



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

Cristina Alia^a, José A. Jofre-Reche^b, Juan C. Suárez^a, José M. Arenas^{a,*},
José M. Martín-Martínez^b

^a Universidad Politécnica de Madrid, Structural Materials Research Centre (CIME), 28040 Madrid, Spain

^b Adhesion and Adhesives Laboratory, University of Alicante, 03080 Alicante, Spain

ARTICLE INFO

Article history:

Received 6 May 2017

Received in revised form

19 March 2018

Accepted 9 April 2018

Available online 14 April 2018

Keywords:

Vinyl ester resin

Thermal degradation

Adhesion

Mechanical characterization

Electron microscopy

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.

© 2018 Elsevier Ltd. All rights reserved.

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 (T_g) 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 crosslinking depended on the post-curing temperature; curing completed when post-curing above 100 °C, a temperature close to the T_g of the completely cross-linked polymer (115 °C). To fully

* Corresponding author.

E-mail address: josemanuel.arenas@upm.es (J.M. Arenas).

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%,

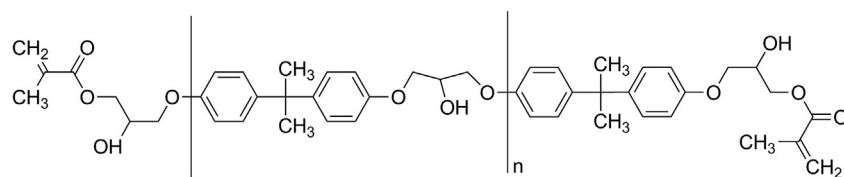


Fig. 1. Chemical structure of the vinyl ester resin monomer.

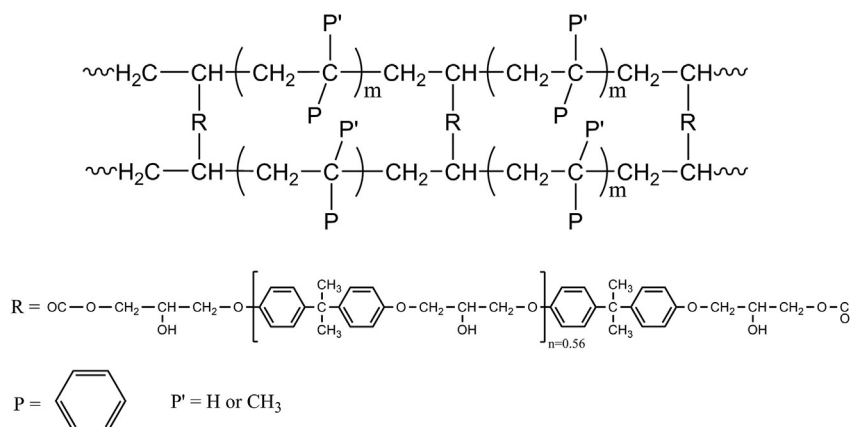


Fig. 2. The structure of the vinyl ester/reactive diluent network.

Download English Version:

<https://daneshyari.com/en/article/7823972>

Download Persian Version:

<https://daneshyari.com/article/7823972>

[Daneshyari.com](https://daneshyari.com)