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Material characterization of a polyester resin system for the pultrusion process

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ABSTRACT

In the present work, the chemo-rheology of an industrial "orthophthalic" polyester system specifically prepared for a pultrusion process is characterized. The curing behaviour is first characterized using the differential scanning calorimetry (DSC). Isothermal and dynamic scans are performed to develop a cure kinetics model which accurately predicts the cure rate evolutions and describes the curing behaviour of the resin over a wide range of different processing conditions. The viscosity of the resin is subsequently obtained from rheological experiments using a rheometer. Based on this, a resin viscosity model as a function of temperature and degree of cure is developed and predicts the measured viscosity correctly. The evolution of the storage and loss moduli are also measured as a function of time using the rheometer which provides an information about the curing as well as the gelation. The temperature- and cure-dependent elastic modulus of the resin system is determined using a dynamic mechanical analyzer (DMA) in tension mode. A cure hardening and thermal softening model is developed and a least squares non-linear regression analysis is performed. The variation in elastic modulus with temperature and phase transition is captured for a fully cured resin sample.

1. Introduction

Pultrusion is a continuous process in which constant cross sectional composite profiles are manufactured. The reinforcements can be in the form of uni-directional (UD) roving or continuous filament mat (CFM). A thermosetting resin system (containing the unsaturated resin, fillers and specialized additives) is used to impregnate the reinforcements in a resin bath. The wetted-out raw materials are pulled through a heated steel forming die using a continuous pulling mechanism. The curing as well as the exothermic chemical reaction is initiated by the heaters located on the die. The cured and solidified profiles are cut into the desired length by a cut-off saw at the end of the process. A schematic view of the pultrusion process is shown in Fig. 1.

Several studies with the aim of obtaining a better understanding of the pultrusion process can be found in literature [1–13]. The curing behaviour of an unsaturated polyester resin with mixed initiators was investigated both experimentally and theoretically and subsequently used in a thermo-chemical analysis of the pultrusion process [1,2]. Cure kinetics of the processing resin system (epoxy based) has been investigated experimentally in [3,4] to predict the temperature and degree of cure distributions inside the part. The temperature of the part exceeds the heater temperatures during the process due to the internal heat generation inside the resin [5–8]. In order to model this phenomenon, the total heat of reaction of the resin material has to be modelled correctly. Pulling force models were developed considering the viscosity evolution and the contact pressure at the die–part interface [9,10]. The process induced residual stresses and distortions were predicted in [11]. In [12], two different numerical simulations were performed for the pultrusion of a C-shaped composite using the finite difference method and the finite element method. It was concluded that similar results were obtained from both methods. The pultrusion process was optimized based on the numerical model in [12] by means of a genetic algorithm and the simplex method in [13]. The variance of the cure degree evaluated at the exit cross section was minimized by an iterative procedure based on the combination of the above techniques. In this work a temperature- and cure-dependent resin modulus was utilized for an epoxy resin system. The parameters in the modulus model were taken from an experimental analysis of a resin transfer moulding process (RTM) since so far there has been no available experimental data specific to the Young's modulus development of a pultrusion resin in literature.

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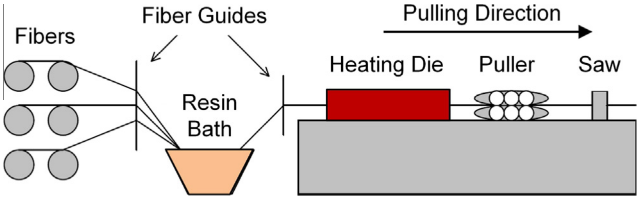

Fig. 1. Schematic view of a pultrusion process.

A precise constitutive model is essential in order to numerically simulate and optimize the pultrusion process properly. The thermo-mechanical and rheological properties of the thermosetting resin change due to thermal softening and cure hardening. Hence, the cure kinetics and rheological behaviour together with the stiffness variations have to be addressed carefully for the processing resin system. However, the material properties of the reinforcements are in general assumed to remain constant throughout the composite manufacturing processes.

Among all the thermosetting resin systems, polyester resins play an important role in the pultrusion industry because of their versatility in properties, flexibility in processing and low cost of manufacture [14]. Unsaturated polyester resins (UPRs) are all based on the use of an unsaturated monomer within a polymer backbone, formed by reacting diacids and glycols which dissolve the UPR in a reactive diluent, typically a styrene monomer. Either maleic anhydride or fumaric acid are used as the unsaturated monomer for all commercial polyesters [15]. The major three types of UPR are the “orthophthalic” anhydride polyesters, “isophthalic” acid polyesters and “terephthalic” acid polyesters. Each system have specific chemical and mechanical properties [15].

