Thermochimica Acta 604 (2015) 52–60

Contents lists available at ScienceDirect

Thermochimica Acta

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

Kinetic analysis and characterization of an epoxy/cork adhesive

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ARTICLE INFO

Article history:
Received 19 November 2014
Received in revised form 27 January 2015
Accepted 29 January 2015
Available online 30 January 2015

Keywords:
Thermosetting resin
Curing process
Kinetics
Cork micro-particles
Differential scanning calorimetry

ABSTRACT

Epoxy resins are the most common structural adhesives due to their good mechanical, thermal and chemical properties. However, the structure of these thermoset polymers, due to the high crosslinking, also causes brittleness, with a low resistance to the initiation of cracks and their propagation. The inclusion of particles (nano or micro) is a common method to improve the mechanical properties such as toughness of structural adhesives. In the present study, natural micro particles of cork were used to increase the toughness of a brittle epoxy adhesive. The main objective of this research was to investigate the effect of the amount of cork particles in the cure reaction of a brittle epoxy, knowing that the amount present influences the mechanical properties. This study was developed using specimens with 0.5, 1, 2 and 5% (volume) of cork and without cork, as reinforcement material of a brittle resin. In general the cork particles do not influence the curing process, although they slightly change the curing mechanism. Also, cork particles decrease the glass transition temperature (T_g) and have a plasticizer effect in the epoxy resin.

1. Introduction

One of the most common structural adhesive is the epoxy resin, due to its good mechanical, thermal, adhesion and chemical properties. The densely cross-linked molecular structure of structural adhesives is responsible for the good properties of these materials, but unfortunately it also makes them inherently brittle (low ductility and toughness) with poor resistance to crack propagation [1,2]. Epoxy resins are the most important thermosetting polymers widely used as matrices in reinforcement composites. Most of the commercially available are oligomers of diglycidyl ether of bisphenol (DGEBA) [3,4].

Polymer composites, such as brittle resins with micro cork particles [5,6], are made of reinforcing particles in an embedded brittle epoxy matrix. However, the ratio between particles/epoxy and the effect of the interface present a major influence on the mechanical behaviour of the composite and on the cure conditions [7]. The effect of particles in the curing process of an adhesive will vary according to the nature of these same particles. There are studies showing that the addition of boron carbide particles in an adhesive does not affect the degree of conversion. However, the particles can act as an accelerator or retarder of the reaction [8]. Erdogan et al. [4] studied the same effect with zeolite particles and concluded that the cure rate was increased by the addition of zeolite. Zeolite particles act as catalyst for epoxy systems. Zuiderduin et al. studied the toughening of polypropylene with calcium carbonate particles and concluded that $CaCO_3$ particles do not act as a nucleating agent in polypropylene since the crystallinity is not increased [8]. Also, Abenojar et al. studied the boron effect in low density polyethylene [9]. In this case the crystallinity and melting temperature increase with boron content.

It is well known by the scientific community that the physical properties of cured epoxy resins depend on the structure [10,11], time and temperature of cure [12–15]. Therefore, it is of major interest to know and understand the relationship between the mechanical properties and the structure network, in order to obtain composites with high performance application [3,5,16,17]. The curing of epoxy resins involves the transformation of monomers or pre-polymers with low molecular weight into 3D structure networks. In the polymer curing process, the glass transition temperature (T_g) of the material increases as a consequence of the increases in the cross-linking density [6]. T_g is a very important property of an adhesive, and is very useful to make the link between the mechanical properties and the cure process.

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http://dx.doi.org/10.1016/j.tca.2015.01.025
0040-6031/

There are several methods to analyse the cure kinetics of epoxies, such a magnetic resonance spectroscopy (NMR) and high pressure liquid chromatography (HPLC) [18–20], Fourier transform infrared spectroscopy (FTIR) [20], and in special differential scanning calorimetry (DSC) [21–24].

The main objective of this research was to investigate the effect of the amount of cork particles in the cure reaction and thermal properties of a brittle structural adhesive. Since, besides changing the mechanical properties of the resin, the cork could modify the crosslinking process and curing mechanism. Also the amount of cork added to the resin could. This study was developed using specimens with 0.5, 1, 2 and 5% (volume) of cork and without cork, as reinforcement material of a brittle resin. The curing process was achieved using DSC and FTIR measurements. The mechanical properties of the modified epoxy were carried out by tensile test.

2. Experimental procedure

2.1. Materials

The selected adhesive was Araldite 2020, from Huntsman Advanced Materials (Pamplona, Spain). This is a two component adhesive (100/30 by weight), low viscosity (150 mPa s), transparent epoxy adhesive that cures at 100 °C, within 15 min. Component A, the epoxy resin, is composed by diglycidyl ether of bisphenol A, (DGEBA) and diglyciddyl ether of 1,4-butanediol (DGEBOH). On the other hand, component B (hardener) is composed by isophorone diamine (IPDA)

Cork powder with 125–250 μm size was used. The cork used was supplied by Amorim Cork Composites (Mozelos, Portugal), without any treatment. Specimens with different amount of cork particles (neat, 0.5, 1, 2 and 5% in volume) were manufactured.

