

INVESTIGATION ON THE REACTION KINETICS OF ADIABATIC POLYMERISATION OF ANIONIC PA-6.

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ABSTRACT: Semi-adiabatic temperature measurements were recorded and used to define semi-empirical equations for the simulation of the anionic PA-6 reaction kinetics. The reaction could be described by autocatalytic polymerisation and isothermal crystallisation models. The resin mixture used in this research has a long infusion window, before the reaction starts. Therefore, research was done on the prediction of the infusion window, defined as the induction time. A linear relationship was found between the induction time and the product of the initial resin temperature and the temperature difference between the mould and the resin. It is expected that the infusion window will be reduced when long pot life times and high initial temperatures of the reactive mixture/buffer vessel are used. Hence, the effect of the pot life (time and temperature) on the reaction kinetics was investigated. It was seen that for a longer pot life time and higher initial pot life temperature, the reactivity of the resin during the exothermal reaction decreased while the induction time slightly increased.

KEYWORDS: Cure behaviour, rheological properties, semi-empirical modelling, thermoplastic resin.

INTRODUCTION

In order to produce thicker and bigger thermoplastic composite parts for use in offshore wind turbine blades the traditional melt processing technique, which requires high temperatures and pressures, has been substituted with a vacuum infusion process. To overcome the high resin viscosity of thermoplastic resins, a reactive resin system is used for the vacuum infusion of glass fibre reinforced anionic polyamide-6 (APA-6) composites. The high molecular weight APA-6 is obtained, after a high temperature infusion process, through ring-opening polymerisation. The infusion of thick-walled, large wind turbine blades requires long residence times for the reactive resin in the buffer vessel prior to infusion.

Previous work showed that the processing temperature is the most important parameter in the infusion of APA-6 composites. The processing temperature results from the sum of the external heat (heating device) and the internal heat (exothermic reaction of the resin). The effect of the temperature is thought to be significant for every stage in the infusion process. In this paper, the effect of pot life, buffer vessel and mould temperature will be investigated in order to predict the infusion window and the temperature rise during reaction. It is expected that the infusion window will be reduced when long pot life times and high initial temperatures of the reactive mixtures are used.

Testing and modelling the reaction kinetics of the resin is the first step to understand the reaction itself. For this purpose, adiabatic reaction tests were performed in which the temperature of the reaction was recorded and was used to define the semi-empirical equations for the simulation of the APA-6 reaction kinetics. In this paper, the reaction kinetics of the resin system will be described and the effect of the pot life (time and temperature) on the reaction of the resin will be investigated.

EXPERIMENTAL

Materials

A reactive resin mixture is used, which consists of three components: the anionic polymerisation grade ϵ -caprolactam monomer, the activator and the initiator which were all supplied by Brüggemann Chemicals, Germany.

Adiabatic Polymerisation

Reaction kinetics tests were performed to investigate the adiabatic temperature build-up. To simulate the adiabatic conditions of the polymerization in thick laminates, a wide 600 ml beaker with a diameter of 8 cm, was used as a mould. A cover lid was designed to ensure the correct and consistent placement of the straight thermocouple in the middle of the beaker and to ensure a nitrogen protective environment during the whole polymerization. The polymerization mixture was prepared in the mini-mixing unit (MMU), which was set to 85, 100 or 115°C. The glass beaker with the reactive mixture was then transferred into an oil bath at polymerisation temperature, which was set to 140, 150 or 160°C, after which the temperature measurements were started. To verify the repeatability of the reactions, all the tests were duplicated.

Effect of Pot Life

To simulate the effect of the pot life on the reaction, the beaker which was filled with the reactive mixture, was placed in an oil bath which was set to the same temperature as the MMU (85 or 115°C). After 5 or 20 minutes, the beaker was placed into the second oil bath set to a higher temperature (140, 150 or 160°C) for the polymerization reaction to take place, simulating the heating phase of thick laminates by contact heating. Temperature measurements were done as described above and repeated twice. The temperature measurements were compared with those corresponding to the reaction kinetics of the resin without any residence time in the buffer vessel.

RESULTS AND DISCUSSION

Semi-empirical Approach to Reaction Kinetics

From the experimental data, the temperature rise over time was recorded. The fractional degree of conversion β can be obtained from the adiabatic temperature measurements [1-2]:

$$\beta = \frac{T - T_0}{T_f - T_0} \quad (1)$$

Where T is temperature at time t , T_0 and T_f are the initial and maximum temperature of the reaction respectively. To obtain the heat of reaction (both polymerization and crystallisation) from the start of reaction, the following data analysis was done; for each set of data, temperature measurements were done for pure caprolactam monomer as well. This data was subtracted from the temperature data of the reaction. The time where the temperature rise of the monomer and the reactive mixture started to deviate was taken as the induction time of the reaction (t_i). The start of the temperature deviation between the two curves was chosen to be at 30% of the maximum slope of the reaction,

giving the most consistent results for all data sets. The temperature of the reactive mixture corresponding to this induction time was considered to be T_0 .