The low viscosity of polyester resin systems promotes quick and total reinforcement wet-out during processing and their high polymerisation reactivity allows for a fast but controllable cure within the pultrusion die. They are available in various formulations containing inhibitors, initiators, functional additives, etc. These formulations are prepared to meet the desired performance of the specific product and the pultrusion process. As a consequence, the processing conditions such as pulling rate, temperature of the heaters and the die geometry differ due to the specific resin system used in the pultrusion process. In addition, the thermal, chemical and mechanical behaviour of the processing composite also change depending on the resin system.

The cure kinetics, rheological and mechanical characteristics of polyester resins have been intensively studied in literature [14,16–30]. The curing behaviour of unsaturated polyester was investigated in [14,16–23] by performing differential scanning calorimetry (DSC) tests. Isothermal and dynamic scans were conducted using the DSC to measure the overall reaction rate and calculate the total heat of reaction during curing. It is assumed that the heat produced during cure is proportional to the extent of the curing reaction. The reaction and the conversion rates are defined based on the total heat calculated from the area under the measured heat flow curves. The glass transition temperature can also be determined from the DSC tests. The cure reaction of the unsaturated polyester resin is quite complex and an early formation of micro-gels occurs even at conversion levels as low as 3–4% due to the rapid build-up of a crosslinked network [14]. In addition to the DSC, Fourier transform infrared spectroscopy (FTIR) measurements were carried out to characterize the curing behaviour of the unsaturated polyester [19,22,23]. In general a good agreement was found between the conversion rates obtained from the DSC and the FTIR. A cure kinetics model was also developed to simulate the curing behaviour [17–21] and the parameters used in the model were calculated from the measured heat flow and conversion rates.

The phase of the polyester changes from a liquid (viscous) to a gel (rubbery) and then a stiff solid (glassy) state during curing. Thus, the rheological and mechanical properties change significantly during processing. The rheology of the polyesters have been studied using a rheological testing or dynamic mechanical analyser (DMA) [14,24–30]. Rheological measurements were employed to test the viscosity change during reaction of the polyester resin systems [14,27,28] using a rheometer in oscillatory mode. The gel point and the corresponding temperature can be determined at which the viscosity starts to grow and the hardening stage begins near gelation. In addition to the viscosity, the developments of the storage modulus and the loss modulus can also be obtained from rheological measurements. From DMA tests, the glass transition temperature is calculated from the ratio of the loss modulus to the storage modulus.

An industrial polyester resin system specifically prepared for a pultrusion process is characterized in the present work. The resin system is based on an “orthophthalic” polyester with medium reactivity and already contains the required fillers, initiators and chemical additives. From a process point of view, the resin is specific but can be considered generic for pultrusion. The curing, rheological and mechanical characteristics are analysed by performing experimental tests and developing the corresponding constitutive material models. A DSC is used to obtain the curing kinetics such as curing rate as a function of time and temperature. The total heat of reaction released during curing is also measured using the DSC. A weighted least squares non-linear analysis is performed to fit the auto-catalytic cure kinetics model to the measured data. The viscosity evolution is obtained using a rheometer in oscillatory mode with circular plates. A temperature- and cure-dependent viscosity model is developed to predict the measured viscosity. The gelation point is also determined based on the viscosity profile together with the corresponding degree of cure profile calculated using the cure kinetics model. The modulus of the resin changes with the temperature and transitions (glassy to rubbery zone). The modulus development as well as the glass transition temperature at fully cured state is obtained by performing a DMA analysis in tension mode. A temperature- and cure-dependent modulus model is used to estimate the measured data.

2. Cure kinetics

The temperature and the degree of cure distributions inside the processing material have to be analysed in order to investigate the pultrusion process precisely. The chemical exothermic reaction takes place when the composite reaches the reaction initiation temperature inside the die. The direction of the heat flux from the heaters is inverted such that the heat flow is transmitted from the composite to the die due to the internal heat generation. Hence,at some point the composite temperature exceeds the die temperature during curing. In order to capture these thermo-chemical aspects in pultrusion, the cure behaviour has to be well identified.

The cure characteristics of an industrial pultrusion polyester resin are obtained performing DSC tests using Mettler Toledo DSC822. The difference in the heat flows from the sample and the reference side of the sensor is measured in the DSC as a function of temperature or time with a sampling rate of 1 value per second. A variation in the heat flow arises when the resin sample absorbs or releases heat due to the thermal effects such as the exothermic reaction during curing. The temperature spectrum used in the DSC is determined based on the processing conditions provided by the pultruder. Three different dynamic and isothermal experiments are performed in order to specify the parameters used in the cure kinetics model which describe the curing behaviour of the resin over a wide range of different processing conditions.

