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Effect of binder powders added to carbon fiber reinforcements on the chemoreology of an epoxy resin for composites

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Abstract

The growing use of reinforcement preforms during composite manufacturing requires resin soluble binders which significantly affect the properties of crosslinking thermosetting resins. In this study, for the first time the influence of an epoxy preforming binder on the curing kinetics and chemorheological behavior of a crosslinking epoxy matrix was studied. The results proved that the addition of the binder lead to a significant change of the curing behavior suggesting that the epoxy binder was an essential component needed to complete the stoichiometry of the resin-hardener mixture. The developed kinetic and chemorheological model of the experimental results could be used for process optimization.

Keywords: A. Thermosetting resin; B. Cure behavior; B. Rheological properties; D. Thermal analysis

1. Introduction

Liquid Composite Molding (LCM) processes are becoming a popular alternative to the autoclave technology to meet the increased demand for advanced composites with complex shapes, shorter production times and lower costs [1]. One of the most used thermosetting matrices in LCM processes is epoxy resin due to its favorable properties such as high tensile strength and modulus, excellent chemical resistance and high thermal stability. These properties, which make epoxy resins widely applied as matrices for high-performance composites [2] and nanocomposite materials [3],[4], [5], [6] and as adhesives and coatings [7], [8], are reached if the crosslinking process, also named curing, is properly carried out. During curing, epoxy resin changes irreversibly from viscous liquid with low molecular weight into a rubbery and then a solid glass state[9]. During the processing of epoxy based composites, if proper temperature and time are not used, the variation of the degree of cure leads to defect in the composite. If a composite laminate is undercured due to insufficient time in the mold, the matrix has lower properties than those which would develop in a fully cured state. As a consequence, the interlaminar shear strength and the creep resistance of the composite will be reduced and fine interlaminar cracks or delamination can occur. Conversely, if the laminate is overcured, it may result in brittle matrix susceptible to crazing under stress[10].

Moreover, in Liquid Composite Molding processes, the flow behavior of the resin through the fibrous reinforcement during mold filling is an essential factor that influences the final quality of the products. The viscosity, which is a

function both of the temperature and degree of cure, is not constant but evolves during filling and curing. A proper model for viscosity is very important in order to assure a good impregnation of the fiber reinforcement [11].

In the last two decades, preforms of dry reinforcement are increasingly being used in LCM processes as a consequence of the high fiber volume fraction needed in demanding high performance applications. The preforms usually consist out of several layers of stacked and aligned textile reinforcements, which are sized with an appropriate binder, usually in the form of sprayed powders or coatings, and bound by a thermoforming process [12], [13]. The advantages of preforms include: easy handling and mold placement of the reinforcement material, control of fiber alignment, prevention of unwanted wrinkling of layers, accurate control of part thickness and of the final fiber volume fractions in the cured composite [14], [15]. Most of the binders commonly used for performing operations are low melting thermoplastic materials (polyester, polyamide) or thermosetting resins (epoxy, cyanoacrylate), which are solid at room temperature but they dissolve in the liquid resin during the infusion process and are often designed to react with the resin [16]. The binder content is usually less than 10% of the weight of the reinforcement. In many cases, the binder acts as a toughening agent for the matrix, after its solubilization and eventual reaction with the other components of the reactive matrix. If high molecular weight oligomers are added to the matrix, the viscosity of the resin will be too high for resin injection. For this reason, differently from prepreg matrices, it cannot be added directly to the resin used for LCM processes. It is then evident that the reactive binder may play a significant role in the curing kinetics and flow behavior of the matrix during LCM processes. Therefore, the presence of the binder must be taken into account in the kinetic and chemorheological models, needed for mold filling and cure modeling. In particular, each epoxy-hardener system has specific kinetic and chemorheological parameters such as kinetic constants, activation energies, order of reaction, etc. These parameters can be obtained by using different techniques able to measure some physical related to the state of the reacting system, such as differential scanning calorimetry [17], [18],[19], [20], dielectric analysis[21][22],[23] ultrasound wave propagation [24],[25],[26], [27], [28], [29], Fourier Transform Infrared spectroscopy [30], [31], rheology [32], [33], [34], [35],[36], etc.

In the literature, the influence of the binder on the properties of the matrix has been little explored. Brody and Gillespie[14] characterized and evaluated the effect of a thermoplastic polyester preform binder on vinyl ester resin. Wu et al. [15] studied the influence of an epoxy preforming binder on polymerization and crystallization of catalyzed Cyclic Butylene Terephthalate (CBT) oligomers while Hsu et al. [37] analyzed the effects of thermoplastic additives on the cure of unsaturated polyester resins. However, up to our knowledge, the role of the reactive binder on curing behavior of the epoxy matrix has been completely ignored in the literature.

In this work, for the first time the effect of the addition of an epoxy binder on the curing kinetics and the chemorheological behavior of an epoxy resin is evaluated. The very popular RTM6 resin from Hexcel, widely used for

the manufacturing of carbon fiber-reinforced composites by LCM processes, has been chosen for this study. Very recently, there has been a renewed interest in studying the curing kinetics of this matrix in view of new potential applications in the field of composite joining with partially cured and fresh resin [38]. Although the curing process of the RTM6 resin has been already studied by calorimetric, dielectric and optical techniques [39],[40],[41],[42],[43], [44], [45], [18], the effect of a reactive epoxy binder powder on curing kinetics and rheology has been completely ignored and could lead to relevant differences in the optimization of cure cycle. The manufacturer recommends preheating and injection of the RTM6 resin at 80 °C and the use of a specific epoxy bindered carbon fabric. In this study, the binder powder has been extracted by the carbon fabric and mixed with the resin. Differential scanning calorimetry and rheological analysis have been carried out in not isothermal mode at several heating rates. A kinetic and a chemorheological model of the experimental results have been developed and compared to former kinetic studies on the same resin, lacking of the binder component.

2. Experimental

2.1 Materials

The investigated epoxy system is HexFlow® RTM6, a monocomponent resin designed for Resin Transfer Molding (RTM) and infusion processes supplied by Hexcel. RTM6 system includes a multifunctional epoxy resin based on tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM) and a mixture of amine hardeners of different functionalities [17], [45]. At room temperature it is a brown translucent paste but its viscosity decreases quickly by increasing the temperature. When it is uncured, the resin has a density of 1.11 g/cm³, which becomes 1.14 g/cm³ in the fully cured state. The resin is usually stored at -20 °C to freeze the macromolecular chains mobility and avoid curing reactions. During composite processing, RTM6 is preheated at 80 °C, injected in a preheated mold at 120 °C under vacuum/low pressure (from 1 to 5 bar) and cured usually at 180 °C [44],[46].

RTM6 is recommended by the manufacturer to be used together with a carbon fabric with the commercial name of G0926 HS06K. It is a 5H satin with HEXTOW AS4C GP 6K yarns, having a nominal weight of 375 g/m². As reported in the technical data sheet, the carbon fabric contains on one side some powder in the amount of 15 g/m² (4% by weight), acting as a binder coating. The binding powder, produced by Hexcel with the commercial name of HP03, is added to the fabric in order to promote adhesion between plies in the stacking/pre-forming process performed before resin infusion processes. The preforms are obtained by thermoforming, i.e. by applying heat and pressure on the carbon fabrics. The binder powders are then soluble at 120 °C in epoxy resin during resin infusion process. These powders are a reactive compound that complete the stoichiometry of the reactive epoxy, which should be not used in combination with reinforcements not containing such powders. In order to assess the effect of the binder powders on the curing behavior of RTM6 system, they were extracted from carbon fabric. Specimens of 200 x 200 mm² size were cut from

G0926 carbon fabric and placed in an aluminum container filled with acetone for about 30 min. After being detached from the fibers, powders were dissolved in acetone. The dispersion was left at room temperature to allow both acetone evaporation and binder harvesting. Before analysis, the resin was conditioned at room temperature for a day. The binder, reduced to a powder with the aid of a mortar, was mixed with the epoxy resin in an appropriate amount which was chosen according to the typical fiber content recommended by the manufacturer in the datasheet, i.e. 57% by volume: this corresponds to 8.5 wt% of binder added to neat resin. Then, the resin-binder mixture was magnetically stirred at 70 °C for 45 min until the complete dissolution of the binder powder. The dissolution time of 45 min was obtained by tests at 70 °C using a Carl Zeiss Axio Imager A2M optical microscope, equipped with a high-speed digital video camera and a THMS600 hot stage (Linkam Scientific Instruments Ltd.) able to heat the sample at a given rate. The complete solubility of binder in the RTM6 resin was obtained when the binder particles disappear and no solid residue could be distinguished.

