Experimental and computational analysis of the polymerization overheating in thick glass/Elium® acrylic thermoplastic resin composites

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ABSTRACT

The exothermic reaction and overheating during radical polymerization of an Elium® resin and glass fiber reinforced Elium® composites are critically evaluated in this work. The polymerization kinetics of the Elium® resin is obtained by performing differential scanning calorimetry (DSC) scans. The measured data is fit to a temperature and degree of polymerization (DoP) dependent kinetics model. A coupled thermo-chemical process model is developed to predict the temperature evolution and DoP. First, the model is validated with the water bath experiments in which the pure Elium® resin is polymerized at different temperatures (30, 50 and 70 °C). The validated process model is then applied to a vacuum infusion process of glass reinforced Elium® composite laminates with different thicknesses (3.8, 7.5 and 11.3 mm) at room temperature. The produced laminates have the void content lower than 1%. The peak temperature is found to be approximately in the range of 155-160 °C during the water bath experiments. On the other hand, the peak exothermic temperature is approximately 49 °C and 70 °C for 3.8 mm and 11.3 mm thick laminate, respectively. The developed polymerization kinetics model is found to be effective as the predicted temperature evolutions match well with the measured temperatures for different laminates. The effect of laminate thickness and processing temperature on the peak temperature is studied by the developed numerical model. The thermo-chemical process model developed in this work is therefore capable of predicting the polymerization overheating for Elium® composites and can enable the optimization of the manufacturing process to control the thermal and DoP histories.

1. Introduction

Fiber reinforced thermoplastic composites (FRTPCs) are widely used in high-end aerospace and aircraft industries due to their high strength-to-weight ratio, fracture toughness and damage tolerance. The processing speed of thermoplastic composites is relatively fast as compared with their thermoset counterparts. In general, a melt process is used to manufacture structural FRTPCs in which the thermoplastic resin is melted, formed and solidified. The significant drawbacks of this thermal processing are the high processing temperatures and pressures together with their thermoset counterparts. In general, a melt process is used to manufacture structural FRTPCs in which the thermoplastic resin is melted, formed and solidified. The significant drawbacks of this thermal processing are the high processing temperatures and pressures together with relatively high viscosity of the thermoplastic material which limit the manufacturing of FRTPC parts in size and thickness [1]. An alternative to melt processing of the FRTPCs is the in-situ polymerization of monomeric or oligomeric thermoplastic materials. Some examples of reactive thermoplastic resins are the thermoplastic polyurethanes (TPUs), polyamides (PAs), polyethyleneteraphthalate (PET), polybutyleneteraphthalate (PBT) and Polycarbonate (PC) [1]. Another example is the recently developed Elium® acrylic resin which is composed of 2-Proponoic acid, 2-methyl-, methyl ester or methyl-methacrylate monomer (MMA) and acrylic copolymers in which MMA undergoes a free radical polymerization to its polymer PMMA. The advantage of commercially available Elium® is that the polymerization can take place at relatively low temperatures even at room temperature.

In reactive processing of Elium® composites, the fiber reinforcements are first impregnated with the resin which is in a liquid state at room temperature with a relatively low viscosity. Afterwards, the in-situ polymerization takes place by mixing the MMA monomers with compatible initiator systems such as a peroxide and applying stimuli such as heat, microwave or ultraviolet. One of the major challenges in processing fiber reinforced Elium® composites is the presence

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of internal overheating due to the exothermic reaction of the radical polymerization which is also seen in thermoset resins during the curing or cross-linking of the molecular groups. This might result in boiling of the thermoplastic resin and hence voids in the composite part. In addition, the large temperature difference can take place in thick composite manufacturing, which results in unwanted residual stresses and shape distortions as extensively investigated in thermoset composites [2–4]. Therefore, the polymerization reaction of Elium® composites has to be understood, described and predicted well in order to develop reliable FRTPCs by using the reactive manufacturing processes such as vacuum assisted resin transfer molding and pultrusion. The previous researches on Elium® resins and their composites are summarized in the following.

Barbosa et al. [5] compared the behavior of Elium® 150 in mode II interlaminar fracture with the traditional epoxy matrix, and found that it can resist up to 40% more than epoxy matrix composites based on the end notched flexure tests. With the optimized welding parameters of a weld time of 1.5 s and a weld pressure of 3 bar, the maximum lap shear strength of the welded carbon/Elium® composite laminate was found to be 23.2% higher than the adhesively bonded Elium® laminates [6]. Bhudolia et al. [7] studied mode I interlaminar fracture toughness (ILFT) behavior of Elium® composites. The results showed that the ILFT properties of thin ply thermoplastic composites was found to be 30% higher than the thick ply thermoplastic composites. Zoller et al. [8] optimized the process temperature by analyzing the radical polymerization of the acrylic resin and compared the conversion degree of the resin with different types of initiators. Elium® composites exhibited lower damage and higher residual strain than the epoxy composite through the load-unload cycles as reported in [9]. The advantage of the Elium® resin composite system in the vibration damping was presented in [10] by vibration and dynamic mechanical analysis tests and its structural damping was found to be 27% higher than the epoxy composites. Bouambilba et al. [11] found that the addition of acrylic tri-block copolymers led to an increase in impact resistance for test temperatures of 80 °C. This improvement was approximately 24% in terms of the penetration threshold. Kinvi-Dossou et al. [12] investigated the impact performances of Elium® composites and found that the delamination extension of acrylic composite was smaller than the one for epoxy composites.

