Article

An Efficient Thermal Cure Profile for Thick Parts Made by Reactive Processing of Acrylic Thermoplastic Composites

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Abstract: The process of curing of large thick composite parts needs attention regarding the formation of residual stresses. Similarly, novel reactive thermoplastics need investigating to produce an efficient thermal cure profile that decreases the risk of warpage and residual stress. In this work, the polymerization kinetics of the Elium resin system is investigated by differential scanning calorimetry (DSC) tests, the analysis of thermo-grams, and the parameters of Kamal and Sourour’s semi-empirical model. A numerical model based on finite elements was set up to reproduce the temperature fields during part consolidation. Several processing conditions were investigated (dwell temperature, environment, heat exchange) in order to predict the thermal gradient within the part. The optimal cure profile was identified as a function of process parameters with the aim of minimizing the thermal gradient within the composite element. The analysis revealed that, for the reactive thermoplastic Elium, the consolidation in facilities with high thermal exchange may increase the risk of residual stresses within the parts, erasing the advantage of short cure cycles.

Keywords: reactive thermoplastic; process model; exothermic reaction; FRP; kinetic model

1. Introduction

Demand for fibre reinforced thermoplastic composites in the aerospace and aircraft industries is increasing due to several benefits compared to thermoset composites, including short process times, superior toughness, possible automation, and easier recyclability [1].

Typically, a melting process is used as the manufacturing process for structural thermoplastic composite components; the thermoplastic resin is melted, formed, and solidified. The principal disadvantage of this type of matrix is its relatively high viscosity, limiting the size and shape of the manufacturing component [1]. As an alternative to the melting process, a new class of reactive thermoplastic resins was developed, for example, polyurethanes (TPUs), polyamide (PA), polyethyleneteraphtalate (PET), polybutylene terephthalate (PBT), and polycarbonate (PC) [1].

Recently, Arkema developed a system based on methyl methacrylate (MMA), its trade-name being Elium®, which is an ideal candidate for substitution epoxy and thermoplastics in manufacturing composites. It is easy to process, and it is suitable for further reprocessing, such as joining [2] and recycling [3].

Elium® is a mixture of 2-Propenoic acid, 2-methyl-, methyl ester or methyl methacrylate (MMA) monomer and acrylic co-polymers. MMA undergoes a free radical polymerisation and converts into PMMA. The main advantage of the Elium® resin is the possibility to pre-impregnated the fibre reinforcement due to the liquid state at room temperature and the relatively low viscosity of 0.2 Pa·s and is suitable for VARI and RTM processes [4,5].

During the fibre reinforced Elium® composite processing, internal overheating may occur due to the exothermic reaction of radical polymerisation, as occurs in thermosetting resins. This further exothermic heating can lead to boiling the thermoplastic resin with
the consequent presence of voids in the composite parts. In addition, the high thermal gradient through the thickness of the composite can cause unwanted residual stress and shape distortion, as studied in thermoset composites [6–8].

Several studies have focused on Elium® resins and their composites, particularly on mechanical behaviour and fracture response, compared to the conventional thermosetting matrix. For example, the interlaminar Mode I fracture toughness (ILFT) behaviour was studied by Budholia et al. [4], showing that the ILFT response of the Elium® composites was comparable to the epoxy. Mode II interlaminar fracture was also compared with the epoxy matrix by Barbosa et al. [9] and was found to be up to 40% higher. Additionally, Cadieu et al. [10] proposed an optimised thermal cycle for the polymerisation of Elium® 150 resin, based on the loading rate effect on the mechanical properties of laminated composites.

One of the principal advantages of the thermoplastic resins is the possibility of welding as joining technologies, as investigated by Bhudolia et al. [11]; in particular, the authors optimised ultrasonic welding parameters, obtaining a maximum lap shear carbon/Elium® composite of 23.2% higher than the adhesively bonded Elium® laminates. The impact performances of Elium® composites have been studied and compared with the epoxy composites. In particular, the Elium® resin system presents a smaller delamination extension than for the epoxy composite, as demonstrated by Kinvi-Dossou et al. [12]. Additionally, Boumbimba et al. [13] highlighted the increase in impact resistance at the temperature of 80 °C due to the addition of tri-block copolymers.