The cure kinetics was monitored by differential scanning calorimetry (DSC) on uncured samples in non-isothermal scans at 0.75, 1, 2, 5 and 10 °C/min from 25 to 300 °C under nitrogen. AMettler-Toledo DSC 822e differential scanning calorimeter was used. Standard aluminum pans were used, with liquid resin mass between 5 and 10 mg. At least three measurements were carried out at each heating rate.

Rheological measurements were carried out in a strain-controlled rheometer (ARES, Rheometrics Scientific) equipped with a parallel plate geometry (50 mm plate diameter) in dynamic mode at 1 Hz and a strain amplitude of 5 %. The tests were performed from 30 °C to 220 °C at 0.75, 1 and 2 °C/min. At least three measurements were carried out at each heating rate.

Results and Discussion

DSC results

In Figure 1 an exothermic reaction, beginning at around 120 °C with a peak at approximately 170 °C, is shown by the HP03 binder upon heating in the DSC. The exothermic peak can be ascribed to a crosslinking reaction, characterized by an enthalpy of reaction of 105 J/g. The second dynamic DSC scan shows no residual enthalpy but only a discontinuity in the heat flux related to the glass transition at 90 °C. The DSC results confirm that the epoxy binder is reactive.

Dynamic DSC runs at constant heating rates have been performed in order to determine the conversion profile and the total heat of reaction released during non isothermal curing of the studied resin systems. The comparison of the thermograms obtained on the RTM6resin and the RTM6-binder mixture at different heating rates is reported in Figure 2 and 3, respectively. The thermograms are characterized by the presence of a single peak, which is indicative of a single autocatalytic polymerization reaction, as typically observed in epoxy/amine formulations [17], [47]. As expected, the

exothermal peak temperature, T_{peak} , and the onset temperature for the reaction increase with increasing heating rate [40]. In Figure 3, the presence of only one exothermal peak in the resin-binder mixture is indicative of the full dissolution of the binder in the matrix as also reported by Schmidt et al. [13]. The presence of the binder in RTM6 resin anticipates the beginning of the crosslinking reaction at around 100 °C instead of 125 °C, as in the case of the neat RTM6 resin. Also the temperature of the exothermic peak of the RTM6-binder system is lower than that of the RTM6resin, as can be inferred from Table 1, where the results of the dynamic DSC scans on neat RTM6 resin and RTM6-binder system are reported.

The total heat of reaction necessary to complete the polymerization, ΔH , has been obtained by integrating the heat flow curve. As inferred from Table 1, the ΔH values of the neat RTM6 resin at different heating rates are comparable with the literature data [17], [39], [40]. Moreover, the average heat of reaction necessary to complete the polymerization of the RTM6-binder system, 501 ± 20 J/g, is higher than the average value for the neat RTM6 resin, which is 458 ± 12 J/g. This confirms that the binder has an active role in the crosslinking reaction of the neat RTM6 resin. The calorimetric results suggest that there are still unreacted groups in RTM6 cured resin and that the mixture stoichiometry is completed in the presence of the reactive binder of the carbon fabric.

Assuming that the heat flow measured in a DSC experiment is proportional to the rate of the exothermic crosslinking reaction, the rate of conversion $d\alpha/dt$ has been determined as the ratio of the heat output rate at time t (dH/dt) to the overall heat of reaction, ΔH [48], [30][49]:

$$\frac{d\alpha}{dt} = \frac{1}{\Delta H} \frac{dH}{dt} \quad (1)$$

The degree of cure, α , can be then determined by the integration of the rate of conversion as follows:

$$\alpha = \int_0^t \frac{d\alpha}{dt} \cdot dt \quad (2)$$

Figure 4 and 5 show the temperature dependence of the degree of cure obtained at different heating rates on RTM6 and RTM6-binder systems, respectively. At the same heating rate, the resin system with the binder reaches a higher degree of cure at lower temperatures. For example, at a heating rate of 10 °C/min, the degree of cure of 0.4 is reached at 238 °C and 218 °C for RTM6 and RTM6-binder systems, respectively. In Figure 6 and 7, the reaction rates for the studied systems at different heating rates are reported. Both RTM6 and RTM6-binder systems present small shoulders at a high degree of cure, which are more pronounced when higher temperature are reached in correspondence of higher heating rates. These shoulders could be ascribed to the competition between the epoxy-amine reaction and the epoxy-hydroxyl reaction, as suggested by Navapour et al. [40].

Kinetic modeling of not isothermal reactions

The kinetic analysis of the curing process is based on the simplifying assumption that the transformation rate $d\alpha/dt$ during a reaction is the product of two functions, one depending completely on the temperature, T , and the other depending completely on the transformed fraction, α [30]:

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

where $k(T)$ is a temperature-dependent reaction rate function and $f(\alpha)$ a kinetic-dependent model function. An Arrhenius type function is generally assumed for $k(T)$:

$$k(T) = A \exp\left(-\frac{E_a}{RT}\right) \quad (4)$$

where A is the pre-exponential factor, E_a is the apparent activation energy and R is the universal gas constant.

During the curing of epoxy resins, multiple events may occur simultaneously and lead to very complicated reactions, consequently, the use of multiple rate constants can provide more accurate modeling results. Kamal's model [50] represents the most general form that can be adopted for modeling the reactive behavior of epoxy resins. It is based on the use of two rate constants, expressed in the following equation:

$$\frac{d\alpha}{dt} = (k_1 + k_2 \alpha^m) * (1 - \alpha)^n \quad (5)$$

where k_1 and k_2 are the rate constants and m and n are the reaction orders. In the specific case of neat RTM6 resin, Karkanis and Partridge [51] modified the Kamal's model (Equation 5) with two different reaction orders, n_1 and n_2 , obtaining a very accurate fitting of the experimental curves. The model presents the form expressed in equation:

$$\frac{d\alpha}{dt} = k_1 (1 - \alpha)^{n_1} + k_2 \alpha^m (1 - \alpha)^{n_2} \quad (6)$$

Karkanis and Partridge's model describes independently the two main chemical reactions that typically occur in epoxy-amine systems. It is well known that the uncatalyzed reaction of an epoxide with a primary amine produces a secondary amine which reacts with another epoxy group to form a tertiary amine. These reactions are auto-accelerated by the hydroxyl groups formed in the reactions. At higher temperature condensation of OH groups with epoxy rings is also favored [52].

Considering the Arrhenius dependence of k_1 and k_2 constants from the temperature, equation 6 can be written also as:

$$\frac{d\alpha}{dt} = A_1 \exp\left(-\frac{E_{a1}}{RT}\right) (1 - \alpha)^{n_1} + A_2 \exp\left(-\frac{E_{a2}}{RT}\right) \alpha^m (1 - \alpha)^{n_2} \quad (7)$$

The parameters A_1 , E_{a1} , A_2 , $E_{a2,m}$, n_1 and n_2 have been determined by minimizing the sum of the squared differences between experimental and predicted reaction rates according to the Levenberg-Marquardt numerical method available in Microcal Origin software. The experimental reaction rates as a function of the temperature (discrete dots) and model predictions (full line) are compared in Figures 6 and 7 for neat RTM6 and RTM6-binder systems, respectively. At all the investigated heating rates, there is a very good correspondence between the non linear fit and the experimental results over the whole range of curing temperatures.