In addition, the moisture diffusion behavior of Elium® composites was investigated in [13]. The results indicated that the weight gain at the saturation of flax-acrylic composite was found to be lower than that of flax-epoxy composite. The characterization of Elium® 150 polymerization reaction was studied in [14] and it was shown that the polymerization was influenced both by the peroxide initiator and the temperature. An optimized thermal cycle for the polymerization of Elium®150 resin was proposed in Cadieu et al. [15] studied the loading rate effect on the mechanical properties of a glass/Elium® 150 laminated composites. The results indicated that the loading rate had a significant influence on the macroscopic parameters of the behavior of the samples. Nash et al. [16] investigated the effect of environmental conditioning on the apparent interlaminar shear strength and dynamic mechanical properties of well-established marine resin systems- and Elium® -matrix composite materials. It was demonstrated that the insusible Elium® resin could be a candidate for the use in marine structures. Kazemi et al. [17] studied the mechanical properties of an ultra-high-molecular-weight polyethylene fabric/Elium® laminates and found that Elium® can be a competitive resin to replace the traditional resin in the fabrication of composite structures. An advanced cure monitoring system and a microwave system were developed and utilized to manufacture Elium® composites in [18]. The temperature evolution and resistance of Elium® composite were determined to obtain a better microwave heating by achieving a 25% increase in the speed of Elium® reaction. The chemical kinetics and rheology of a partially polymerized carbon/PMMA prepregs were investigated in [19] to develop materials processing guidelines for reactive thermoplastic prepregs.

Although Elium® thermoplastic resins and their composites were investigated by several researchers, to date there has been a limited focus on the exothermic reaction and resulting polymerization overheating in literature. It was stated in [20] that the highly exothermic reaction during the manufacturing of thick Elium® composites (12 mm or greater) could cause the peak temperature being higher than the resin boiling temperature of 100 °C. This might cause an uncontrolled temperature distribution and growth as well as process instabilities and unwanted monomer loss due to the boiling of the resin.

The objective of this paper is therefore to critically assess the exothermic reaction and overheating during manufacturing Elium® composites which have been overlooked in the literature. The polymerization kinetics of the Elium® resin is investigated by performing isothermal and dynamic differential scanning calorimetry (DSC) tests. To this end, a temperature dependent kinetics model is developed based on the data fitting analysis. The obtained kinetics model and the total heat of polymerization reaction are used in the transient thermochemical model to predict the temperature and degree of polymerization (DoP) evolutions during the manufacturing process. First, the transient thermo-chemical model is validated by measuring the temperature evolution during the reactive processing of the pure Elium® resin at different temperatures in a water bath. Then, the validated polymerization process model is used to predict the temperature evolution and overheating during the vacuum infusion process of glass fiber reinforced Elium® laminates with different thicknesses and process temperatures. The model predictions are compared with the measurements. The quality of the produced laminates with different thickness are evaluated by performing a microscopy analysis for the cross sections of the manufactured laminates.

2. Experiment

2.1. Materials

Elium®150 resin supplied from Arkema was used in this work. As an initiator, 2% Perkadox CH-50X Peroxide was mixed with the Elium® resin as recommended by the resin manufacturer [21]. A unidirectional (UD) glass fabric with an areal weight of 750 gsm (consisting of 660 gsm roving and 90 gsm random filament stitching) was used as the reinforcing fabric.

2.2. DSC analysis

DSC experiments were used to obtain the parameters necessary for the polymerization kinetics model of the liquid resin and the heat capacity for the fully polymerized resin and composites. The polymerization reaction of Elium® begins after mixing it with the peroxide at room temperature. The non-polymerized samples for DSC tests had a weight of approximately 10 mg. All samples were prepared with the same peroxide proportion, roughly the same weight, the same stirring time and the same total time from making the specimen to data recording. The polymerization characteristics of the Elium® resin was obtained by performing DSC tests using the Mettler Toledo DSC822e. It had two pans, a pan with the sample and another pan which was empty as a reference to track the heat flow. Hence, the heat flow was recorded by comparing the heat flow change in the pans during the DSC tests. The heat capacity was measured by using the fully polymerized pure Elium® (5 g) and Elium® composite by sweeping the temperature from −10 °C to 200 °C in the DSC experiments. Each experiment was repeated twice in order to have a repeatable and reliable measurements.

To develop a polymerization kinetics model, isothermal and dynamic DSC experiments were carried out. The isothermal experiments were performed at three different temperatures 30 °C, 50 °C and 70 °C. It should be noted that it is a difficult task to reach a fully polymerized state after the isothermal polymerization at lower temperatures [22]. Therefore, dynamic DSC scans were also performed to obtain a complete polymerization and determine the corresponding total heat generation.
during the polymerization process. The dynamic DSC scans were carried out at three different heating rates of 5 °C/min, 7.5 °C/min and 10 °C/min. Nitrogen was used as a purge gas in the DSC experiments to prevent possible reaction inhibitions and oxidation of the polymer.