The Elium® 150 polymerisation reaction was investigated in [14], highlighting its influence by temperature and the peroxide initiator. The effect of environmental conditioning was investigated by Nash et al. [15] for possible marine application; it was demonstrated that the interlaminar shear strength and dynamic mechanical properties were comparable to the traditional marine resin systems. Kazemi et al. [16] investigated the mechanical properties of the ultra-high-molecular-weight polyethylene fabric/Elium® laminates and also demonstrated that Elium® can replace traditional resins for the fabrication of composite structures.

Therefore, an advanced cure monitoring system and microwave were developed and applied by Pantelelis et al. [17] to manufacture Elium® composites. In particular, the authors achieved a 25% increase of the Elium®’s speed reaction, determining the temperature evolution and resistance of the Elium® composite. Shin et al. [18] studied the chemical kinetics and rheology of partially polymerised carbon/PMMA prepregs to develop a standard method for material processing for reactive thermoplastic prepregs. Although several researchers studied Elium® thermoplastic resins and their composites, there is a lack of literature on the exothermic reaction and kinetic analysis of polymerisation. Han et al. [19] proposed a polymerisation kinetic model for the Elium® 150 system; however, it was also stated that a highly exothermic reaction occurs during the manufacturing of Elium® composites that can cause peak temperatures higher than the boiling temperature of resin at 100 °C. Obande et al. [20] reported the need for a proprietary exothermic control agent to produce glass fibre-reinforced acrylic laminates. These results were confirmed by Charlier et al. [21], who showed a constant heat flow and reaction rate of up to 40% conversion and subsequently a rapid increase in reaction rate of up to 100% conversion. This phenomenon, linked to an auto-acceleration phenomenon (the gel effect), reported inducing a high degree of exotherm in bulk free radical polymerisation; this can produce an uncontrolled and nonuniform temperature distribution and subsequently residual stresses in the Elium® composite laminate.

During the manufacturing process of composite materials, the final shape and dimension of the parts cannot accurately reproduce the mould shape due to the residual stress generated inside the part by the temperature gradients during the cure. Many papers have been published that focus on the rise of thermal distortion due to thermal gradients during consolidation [22]. As demonstrated by Yuan et al. [23], internal stresses also occur during
the heating and dwell stage and not only during the cooling down until room temperature stage. This phenomenon is related to matrix curing due to the exothermal reaction.

Novel reactive thermoplastics open the chance to consider processing methodologies of a thermoset to a new class of materials. However, there is a lack of work investigating the effects of thermal distribution within the manufacturing of large parts by such materials. This paper aims to assess the exothermic reaction and a polymerisation kinetic model for the Elium\textsuperscript{®} 188 system composite. In particular, the polymerisation kinetics of the Elium\textsuperscript{®} resin is investigated by conducting isothermal and dynamic differential scanning calorimetry (DSC) tests and, based on the fitting data analysis, a temperature-dependent kinetics model is proposed. The founded kinetic model and the average of the total heat of polymerisation reaction was implemented in the FE model that was developed to predict the temperature distribution and the degree of polymerisation during the autoclave and oven curing of the GF/Elium\textsuperscript{®} laminates. The final target of the present work is to investigate the advantages and disadvantages related to the use of more efficient procedures (i.e., autoclave curing) in the fabrication of Elium-based components.

2. Materials and Methods

2.1. Materials

Arkema supplied Elium\textsuperscript{®} 188 resin, and 3\% of dibenzoyl peroxide (BPO, Carlo Erba Reagents, Milano, Italy) was used as initiator as prescribed by the resin manufacturer (Arkema, Colombes Cedex, France)\textsuperscript{[24]}. The samples for the differential scanning calorimetry (DSC) tests were prepared by mixing Elium\textsuperscript{®} with the BPO at room temperature. Before using the BPO powder, it was shaken as reported in the manufacturer’s manual. Then, BPO and liquid resin were mixed using a Centrifugal Vacuum Mixer combining two different stages: the first was a planetary mixing at 1000 rpm for 1 min, the second was a combining vacuum pressure reduction with mixing at 500 rpm for 4 min. This procedure allows reaching a homogeneous solution with no particles or air bubbles visible.