The parameters for the analyzed systems are reported in Table 2. For neat RTM6 resins, a very good agreement of the kinetic parameters with the literature data is clearly observable, while the kinetic parameters obtained on neat resin and resin-binder system are significantly different. In particular, in the RTM6-binder system the pre-exponential factors are larger than those of neat resin while the reaction order m and n_1 are significantly different. This suggests that the presence of the binder plays a key role in the cure reaction by affecting the competition between the epoxy-amine reaction and the epoxy-hydroxyl reaction. In particular, the presence of unreacted groups in the neat RTM6 resin is probable, being the stoichiometry completed by the presence of the binder powder of the carbon fabric. Therefore, it is correct to account for this contribution for kinetic modeling of these matrices when used in RTM processes.

Rheological results

Rheological analysis has been carried out by oscillatory rheometry in order to study the viscosity evolution of the resin system as a function of the temperature and degree of reaction. The dependence of viscosity upon heating is relevant in composite processing, being related to resin flow and volatile evolution, both responsible of the final porosity content. The rheological curves, experimentally obtained at different heating rates, are reported in Figures 8 and 9 for the RTM6 and RTM6-binder systems, respectively. As reported in literature for thermoplastic and thermoset binders, the presence of binders increases the initial viscosity [13]. In the present case, the initial viscosity at 40 °C doubles due to the addition of the epoxy binder.

As expected for a crosslinking thermosetting resin undergoing a heating cycle, the viscosity is governed by two competing phenomena: the effect of the temperature on the molecular mobility, which reduces the viscosity, and the growing size of the macromolecules due to the chemical reaction, which increases the viscosity [33]. Therefore, a decrease of the viscosity with the temperature is observed when the effect of temperature is dominant. Then, as the rate of reaction increases, a minimum of viscosity is observed. The steep increase of the viscosity is indicative of gelation, the stage at which the resin changes from a viscous liquid to an elastic gel due to the formation of a three-dimensional network.

According to the ASTM D4473 standard, the dynamic gel temperature (DGT) and the gel point in isothermal condition have been taken as the temperature at which the viscosity of the curing system has reached the values of 100 Pa*s

during heating at a constant heating rate and as the time at which the crossover of G' and G'' moduli occurs in isothermal conditions, respectively. The values obtained at different heating rates and temperatures for the studied epoxy systems are reported in Table 3. The addition of the binder to the RTM6 resin leads to a reduction of the gel temperature of 9-14 °C depending on the heating rate. The anticipated DGT of RTM6-binder systems, determined by rheological measurements, is in agreement with the anticipated T_{peak} obtained by calorimetric analysis. They are indicative of an unbalanced stoichiometry of neat resin, probably lacking of some functional groups present in the binder. The gel time is an indication of the processability of the resin matrix. As inferred by Table3, the addition of preforming binder leads to a significant reduction of the processing time, which is almost halved compared with the referencematrix system without any preforming binder. This result is very important from a technological point of view, since the working time and temperature during composite processing have to be chosen on the basis of the RTM6-binder system and not on the neat RTM6 resin.

A proper rheological model has been used, able to interpolate the experimental data, which is given by the product of a function of the temperature and a function of the degree of reaction:

$$\eta(T, \alpha) = f(T) * g(\alpha) \quad (8)$$

In recent years, different models have been proposed to predict the viscosity behavior of epoxy resins under non-isothermal curing conditions. One of the most used is the Castro-Macosko model[53] -[54], which accounts for the chemical reaction in isothermal curing:

$$\eta = \eta_{g0} * \left(\frac{\alpha_g}{\alpha_g - \alpha} \right)^{A+B\alpha} \quad (9)$$

where η_{g0} is the viscosity of the unreacted resin, α_g is the degree of cure at the gel temperature, while A and B are constants.

To account also for the variation of viscosity with the temperature during heating, Kenny and Opalicki have proposed the following chemorheological model [55]-[21]:

$$\eta = \eta_{g0} * \exp\left(\frac{-C_1 * (T - T_{g0})}{C_2 + T - T_{g0}}\right) * \left(\frac{\alpha_g}{\alpha_g - \alpha}\right)^n \quad (10)$$

where T_{g0} is the initial glass transition temperature, while C_1 , C_2 , A and B are constants.

Since the modeling of the viscosity curves of the studied systems at different heating rates with the Kenny and Opaliki model is not satisfactory, a chemorheological model based on a modified version of Kenny and Opalicki model has been used:

$$\eta = \eta_{g0} * \exp\left(\frac{-C_1 * (T - T_{g0})}{C_2 + T - T_{g0}}\right) * \left(\frac{\alpha_g}{\alpha_g - \alpha}\right)^{A+B\alpha} \quad (11)$$

where η_{g0} is the viscosity of the unreacted resin at the initial glass transition temperature T_{g0} , α_g is the degree of cure at the gel temperature, while C_1 , C_2 , A and B are constants. The degree of reaction used in the chemorheological model has been obtained from dynamic calorimetric measurements, as reported in Figures 4 and 5. The proposed model accounts for the twofold effect of the temperature: an increase of the temperature lowers the viscosity of the resin but simultaneously promotes the curing reaction and therefore increases the viscosity.

For the identification of the first three parameters, i.e. the viscosity η_{g0} at T_{g0} and C_1 and C_2 constants, the initial part of the rheological curve, until a temperature lower than the onset temperature of reaction peak observed in a DSC experiment, has been considered. In this part of the rheological curve, the effect of the resin reaction has been neglected in a first approximation and the dependence of the viscosity from the temperature has been considered. Once obtained the values of η_{g0} , C_1 and C_2 constants from the non linear fitting of the initial part of the curve, the overall viscosity curve has been non linearly fitted with equation (8), obtaining the parameters reported in Table 5.

As can be seen from α_g values, the gelation of neat RTM6 resin and RTM6-binder system occurs at 0.4 and 0.42, respectively. These values are in agreement with literature data for resin systems, where the degree of cure at gelation is in the range between 0.4 and 0.5[32].

The comparison between the experimental rheological curves and the non linear fit at different heating rates, reported in Figure 8 and 9 is very satisfactory. The model is able to predict either the initial viscosities and their decreasing slope up to the gelation either the fast increase of viscosity at gelation.

Conclusions

The curing kinetics and the chemorheological behavior of a commercial epoxy resin used in aeronautical applications has been investigated with the aim of assessing the effect of the addition of a binder used in the carbon fabric recommended by the supplier for that resin, for performing operations. The autocatalytic cure model by Karkanis and Partridge has been successfully applied to describe the cure kinetics of the investigated epoxy systems. A modified version of the classical Williams–Landel–Ferry(WLF) equation that took into account the gelation and the effects of crosslinking was used as a chemorheological model.

The DSC and rheological results prove that the addition of the binder generally causes a significant change in the kinetics of the cure reaction. This is evident from the shift to lower temperatures of the beginning of the crosslinking reaction, the heat flow peak and the dynamic gel temperature. Furthermore, the heat of reaction developed by the system mixed with binder is higher than that developed by the neat RTM6 resin, indicating that the binder is needed to

complete the stoichiometric balance of the resin-hardener mixture. Finally, the addition of preforming binder leads to a significant reduction of the processing time of the resin matrix.

Most of the literature devoted to the study of the reactive behavior of neat RTM6 is of limited practical interest, dealing with a commercial system never used without the reactive binder, essential to reach the target properties. Therefore, the knowledge gained in this study is very useful for the manufacturing optimization of cure cycles, where the data on the RTM6-powder system and not only on the neat RTM6 resin should be taken into account.

