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Material Behaviour

Thermal, rheological, and dielectric analyses of the polymerization reaction of a liquid thermoplastic resin for infusion manufacturing of composite materials

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ABSTRACT

The use of thermoplastics in advanced composites has increased in recent years due to their recyclability and rapid processing. It is thus important to establish an appropriate thermal cycle processing method in order to achieve parts with high mechanical performance. Elium® thermoplastic resins from Arkema constitute an innovation in the composites processing field for their ability to adapt to thermoset infusion processing methods already in use. Some studies on these new resins can already be found in literature. However, these studies address their mechanical behavior, and none so far focuses on polymerization reactions. Therefore, the present study uses thermal, rheological and dielectric measurements to characterize these acrylic resin polymerization reactions. The results show that both the initiator and temperature have an influence on these reactions, and that a multiple step isothermal cycle allows for the full polymerization of the resin. Also, an optimized thermal cycle for Elium®150 Arkema processing was suggested using dielectric analysis and validated by differential scanning calorimetry.

1. Introduction

The use of thermoplastics as a matrix for advanced composites has undergone considerable growth in recent years due to their attractive properties such as their recyclability and rapid processing capabilities [1]. Elium®150 liquid thermoset resin for infusion from Arkema has proven to be a breakthrough technology in this sense due to its infusion molding capabilities, which, according to supplier, can be molded into large and stiff structural parts while maintaining excellent toughness [2].

The Elium®150 resin is based on a mixture of a 2-propenoic acid, 2-methyl-, methyl ester and acrylic copolymers (non-specified due to trade secret information). According to the supplier, this resin can be combined with benzoyl peroxide and polymerized at room temperature, and can achieve high conversion rates with no need for post-heating. However, it is also stated that an additional post-heating step of 4 h at 80 °C may be necessary to maximize its mechanical properties and achieve mechanical behavior comparable to well established thermosets matrices for advanced composites.

The final properties of the acrylic cured resin depend on the polymerization reactions, and it is for this reason that a well-defined thermal processing cycle must be established in order to improve acrylic resin properties and performance. So far, most studies on the Elium® resins family focus solely on the final mechanical properties of the composite material [3–5], without any special attention being given to the processability and thermal cycle of polymerization reactions.

Along with thermal and rheological analyses, dielectric analysis should be mentioned as an extremely important validation tool for characterizing polymerization reactions [6,7]. This affirmation stems from the fact that this sort of analysis is based on ion and dipole mobility measurements, reflecting the structural changes in the material derived from chain growth during polymerization. Therefore, these techniques are commonly combined for polymerization reaction studies [8–11] and can be considered powerful methodologies for establishing and optimizing these materials' processing cycles.

In this context, the present study seeks to characterize Elium®150 polymerization by means of differential scanning calorimetry (DSC), rheology and dielectric analysis (DEA). Based on the results of these

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characterization techniques, this study can offer a more in depth understanding of the ongoing modifications that occur during the supplier's suggested thermal cycle for resin processing. Also, a proposal for cycle optimization is given which seeks to achieve higher final conversion rates by reducing time while still maintaining final properties with high quality.

2. Materials and methodology

2.1. Materials

Acrylic resin system samples were prepared by using a mixture of 98.8% weight Elium®150 resin and 1.2% weight Luperox®78 initiator, both components supplied by Arkema. This proportion was established based on the supplier's data sheet suggestion [2]. The samples were then weighed and prepared according to the requirements of each experiment.

According to the supplier, the resin system is a low viscosity liquid and can be used as a matrix to fabricate structural composites reinforced by glass, carbon or other continuous fibers. The resin undergoes radical polymerization to produce thermoplastic matrices by peroxide compound initiation.

2.2. Differential scanning calorimetry (DSC)

DSC analyses were performed in a DSC Q20 2151 calorimeter from TA Instruments in an inert nitrogen (N_2) atmosphere with a 30 ml/min flow rate. A primary dynamic analysis was performed by placing an acrylic resin system sample of approximately 5 mg in a hermetic aluminum sample holder and subjecting it to a temperature run from 25 to 200 °C, with a 10 °C/min heating rate.

From this analysis, the onset (T_{onset}) and reaction peak (T_{max}) temperatures were obtained using the TA Universal Analysis software, which also allowed calculation of the total reaction enthalpy values (ΔH) and the conversion or polymerization degree (α), as presented in Equation (1), in which H_i is the partial enthalpy value at a given reaction time (i):

$$\alpha = \frac{H_i}{\Delta H} \tag{1}$$

The results mentioned above were used in the ASTM E2041 methodology in order estimate the kinetic parameters of activation energy (E_a), reaction order (n) and pre-exponential factor (A), according to the Borchardt and Daniels kinetic model.