Isothermal experiments are carried out at temperatures 120 °C, 130 °C and 140 °C using a resin sample of 10 mg. On the other hand, dynamic scans are performed by heating the sample from 25 °C to 200 °C with a heating rate of 5 °C/min, 7.5 °C/min and 10 °C/min. It should be noted that high heating rates are employed in pultrusion such that the peak temperature (~170 °C) is obtained by heating the sample from room temperature (~25 °C) within 1–2 min inside the heating die. Figs. 2 and 3 show the heat rate evolved during the isothermal and dynamic experiments, respectively. It is seen from Fig. 2 that the reaction heat as well as the peak of the heat flow increases with the isothermal set temperature. On the other hand the duration of the exothermic reaction decreases with the temperature. Similarly, using a higher heating rate results in a higher reaction heat at earlier stages during the dynamic DSC scans as seen in Fig. 3. The total exothermic heat of reaction (H_{tr}) released during cure is calculated approximately as 175 ± 15 kJ/kg by obtaining the integral of the heat flow-time plots for the dynamic DSC experiments. Here, a straight baseline between the onset and the end of the reaction is considered as suggested in [31]. The rate of degree of cure ($d\alpha/dt$) is assumed to be proportional to the rate of heat flow (dH/dt) [31] and expressed in Eq. (1). The corresponding evolutions of $d\alpha/dt$ as a function of time are depicted in Fig. 4 for the isothermal DSC experiments.

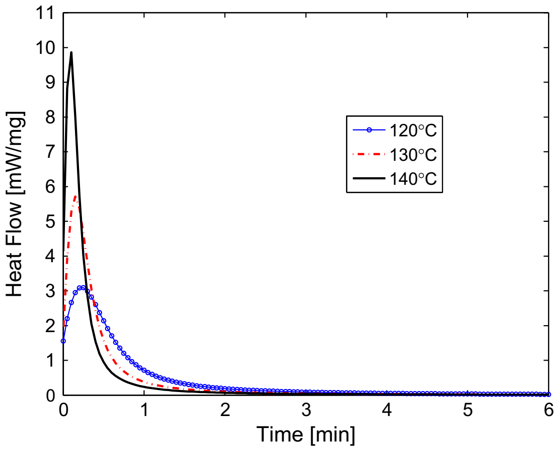

Fig. 2. The evolution of the heat flow for the isothermal DSC experiments.

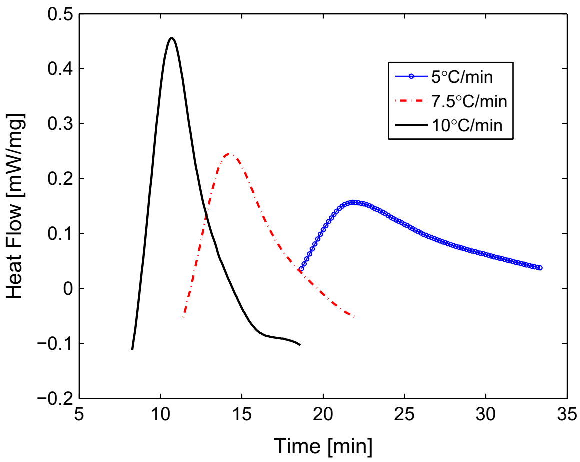

Fig. 3. The evolution of the heat flow for the dynamic DSC experiments.

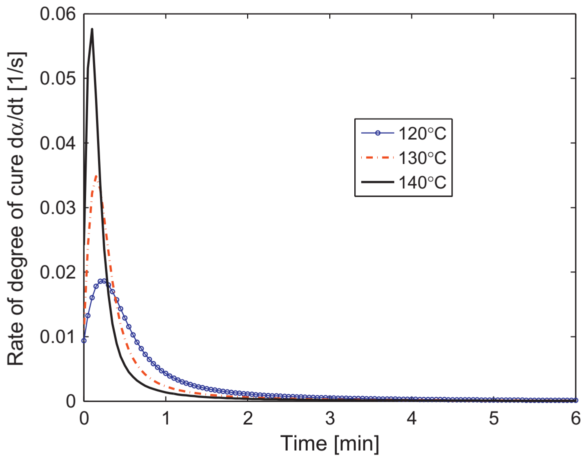

Fig. 4. The rate of the degree of cure ($d\alpha/dt$) as a function of time obtained from the isothermal DSC scans.

Table 1
The estimated cure kinetics parameters of the polyester (Eq. (2)).