From DSC experiments, heat flow vs. time and heat flow vs. temperature curves were obtained using the STAR® thermal analysis software. The total heat of reaction (ΔHtot) was calculated by integrating the heat flow with respect to time from the dynamic DSC tests. The final DoP (α) was calculated as:

\[ \alpha = \frac{\Delta H}{\Delta H_{\text{tot}}} \]  (1)

where ΔH was the heat generated by the reaction per unit mass of the resin at the end of the isothermal DSC tests. The resin was considered to be fully polymerized at \( \alpha = 1 \) where \( \alpha \) was the DoP. The rate of DoP, i.e. \( \frac{d\alpha}{dt} \), was assumed to be proportional to the rate of heat flow \( \frac{d(\Delta H)}{dt} \) which is expressed as:

\[ \frac{d\alpha}{dt} = \frac{d(\Delta H)}{dt} - \frac{1}{\Delta H_{\text{tot}}} \]  (2)

Different polymerization kinetics models have been proposed and analyzed to describe the polymerization of the PMMA thermoplastic resin systems [23,24]. A well-known semi-empirical Arrhenius type autocatalytic model was used in this work for the rate of DoP as:

\[ \frac{d\alpha}{dt} = A_i \exp\left(-\frac{E_i}{RT}\right)(1-\alpha)^{n_i} + A_2 \exp\left(-\frac{E_2}{RT}\right)\alpha^{n_2}(\alpha_{\text{max}} - \alpha)^{n_3} \]  (3)

where the reaction rate \( \frac{d\alpha}{dt} \) was defined as a function of the DoP (\( \alpha \)) and the absolute temperature \( T \), with seven polymerization kinetic parameters namely the re-exponential constant \( A_i \)(\( i = 1, 2 \)), the activation energy \( E_i \)(\( i = 1, 2, 3 \)) and the universal gas constant \( R \), which was equal to 8.314 J/(mol K). In Eq. 3, \( \alpha_{\text{max}} \) was the maximum DoP that can be achieved at a certain isothermal temperature. Based on the obtained measured DoP rate from Eq. (1) and Eq. (2), the parameters in Eq. (3) were obtained by using the least squares nonlinear regression analysis in Matlab.

2.3. Exothermic reaction in a water bath

The exothermic temperature evolution was characterized during the polymerization of the Elium® resin mixture in a water bath by measuring the temperature evolution. A plastic cup with Elium® mixture was fixed in a heated water bath using fixture clamps as shown in Fig. 1(left). Three different water temperatures (30 °C, 50 °C and 70 °C) were used in the tests. Resin temperature as a function of time was measured by using thermocouples and a data logger from National Instruments. J-Type thermocouples were connected to a 4-Ch thermocouple input (NI 9211), and data were collected with a USB data logger (NI cDAQ-9171). Fig. 1(right) shows the Elium® resin mixture before reaction. The location of the thermocouple was fixed inside the resin using a plastic pipe and a metal stick. It should be noted that the mixture was immersed fully in the water bath.

A schematic view of the 2D geometry of the water bath experiment is shown in Fig. 2. The diameter of the cup was 59.2 mm, and the height of the Elium® mixture in the cup was 23.6 mm. The thermocouple was placed at around 20 mm from the sidewall and around 7.8 mm from the bottom surface. The total time of the water bath experiments was approximately 5000 s.

2.4. Vacuum assisted infusion of glass/Elium® laminates

Three different thermoplastic laminates with different thicknesses (3.8 mm, 7.5 mm, 11.3 mm) were fabricated at room temperature by using a vacuum assisted resin infusion process. The 3.8 mm, 7.5 mm and 11.3 mm thick laminates consisted of 4, 8, 12 UD glass fabric layers, respectively. The vacuum infusion process layout is shown in Fig. 3. The fabrication process started with cutting the dry glass fabrics. A glass plate was used as a mold which was first cleaned with an ethanol and then waxed with the 227-CEE release agent at least four times to demold the laminated composites easily. Afterwards, the UD glass fabrics were laid on the waxed mold, which was followed by the placement of the peel ply and flow mesh, as seen in Fig. 3. The thermocouples as the same type used in the water bath experiment were used to measure the temperature evolution in the laminate. The whole vacuum infusion system was sealed by a plastic bag with a sealant tape. Moreover, a leakage test was performed, which lasted 20 min to ensure that there was no air leakage. In order to decrease the void content in the produced laminate, the Elium® resin mixture was prepared and put in a vacuum chamber to degas for 2 min before the resin infusion as also done in [25]. The infused glass fiber reinforced Elium® laminates were kept at room temperature for around 3 h and afterwards demolded.

A schematic view of the vacuum infusion domain for the glass/Elium® laminates is seen in Fig. 4. The three laminates had the same length and width (150 mm × 150 mm) and a different uniform thickness of 3.8 mm, 7.5 mm and 11.3 mm after the manufacturing process. The fiber direction of the layers was in the X-direction. Only one thermocouple was placed at the center of 3.8 mm and 7.5 mm thick laminates. On the other hand, a total of three thermocouples was placed at the top (under the first fabric layer), center and bottom (between the glass mold and the last fabric layer) of 11.3 mm thick laminate as shown in Fig. 4(a).