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References

- [1] Kumar AA, Sundaram R. Cure cycle optimization for the resin infusion technique using carbon nanotube additives. *Carbon* N Y 2016;96:1043–52.
- [2] Greco A, Lionetto F, Maffezzoli A. Processing and characterization of amorphous polyethylene terephthalate fibers for the alignment of carbon nanofillers in thermosetting resins. *Polym Compos* 2015;36:1096–103.
- [3] Chiacchiarelli LM, Escobar MM, Kenny JM, Torre L, Vazquez A. The role of the interphase on the shear induced failure of multiwall carbon nanotubes reinforced epoxy nanocomposites. *J Appl Polym Sci* 2015;132.
- [4] Lettieri M, Lionetto F, Frigione M, Prezzi L, Mascia L. Cold-cured epoxy-silica hybrids: Effects of large variation in specimen thickness on the evolution of the T_g and related properties. *Polym Eng Sci* 2011;51:358–68.
- [5] Corcione CE, Freuli F, Maffezzoli A. The aspect ratio of epoxy matrix nanocomposites reinforced with graphene stacks. *Polym Eng Sci* 2013;53:531–9.
- [6] Lionetto F, Caldò E, Di Benedetto F, Pisignano D, Maffezzoli A. A methodology to orient carbon nanotubes in a thermosetting matrix. *Compos Sci Technol* 2014;96:47–55. doi:10.1016/j.compscitech.2014.02.016.
- [7] Lionetto F, Frigione M. Mechanical and natural durability properties of wood treated with a novel organic preservative/consolidant product. *Mater Des* 2009;30:3303–7. doi:10.1016/j.matdes.2008.12.010.
- [8] Lionetto F, Frigione M. Effect of novel consolidants on mechanical and absorption properties of deteriorated wood by insect attack. *J Cult Herit* 2012;13:195–203. doi:10.1016/j.culher.2011.09.007.
- [9] Lionetto F, Tarzia A, Maffezzoli A. Air-coupled ultrasound: A novel technique for monitoring the curing of thermosetting matrices. *IEEE Trans Ultrason Ferroelectr Freq Control* 2007;54:1437–43.

doi:10.1109/TUFFC.2007.404.

- [10] Khan LA, Kausar A, Hussain ST, Iqbal Z, Day RJ, Syed AS, et al. Cure characterization of Cycom 977-2A carbon/epoxy composites for quickstep processing. *Polym Eng Sci* 2014;54:887–98.
- [11] Lionetto F, Dell'Anna R, Montagna F, Maffezzoli A. Modeling of continuous ultrasonic impregnation and consolidation of thermoplastic matrix composites. *Compos Part A Appl Sci Manuf* 2016;82:119–29.
- [12] Daelemans L, van der Heijden S, De Baere I, Muhammad I, Van Paepegem W, Rahier H, et al. Bisphenol A based polyester binder as an effective interlaminar toughener. *Compos Part B Eng* 2015;80:145–53.
- [13] Schmidt S, Mahrholz T, Kühn A, Wierach P. Powder binders used for the manufacturing of wind turbine rotor blades. Part 1. Characterization of resin-binder interaction and preform properties. *Polym Compos* 2016.
- [14] Brody JC, Gillespie Jr JW. Reactive and Nonreactive Binders in Glass/Vinyl Ester Composites. DTIC Document; 2004.
- [15] Wu W, Xie L, Jiang B, Ziegmann G. Influence of textile preforming binder on the thermal and rheological properties of the catalyzed cyclic butylene terephthalate oligomers. *Compos Part B Eng* 2013;55:453–62.
- [16] Chen J, Backes D, Jayaraman K. Dynamics of binder displacement in liquid molding. *Polym Compos* 1996;17:23–33.
- [17] Kazilas MC, Partridge IK. Exploring equivalence of information from dielectric and calorimetric measurements of thermoset cure—a model for the relationship between curing temperature, degree of cure and electrical impedance. *Polymer (Guildf)* 2005;46:5868–78.
- [18] Bhunia S, Niyogi D, Marru P, Neogi S. Modelling of curing kinetics of amine cured epoxy resins for vacuum assisted resin infusion molding. *Can J Chem Eng* 2014;92:703–11.
- [19] Cebrián AS, Zogg M, Ermanni P. Methodology for optimization of the curing cycle of paste adhesives. *Int J Adhes Adhes* 2013;40:112–9.
- [20] Henne M, Breyer C, Niedermeier M, Ermanni P. A new kinetic and viscosity model for liquid composite molding simulations in an industrial environment. *Polym Compos* 2004;25:255–69.
- [21] Maffezzoli A, Trivisano A, Opalicki M, Mijovic J, Kenny JM. Correlation between dielectric and chemorheological properties during cure of epoxy-based composites. *J Mater Sci* 1994;29:800–8.
- [22] Corcione CE, Maffezzoli A. Transport properties of graphite/epoxy composites: Thermal, permeability and dielectric characterization. *Polym Test* 2013;32:880–8.
- [23] Lionetto F, Maffezzoli A. Relaxations during the postcure of unsaturated polyester networks by ultrasonic wave propagation, dynamic mechanical analysis, and dielectric analysis. *J Polym Sci Part B Polym Phys* 2005;43:596–602. doi:10.1002/polb.20359.

- [24] Lionetto F, Maffezzoli A. Monitoring the cure state of thermosetting resins by ultrasound. *Materials (Basel)* 2013;6:3783–804. doi:10.3390/ma6093783.
- [25] Lionetto F, Montagna F, Maffezzoli A. Ultrasonic transducers for cure monitoring: design, modelling and validation. *Meas Sci Technol* 2011;22:124002. doi:10.1088/0957-0233/22/12/124002.
- [26] Ávila-Orta C, Espinoza-González C, Martínez-Colunga G, Bueno-Baqués D, Maffezzoli A, Lionetto F. An overview of progress and current challenges in ultrasonic treatment of polymer melts. *Adv Polym Technol* 2013;32:E582–602.
- [27] Samet N, Maréchal P, Duflo H. Ultrasonic characterization of a fluid layer using a broadband transducer. *Ultrasonics* 2012;52:427–34.
- [28] Ghodhbani N, Marechal P, Duflo H. Curing and post-curing viscoelastic monitoring of an epoxy resin. *Phys Procedia* 2015;70:106–9.
- [29] Espinoza-Gonzalez C, Avila-Orta C, Martinez-Colunga G, Lionetto F, Maffezzoli A. A Measure of CNTs Dispersion in Polymers with Branched Molecular Architectures by UDMA. *IEEE Trans Nanotechnol* 2016;15:731–7. doi:10.1109/TNANO.2016.2530697.
- [30] Lionetto F, Timo A, Frigione M. Curing kinetics of epoxy-deep eutectic solvent mixtures. *Thermochim Acta* 2015;612:70–8. doi:10.1016/j.tca.2015.05.004.
- [31] Haq EU, Padmanabhan SK, Karim MRA, Licciulli A. Setting and curing of mortars obtained by alkali activation and inorganic polymerization from sodium silicate and silica aggregate. *Constr Build Mater* 2016;105:291–6.
- [32] Garschke C, Parlevliet PP, Weimer C, Fox BL. Cure kinetics and viscosity modelling of a high-performance epoxy resin film. *Polym Test* 2013;32:150–7.
- [33] Faria H, Pires FM, Marques AT. Modeling the rheology of SR1500 and LY556 epoxies under manufacturer's recommended cure cycles after viscosimetry and rheometry characterization. *Polym Eng Sci* 2014;54:831–9.
- [34] Lelli G, Terenzi A, Kenny JM, Torre L. Modelling of the chemo-rheological behavior of thermosetting polymer nanocomposites. *Polym Compos* 2009;30:1.
- [35] Chiacchiarelli LM, Kenny JM, Torre L. Kinetic and chemorheological modeling of the vitrification effect of highly reactive poly (urethane-isocyanurate) thermosets. *Thermochim Acta* 2013;574:88–97.
- [36] Lionetto F, Sannino A, Mensitieri G, Maffezzoli A. Evaluation of the Degree of Cross-Linking of Cellulose-Based Superabsorbent Hydrogels: A Comparison between Different Techniques. *Macromol Symp* 2003;200:199–207. doi:10.1002/masy.200351020.
- [37] Hsu CP, Kinkelaar M, Hu P, Lee LJ. Effects of thermoplastic additives on the cure of unsaturated polyester

