



Polymerization and curing kinetics of furan resins under conventional and microwave heating



Unai Lopez de Vergara^{a,b,*}, Mariasun Sarrionandia^b, Koldo Gondra^a, Jon Aurrekoetxea^b

^a Plastics and Composites Department, Gaiker IK4 Research Centre, Parque Tecnológico, Ed. 202, 48170 Zamudio Spain

^b Mechanical Engineering and Industrial Manufacturing Department, Mondragón Unibertsitatea, Loramendi 4, 20500 Mondragón Spain

ARTICLE INFO

Article history:

Received 2 December 2013

Received in revised form 18 February 2014

Accepted 20 February 2014

Available online 28 February 2014

Keywords:

Furan resin

Renewable polymer

Kinetics

Polymerization

Microwave curing

ABSTRACT

The challenge of this work is the microwave curing study of low free-furfuryl alcohol content furan resins. The chemical characterization of the furan resins has been made by infrared spectroscopy and nuclear magnetic resonance spectroscopy. The chemical composition of the resin and its reactions with *p*-toluenesulfonic acid are proposed, with the aim of understanding the mechanism responsible for the main reactions. The results show the presence of methyl and ether bridges between the furan rings, and the formation of ketone and conjugated structures. Furthermore, the curing kinetics of the furan resins has been characterized by differential scanning calorimetry. Different methods have been applied in order to obtain and compare the activation energy of the process. Vyazovkin numerical analysis was found the most accurate method. Finally, microwave and conventional curing processes has been compared. The analysis showed that microwave curing of furan resins was twice faster than thermal curing.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Fiber reinforced polymer composites have gained substantial interest over the last years, mainly due to their high specific stiffness and strength, high impact energy absorption per unit of weight, noise suppression capabilities and excellent resistance to fatigue [1,2]. However, for composites to be extensively used, environmental-friendly materials and cost-effective manufacturing processes should be developed [3].

The dwindling of the fossil resources and their unpredictable price have increased the interest on developing renewable feedstock for new polymers [4]. Furan resin is one of such polymer [5–7], especially for replacing the most widely used phenolic resins in fire applications. In furan resin the toxic formaldehyde of the phenolic is replaced by the furfural. So, it could be possible to reduce the environmental impact since furan can be synthesized from renewable resources [8] and reduces formaldehyde emissions.

As a new and effective way of heating, microwave (MW) technology was found to be a viable alternative method for the curing of thermoset polymers, with the advantages of shorter processing time, improved energy efficiency, and the potential of lower

processing temperature and improved product performance [9,10]. The microwave energy is transferred directly to the materials, through a molecular dielectric interaction with the electromagnetic field, generating the heat throughout the entire material volume simultaneously. Furthermore curing can take places with a cold mold, so faster heat transfer and lower temperatures during processing can be achieved [9–16]. Furan resins are particularly attractive for this type of curing due to its high hydroxyl group and water content, but there is no published works related to the microwave curing of this kind of composite, so the present paper aims to fill this knowledge gap. So, the scope of the present work is to study the microwave curing mechanisms and kinetic of furan resins, comparing then to those of the conventional thermal method.

2. Experimental

2.1. Materials

The furan resin employed, coded as FuroLite, is developed by Transfurans Chemicals (Belgium), which principal characteristics are: $\mu = 200\text{--}400$ cP, $\rho(20^\circ\text{C}) = 1.21$ g cm⁻³, M_n (Da) = 139, PDI (M_w/M_n) = 2.33. The used cure agent is *p*-toluenesulfonic acid catalyst coded as S-type catalyst (Transfurans Chemicals). Four different amounts of catalyst were used to cure resin: 4%, 6%, 8% and 10% (w/w).

* Corresponding author at: Plastics and Composites Department, Gaiker IK4 Research Centre, Parque Tecnológico, Ed. 202, 48170 Zamudio, Spain.

Tel.: +34 94 600 23 23; fax: +34 94 600 23 24.

E-mail address: bergara@gaiker.es (U. Lopez de Vergara).

2.2. Chemical characterization techniques

The curing reaction of the furan resin was monitored in situ by Fourier transform infrared spectroscopy (FTIR). The FTIR measurements were carried out, at 4 cm^{-1} resolution, using a Perkin Elmer Spectrum 100 and Nicolet Nexus spectrometers, equipped with a heating furnace and Universal ATR Sampling Accessory. Spectres were scanned from 520 to 4000 cm^{-1} at 353 K. The attenuated total reflectance (ATR) mode was used to characterize the furan resin (0.05 ml) and also the totally cured thermoset (1 g).

Liquid nuclear magnetic resonance spectroscopy (NMR) spectra were measured using a Bruker Advance 500 spectrometer at the resonance frequencies of 500 MHz (^1H) and 125.7 MHz (^{13}C). The samples (15 mg) were dissolved in 0.7 ml of acetone- d_6 and TMS was used as internal reference.

2.3. Curing kinetic techniques

The states of curing and kinetic parameters are required in order to elucidate the best manufacturing process. Many complex reactions take place during the curing stage of thermosetting polymers, so this step determines the material's final properties and the study of the cure kinetics significantly contributes in the improvement of the final product performance and quality [7].