2.5. Density measurement

The density of the produced Elium® composite laminates was esti-
mated by using the Archimedes principle. Total of four samples was prepared from each composite laminate with different thicknesses. The nominal dimensions of the specimens were approximately 30 mm × 15 mm for the laminate thicknesses of 3.8 mm, 7.5 mm, 11.3 mm. The specimens were fully submerged in the ethanol at room temperature during the tests, and the density was calculated by using the following relation:

\[ \rho_c = \rho_e m_c m_e \]  

(4)

where \( \rho_c \) and \( \rho_e \) represented the density of the specimen and the fluid (ethanol), respectively, \( m_e \) and \( m_c \) were the mass of the specimen which is fully submerged in the ethanol and the air, respectively.

2.6. Fiber volume fraction

The mass fraction of the fiber and the matrix was obtained by burning off the resin from the specimen. The specimens were utilized in the burning experiment after the density measurement. The required temperature to fully burn off the Elium® resin was determined to be 500 °C based on the Thermogravimetric analysis (TGA) tests performed in [26]. Accordingly, the specimens were put in ceramic crucibles in an oven at 500 °C for 3 h after which the resin was completely burned off in the oven, and only fiber reinforcement was left. The volume fraction of the fiber was then calculated by using the following relation:

\[ V_f = \frac{1}{1 + \frac{\rho_e}{\rho_r} \left( \frac{w_f}{w_r} - 1 \right)} \]  

(5)

where \( \rho_r \) and \( \rho_f \) represented the density of the resin and the fiber, respectively, \( V_f \) was the fiber volume fraction, \( w_f \) and \( w_r \) were the fiber and resin mass fraction, respectively, where \( w_f = 1 - w_r \). The resin mass fraction \( w_r \) was estimated by using Eq. (6).

\[ w_r = \frac{m_b - m_a}{m_c} \]  

(6)

where \( m_b \) was the total weight of cup and composites specimen before burning, \( m_a \) was the weight of the cup and composite specimen after burning and \( m_c \) was the mass of the composite specimen.

2.7. Microscopy analysis

Two samples were cut from each produced laminate and embedded in an epoxy resin which was cured for at least 24 h. Afterwards, the samples were polished using a Struers Tegramin-30 semiautomatic grinding and polishing machine for the microscopy analysis. The polished cross-sections and the internal microstructure of the produced glass/Elium® laminates were observed by using the Keyene VHX digital microscope.

3. Thermo-chemical process model

3.1. Governing equations

The general governing equation for the heat transfer problem was derived from the Fourier’s heat conduction equation [27]:

\[ \rho C_p \frac{\partial T}{\partial t} = k_x \frac{\partial^2 T}{\partial x^2} + k_y \frac{\partial^2 T}{\partial y^2} + k_z \frac{\partial^2 T}{\partial z^2} + Q' \]  

(7)

where \( T \) is the temperature, \( t \) is the time and \( x, y, z \) are spatial co-
ordinates in the Cartesian coordinate system, \( \rho \), \( C_p \) and \( k_i \) are the composite material’s density, specific heat and thermal conductivity, respectively. The volumetric heat source term (\( Q'' \)) represents the internal volumetric heat generation taking place during the polymerization of the resin and is expressed as,

\[
Q'' = \rho \Delta H_{\text{tot}} \left( 1 - V_f \right) \frac{d\alpha}{dt} \tag{8}
\]

where \( \Delta H_{\text{tot}} \) was the total reaction enthalpy during polymerization, \( V_f \) was the fiber volume fraction, \( d\alpha/dt \) was the rate of polymerization reaction which was a function of DoP (\( \alpha \)) and temperature (\( T \)) as shown in Eq. (3).

### 3.2. Numerical process model for polymerization of pure Elium®

A three dimensional (3D) finite element (FE) model of the Elium® polymerization process was built according to the water bath experiments described in section 2.3. The developed process model was used to validate the polymerization kinetics model. The transient heat conduction equation given in Eq. (7) was coupled with the resin polymerization kinetics model given in Eq. (3). The numerical process model was developed by using a general purpose FE software package ABAQUS to simulate the polymerization of the resin in the water bath.

The following assumptions were made in the 3D FE model: i) The material was homogenous, isotropic and well-mixed reaction system, ii) the density, specific heat capacity and heat conductivity were constant and iii) the effect of the plastic cup on the heat transfer was neglected.

The properties of the Elium® resin used in the FE model are shown in Table 1. The density of Elium® was obtained from the density measurement experiments. The heat capacity was obtained from the DSC experiments. The thermal conductivity was taken from [28]. For the sake of simplicity in the numerical simulations, the thermal properties of the Elium® resin were assumed to be constant as aforementioned which was also the case in [29] for PMMA since the changes in the thermal properties were described as relatively small during the polymerization.

The applied boundary conditions (BCs) in the model are shown in Fig. 5 (left). The top surface of the resin was assumed to be exposed to the ambient temperature (\( T_{\text{amb}} = 26 \, ^\circ\text{C} \)) via a convective heat transfer coefficient (\( h_t \)) of 5 W/m\(^2\)K by considering the free convection of air surrounding the top surface of the water bath. The side and bottom BCs were assumed to be exposed to the water temperature (\( T_{\text{water}} = 30 \, ^\circ\text{C}, 50 \, ^\circ\text{C}, 70 \, ^\circ\text{C} \)) via a relatively larger convective heat transfer coefficient (\( h_{bs} \)) of 100 W/m\(^2\)K. The simulation time was the same as the experimental time which was 5000 s. Fig. 5 (right) shows the mesh employed in the model. The element type used was the 8-nodes linear heat transfer brick (DC3D8) elements with a size of 1.31 mm, and the total number of elements used in the 3D FE model was 44,208.