2.2. DSC Analysis

Samples of approximately 15 mg were tested by DSC Discovery series supplied by TA Instruments, New Castle, DE, USA. Tests were conducted under nitrogen as a gas purge to avoid a possible reaction and oxidation of the polymer and to cool the specimens rapidly.

Dynamic and isothermal DSC experiments conducted by Dynamic DSC scans were performed to obtain a complete polymerisation and the corresponding total heat generation; in particular, they were conducted at three different heating rates of 1, 5, and 10 °C/min; the results are reported in Table 1. Moreover, the isothermal tests were conducted at temperatures of 25, 60, and 100 °C. All the experiments were repeated three times due to obtaining a repeatable and reliable measurement. The total heat of reaction ($\Delta H_{tot}$) was estimated from DSC experiments by integrating the heat flow from the dynamic DSC tests. At the same time, isothermal scans were adopted to evaluate the polymerisation kinetics.

| Heating Rate (°C/min) | 1    | 5    | 10   | Average |
|-----------------------|------|------|------|---------|
| $\Delta H_{tot}$ (J/g) | 251.15 | 240.35 | 234.98 | 242.16 |

The final degree of polymerisation (DoP), $\alpha$, was calculated as:

$$\alpha = \frac{\Delta H}{\Delta H_{tot}}$$ (1)
where $\Delta H$ was the heat generated by the reaction of a unit mass of the resin at the end of the isothermal DSC tests, the resin is considered fully polymerised when $\alpha = 1$. Therefore, the rate of DoP, $d\alpha/dt$, is proportional to the rate of heat flow:

$$
\frac{d\alpha}{dt} = \frac{\Delta(H)}{dt} \frac{1}{\Delta H_{\text{tot}}}
$$

(2)

Different polymerisation kinetics models have been proposed and analysed in the literature to describe reactive PMMA polymerisation [19,25]. In the present work, a semi-empirical autocatalytic model (Kamal and Sourour [26]) was adopted:

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

(3)

where l and m are the reaction orders of the four parameters model, while $k_1$ and $k_2$ are the rate constants defined by an Arrhenius expression:

$$
k(T) = A e^{-\frac{E}{RT}}
$$

(4)

E is the activation energy, A is the pre-exponential factor, R is the gas constant (8.314 J/mol K), and T is the absolute temperature (K).

A MATLAB script was implemented in order to estimate the kinetic parameters of the system. The numerical procedures rely on the least square regression of experimental DoP according to the model described by Equations (1)–(3).

3. Modelling

The model was developed to study the time variation of temperature and the degree of cure (DoP) of the thermo-reactive resin. The Equation governing heat transfer in the resin during the manufacturing process is [27]:

$$
\rho C_p \frac{\partial T}{\partial t} = k_x \left( \frac{\partial^2 T}{\partial x^2} \right) + k_y \left( \frac{\partial^2 T}{\partial y^2} \right) + k_z \left( \frac{\partial^2 T}{\partial z^2} \right) + \rho \Delta H_{\text{tot}} \frac{\partial \alpha}{\partial t} (1 - V_f)
$$

(5)

where $T$ is the temperature, $t$ is the time, and $x,y,z$ are spatial coordinates in the Cartesian coordinate system, $C_p$, $\rho$, and $k_i$ are the composite material’s specific heat, density, and thermal conductivity.

The second part of this Equation represents the internal volumetric heat generation occurring during the polymerisation of the resin. $\Delta H_{\text{tot}}$ and $V_f$ represent the total reaction enthalpy and the volume fibre, respectively, while $\partial \alpha / \partial t$ is the rate of polymerisation, which is a function of DoP and temperature as reported in Equation (3). In order to resolve the time derivative of the degree of cure, the ordinary differential equations (ODEs) and differential algebraic equations (DAEs) interface was added to the heat transfer. Equation (3) is indicated as $f$ and the Equation assuming is:

$$
e_a \frac{\partial^2 \alpha}{\partial t^2} + d_a \frac{\partial \alpha}{\partial t} = f
$$

(6)

where $d_a$ damping term is unity, and the mass coefficient $e_a$ is zero. The initial condition of zero indicates that the material is modelled starting from the uncured state.