A_0 (1/s)	E_a (kJ/mol)	m	n
7.5581×10^9	82.727	0.63	1.847

$$\frac{d\alpha}{dt} = \frac{1}{H_{tr}} \frac{dH}{dt} \tag{1}$$

The degree of cure is then calculated by obtaining the areas under the curves depicted in Fig. 4 by integration. In literature, several cure kinetics models have been proposed and analysed to describe the curing of the thermosetting resin systems [32,33]. A well known semi-empirical autocatalytic model [34] which is an Arrhenius type of equation is utilized. The corresponding expression is given as:

$$R_r(\alpha, T) = \frac{d\alpha}{dt} = A_0 \exp\left(\frac{-E_a}{RT}\right)\alpha^m(1-\alpha)^n \tag{2}$$

where A_0 is the pre-exponential constant, T is the absolute temperature, E_a is the activation energy, R is the universal gas constant and m and n are the order of reaction (kinetic exponents). The parameters in Eq. (2) are obtained using a weighted least squares nonlinear regression analysis including the experimental data from both isothermal and dynamic DSC scans. The estimated best fit parameters are given in Table 1. As seen from the best fit between the experimental data and the predictions in Fig. 5, the autocatalytic model accurately predicts the degree of cure as well as the cure rate evolutions for all three isothermal temperatures. Fig. 6 shows that a reasonably good fit is also obtained between the measured and the estimated degree of cure as well as cure rate for different heating rates in dynamic DSC scans.

3. Rheological behaviour

In pultrusion, the rheological behaviour of the processing resin system directly affects the viscous force development at the die–part interface. The viscous force is one of the contributions (the collimation, the bulk compaction, the viscous and the frictional force) to the pulling force [10]. Before the gelation point, a viscous drag occurs at the die–part interface. The viscous force can be defined as a function of the viscosity profile for pultrusion [35]. In order to predict the viscous force correctly, the rheological properties of the processing resin have to be characterized.

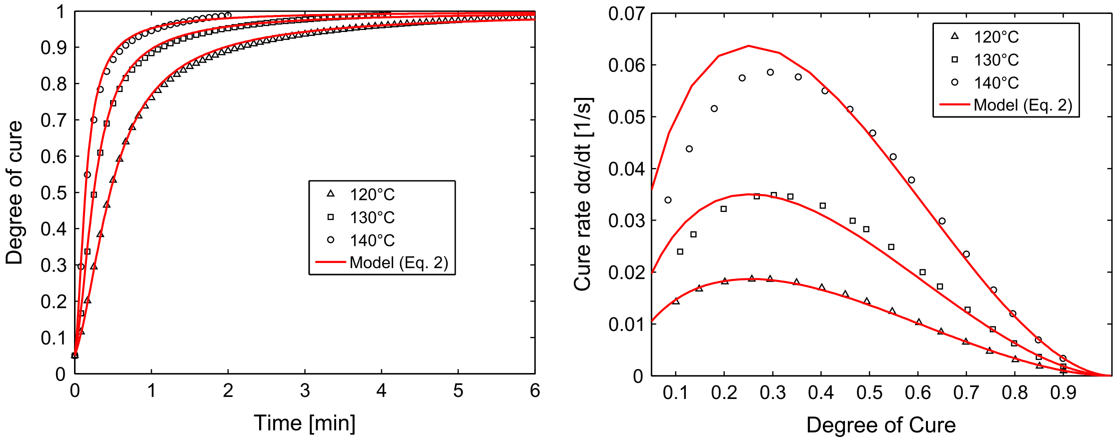

Fig. 5. The experimental and predicted (best fit) degree of cure evolutions (*left*) and the cure rate as a function of degree of cure (*right*) for the isothermal DSC scans.

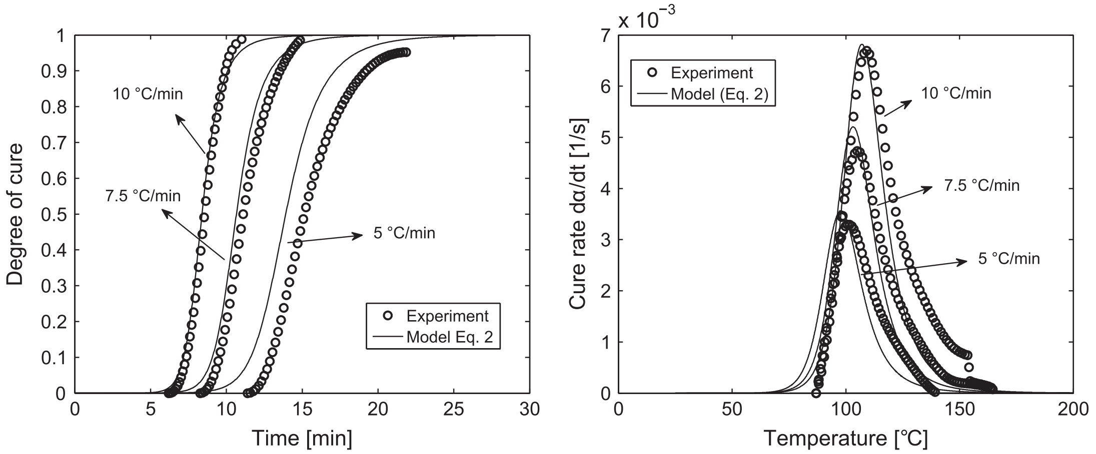

Fig. 6. The experimental and predicted (best fit) degree of cure evolutions (*left*) and cure rate as a function of temperature (*right*) for different heating rates used in dynamic DSC scans.