- resins. *Polym Eng Sci* 1991;31:1450–60.
- [38] Moosburger-Will J, Sause MGR, Horny R, Horn S, Scholler J, Llopard Prieto L. Joining of carbon fiber reinforced polymer laminates by a novel partial cross-linking process. *J Appl Polym Sci* 2015;132.
- [39] Karkanis PI, Partridge IK. Cure modeling and monitoring of epoxy/amine resin systems. II. Network formation and chemoviscosity modeling. *J Appl Polym Sci* 2000;77:2178–88.
- [40] Navabpour P, Nesbitt A, Degamber B, Fernando G, Mann T, Day R. Comparison of the curing kinetics of the RTM6 epoxy resin system using differential scanning calorimetry and a microwave-heated calorimeter. *J Appl Polym Sci* 2006;99:3658–68.
- [41] Aduriz XA, Lupi C, Boyard N, Bailleul J-L, Leduc D, Sobotka V, et al. Quantitative control of RTM6 epoxy resin polymerisation by optical index determination. *Compos Sci Technol* 2007;67:3196–201.
- [42] Gerlach R, Siviour CR, Petrinic N, Wiegand J. Experimental characterisation and constitutive modelling of RTM-6 resin under impact loading. *Polymer (Guildf)* 2008;49:2728–37.
- [43] El Sawi I, Olivier PA, Demont P, Bougherara H. Investigation of the effect of double-walled carbon nanotubes on the curing reaction kinetics and shear flow of an epoxy resin. *J Appl Polym Sci* 2012;126:358–66.
- [44] Causse N, Benchimol S, Martineau L, Carponcin D, Lonjon A, Fogel M, et al. Polymerization study and rheological behavior of a RTM6 epoxy resin system during preprocessing step. *J Therm Anal Calorim* 2015;119:329–36.
- [45] Moosburger-Will J, Greisel M, Sause MGR, Horny R, Horn S. Influence of partial cross-linking degree on basic physical properties of RTM6 epoxy resin. *J Appl Polym Sci* 2013;130:4338–46.
- [46] Hexcel. HexFlow RTM 6 180°C epoxy system for Resin Transfer Moulding monocomponent system. *Monocomponent Syst* 2011:1–4.
- [47] Pascault J-P, Sautereau H, Verdu J, Williams RJJ. *Thermosetting polymers*. vol. 64. CRC Press; 2002.
- [48] Ruiz E, Billotte C. Predicting the cure of thermosetting polymers: The isoconversion map. *Polym Compos* 2009;30:1450–7.
- [49] Greco A, Lionetto F, Maffezzoli A. *Orientation of graphene nanoplatelets in thermosetting matrices* 2016.
- [50] Kamal MR. Thermoset characterization for moldability analysis. *Polym Eng Sci* 1974;14:231–9.
- [51] Karkanis PI, Partridge IK, Attwood D. Modelling the cure of a commercial epoxy resin for applications in resin transfer moulding. *Polym Int* 1996;41:183–91.
- [52] Faria H, Pereira CMC, Pires FMA, Marques AT. Kinetic models for the SR1500 and LY556 epoxies under manufacturer's recommended cure cycles. *Eur Polym J* 2013;49:3328–36.
- [53] Castro JM, Macosko CW. Studies of mold filling and curing in the reaction injection molding process. *AIChe J*

1982;28:250–60.

[54] Macosko CW, Rheology P. Measurements and Applications. VCH, New York 1994.

[55] Kenny JM, Oplicki M. Influence of the chemorheology of toughened epoxy matrices on the processing behavior of high performance composites. Makromol. Chemie. Macromol. Symp., vol. 68, Wiley Online Library; 1993, p. 41–56.

Table 1: Comparison of the results of dynamic DSC scans on RTM6-binder mixture with those on neat RTM6 resin and literature data available for RTM6

Heating Rate (°C/min)	Experimental Results on RTM6		Literature Results on RTM6	Experimental Results on RTM6-binder	
	ΔH (J/g)	T_{peak} (°C)	ΔH (J/g)	ΔH (J/g)	T_{peak} (°C)
1	469	170	432 [17]	502	163
2	441	195	436 [51] 401 [40]	528	179
5	464	220	437 [51] 413 [40]	475	203
10	458	242	438 [51] 428 [40]	496	224

Table 2 Fitting parameters for the neat RTM 6 and RTM6-binder systems

	A_1 (s ⁻¹)	E_1 (kJ/mol)	A_2 (s ⁻¹)	E_2 (kJ/mol)	m (-)	n_1 (-)	n_2 (-)
Neat RTM6	39111	73.70	5432	51.78	1.35	0.57	1.99
Literature data	20340 [51] 39300 [40]	70.20 [51] 74.00 [40]	5400 [51] 5216 [40]	51.50 [51] 50.75 [40]	1.40 [51] 1.48 [40]	0.45 [51] 0.46 [40]	1.83 [51] 1.90 [40]
RTM6-binder	69309	74.02	54551	60.36	0.52	0.82	2.01

Table 3 Results of rheological analysis on neat RTM6 and RTM6-binder mixture.

Experimental Results – Dynamic Gel Temperature (°C)		
Heating Rate (°C/min)	neat RTM6	RTM6-binder
2	189	175
1	171	157
0.75	161	150
Experimental Results - Gel Point in isothermal conditions (°C)		
Temperature (°C)	neat RTM6	RTM6-binder
160	40	23
180	30	17

Table 4 Fitting parameters for neat RTM6 and RTM6-binder mixture.

	η_{g0} (Pa·s)	C_1 (-)	C_2 (K)	α_g (-)	A (-)	B (-)
neat RTM6	$2.00 \cdot 10^9$	31.60	33.50	0.42	5.58	7.20
RTM6-binder	$1.99 \cdot 10^{10}$	32.96	30.92	0.39	5.04	8.64

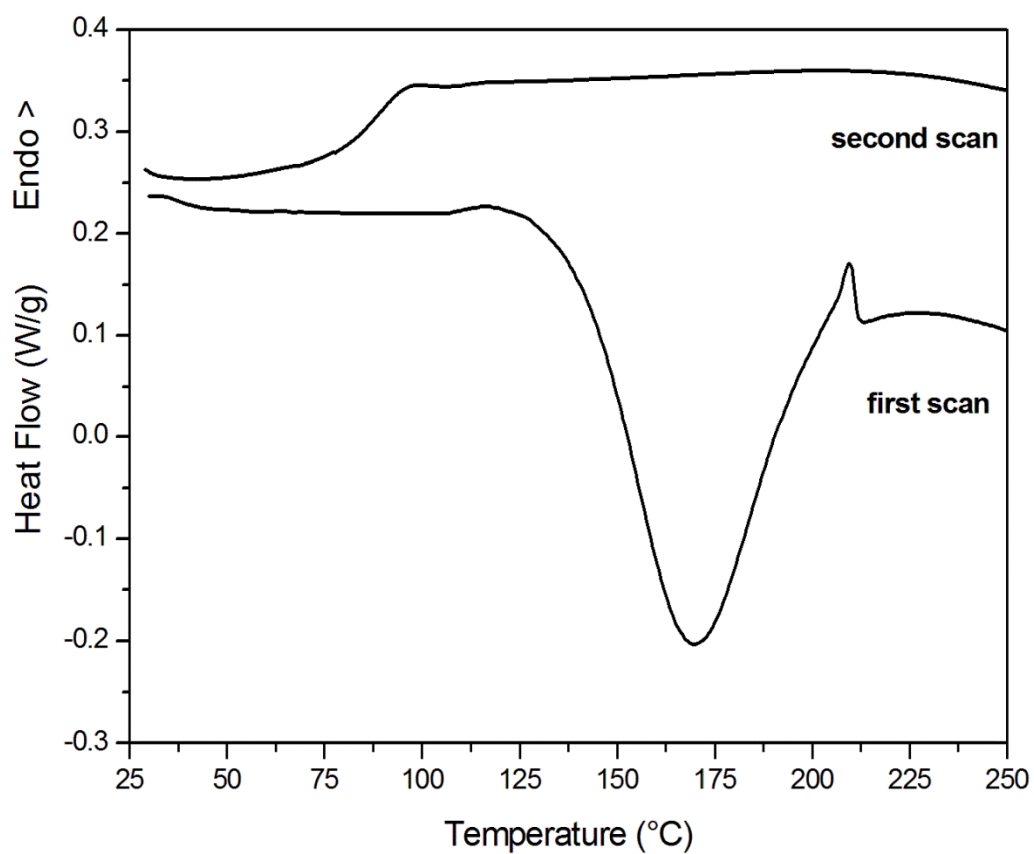


Figure 1 DSC thermograms of HP03 preforming binder.