Finite Elements Analysis

A 3D finite element model of the Elium® polymerisation process, both for the autoclave cure and the oven cure cycle, was created using the Comsol Multiphysics software. The developed model was conducted to validate the assumed kinetic model. As a result, the transient thermal conduction is given by the first term of Equation (5), coupled with the resin polymerisation equation’s kinetic model (3).
The following assumptions were made in the 3D model, both for the workpiece and the mould: (i) the material was considered homogeneous, isotropic, and well mixed; (ii) the density, specific heat capacity, and thermal conductivity were considered constant; and (iii) heat transfer between the workpiece and the mould was considered.

The Elium® resin and mould properties used in the FE model are shown in Table 2. The density of Elium® resin and the thermal capacity was obtained from data reported in the literature [28,29], while the thermal conductivity was obtained by applying the mixture rule [30], considering the value for the glass fibres equal to 0.18 W/(m*K).

Table 2. Thermal properties of the glass/Elium® components and aluminium mould used in the thermal simulation of the polymerisation curing process.

| Material       | Parameter | Value | Unit     |
|----------------|-----------|-------|----------|
| Aluminium      | ρ         | 2700  | kg/m³    |
|                | Cp        | 900   | J/(kg*K) |
|                | kx = ky = kzz | 79.5 | W/(m*K)  |
| Elium®/GF      | ρ         | 1910  | kg/m³    |
|                | Cp        | 1200  | J/(kg*K) |
|                | kx = ky = kzz | 0.8  | W/(m*K)  |

Two case studies were selected to investigate the temperature gradient within the composite part during consolidation, at low heat transfer (10 W/m² K) and high heat transfer (100 W/m² K), reproducing the boundary conditions in the cases of out of autoclave and autoclave curing, respectively [27]. Furthermore, to consider the decrease of energy transfer during the cooling down stage, the environmental parameters were halved during the cooling. In order to introduce the energy released due to the Elium conversion (exothermic reaction [19]), a heat generation contribution was added to the energy balance in correlation of the composite part (Figure 1b).

Figure 2 shows the mesh used in the FE model; the legends indicate the quality of the mesh elements.
For studying the temperature evolution during the cure, three different thermal cycles were considered. Table 3 reports dwell times for each cycle heating rate, and the cooling rate was considered similar for each cycle, 5 and 2 °C/min, respectively.

Table 3. Thermal cycle imposed.

| Tmax (°C) | 25  | 60  | 100 |
|----------|-----|-----|-----|
| Dwell time (min) | 360 | 90  | 30  |

The proposed alternative cure cycles aim to provide a shorter process time; however, shortening the thermal cycle leads to an increase in thermal mismatches within the parts, which can promote the formation of residual stresses or geometrical distortion of the composite part. The present investigation aims to identify an optimised cure profile that allows shortening of the processing time and concurrently minimising the thermal gradient.

4. Results

4.1. Kinetics Model

The DoP was estimated using the obtained total heat of reaction using Equations (1) and (2) for isothermal DSC experiments. The averaged heat of reaction estimated by the dynamic DSC test was 242 J/g for a fully polymerised resin.

The best fit parameters obtained for the polymerisation kinetics model expressed in Equation (3) are presented in Table 4. Figure 3 shows the fitting curves compared with the experimental data. It is seen that the fitted model accurately predicted the trends of the DoP as well as the polymerisation rate evolutions for all three isothermal temperatures. Furthermore, the obtained rate of polymerisation and DoP are consistent with the obtained observations reported in [31]. However, as previously noticed by Kuppusami et al. [26], the autocatalytic model considered is less accurate at lower temperatures.
Table 4. Kinetics parameters estimated for the Elium 188-O/3%wt BPO system.

| Parameter | Value       | Unit       |
|-----------|-------------|------------|
| $A_1$     | $1.8 \times 10^3$ | 1/s        |
| $A_2$     | 1.99        | 1/s        |
| $l$       | 1.30        |            |
| $m$       | 1.75        |            |
| $E_1$     | $4.34 \times 10^4$ | J/mol     |
| $E_2$     | $1.50 \times 10^4$ | J/mol     |
| $\Delta H_{\text{tot}}$ | 242         | kJ/kg      |
| $R_{\text{gas}}$ | 8.314       | J/(mol*K)  |

Figure 3. The polymerisation rate as a function of DoP for the experimental and predicted (best fit) DoP evolutions.