The adiabatic temperature rise can be described from the energy balance as the heat build-up due to polymerisation and crystallisation (\dot{q}) and the heat loss due to thermal conduction [2]:

$$C_p \frac{dT}{dt} = \frac{dq}{dt} - U(T - T_{amb}) \quad (2)$$

Where U is the overall heat transfer coefficient, T_{amb} is the ambient temperature, C_p is the heat capacity, which is a function of the degree of conversion of the resin and temperature.

According to Lee [2] and Bolgov [3], the heat flux from both polymerisation and crystallisation can be described as follows:

$$\dot{q}(t) = Q_1 \dot{\beta}(t) + Q_2 \dot{\alpha}(t) \beta(t) \quad (3)$$

In which α is the degree of crystallinity at time t , Q_1 the heat of polymerization, Q_2 is the heat of crystallization.

It is known that isothermal crystallisation can be described by an adapted Avrami equation [3], although it only considers single stage crystallisation, and is insufficient in describing secondary crystallisation within the process. The data recording for this paper was stopped once the polymerisation plateau was reached, hence excluding the secondary crystallisation from the measurements.

$$\alpha(t) = 1 - \exp\left[-\left(\frac{t}{t_0}\right)^n\right] \quad (4)$$

This equation (eq. 4) showed good accuracy with the obtained measurements. It can be concluded that the system used allows to be fitted with isothermal crystallization kinetics. The characteristic crystallization time t_0 can be described as follows [3]:

$$t_0 = c \exp\left(\frac{\psi T_m^0}{T(T_m^0 - T)}\right) \quad (5)$$

Whereby n , c and ψ are constants and T_m^0 the melting point of the polymer = 214°C.

In order to find the adiabatic polymerisation kinetics of anionic PA6, an autocatalytic model has been suggested by several researchers [1-2]:

$$\frac{d\beta}{dt} = A_0 \exp\left(-\frac{E}{RT}\right) (1 - \beta)^n (1 + B_0 \beta) \quad (6)$$

In which, A_0 and n are constants, E the activation energy and B_0 the autocatalytic factor. The experimental data obtained were used to find the reaction kinetics by a nonlinear least squares method fit with eq. 1-6. Together with the reaction kinetics constants, the correlation coefficient R^2 was calculated.

Adiabatic Reaction Kinetics

A typical example of the adiabatic temperature evolution and the fitted curve is shown in Fig. 1. It could be seen that the fitting model as described above gives repeatable results and good correlation coefficients (97% or higher). The average kinetic parameters describing the material system used are shown in Table 1. It was seen that the values for E , n and B_0 comply well with values found in literature [1-2]. However, the autocatalytic factor B_0 for mould temperatures of 160°C is significantly higher. The

activator used in this study shows a different polymerisation reaction from temperatures above 160°C which results into higher B0 values. It can also be seen that the A0 values for a MMU temperature of 85°C are lower than compared with the higher MMU temperatures. Due to the low initial temperature and hence longer heating time before reaction starts, fewer interactions between the different molecules are present, resulting in the lower A0 value.

Table 1 Kinetic parameters for polymerisation for various MMU temperatures and pot life times

Temp MMU [°C]	85			100			115		
Mould temp [°C]	140	150	160	140	150	160	140	150	160
A0 x10 ⁵ [1/s]	2.52	3.25	3.62	5.75	5.42	4.84	5.71	5.33	4.82
E x10 ⁴ [J/mol]	6.82	6.81	6.75	6.96	6.88	7.09	7.1	6.94	7.04
n [-]	1.01	0.99	1.09	0.99	0.93	1.08	1.2	1.04	1.04
B0 [-]	7	9	11	7	9	21	14	11	16
R ² [%]	97.7	99.4	99.1	99.2	99.9	99.8	98.4	99.7	99.7

In order to describe the temperature behaviour of the resin during the heating phase in composites, further insight in the prediction of the induction time t_i and the initial temperature T_0 is needed. As can be seen in Fig. 2, the induction time is linearly dependent on the product of the MMU temperature and the temperature difference between the MMU and the mould temperature (oil bath). The slopes of the curves for different MMU temperature, as shown in Fig. 2 are approximately the same, -0.228 ± 0.027 on average, while the interception of the curves with the y-axis seems to be linearly dependent on MMU temperature ($y_{intercept} = -12,3 * T_{MMU} + 3200,7$). The proposed equation for prediction of the induction time is described in eq. 7. Further work is needed on establishing the relation between t_i and T_0 .

$$t_i = A \cdot T_{MMU} \cdot (T_{mould} - T_{MMU}) + (B \cdot T_{MMU} + C) \quad (7)$$

With $A = -0,228 [1/(\text{°C})^2]$, $B = -12,3 [1/\text{°C}]$ and $C = 3200,7 [\text{sec}]$.