These parameters were then applied to forecast the polymerization or conversion degree reached in the acrylic resin by being held at a certain temperature (T) for a determined time (t) according to Equation (2). In this equation, R is the gas constant [12].

$$\alpha = 1 - \left[1 - (1 - n).\, A.\, t.\, \exp\left(\frac{-E_a}{RT}\right)\right]^{\left(\frac{1}{1-n}\right)} \tag{2}$$

This forecast allowed for the establishment of a thermal cycle that assures a conversion degree of approximately 100% ($\alpha \cong 1$) for the polymerization of the acrylic resin. A new DSC dynamic analysis was performed in an air oven on a sample that was previously subjected to the established thermal cycle to validate this cycle. The thermal cycle validation is based on the absence of exothermal peaks in the dynamic DSC results, which could be associated with an incomplete polymerization reaction.

Also, a similar thermal cycle test was performed to validate the optimized cycle proposed from the analysis of the DEA results. A sample subjected to the proposed three-step cycle was again tested via dynamic DSC analysis to search for the remaining reaction peaks. A heating rate of 10 °C/min and a temperature range from 25 to 400 °C was used along with the same conditions used in the first dynamic DSC analysis.

2.3. Dielectric analysis (DEA)

DEA tests were performed using a dielectric module based on an impedance converter and an inter-digital sensor. The measurement array details and calculations were performed as described in a previous work [13]. The analyses were performed using a work frequency of 1 kHz.

The tests were divided into three parts. This was based on the thermal polymerization cycle previously established by the Borchardt and Daniels kinetic study. Additionally, it was observed that placing the acrylic resin samples in the air oven directly at 80 °C may lead to bubble formation in the samples. To prevent this, a 25 °C initial step was added to promote a slow reaction start, thus avoiding bubble formation. The second part was performed at 80 °C for 120mins, while the third part was performed at 110 °C for 120mins. All three parts took place in an air-circulating oven.

The results were analyzed seeking to both validate and optimize the previously established thermal polymerization cycles based on the resistivity (ρ) behavior of the samples during the three steps of the thermal cycle.

3. Results and discussion

3.1. Polymerization reaction characterization

Fig. 1 presents the heat flux (Q) as a function of temperature (T) for the dynamic DSC run of the acrylic resin system sample. From these values, the total enthalpy (ΔH), conversion degree (α) and the kinetic parameters (E_a, lnA, n) were estimated by the peak total and partial integrations, respectively, using the Borchardt and Daniels method as described in the methodology. The onset and peak temperatures were also calculated. These are summarized in Table 1 along with the results mentioned above. One can see that the activation energy value is approximately 43.60 kJ/mol, which is comparable to the values found in literature for acrylic resin polymerization reactions [14,15]. The reactions also present a non-integer order number ($n \sim 1.06$), which is associated with complex reaction mechanisms [16].

Fig. 2 presents the dynamic rheometer run for the acrylic resin system, in which the effects of both initiator and heat in the polymerization reaction can be seen. Initially, a constant viscosity plateau can be observed that is associated with the induction period preceding the initiation step. This plateau is extended until approximately 40 °C,

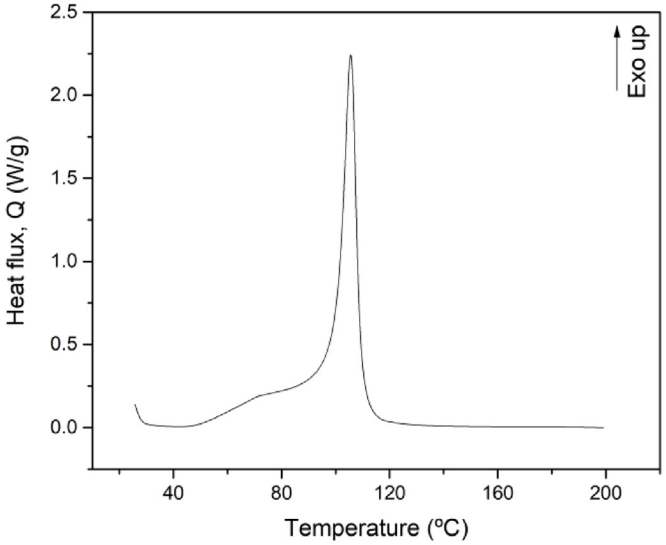

Fig. 1. Dynamic DSC of acrylic resin system (Elium®150 and 1.2% of Luperox®78) sample of approximately 5 mg.