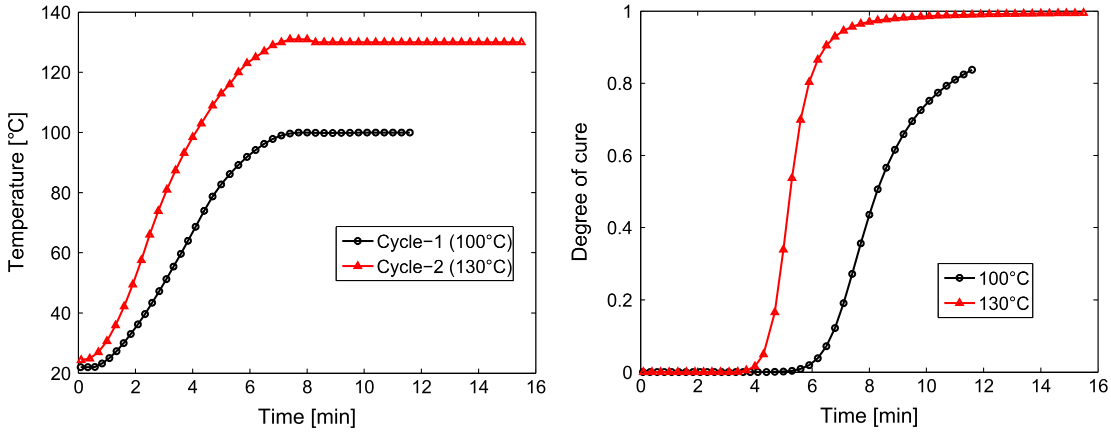

Fig. 7. The measured temperature scan in the rheometer (*left*) and the corresponding degree of cure evolutions calculated using the cure kinetics model (Eq. (2)) (*right*).

In this work, rheological measurements are carried out using Anton Paar-Physica MCR 501 rheometer in "plate–plate" mode for the polyester resin system and 200 measuring points are used in the experiments. The neat polyester is prepared in liquid form with dimensions of ∼30 mm (diameter) and ∼2 mm (thickness). Circular plates are used in oscillatory mode at 1% strain and 1 Hz. Two temperature cycles (Cycle-1 and Cycle-2) having different heating rates are used in the rheometer as seen from Fig. 7(*left*). A hold temperature of 100 °C and 130 °C are considered in Cycle-1 and Cycle-2, respectively. The corresponding degree of cure

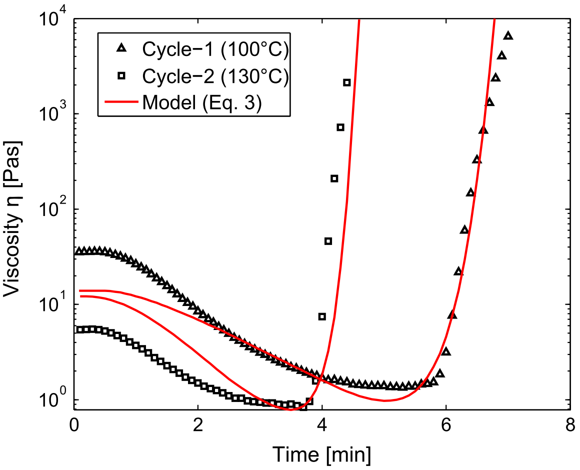

Fig. 8. The measured and predicted (best fit) viscosity evolutions as a function of time for two different rheometer temperature cycles.

evolutions are calculated using the developed cure kinetics model (Eq. (2)). It is seen from Fig. 7(*right*) that higher cure rate and degree of cure are obtained for temperature Cycle-2 (130 °C). The viscosity evolutions as well as the variations in the storage modulus (G') and the loss modulus (G'') are measured. A well known temperature- and cure-dependent viscosity model is implemented to predict the viscocity development and expressed as [36,37]:

$$\eta = \eta_\infty \exp\left(\frac{\Delta E_\eta}{RT} + K\alpha\right) \tag{3}$$