### Table 1

<table>
<thead>
<tr>
<th>Material</th>
<th>( \rho ) [kg/m(^3)]</th>
<th>( C_p ) [J/kg K]</th>
<th>( k ) [W/m K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elium®</td>
<td>1183 (measured)</td>
<td>1550 (measured)</td>
<td>0.18 [28]</td>
</tr>
</tbody>
</table>

Fig. 4. Schematic view of the vacuum assisted resin infusion process domain for the glass/Elium® composite a) side view and b) top view. All dimensions are in mm.
Two subroutines were implemented in ABAQUS to couple the general heat transfer equation with the polymerization kinetics model. In the subroutine USDPLD, DoP was calculated by using a Fortran code by employing the following relation in the time domain:

\[ \alpha^{n+1} = \alpha^n + \left( \frac{d\alpha}{dt} \right) \Delta t, \quad n = 1, 2, \ldots \quad (9) \]

where \( \alpha^{n+1} \) was the DoP at the actual time step and \( \alpha^n \) represented the DoP at the previous time step. The variable \( \alpha \) had to be initialized, and the value of 0.0001 was set as the initial DoP. The second subroutine HETVAL was employed to calculate the internal heat generation due to the exothermic reaction. The FE software solves the coupled equations and outputs the temperature and DoP, allowing one to trace the thermal and polymerization histories during polymerization of the Elium® resin.

### 3.3. Numerical process model for polymerization of a fully infused laminate

In order to estimate the temperature and DoP evolutions during the vacuum infusion of glass/Elium® composites, a 3D model was developed in ABAQUS. The thermal conductivity of Elium® composites was obtained by the rule of mixture [30]. Here the thermal conductivity of the glass fiber was used as 0.18 W/(m·K) [27]. The employed dimensions of the laminates and the thermal properties used in the 3D thermal model are listed in Table 2.

![Fig. 5](image)

**Fig. 5.** The applied boundary conditions of the 3D FE model from side view (left) and the used FE mesh in the 3D thermo-chemical process simulations for the pure Elium® resin in the water bath (right).

The thermal properties and geometrical parameters of the glass/Elium® laminates used in the thermo-chemical simulation of the polymerization in vacuum assited resin infusion process are shown in **Table 2**.

![Laminate properties](image)

**Table 2**

Thermal properties and geometrical parameters of the glass/Elium® laminates used in the thermo-chemical simulation of the polymerization in vacuum assited resin infusion process.

<table>
<thead>
<tr>
<th>Name</th>
<th>Value</th>
<th>Unit</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>150</td>
<td>mm</td>
<td>Length and the width of the laminates.</td>
</tr>
<tr>
<td>h</td>
<td>3.8,7,5,11.3</td>
<td>mm</td>
<td>Thickness of the laminates.</td>
</tr>
<tr>
<td>( T_{\text{amb}} )</td>
<td>24</td>
<td>°C</td>
<td>Ambient temperature (Room temperature).</td>
</tr>
<tr>
<td>( h_s, h_{bs} )</td>
<td>5,20</td>
<td>W/ (m²·K)</td>
<td>Surface film condition [31].</td>
</tr>
<tr>
<td>( \rho_{C} )</td>
<td>1910</td>
<td>kg/m³</td>
<td>Density of the composite obtained from experiments.</td>
</tr>
<tr>
<td>( C_p )</td>
<td>1200</td>
<td>J/(kg·K)</td>
<td>Heat capacity of the composite obtained from experiments.</td>
</tr>
<tr>
<td>( k_x, k_y )</td>
<td>0.8,0.34,0.34</td>
<td>W/(m·K)</td>
<td>Thermal conductivity of the composite in x, y and z directions, respectively [30].</td>
</tr>
<tr>
<td>( \rho_r )</td>
<td>1180</td>
<td>kg/m³</td>
<td>Density of the resin obtained from experiments.</td>
</tr>
<tr>
<td>( \rho_f )</td>
<td>2620</td>
<td>kg/m³</td>
<td>Density of the E-glass fiber [32].</td>
</tr>
</tbody>
</table>
| \( V_f \) | 0.55 ± 0.04 | % | Fiber volume fraction obtained from experiments.

### 4. Results and discussion

#### 4.1. Polymerization kinetics

**Fig. 7** shows the heat flow evolution during isothermal DSC experiments at different temperatures. Elium® polymerization first went through a brief induction period, after which the rate of polymerization slightly decreased until it reached a minimum, as anticipated by the classical free-radical polymerization theory [33,34]. After this local minimum, the polymerization rate deviated from the classical theory by rapidly accelerating and then decelerating until the polymerization attained completion. This auto-acceleration phenomenon was known as the Trommsdorff effect or gel effect [34]. The onset of the auto-acceleration (point M) was defined as the moment when the polymerization rate departed from a certain value according to the classical theory of free-radical polymerization [35–37]. Then the polymerization rate reached the maximum (point S), followed by the deceleration stage and the end of polymerization (point K). The endpoint K is determined when the rate of the polymerization becomes close to zero [34]. The temperature, the type and the concentration of the initiator were the factors determining the onset and the intensity of autoacceleration [35,38]. The time of reaching point M was advanced with the increase of temperature, and the peak of the heat flow increased by increasing the temperature.

