International Journal of Adhesion & Adhesives 61 (2015) 99–111

Contents lists available at ScienceDirect

International Journal of Adhesion & Adhesives

journal homepage: www.elsevier.com/locate/ijadhadh

Post-curing process and visco-elasto-plastic behavior of two structural adhesives

Ignacio-Alberto Estrada-Royval, Alberto Díaz-Díaz *

Centro de Investigación en Materiales Avanzados, S.C. Miguel de Cervantes 120, Complejo Industrial Chihuahua, Chihuahua 31109, Mexico

ARTICLE INFO

Article history:
Accepted 29 May 2015
Available online 6 June 2015

Keywords:
Epoxides
Thermal analysis
Glass transition temperature
Mechanical properties of adhesives

ABSTRACT

The aim of this paper is to reveal original visco-elasto-plastic phenomena for two commercial epoxy adhesives (D609 and E20HP) subjected to uniaxial tension and compression. First, a post-curing heat treatment is proposed by means of thermal analyses in order to ensure stable mechanical properties. Bulk adhesive specimens are prepared to analyze the mechanical response of both materials. Monotonic tensile and compressive tests are carried out at different strain rates. Both adhesives exhibit first a linear elastic behavior but once a yield stress is reached, a visco-elasto-plastic behavior appears. Creep tensile tests are also carried out and confirm that strain rate phenomena take place and that non-negligible negative volumetric inelastic strains appear. Cyclic tests are also performed and reveal ratcheting effects. The applicability of the results to thin bondlines is discussed. The experimental observations must be taken into account in any model which aims at predicting accurately the behavior of the adhesives considered in this paper.

1. Introduction

Adhesive joints represent great advantages over other assembly techniques and their applications are increasing every day. In order to optimize the design of this type of joints, it is important to know the adhesive behavior up to failure. Generally, this behavior is nonlinear because of phenomena such as plasticity [1], damage [2] and visco-elasto-plasticity [3]. Several experimental and theoretical studies focused on the non-linear behavior of polymers and adhesives have been published. Wang and Chalkley [4] carried out modified Iosipescu tests (multiaxial testing) with specimens of a commercial adhesive, and showed that a Drucker–Prager-type modified function adequately predicts yielding. By means of modified ARCAN tests, Cognard et al. [5] studied the elastoplastic behavior of another commercial epoxy adhesive at low temperatures to minimize the effects of viscosity. It was demonstrated that the hydrostatic stress has an effect on the non-linear behavior of the adhesive. On the other hand, it is worth stating that, for some adhesives, the loading rate may affect the mechanical response at room temperature [6]. For example, Pap et al. [3] tested under tension and compression, a commercial adhesive, put in evidence a strain rate-dependent behavior, and used a linear viscoelastic model which failed to correctly predict the behavior because it did not include plasticity. In [7], Cognard et al. tested another commercial epoxy adhesive at room temperature by means of modified ARCAN cyclic tests, and at different rates. It was demonstrated that the behavior of the studied adhesive was visco-elasto-plastic.

The visco-elasto-plastic behavior of polymers has been widely studied but a general 3D model validated by 3D tests has not been yet developed. This is surely due to a lack of experimental data. Drozdov has developed 1D visco-elasto-plastic models based on uniaxial tensile tests and which predict accurately axial strains and stresses for several polymers [8–11]. Mahnken et al. developed a 3D visco-plastic model for a glassy polymer and compared its predictions to the axial strains and stresses in uniaxial tensile and compressive monotonic tests carried out at different strain rates [12]. This model reproduced well the experimental asymmetry: maximum stresses in compression were higher than those in tension. Chaboche [13] and Poulain et al. [14] also developed 3D viscoplastic models but only confronted their predictions to the axial strains and stresses in uniaxial tensile and compressive monotonic tests. In fact, the measurement of the transverse strains is seldom reported and without it, a full description of the strain state cannot be achieved. This measurement not only provides a Poisson's ratio but also valuable information about inelastic volumetric strain rates which may help, for example, to test the accuracy of a von Mises-type yield criterion that predicts, in the case of associative plasticity, a zero volumetric strain rate [15].

It is important to note that the mechanical characterization of a thermosetting adhesive cannot ignore a thermal study of the adhesive and its curing. Remaining chemical reactions may occur

* Corresponding author. Tel.: +52 614 4394802.
E-mail address: alberto.diaz@cimav.edu.mx (A. Díaz-Díaz).

http://dx.doi.org/10.1016/j.ijadhadh.2015.06.001
0143-7496/

after curing and the mechanical properties may vary with time and temperature [16]. A post-curing heat treatment at a moderate temperature above the glass transition temperature (Tg) may help to achieve the thermal stability of the polymer [17]. Care must be taken in the selection of the post-curing temperature because if it is too high, it may cause a degradation of the mechanical properties of the polymer [16,18]. Several authors suggest and apply a post-curing heat treatment to adhesives in structural assemblies and resins in dental applications to ensure stable mechanical properties and to improve them [19–21]. For example, Cognard et al. [22] proposed a post-curing process of 50 °C during 4 h for aluminum adhesive joints using an epoxy adhesive (Vantico Redux 420). In spite of the publications involving post-curing heat treatments to adhesives, little or no information of the procedure adopted to select the temperature and duration of the treatment is provided.