where ΔE_η is the viscous activation energy, η_∞ is the initial viscosity, K is a constant, R is the universal gas constant, T is the absolute temperature. A least squares non-linear regression analysis is performed upon the measured data in order to determine the constants in the viscosity model. Figs. 8 and 9 show the viscosity evolutions as a function of time and temperature, respectively. The estimated model constants are given in Table 2. It is seen that a good agreement is found between the measured and estimated (best fit) viscosity profiles for the two different temperature scans. The viscosity increases rapidly after some time owing to the curing of the sample. The viscosity for Cycle-2 starts increasing earlier (~4.6 min) than Cycle-1 (~6.7 min) since curing takes place at earlier stages in time for Cycle-2. The estimated initial viscosity slightly deviates from the measured one, nevertheless this does not have an important effect on the thermo-mechanical analysis of the pultrusion process since the stiffness of the liquid resin is not high enough to build up stresses. The gelation is defined as the point at which the state of the resin changes from a viscous liquid to a rubbery gel. As reported in [26], the gelation occurs when the viscosity of the resin increases to infinity. However, measuring an infinite viscosity is not practical and hence it is accepted to define the gel point when the viscosity reaches a value of $\sim 10 \times 10^4$ Pas [26,38]. Keeping this in mind the degree of cure at gelation is calculated approximately as 0.12 and 0.14 for Cycle-1 and Cycle-2, respectively (Fig. 7(*right*)) by obtaining the gel time at $\eta \approx 10 \times 10^4$ from Fig. 8. This indicates that the polyester system used in this study is a highly reactive resin. The predicted degree of cure at gelation is found to be in the conversion range (0.1–0.3) provided in [15].

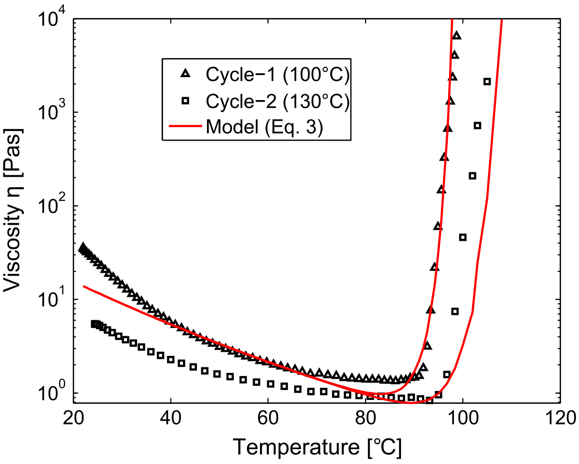

Fig. 9. The measured and predicted (best fit) viscosity evolutions as a function of temperature for two different rheometer temperature cycles.

Table 2
The estimated constants used in the viscosity model (Eq. (3)).

η_∞ (Pas)	ΔE_η (kJ/mol)	K
1.08×10^{-6}	40.147	83.39

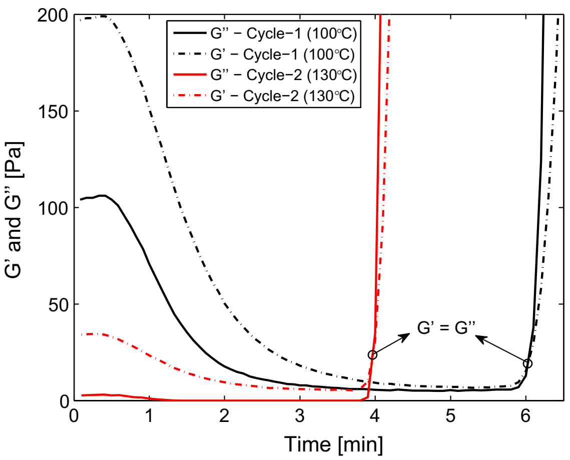

Fig. 10. The measured storage (G') and loss (G'') moduli as a function of time in the rheometer experiments.

Fig. 10 shows the development of G' and G'' as a function of time for Cycle-1 and Cycle-2. Both G' and G'' increase as the crosslinking reaction occurs. The gel time is taken as the point at which the crossover of G' and G'' takes place during curing [26,39], nevertheless, it may not be equal to the one calculated at $G' = G''$ for several resin systems [26,40]. The gel time determined from $G' = G''$ is found to be somewhat less than the one obtained from $\eta \approx 10 \times 10^4$ Pas for unsaturated polyester resins [41]. As seen from Fig. 10, the gel time is determined to be ~4 min and ~6 min for Cycle-2 and Cycle-1, respectively which is less than the gel time measured from $\eta \approx 10 \times 10^4$ Pas.

4. Elastic modulus

A proper mathematical description of the different mechanical moduli is required for the calculation of the process induced stresses and the dimensional variations in pultrusion. Hence, a temperature- and cure-dependent modulus model is considered in the present study. A DMA (Metravib Viscoanalyser VA2000) is utilized in tension mode by applying a sinusoidal deformation/strain to the sample. The stiffness (modulus) and damping (tan δ) are measured as a response in the DMA and 200 measuring points are used in the experiments. The modulus can be described by two components: an in-phase component, the storage modulus (elastic behaviour)

(E'), and an out-of-phase component, the loss modulus (E''). The damping ($\tan\delta$) is defined as the ratio of the loss modulus to the storage modulus and represents the energy dissipation in the sample. The peak of $\tan\delta$ at which the difference between E' and E'' is minimum indicates the glass transition temperature T_g.