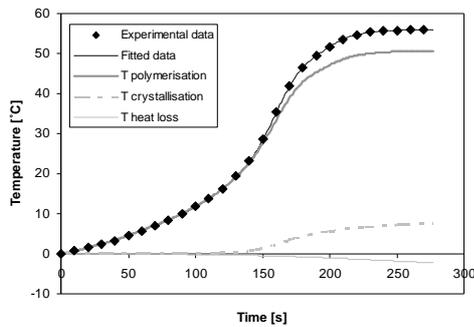


Fig. 1 Typical graph of adiabatic temperature measurements and kinetic model. Temperature MMU-mould: 85-140°C

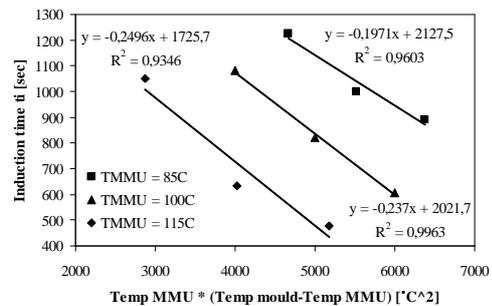


Fig. 2 Induction time t_i versus MMU temperature times the difference between mould and MMU temperature for different initial reactive mixture temperatures (85-100-115°C)

Effect of Pot Life

It is expected that the infusion window will be reduced when long pot life times and high initial temperatures of the reactive mixture/buffer vessel are used. After 5 min of pot life, both the time of maximum slope of the reaction and the reaction itself, represented by the activation energy E are comparable with the baseline, as can be seen in Fig. 3 and Fig. 4 respectively. However, for a longer pot life time, the resin already starts reacting while in the buffer vessel, therefore increasing the viscosity of the resin, especially for the higher pot life temperatures. As the heat transfer to the middle of the beaker is mainly driven by convection, the heating of the resin is inhibited by the higher

viscosity and the reaction of the resin is dependent on only the internal heat available in the reactive system. This effect is visible in Fig. 3 when the heating up of the curve for 85-160°C and 115-160°C for 20 min are compared with each other. For a pot life temperature of 85°C, the resin still heats up due to the applied external heat, which is in contrast with the results for 115°C. The effect of reaction of the resin in the buffer vessel with the longer pot life times is also visible in the reduction in activation energy E, see Fig. 4. It can therefore be concluded that less energy is needed for the reaction to take place as part of the energy is already supplied during the pot life, resulting in a lower activation energy.

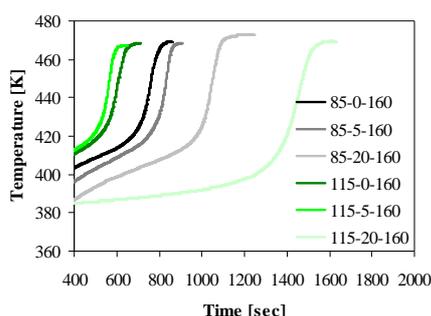


Fig. 3 Adiabatic temperature rise for different pot life times (0-5-20 min) and initial pot life temperatures (85-115°C) for a mould temperature of 160°C.

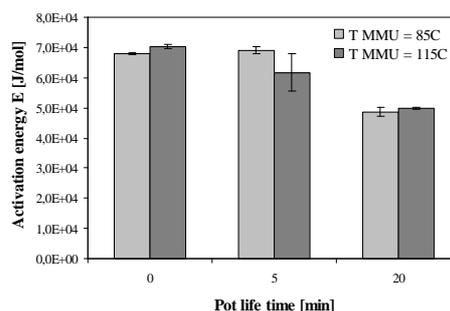


Fig. 4 Average activation energy for different pot life times and pot life temperatures.

Since the induction time is calculated at 30% of the maximum slope of the reaction and the slopes for the longer pot life times are less steep when compared to the 5 min pot life, the induction time only shows a small increase for the higher pot life temperature; 1.2 min for 140°C and 1.9 min for 160°C, while the induction time for 150°C remained approximately the same. For the lower pot life temperatures, the induction times were almost stable for 5 and 20 min for high mould temperatures, while even a decrease of 1.8 min was observed for 140°C. It could be concluded that the induction time as calculated in this paper is not predictable yet when pot life is taken into account while it could be seen that the induction time with pot life did not change more than ± 3 min compared with the baseline for all pot life conditions tested.

CONCLUSIONS

By means of a semi-empirical approach, the reaction kinetics of anionic PA-6 could be successfully be described. It was found that the adiabatic polymerisation could be predicted with the autocatalytic model and the crystallisation by means of the isothermal crystallisation model. When investigating the effect of pot life on the reaction kinetics, it was seen that for a longer pot life time and higher initial pot life temperature, the reactivity of the resin during the exothermal reaction decreased while the induction time slightly increased.

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