In this document, the mechanical response of two commercial epoxy adhesives is studied. Uniaxial tensile and compressive tests are performed at room temperature. A post-curing heat treatment is developed and proposed to achieve stable mechanical properties. The effect of the temperature reached during curing on the properties of the adhesives and the applicability of the experiments in this paper to adhesive joints are discussed. The mechanical tests performed are monotonic at different strain rates, of creep- and cyclic-type. Axial and transverse strains are measured to provide a full description of the strain state in the specimens. In the mechanical tests, visco-elasto-plastic phenomena which have not been reported previously for thermosetting polymers are put in evidence. For example, the volumetric inelastic strains are non-negligible and volumetric strains may be negative in tensile tests. Negative volumetric strains in uniaxial tension have not been reported for epoxy polymers [23], but only for thermoplastic polymers such as polyvinylidene fluoride in large strains in a rubbery state [24,25] and polycarbonate in a glassy state [26]. Taking into account the experimental observations, recommendations are made for future models aimed at predicting correctly the mechanical behavior of epoxy adhesives.

In this article, the materials and methods used are presented first. The results are provided later. Then, a discussion of these results is presented with an emphasis on the new elements provided by the research presented herein. The conclusions of this work are presented at the end of the document.

2. Materials and methods

2.1. Materials

The epoxy adhesives studied are D609 and E20HP, both fast curing two-component structural adhesives from Hysol line by Henkel. These adhesives are recommended to be used with metals, polyester, glass, wood, etc. The manufacturer recommends a curing temperature of 25 °C for 24 h for both adhesives. D609 is recommended for applications at low temperatures and, as for E20HP, there is no recommendation on the working temperatures in the specifications but a graph is provided, showing that the strength of an adhesive joint with aluminum decreases as the temperature increases from 25 °C, approximately. The Tg is only provided for E20HP: 60 °C.

The manufacturer indicates that the D609's resin is composed of epichlorohydrin-4,4′-isopropylidene diphenol, while the E20HP's resin contains acrylic polymers. The D609's hardener consists of a polymercaptan and a tertiary amine. The E20HP's hardener consists of polyamine, polyglycol diamine, salicylic acid, glycerol, aminophenol, diethyleneglycol monoethyl ether and ethylene glycol. Each two-component adhesive is contained in a cartridge. A mixing nozzle is used with the cartridge to apply the mixture of resin and hardener. The mechanical properties of adhesives depend on the curing condition and degree. According to the manufacturer, both adhesives (D609 and E20HP) have a maximum strength after having cured for 24 h at 25 °C. However, there is no guarantee whatsoever that under these conditions, all reactions will be completed and that the mechanical properties will remain stable after being subjected to temperature variations [16]. In this sense, in this work, the choice has been made to determine a post-cure heat treatment. It would have been possible to think of a curing at a higher temperature, but this method was discarded because of the advantage of handling and curing an adhesive within an adhesive joint at room temperature.

2.2. Post-curing heat treatment

This treatment is aimed at stimulating the remaining reactions within the adhesive specimens cured at room temperature in order to achieve a nearly complete curing and stable mechanical properties. This section describes the procedures to determine the temperature and post-curing time for adhesives cured at 25 °C for 24 h.

For each adhesive, we began by carrying out a thermogravimetric analysis (TGA) of the resin, the hardener and the cured adhesive so as to verify that the constituents do not experiment degradation and determine up to which temperature level it is possible to execute the post-cure treatments without degrading the adhesive. One repetition was considered and the heating rate employed was 10 °C/min. Later on, in a differential scanning calorimeter (DSC), analyzing the heat power per unit mass, the adhesives were monitored at 25 °C, to verify the curing time proposed by the manufacturer (one repetition per adhesive was performed). Then, on the same device, a temperature scanning was performed with cured samples in order to verify that there are remaining exothermic reactions. Subsequently, in the DSC, cured samples were subjected to constant temperatures (50 °C, 60 °C, 70 °C, 80 °C, 90 °C, and 100 °C) to select the time and temperature for the post-curing treatment. Finally, the post-cured samples were subjected to a temperature scanning in the same device in order to verify that, virtually, there is no remaining reaction that may be stimulated by a temperature increase. This temperature scanning also made possible to make a first estimation of Tg. It is worth stating that temperature scannings in the DSC were made at a heating rate of 5 °C/min from −50 °C up to 140 °C.

A second estimation of Tg was provided by a dynamical mechanical analysis (DMA) and a temperature scanning. The samples intended for this technique were obtained by pouring the adhesive in urethane molds at room temperature and, after the curing, a heat treatment was applied with the parameters determined by the DSC. Afterwards, the faces were rectified in a milling machine to obtain specimens which are 12 mm wide, 3 mm thick, and 50 mm long. A three point flexural test was carried out with a 44 mm span length. The test frequency and amplitude were 1 Hz and 4.5 N, respectively. A 6 N-preload was used to ensure that the specimen was always in contact with the supports. The dimensions and applied loads yield a 6.41 MPa maximum flexural stress which, at room temperature, does not cause plastic strains in quasi-static monotonic tests (see Section 3.2). The temperature range was from −30 °C to 100 °C at a heating rate of 5 °C/min. One test per adhesive was carried out.

2.3. Uniaxial mechanical testing

Uniaxial tension and compression tests were performed in an electromechanical machine Instron 3382 to study the mechanical behavior of the adhesives and analyze a potential asymmetry. In