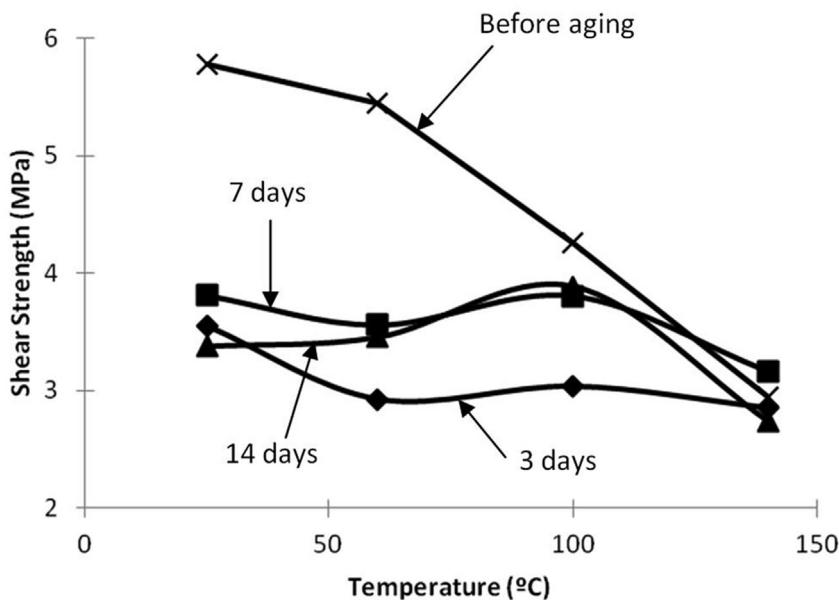


**Fig. 15.** Variation of the single lap-shear strength values of stainless steel/VE resin joints as a function of the post-curing temperature for VE resin postcured at different temperatures and aged at 80 °C for 3, 7 and 14 days.

climate chamber, the mechanical properties of the VE resin improve, due possibly to hydrolytic effects.

## 4. Conclusions

Chemical and structural changes are observed in VE resins after aging in a climatic chamber. Upon aging, a hydrolytic attack of the ester group of the VE polymer is produced, as indicated by modifications in the ATR-IR, and it is linked to the mechanisms of degradations in the polymer throughout the aging periods. Most of the modifications occur within the first 3 days. This is a well-known effect related to the diffusive behavior of water in polymers. The initial rate of water intake is quite high but it starts to decrease as the water diffusing from the outer surface of the specimens need to go through an increasingly thicker layer of water saturated polymer. For the first 3 days the hydrolytic degradation rate is controlled by the kinetics of water molecules attack on ester groups. As aging proceeds, the diffusive process takes the leading role and most of the time is taken by the water traveling through the polymer network. Once the water arrives to non-soaked material the hydrolytic attack stars.

Tg value increases as the post-curing temperature increases, due to the crosslinking of the non-aged polymer. However, when the polymer has been under aging periods ranging for 3–14 days, the crosslinking does not proceed further. Thus, Tg value reaches a limit value for every curing temperature. On the other hand, TGA results show that aging time does not influence the four decomposition temperatures of VE polymer. These are instead related to changes in the molecular structure during aging that are unaffected by the hydrolytic processes.

The mechanical properties decrease with aging temperatures 25 to 140 °C. However, at a temperature near the Tg, no mechanical property changes occur as aging time increases. Finally, the aging decreases the shear strength of single-lap shear joints, but at temperatures above the Tg (i.e., completely cured VE resin), there are no differences in the mechanical properties.

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