The neat resin is first cured in the form of rectangular stripes using an oven. Subsequently, the fully cured ($\alpha = 1.0$) samples are initially conditioned at room temperature (25 °C) for approximately 5 min in the DMA. The sample size is specified as $30 \times 5 \times 2$ mm (length × width × thickness). Dynamic heating scans are performed from 25 °C to 190 °C with a heating rate of 5 °C/min and a frequency of 6.22 Hz [42]. The static and dynamic load strains are set to 1% and 0.1%, respectively.

Fig. 11 shows the measured E' and E'' as well as $\tan\delta$ evolutions. It is seen that the peak of $\tan\delta$ is obtained at ~135 °C which corresponds to T_g at $\alpha = 1.0$. The moduli change with temperature and a transition (glassy to rubbery zone) inside the sample. In order to capture these variations properly, a modified cure hardening instantaneous linear elastic (CHILE) model [31,34] is developed for the measured resin modulus. Note that the developed tangent modulus is convenient for the incremental stress calculation (i.e. $\dot{\sigma} = \mathbf{E}\dot{\varepsilon}$) [11]. The corresponding expression is given as:

$$E_r = \begin{cases} E_0; & T^* \leqslant T_{C1} \\ A_e \exp(K_e T^*); & T_{C1} < T^* < T_{C2} \\ E_1 + \frac{T^* - T_{C2}}{T_{C3} - T_{C2}}(E_\infty - E_1); & T_{C2} < T^* < T_{C3} \\ E_\infty; & T_{C3} \leqslant T^* \end{cases} \tag{4}$$

where T^* represents the difference between the instantaneous glass transition temperature (T_g) and the resin temperature T, i.e. $T^* = T_g - T$ [34]. A_e and K_e are the constants for the exponential term. The other model constants indicate the transition zones and are schematically shown in Fig. 12. Here, T_{C1}, T_{C2} and T_{C3} are defined as the critical temperatures and E_0, E_1 and E_∞ are the corresponding elastic modulus values, respectively, at which the modulus behaviour is changed due to the phase transitions of the resin (viscous–rubbery–glassy state). More specifically, E_0 and E_∞ can be considered as the elastic modulus in the viscous and glassy state, respectively. The glass transition temperature T_g can be defined as a function of the degree of cure [34] in the following way:

$$T_g = T_g^0 + a_{Tg}\alpha \tag{5}$$

where T_g^0 is the glass transition temperature at α=0 and a_{Tg} is a constant. For the sake of convenience, T_g^0 is assumed to be a much lower value than $T_g = 135$ °C obtained from DMA for $\alpha = 1.0$. In the

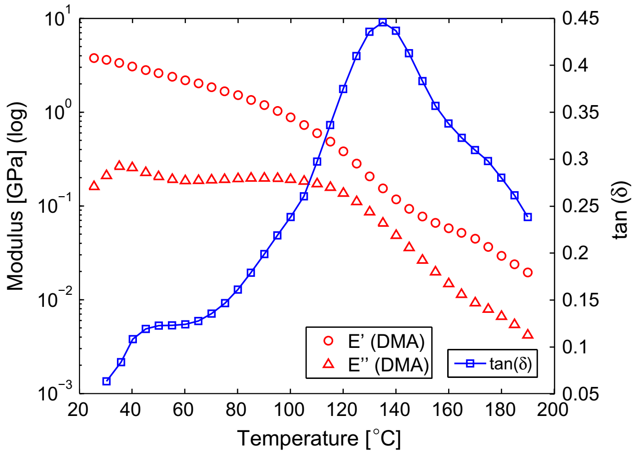

Fig. 11. Measured storage modulus (E') and loss modulus (E'') together with the $\tan\delta$ evolutions from DMA experiments.

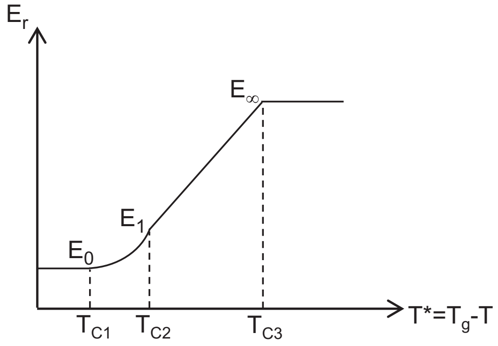

Fig. 12. Schematic representation of the elastic modulus evolution for the polyester resin.

Table 3
The estimated constants used in the modulus model (Eq. (4)).