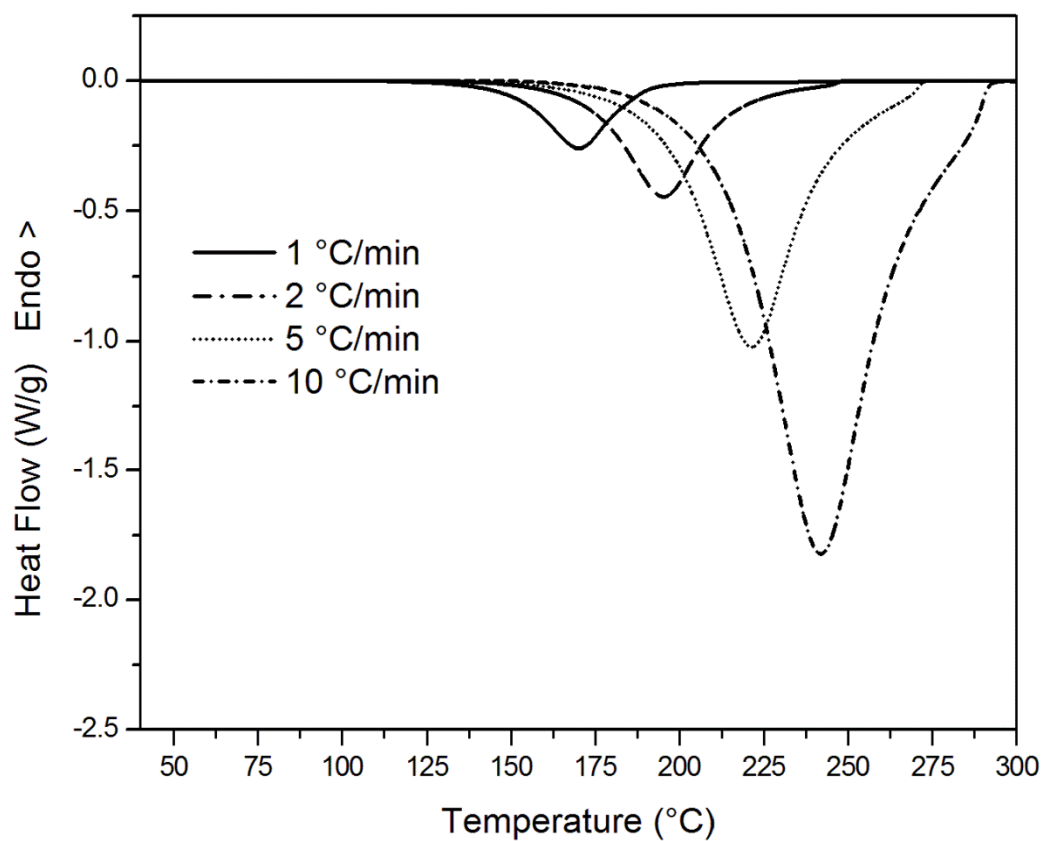


Figure 2 DSC thermograms on neat RTM6 resin at different heating rates.

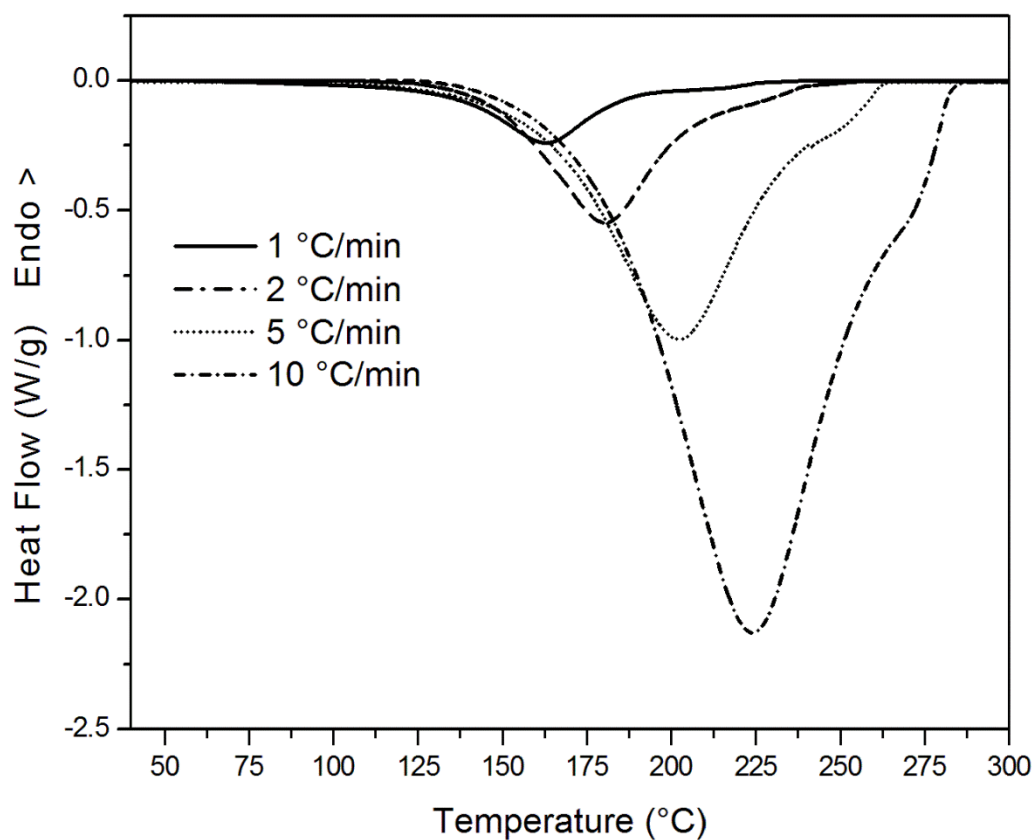


Figure 3 DSC thermograms on RTM6-binder mixture at different heating rates.