2.3.1. Thermal kinetic approach

Differential scanning calorimetry (DSC) is the most common method used to achieve thermal analysis of thermosetting resins and has been widely used to calculate the kinetic parameters of curing reactions through measuring the overall extent of the chemical conversion by different methodologies. Different methods have been used to evaluate the degree of conversion (α), the conversion rate ($d\alpha/dt$) and the activation energy (E_a) [7]. Unless there are secondary enthalpic events, it is possible to assume that the heat flow (dH/dt) is directly proportional to the conversion rate [17]. The α value is determined as the ratio between the heat released up to a certain time t (ΔH_t) and the total heat of reaction (ΔH_{Dyn}) as follows:

$$\alpha = \frac{\Delta H_t}{\Delta H_{\text{Dyn}}} \quad (1)$$

Differential scanning calorimetry was used to evaluate the resin cure by measurement of the heat of reaction (area under the exothermic curve) and the peak reaction temperatures. Dynamical methods were performed in the present work to analyze the curing kinetics of the furan resin. The measurements were performed on a Mettler TC15/DSC 30 using medium pressure (2 MPa) steel sealed capsules and in a controlled atmosphere of N_2 ($50\text{ cm}^3\text{ min}^{-1}$). The temperature range of dynamic scans was from 223 to 523 K at different heating rates (2, 4, 6, 8 and 10 K min^{-1}). Sample weight was between 8 and 10 mg. At least three repetitions were carried out for each sample. The calculations of the curing degree from the DSC thermograms and the kinetic parameters were done with Origin[®] 8 and with STARe Mettler[®] software.

2.3.2. Microwave kinetic approach

In order to study the behaviour of the microwave curing, microwaves have been applied to furan resin samples at different times (from 10 to 100 min) and heating rates (0.5, 0.75 and 1 K min^{-1}). For the comparison between both processes, the curing conditions must be the same. So that, dynamical methods were performed with the DSC at the same heating rates (0.5, 0.75 and 1 K min^{-1}) for thermally cured samples.

The used microwave system, the Hephaistos VHM 100/100 developed by Vötsch Industrietechnik, has 12 magnetrons each with 0.85 kW of power at a fixed frequency of 2.45 GHz. The power

ranges from 5% (i.e. 510 W) to 100%, with a minimum resolution of 0.1%. The system has an internal hexagonal chamber, with a diameter of 1 m and a depth of 1 m. Temperature is controlled by an optical fiber.

In order to compare the curing processes, dynamical DSC scans were carried out to the microwave cured samples from 223 to 523 K at 10 K min^{-1} . For each microwave heating rate-time condition three samples of 8–10 mg were extracted from the centre of the cured resin sample (20 g) and tested on the DSC. It should be noted that at the end of each test, the sample was tempered by putting it into freezer, at a temperature of 253 K to interrupt the crosslinking reaction and to avoid a conversion increase due to the achieved temperature with the microwave heating.

Knowing that the area under the exothermic curve is the heat reaction of the partially cured resin ΔH_{res} , Eq. (2) was applied in order to obtain a representative tendency of the degree of cure with time [18]:

$$\alpha = \frac{\Delta H_{\text{Dyn}} - \Delta H_{\text{res}}}{\Delta H_{\text{Dyn}}} \quad (2)$$

2.3.3. Isoconversional methods

Kissinger and Ozawa have proposed a method that can be used to calculate the activation energy of the overall curing process. As previously said, kinetic analyses of thermosetting resins are usually complex because simultaneous chemical reactions take place during the curing. So that, it is difficult to find a single model which represents the whole system. Therefore, isoconversional methods are the key to describe variations in the curing kinetics throughout the whole process. Isoconversional methods have been previously applied to the cure of many other thermosetting systems and require no knowledge of the reaction model [7].

Kinetics deals with measurement and parameterization of the process rates. Thermal analysis is concerned with thermally stimulated processes, i.e., the processes that can be initiated by a change in temperature. The majority of kinetic methods used in the area of thermal analysis consider the reaction rate to be a function of two variables, the temperature T and the extent of conversion α [19], as follows:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (3)$$

The dependence of the process rate on temperature is represented by the rate constant, $k(T)$, and the dependence on the extent of conversion by the reaction model, $f(\alpha)$.

If the reaction is studied under non-isothermal conditions and considering that the rate constant (k) follows Arrhenius law for a given constant heating rate $\beta = (d\alpha/dt)/(d\alpha/dT)$, Eq. (4) is obtained [7]:

$$\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT} = A e^{-E_a/RT} f(\alpha) \quad (4)$$

where A is the pre-exponential factor, E_a is the activation energy, R is the gas universal constant, T is the absolute temperature and $f(\alpha)$ is the function that describes the kinetic model.

Integrating and rearranging Eq. (4), leads to:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^T e^{-E_a/RT} dT = \frac{A}{\beta} I(E, T) \quad (5)$$

where $g(\alpha)$ is the integral form of the reaction model. For non-isothermal conditions when the temperature is raised at a constant heating rate β , integration of Eq. (5) requires solving the temperature integral $I(E, T)$ which does not have an analytical solution. Its solution is accomplished by using either approximations or numerical integration [20,21].

Download English Version:

<https://daneshyari.com/en/article/673422>

Download Persian Version:

<https://daneshyari.com/article/673422>

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