The dynamic DSC test results are shown in **Fig. 8**. The time at the heat flow peak decreased by increasing the heating rate due to the faster polymerization. **Table 3** shows the total exothermic heat of reaction (\( \Delta H_{\text{ex}} \)) for different heating rates which were obtained by integrating the heat flow versus time plots in the dynamic DSC experiments. The average value was calculated as 241 kJ/kg for a fully polymerized resin after the dynamic DSC scans. Due to the presence of acrylic copolymers within the Elium® resin and the limited increase in the average molecular weight of the polymer depending on the initiator content, the total heat of reaction was found to be lower than the one for MMA (550 kJ/kg [39]). The DoP was estimated by using the obtained total heat of reaction and using Eqs. (1) and (2) for isothermal DSC experiments. The calculated final DoP (\( \alpha_{\text{max}} \)) is listed in **Table 4** for different isothermal DSC temperatures. The final DoP at 30 °C was found to be 0.844 and increased to 0.992 at 70 °C. It shows that \( \alpha_{\text{max}} \) increased with the temperature by approximately 18%. The increase in \( \alpha_{\text{max}} \) was approximately 4% when the temperature increased from 50 °C to 70 °C. Based on the experimentally obtained \( \alpha_{\text{max}} \) seen in **Table 4**, a temperature dependent quadratic function was developed and fit to the estimated \( \alpha_{\text{max}} \) values.
The corresponding expression is given in Eq. (10) with the fitted parameters and the corresponding fitting curve is shown in Fig. 9.

\[
\alpha_{\text{max}} = \begin{cases} 
8.15 \times 10^{-3}T^2 + 0.05647 - 8.75, & 20^\circ C < T \leq 70^\circ C \\
1, & T > 70^\circ C 
\end{cases}
\]  

(11)

It was assumed that \( \alpha_{\text{max}} = 1 \) when the temperature was above 70 °C, as seen in Eq. (9). The DoP increased with increasing temperature when the temperature was below 70 °C [40].

The estimated best fit parameters for the polymerization kinetics model expressed in Eq. (3) are given in Table 5. The fitting curves compared with the experimental data are shown in Fig. 10. It is seen that the fitted model accurately predicted the trends of the DoP as well as the polymerization rate evolutions for all three isothermal temperatures. The obtained rate of polymerization and DoP are in line with the observations reported in [19, 33]. The predicted \( \alpha_{\text{max}} \) was found to be consistent with the experimental results. The DoP at the auto-acceleration region was found to be approximately 0.2 as was the case also in [14, 41].

4.2. Polymerization in water bath

In order to validate the polymerization kinetics model of the Elium® resin, three water bath experiments at different temperatures were

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Table 3

<table>
<thead>
<tr>
<th>Heating rate (°C/min)</th>
<th>( \Delta H_{\text{tot}} ) (kJ/kg)</th>
</tr>
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<tbody>
<tr>
<td>5</td>
<td>231</td>
</tr>
<tr>
<td>7.5</td>
<td>252</td>
</tr>
<tr>
<td>10</td>
<td>240</td>
</tr>
<tr>
<td>Average</td>
<td>241</td>
</tr>
</tbody>
</table>

Table 4

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>( \Delta H ) (kJ/kg)</th>
<th>( \alpha_{\text{max}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>203.4</td>
<td>0.844</td>
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<tr>
<td>50</td>
<td>229.2</td>
<td>0.951</td>
</tr>
<tr>
<td>70</td>
<td>239.0</td>
<td>0.992</td>
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</table>

The total heat of reaction (\( \Delta H \)) obtained from different isothermal polymerization temperatures and the corresponding final DoP (\( \alpha_{\text{max}} \)).

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Fig. 6. The mesh used in the 3D FE model (left) and the corresponding thermal boundary conditions of the 3D model illustrated from the side view (right).

Fig. 7. The heat flow evolution as a function of time obtained from the isothermal DSC tests at 30 °C, 50 °C and 70 °C.

Fig. 8. The heat flow evolution as a function of time obtained from the dynamic DSC tests with heating rates of 10 °C/min, 7.5 °C/min, 5 °C/min.

Fig. 9. Fitting curve for \( \alpha_{\text{max}} \) at different isothermal polymerization temperatures.
carried out. The same weight and percentage of Elium® resin mixture were prepared in a plastic cup and put in the water bath with set temperatures of 30 °C, 50 °C and 70 °C. Fig. 11(a) depicts the measured and predicted temperature evolution at the thermocouple location. It is seen that the thermal process model captured the main trends of the experimentally observed internal heat generation quite well. The peak temperatures for the 30 °C, 50 °C and 70 °C of water bath were found to be approximately 155 °C, 157 °C and 161 °C, respectively. The predicted peak temperatures and the corresponding process time matched quite well with the measured ones.