4.2. Low Thermal Exchange Environment

Figure 4 shows the temperature profile obtained from the simulation of the cycle curing at 25 °C and the dwell time of 360 min. The first evident result is the presence of a temperature peak due to the exothermic polymerisation reaction. This instant coincides with the maximum temperature gradient inside the part, equal to 14.22 °C.

Figure 5a shows the temperature distribution inside the part at the maximum gradient value. This nonuniformity of temperature inside the part is reduced by the dwell time. As highlighted by Figure 5b, the temperature distribution inside the part and the mould after 360 min is uniform.

Figure 6 reports the temperature field at the time related to the complete conversion of the polymer ($\alpha$ is equal to 0.95, vitrification state). This instant is relevant since the temperature mismatch will lead to thermal stresses during the cooling stage and can be released when the mould is removed.
4.2. Low Thermal Exchange Environment

Figure 3. The polymerisation rate as a function of DoP for the experimental and predicted (best fit) DoP evolutions.

Figure 4. Temperature profile inside the part for the hottest and coldest points and their gradient for the cycle at Tmax equal to 25 °C.

As highlighted by Figure 5b, the temperature distribution inside the part and the mould after 360 min is uniform.

Figure 6 reports the temperature field at the time related to the complete conversion of the polymer (\(\alpha\) is equal to 0.95, vitrification state). This instant is relevant since the temperature mismatch will lead to thermal stresses during the cooling stage and can be released when the mould is removed.

Figure 7. Temperature distributions within the mould at the end of the dwell highlight an increase of the thermal gradient as the dwell temperature increased, since the slow heat transfer did not ensure that the mould reached the environment temperature for the considered thermal cycle.
The temperature distributions within the mould (Figure 7) at the end of the dwell highlight an increase of the thermal gradient as the dwell temperature increased, since the slow heat transfer did not ensure that the mould reached the environment temperature for the considered thermal cycle.

Figure 7. Temperature distribution plot in the part and the mould at the end of dwell phase before the cooling ramp for the curing cycle at (a) 60 °C and (b) 100 °C.

Figure 8 shows the trend of the DoP (α) vs. the thermal cycle. The instant in which the resin reaches a value of \( \alpha = 0.95 \), which is conventionally indicated as the complete conversion of the material, depends on the specified boundary conditions.

Figure 8. Thermal cycle vs. \( \alpha \) (DoP) for the curing cycle at (a) 60 °C and (b) 100 °C.

Figure 9 shows the isotherms generated inside the piece and the mould for the value of \( \alpha = 0.95 \) for each case analysed. It can also be seen that the time required for complete polymerisation of the resin decreases as the maximum temperature reached increases; conversely, the temperature distribution is more uniform in inverse proportion to the maximum temperature.
4.3. High Thermal Flow Environment

However, this temperature gradient gradually decreases once the dwell phase begins until it disappears shortly before the cooling phase ends. This is evident from the plots shown in Figure 10 in which the temperature distributions inside the mould and the workpiece are shown just before the cooling phase begins for each case under consideration.

Figure 10. Temperature distribution plot in the part and the mould at the end of dwell phase before the cooling ramp for the curing cycle at (a) 60 °C and (b) 100 °C.

Figure 11 shows how the degree of polymerisation ($\alpha$) varies with the variation of the thermal cycle for the hottest and coldest points, respectively, which confirms what was previously described. The instant in which the resin reaches a value of $\alpha = 0.95$ (conventionally referred to as complete conversion of the material) depends on the specified boundary conditions. Figure 12 shows the isotherm curves generated inside the part and the mould for the value of $\alpha = 0.95$ for each case analysed. It is also possible that the time required for the complete polymerisation of the resin is reduced as the maximum temperature reached increases; conversely, the temperature distribution is more uniform in an inversely proportional trend to the maximum temperature.
5. Discussion

The cure of large components leads to non-homogeneous process due to the exothermic behaviour of Elium 188–0 during its consolidation. This nonuniformity is strictly dependent on the thickness due to the mass effects. This phenomenon is evident from Figure 13, which shows the temperature trend inside the part when the thermal gradient is at its maximum; the warmest point is situated where the thickness is larger.