The cork was initially mixed with the resin using a centrifuge mixing machine, SpeedMixer DAC 150^{TM} by Hauschild Engineering (Hamm, Germany), for 90 s at 1500 rpm. Then, cork was mixed with the resin and after that the hardener was added to the mixture. This procedure was the same for the different amounts of the cork. However, a sufficiently uniform distribution of the cork particles was not reached, due the low density of the cork particles and the adhesive low viscosity. In order to obtain a better particle distribution after mixing, the composite was heated to 50 °C during 15 min, to increase the adhesive viscosity. After this procedure, the composite was mixed again in the centrifuge mixing machine. This procedure permitted to obtain a uniform particle distribution.

After mixing the cork particles with the resin and hardener, the mixture was cast in a pre-heated steel mould. Release agent was applied to the mould to ensure easy release of the bulk specimen. A silicone rubber frame was used to apply a hydrostatic pressure to the adhesive, which was hot pressed (2 MPa) for 15 min at 100 °C (according to the manufacturer's recommendation cure schedule [25]). Specimens were machined from the plates manufactured with the mould. This manufacturing technique was used to produce the specimens used for FTIR and DSC (cured specimens).

2.2. Differential scanning calorimetry (DSC)

To analyse the cure kinetics of specimens with and without cork particles a DSC machine supplied by Mettler Toledo GmbH (Greifensee, Switzerland) was used. Aluminium crucibles of 40 μl, with around 7.5 mg of the composite or neat resin for each test were used. Nitrogen was used as purge gas, at 80 ml/min. Isothermal tests of 30 min, at different temperatures (70, 85 and 100 °C), were chosen; a second segment of dynamic scanning from the isothermal temperature to 200 °C at a scan rate of 5 °C/min was added. This way the total heat of reaction was calculated. Two tests were performed for each condition. Non-isothermal (dynamic) tests were also carried out at different heating rates (5, 10 and 20 °C/min) from 0 at 200 °C.

2.2.1. Operational method

Three methods were compared in the study of the kinetics and the activation energy of the curing reactions. The evaluation of the kinetic parameters was carried out by the empiric method. Through the isothermal DSC curves of curing, it is possible obtain the reaction rate curves. Thereafter, the experimental data were adjusted to a model for heterogeneous reactions, using kinetic equations called autocatalytic or *n*-order. The autocatalytic mechanism is characterized by a maximum reaction rate at about 30–40% reaction curing progress. In these models, the kinetic parameters do not have physicochemical interpretation in many cases and are fitting parameters. For the calculation of the kinetic parameters, the Kamal's method was used [26], according to Eq. (1) where the two mechanisms are included:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1-\alpha)^n \quad (1)$$

In this equation, α and t represent the conversion degree and time, respectively; n and m represent the reaction order and the total reaction order is the sum of them; k_1 and k_2 are the rate constants of the n-order and autocatalytic reaction, respectively [27].

Taking into account that two mechanisms were considered, two rate constants were obtained. In the stages where the chemical kinetics controls the reaction, the rate constants show an Arrhenius type dependence with temperature, as shown in Eq. (2).

$$K = Ae^{-\frac{E_a}{RT}} \quad (2)$$

The kinetics parameters of the curing process can also be examined with isoconversional methods utilizing other empiric models such as those of Flynn–Wall–Ozawa and Friedman used by Zhao et al. [28] in a study of epoxy novolac resin and modified with methanol etherified amino resin. Each model requires different representations and equations, but in all of them at the end an activation energy of the process is obtained. In the present study, the method of Kamal was chosen to have information on the autocatalytic mechanism of the curing reaction.

With non-isothermal (dynamic) tests, the reaction kinetic can also be calculated. The model free kinetic (MFK) [29,30] was used. MFK is based on at least three temperature scans at different rates. This option gives reliable predictions about conversions of reactions under simulated conditions and delivers an activation energy which depends on the degree of conversion. In this study, STARe Software of Mettler Toledo GmbH (Greifensee, Switzerland) was used. The model-free methodology has long proved useful to obtain reliable kinetic information on many different processes. The fundamental assumption of the model-free method is that the reaction model $f(\alpha)$ is not dependent on temperature or heating rate. MFK can be used for epoxy [31] and phenolic resins [32], in curing and degradation processes [33], and in isothermal and non-isothermal curing processes [32,34]. Other empirical models can be used for dynamic kinetic studies such as Kissinger and Flynn–Wall–Ozawa models. For example, Wang et al. [35] used these models for the kinetic study of nanocomposites of carboxyl-modified multi-walled carbon nanotubes/epoxy.

2.2.2. Measurement of the glass transition temperature (T_g)

T_g measurements were carried out by use of a Mettler Toledo GmbH apparatus T_g/DSC (Greifensee, Switzerland). A heat rate of 10 °C/min and 6 mg of composite or neat resin were used, from −20 °C to 200 °C. Two tests were performed for each