Fig. 11(b) shows the plots of the predicted DoP that reached 1 (i.e., fully polymerized) for all the different water temperatures. The polymerization time was approximately 1568s, 1013s, and 719s for water temperature of 30 °C, 50 °C and 70 °C, respectively. The temperature fluctuation can be seen clearly when the temperature reached around 100 °C for the 50 °C and 70 °C water bath experiments in Fig. 11 (a). This may be due to the boiling of resin which was at around 100 °C. These causes some sort of air bubbles and porosities in the polymerized resin which resulted in fluctuations and variations in the temperature measurements at around 100 °C. However, there was no temperature fluctuation for 30 °C water bath experiments. This was the case because the DoP was around 0.62 when the resin temperature reached 100 °C for 30 °C water bath experiments, which was much higher than 0.42 in the 50 °C experiments and 0.28 in the 70 °C experiments as seen in Fig. 11 (b). Hence, the resin did not boil at 100 °C for 30 °C water bath experiments and less bubbles were formed, which had negligible effect on the temperature measurement for the 30 °C experiments. These results imply that for a given 23.6 mm thickness Elium® mixture, there exists a minimum DoP (0.62) that can be used to avoid the boiling because the resin is solidified sufficiently. Fig. 12 shows the formed bubbles and porosities after the polymerization of Elium® resin at the water temperature of 70 °C. Therefore, this can be an explanation for the discrepancy between the predicted and measured temperature history for the resin.

<table>
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<tr>
<th>A_1 [1/s]</th>
<th>A_2 [1/s]</th>
<th>n_1</th>
<th>n_2</th>
<th>n_3</th>
<th>E_1 [J/mol]</th>
<th>E_2 [J/mol]</th>
<th>ΔH_{tot} [kJ/kg]</th>
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<td>3.0202</td>
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<td>7.4876 × 10^3</td>
<td>241</td>
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</table>

Fig. 10. The polymerization rate as a function of DoP for the isothermal DSC scans (left) and the experimental and predicted (best fit) DoP evolutions (right).

Fig. 11. Predicted and measured temperature evolution of the Elium® resin for water temperatures of 30 °C, 50 °C and 70 °C (a). The corresponding DoP evolution (b).
Fig. 13 shows the predicted temperature distributions within the resin with different isothermal water bath temperatures (30 °C, 50 °C and 70 °C) when the temperature reached its peak value due to internal heat generation. A total of 10 points were selected at the center of the resin to investigate the temperature evolution. The peak temperature of Elium® reaction for the different water temperature (30 °C, 50 °C and 70 °C) was obtained as 173.7 °C, 211 °C and 263.7 °C when the polymerization time was approximately 1560s, 1121s and 944s, respectively. It is seen that the regions with higher temperatures were located near the top surface because the heat was transferred in a faster way at the bottom and side surfaces than the top surface. Therefore, the heat was accumulated more near the top surface.

Fig. 14 and Fig. 15 show the temperature and DoP histories of Elium® resin at different location points indicated in Fig. 13. It is seen that the temperature and DoP difference in the through-thickness direction increased with the increase in water bath temperature. In other words, an increase in the applied thermal load resulted in a more non-uniform polymerization reaction. The largest temperature difference was approximately 180 °C for 70 °C water bath. The final DoP was 1 due to the highly exothermal reaction of the Elium®. The polymerization time was different according to the different locations within the resin solution. The region of a relatively fast polymerization time was at the bottom and side surfaces because the heating of the resin initiated earlier at the surfaces in contact with the water.

4.3. Vacuum infusion of laminates

In order to characterize the polymerization overheating in thick glass/Elium® acrylic thermoplastic resin composites, laminates with three different thicknesses were investigated. The 3.8 mm, 7.5 mm and 11.3 mm thick laminates were polymerized at the room temperature. The micrographs of the cross-section of the manufactured laminates are shown in Figs. 16–18. Overall, the void content was found to be below 1% by analyzing the microscopy images. Two different void types were observed namely the micro and meso-voids. The micro-voids were found to be located within the fiber tows of the UD layers. The meso-voids were observed between the UD layers only for 7.5 mm and 11.3 mm thick laminates as seen in Figs. 17 and 18.

Fig. 19 (a) shows a comparison of the temperature evolution at the center point between the simulation and the experimental results. Overall, a good agreement was found between the measured and predicted temperature evolutions. The measured peak temperature was obtained as 48.5 °C, 62.5 °C and 70 °C for 3.8 mm, 7.5 mm and 11.3 mm thick laminates, respectively. The predicted peak temperature was found to be close to the measured ones. Fig. 19(b) shows the predicted DoP for the laminates with different thicknesses. The \( \alpha_{\text{max}} \) was calculated as 0.958, 0.985 and 0.99 for 3.8 mm, 7.5 mm, and 11.3 mm thick laminates, respectively. Due to a lower internal generation and polymerization reaction rate for the 3.8 mm thick laminate, a lower final DoP was obtained. The polymerization time of 3.8 mm, 7.5 mm and 11.3 mm thick laminates were found to be approximately 2708s, 2514s and 2486s, respectively.