In addition, comparing the thermal fields at 60 °C (Figure 13a) and at 100 °C (Figure 13b), the maximum $\Delta T$ occurring in the laminate is lower in the out of autoclave case with respect to the autoclave processing, reducing the possibility of residual stresses.

Since the curing process is an exothermic reaction, the generated heat induces a thermal expansion of the resin system before a shrinkage caused by the phase change (from liquid-state to solid-state, gelation onset).

The stresses built up inside the composite parts as a consequence of temperature distribution (related to the chemical reaction during resin consolidation) and as a consequence of thermal expansion mismatches between fibres and polymers after the gelation point.
Figure 13. Temperature distribution within the part at the time when $\Delta T$ is maximum for the cure at 60 °C (a) and 100 °C (b).

Therefore, internal stress developments are governed by coupling chemistry, thermal distribution, and the local stiffness. The relationship between the curing rate and the shrinkage is linear as reported in [32]. Based on the results reported, the critical value of DoP for the formation of induced residual stress is in the range of 0.5 and 0.7, which identifies gelation and vitrification, respectively (Figure 14).

Figure 14. DoP evolution during the thermal cycle.

The temperature profile associated with the two fast curing cycles as reported in Table 3 are shown in Figure 15. Here, the temperature profiles are compared to the temperature history for the warmest and coolest points inside the workpiece and their temperature gradient.

The component cannot reach the maximum temperature expected, according to the imposed, as highlighted in Figure 16. Although the temperature distributions inside the mould and the work piece are shown for both thermal cycles, the temperature profiles are computed at the end of the dwell time. In both cases, the part did not reach the dwell temperature.
Figure 15. Temperature profile inside the part for the hottest and coldest points and their gradient for the cycle at Tmax equal to 60 °C (a) and 100 °C (b).

The component cannot reach the maximum temperature expected, according to the imposed, as highlighted in Figure 16. Although the temperature distributions inside the mould and the work piece are shown for both thermal cycles, the temperature profiles are computed at the end of the dwell time. In both cases, the part did not reach the dwell temperature.

Figure 16. Temperature distribution within the part at the time when ΔT is maximum for the cure at 60 °C (a) and 100 °C (b).

Figure 17 shows the temperature profile of the maximum and minimum temperature points inside the part and their temperature gradient for the high thermal flow environment. In this case, the temperature gradient is higher than the previous due to the higher convective flux.

According to the numerical procedure developed, the faster the process time, the higher the risk of promoting residual stress build-up. The temperature mismatches can be frozen within the composite parts as the vitrification time is shortened by high temperature cycles (Table 5). Table 5 reports the summary of simulations conducted. The need of a short cure cycle, and low temperature gradients are highlighted as a best cure profile for out-of-autoclave technology with a cure profile at 100 °C, while the best option for autoclave curing appears to be a cure at 60 °C.
Figure 17. Temperature profile inside the part for the hottest and coldest points and their gradient for the cycle at Tmax equal to 60 °C (a) and 100 °C (b) in the high thermal flow environment case.

| T Dwell (°C) | Tmax (°C) | ΔTmax (°C) | Time @ α = 0.95 (min) |
|-------------|-----------|------------|------------------------|
| Out of autoclave | 25 | 25.5 | 14.2 | 58.5 |
| | 60 | 56.8 | 18.5 | 46.5 |
| | 100 | 68.7 | 22.8 | 39.5 |
| Autoclave | 60 | 69.7 | 20.1 | 31.0 |
| | 100 | 96.2 | 43.7 | 21.0 |

6. Conclusions

Computational and experimental characterisation of polymerisation overheating in glass/Elium® acrylic thermoplastic resin composites were studied. First, the polymerisation kinetics model of the pure Elium® resin was developed based on the DSC experiments. Subsequently, the polymerisation kinetics model was coupled with the FE model, considering thermal and chemical coupling. The developed 3D thermal process model considers the polymerisation to be overheating by measuring the temperature evolution during the out of autoclave and autoclave curing processes of the glass/Elium® composites for different temperature processes. The proposed polymerisation kinetics model and the reported polymerisation overheating trend can be used to further optimise the manufacturing processes of Elium® composites. Based on the model set-up, an optimized cure cycle accounting for the need of low thermal gradient with short time was investigated.

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