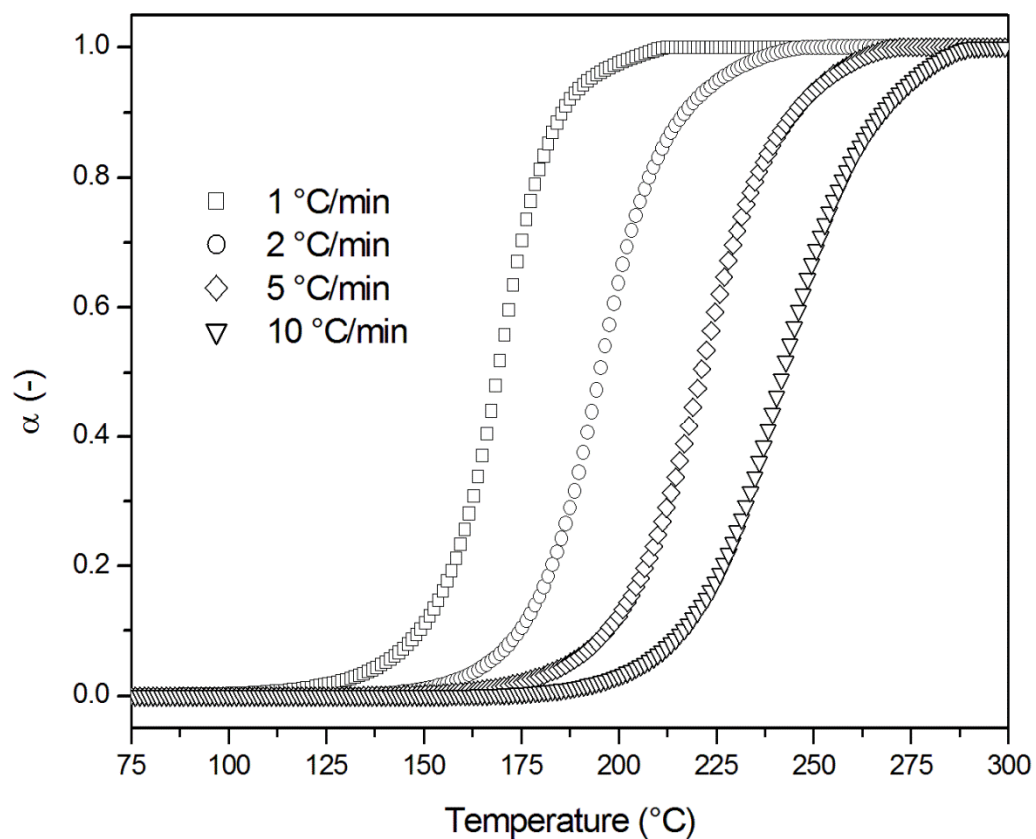


Figure 4 Degree of cure of neat RTM6 resin at different heating rates.

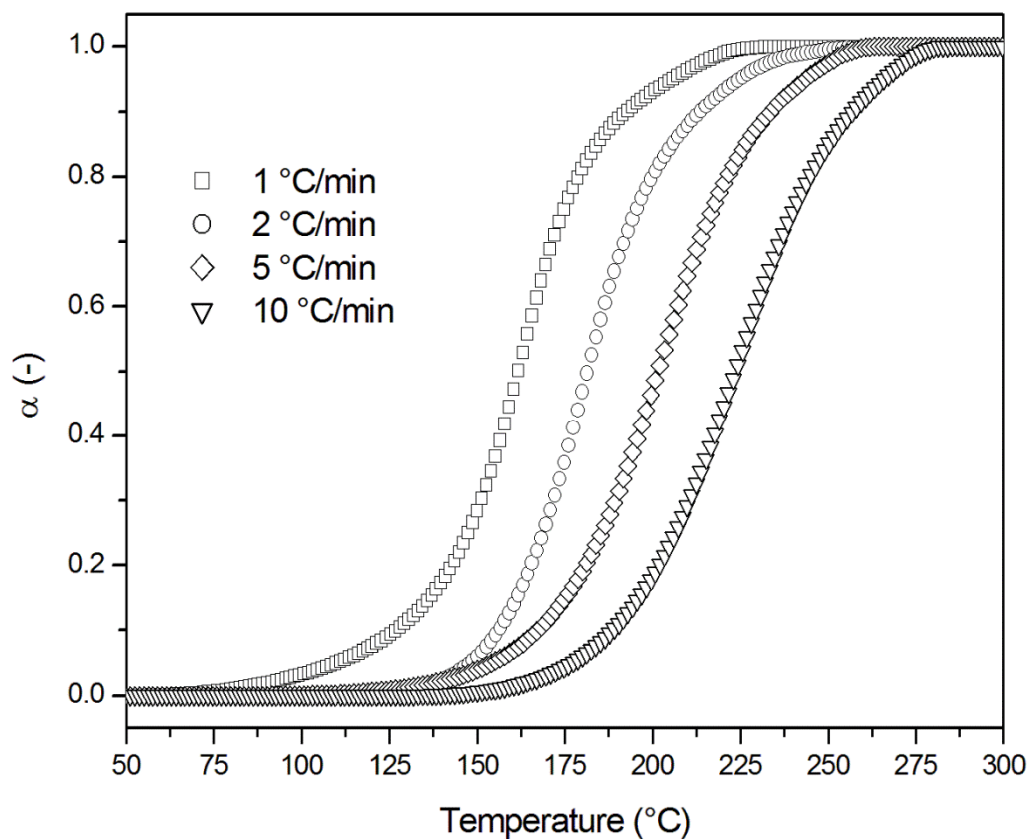


Figure 5 Degree of cure of RTM6-binder mixture at different heating rates.

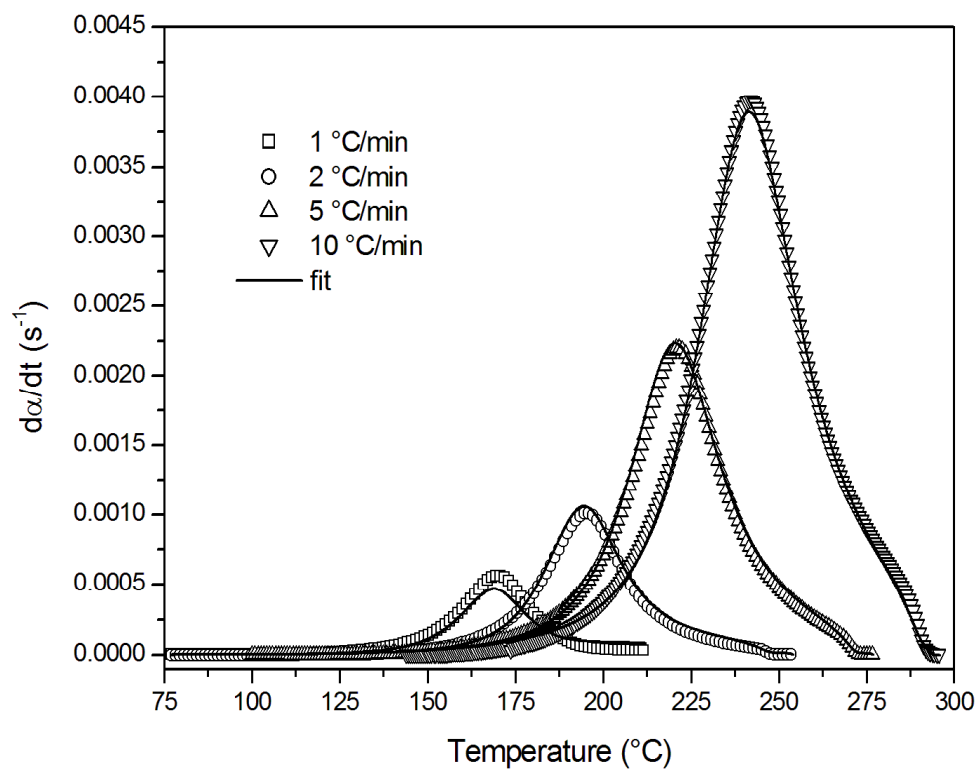


Figure 6: Comparison between the experimental data and the non linear fit for neat RTM6 resin at different heating rates