In Fig. 20, the predicted and measured temperatures at the center, top and bottom of the laminate with 12 plies (11.3 mm thick) are
Fig. 14. Predicted temperature vs. time plots for the pure Elium® resin at different points along the through thickness direction and located at the center of the 3D model for different water bath temperatures (a) 30 °C (b) 50 °C (c) 70 °C.

Fig. 15. DoP vs time plots for the pure Elium® resin at different points along the through thickness direction and located at the center of the 3D model for different water bath temperatures (a) 30 °C (b) 50 °C (c) 70 °C.
presented. The predicted temperature distribution and evolution trends matched well with the experiments. The maximum measured peak temperature was found to be located at the top surface, which was approximately 74 °C. The measured peak temperature at the center and bottom were approximately 70 °C and 58 °C, respectively. The predicted peak temperatures at the center and top were 68 °C and 69 °C which were 2 °C and 5 °C lower than the experimental values. The cooling rate of simulation at the bottom was faster than its experimental result which might be due to the assumptions made in the process model for the boundary conditions and material properties. Nevertheless, the peak temperature at the bottom in the simulation was almost the same as the experimental result.

Fig. 21 shows the contour plots of temperature distributions when the temperature reached the peak value at the polymerization time of 2682s, 2494s and 2466s for the 3.8 mm, 7.5 mm and 11.3 mm thick laminates, respectively. It is seen that the maximum temperatures took place near the top region of the laminates, as also observed with the thermocouple measurements.
Fig. 22 shows the thermal history of different laminates at the selected points as indicated in Fig. 21. The predicted peak temperature for the different thicknesses (3.8 mm, 7.5 mm, 11.3 mm) was found to be approximately 48 °C, 64 °C, 69 °C, where the corresponding location was approximately at 1.9 mm, 5.7 mm, 9.4 mm from the bottom surface, respectively. The maximum through thickness temperature difference of the 3.8 mm, 7.5 mm and 11.3 mm thick laminate was found to be around 3 °C, 8 °C and 10 °C, respectively. The temperature difference in the thickness direction increased with an increase in laminate thickness, which also influenced the DoP, as seen in Fig. 23.

Fig. 23 shows the DoP of different laminates at different points on the centerline along the thickness direction. The DoP was influenced by the temperature history of the laminate. The maximum DoP of 3.8 mm, 7.5 mm and 11.3 mm thick laminate was found to be around 0.958, 0.985 and 0.991, respectively. This indicates that the maximum DoP increases with the increase of thickness of the laminate. The highest difference of DoP for 3.8 mm, 7.5 mm and 11.3 mm thick laminate was found to be approximately 0.01, 0.015 and 0.03, respectively. This suggests that the DoP is different at different positions of laminate, and the highest difference of DoP increases with the increase of laminate thickness. The reason could be the larger internal heat generation for the thicker laminates which results in a larger through thickness temperature and DoP difference [42].

By using the developed numerical process model, the effect of laminate thickness and mold temperature (Room temperature (24 °C), 30 °C and 50 °C) on the temperature peak was investigated as shown in Fig. 24. It is seen that the temperature peak increased with the laminate thickness and the mold temperature with a non-linear trend. The obtained temperature peaks were found to be lower than 100 °C. The change in temperature peak became less as the laminate thickness increased. In other words, the effect of thickness on the temperature peak was found to decrease for relatively thick laminates.

5. Conclusions

Computational and experimental characterization of polymerization overheating in thick glass/Elium® acrylic thermoplastic resin composites was studied. First, the polymerization kinetics model of the pure Elium® resin was developed based on the DSC experiments. Subsequently, the polymerization kinetics model was coupled with the thermal model. The developed 3D thermo-chemical process model was validated with water bath experiments by taking the exothermic internal heat generation into account. The obtained temperature peaks were calculated approximately as 155 °C, 157 °C and 161 °C for 30 °C, 50 °C and 70 °C water bath temperatures, respectively. The Elium® resin mixture was fully polymerized in the water bath experiments within 1725s, 970s and 700s for water bath temperatures of 30 °C, 50 °C and 70 °C water bath temperatures, respectively. Furthermore, the polymerization overheating was investigated by measuring the temperature evolution during the vacuum assisted resin infusion process of the glass/Elium® composites at room temperature. A 3D FE model of the laminate production for different composite thicknesses was developed and validated with thermocouple measurements. It was found that the peak temperature increased from 48.5 °C to 70 °C as the laminate thickness increased from 3.8 mm to 11.3 mm. A non-linear increase in peak temperature was obtained with an increase in laminate thickness and mold temperature. At last, the void content of Elium® composites was investigated and found to be lower than 1% for all the laminates. The proposed polymerization kinetics model, as well as the reported polymerization overheating trend can be used to further optimize the manufacturing processes of Elium® composites. More elaborate investigation of the effect of process temperature on the void formation for fiber reinforced Elium® composites is considered to be a future work.
Fig. 21. The contour plots of the predicted temperature distributions for the laminates with a thickness of (a) 3.8 mm. (b) 7.5 mm. (c) 11.3 mm at process time of 2682s, 2494s and 2466s, respectively. Note that only the half of the simulation domain is shown due to symmetry.

Fig. 22. The predicted temperature vs time plots for different points along the through thickness direction and located at the center of the 3D model for the laminate thickness of a) 3.8 mm. b) 7.5 mm. c) 11.3 mm.
Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

References