T_{C1} (°C)	T_{C2} (°C)	T_{C3} (°C)	E_0 (GPa)	E_1 (GPa)	E_∞ (GPa)	A_e (GPa)	K_e (1/°C)
−60	30	110	0.0195	0.73	3.76	0.20	0.043

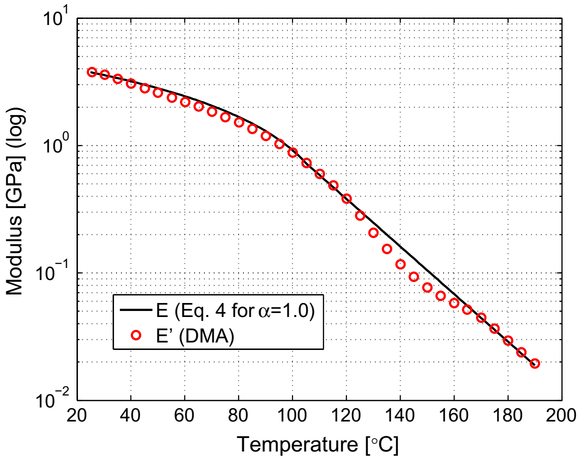

Fig. 13. Comparison of the measured and predicted elastic modulus developments (log scale).

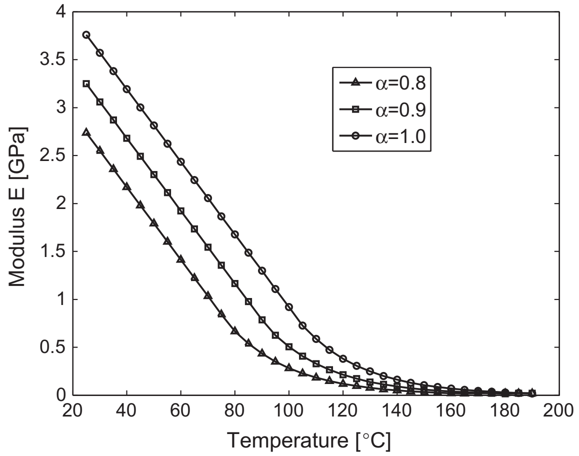

Fig. 14. The Predicted Young's modulus evolutions for different degree of cure values at glassy state.

present work, T_g^0 is hence assumed to be $0\,^{\circ}\mathrm{C}$ as in [43] providing $a_{Tg} = 135\,^{\circ}\mathrm{C}$. The variation in T_g^0 would not have an important effect on mechanical response of the processing part during the pultrusion process since the stiffness of the viscous resin is relatively small to build up induced stresses. Using $T_g = 135\,^{\circ}\mathrm{C}$ at $\alpha = 1.0$, a least squares non-linear regression analysis is performed to obtain the constants in Eq. (4) which give the best agreement with the measured moduli. The estimated parameters are given in Table 3. The calculated elastic modulus evolution (best fit) is compared with the experimental data seen in Fig. 13. A good agreement is found between the measured and the predicted modulus evolution. Eq. (4) is further used to generate the modulus evolutions for different degree of cure values as shown in Fig. 14. It is seen that there is a shift in modulus development as the degree of cure increases. This is an expected outcome and agrees quite well with the experimental observations in [34].

5. Conclusions

The material characterization of an industrial “orthophthalic” polyester resin system specifically prepared for a pultrusion process was investigated by using experimental tests and developing the corresponding constitutive material models. A least squares non-linear regression analysis was conducted to fit the material models to the measured data. The evolution of the degree of cure as well as the cure rate was obtained over a wide temperature range using the isothermal and dynamic DSC scans. A temperature- and cure-dependent viscosity model was developed to estimate the rheological behaviour of the polyester system. A good fit was established between the predicted and the measured viscosity data. The gelation point was determined according to the viscosity value around $\eta \approx 10 \times 10^4$ Pas. The corresponding degree of cure value at gelation was found to be in the range 0.1–0.3 [15] according to the degree of cure evolutions predicted using the cure kinetics model. The gel time determined from $G' = G''$ was found to be less than the gel time measured from $\eta \approx 10 \times 10^4$ Pas. The DMA analysis was carried out to investigate the modulus development as a function of temperature and time. A significant variation was found in modulus due to the temperature change and transition (glassy to rubbery zone). Hence, a cure hardening and thermal softening modulus model (modified CHILE approach) was implemented to predict the elastic modulus evolution.

The proposed constitutive models are crucial to analyze and subsequently control the pultrusion process correctly and can be used for targeted numerical process modelling. The degree of cure and temperature distributions inside the pultruded part can be evaluated by means of the developed cure kinetics model. This gives an idea about the quality of the cure at the end of the process. The developed temperature- and cure-dependent viscosity model can be used to calculate the viscous force at the die–part interface. The proposed cure hardening and thermal softening modulus model can be used for the calculation of the process induced stresses and distortions during processing. Moreover, the developed constitutive models are essential in order to optimize the process via process models.

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