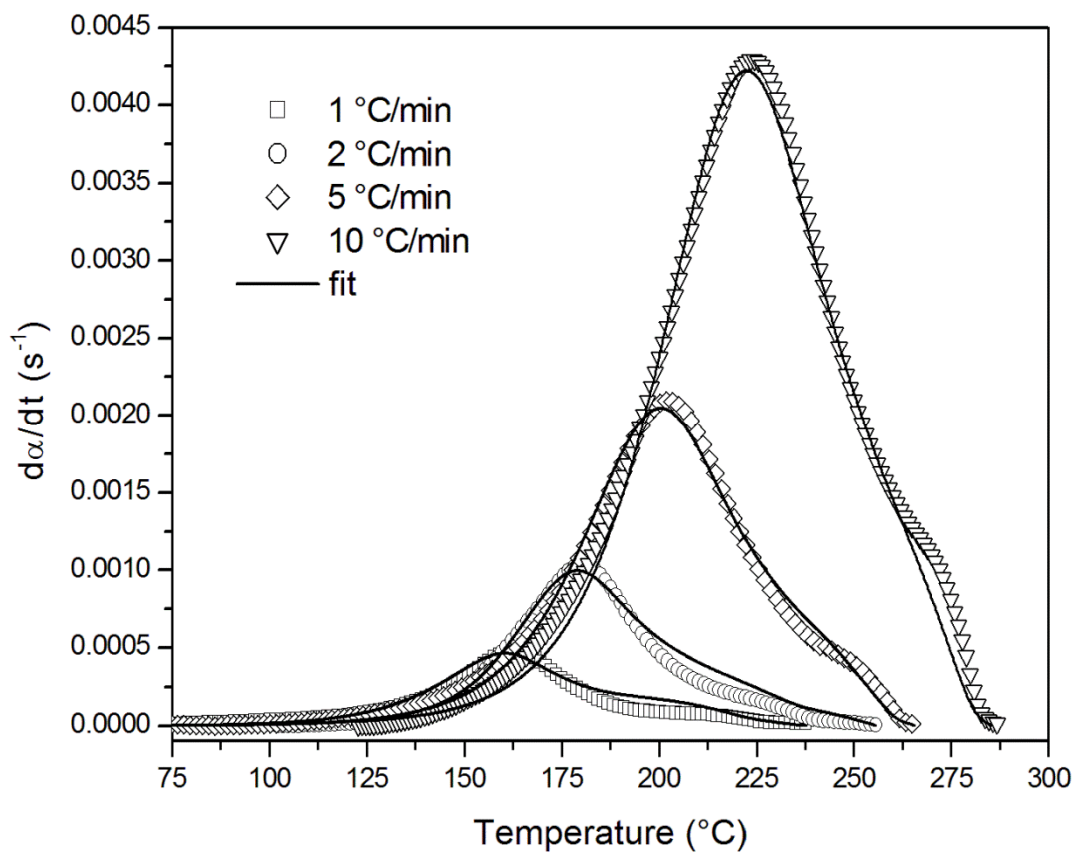


Figure 7 Comparison between the experimental data and the non linear fit for RTM6-binder mixture at different heating rates

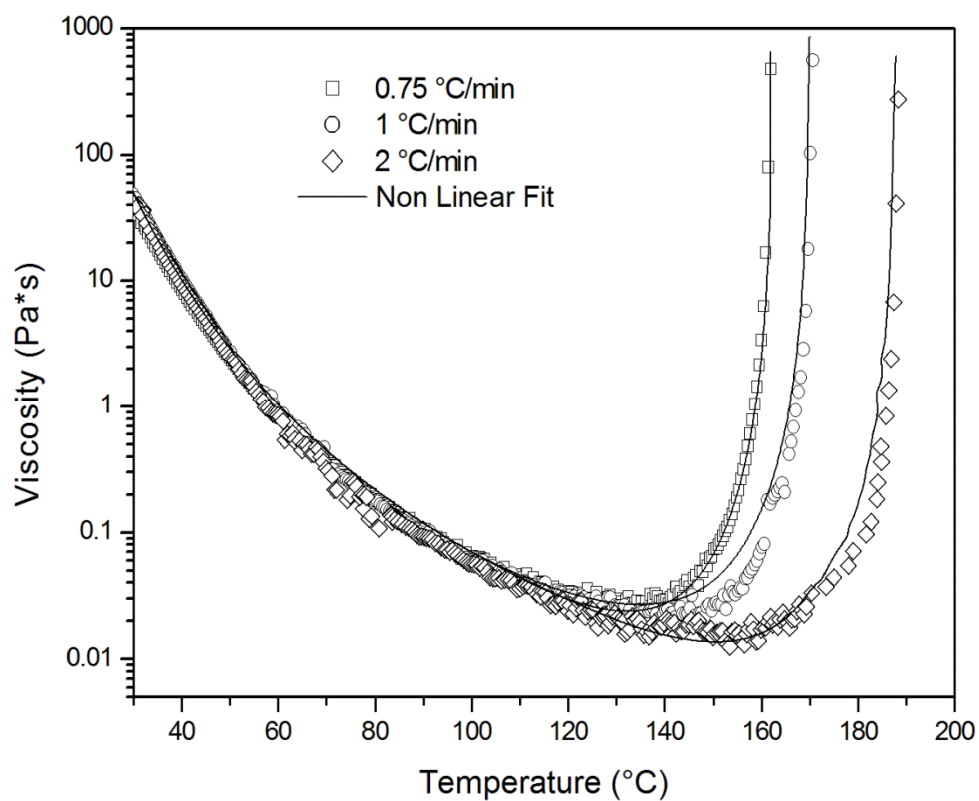


Figure 8 Comparison between the experimental data on neat RTM6 and the non linear fit for different heating rates

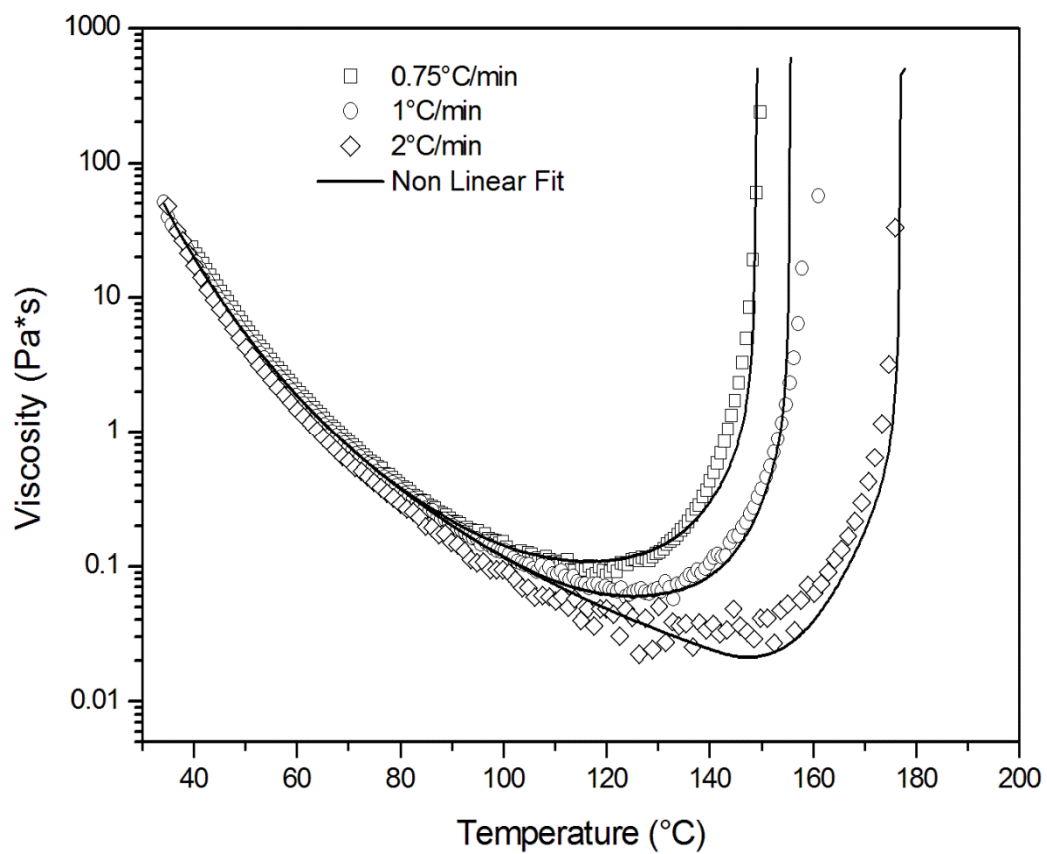


Figure 9 Comparison between the experimental data on RTM6-binder mixture and the non linear fit for different heating rates