



Process modelling in Anionically Polymerised Polyamide-6 (APA6) for the *in situ* polymerisation of composite matrices

J. Humphry^a, N. Wolter^{a,d}, N. Yang^a, L.-J. Vandij^b, R. Truss^{a,b}, D.J. Martin^c, M.T. Heitzmann^{a,*}

^a School of Mechanical and Mining Engineering, The University of Queensland, Brisbane, QLD 4072, Australia

^b School of Chemical Engineering, The University of Queensland, Brisbane, QLD 4072, Australia

^c Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, Brisbane, QLD 4072, Australia

^d Das Faserinstitut Bremen e.V. (FIBRE), University Bremen, 28359 Bremen, Germany

ARTICLE INFO

Keywords:

ϵ -Caprolactam

Polyamide-6

Anionic polymerisation

Ring opening polymerisation

In situ polymerisation

Thermoplastic composites

Reactive-resin transfer moulding

Thermoplastic-resin transfer moulding

Introduction

The *in situ* reactive formation of thermoplastics provides a new and powerful avenue for the generation of tougher, recyclable composite materials. A molten low viscosity monomer is combined with an activator and initiator mixture before being injected into a mould where a rapid, by-product free polymerisation process occurs. The by-product free, anionic ring opening polymerisation of polyamide-6 from ϵ -caprolactam is one such example of a well-developed and commercially available system. Whilst this system is commercially used for the casting of polymer structures, its potential for composite applications is yet to be exploited. Table 1 compares the system to that of an epoxy resin, comparing infusion viscosities, times, and temperatures, showcasing its suitability as a composite matrix.

This new system however, lacks the modelling and history of application of thermosetting resins. It is thus desirable to generate process diagrams (akin to cure diagrams for thermosets), and models for the reaction kinetics, crystallisation, and rheology. Early work in this space by Davé et al. [3,4] and many others, identifies modelling as an essential and by no means trivial endeavour, mainly due to crystallisation and polymerisation phenomena occurring simultaneously. The impact of the concurrent polymerisation and crystallisation is not only a theme of academic research but also of commercial significance, including the following complications/limitations arising as a result:

- Early crystallisation leads to the trapping of monomers and results in reduced final conversion, whereas
- Late crystallisation leads to an increased time to demould, and thus less economic process overall,
- Late crystallisation also leads to polymer chain branching and other side-reactions being allowed to occur in the product, inhibiting the ultimate quality of the polymer crystals.
- The simultaneous phenomena significantly inhibits the ability to analyse the system with thermal analysis, due to the difficulty of dissociating the thermal contribution of crystallisation from that of the polymerisation.
- Finally, the autocatalytic effect of crystallisation (due to exothermic heating) may exaggerate thermal gradients, depending on part geometry.

These complex interactions can be summarised in the roadmap schematic displayed in Fig. 1.

Analytics and corresponding models

Most impactful in the field of the kinetic modelling of anionically polymerised polyamide-6 is the work of Malkin et al. [6–8]. Malkin attempts to derive a kinetic model semi-mechanistically, involving an autocatalytic term (proportional to conversion) and an initiation term

* Corresponding author.

E-mail address: m.heitzmann@uq.edu.au (M.T. Heitzmann).

Table 1
Comparison of typical key cure parameters for Anionically Polymerised Polyamide-6 (APA-6) and typical epoxy-amine thermosetting resin.

	Initial Viscosity	Cure time	Cure Temperature	Reference
APA-6	3 mPa s	3–30+ min	120 °C–200+ °C	Van Rijswijk and Bersee [1]
Epoxy ^a	500 mPa s–13 Pa.s	5 min–18+ h	25 °C–200+ °C	Aronhime and Gillham [2]

^a Epoxy reactive systems are very diverse and numbers included purely as a ballpark.

(nth order reaction term). Several works have aimed to improve upon the Malkin model, including the works of Sibal et al. [9] and Lin et al. [10]. The most recent work of Teuwen et al. [11], found that the use of a similar autocatalytic model, originally used for thermosetting resins, the Kamal and Sourour [12] model (Eqs. 1 and 2) achieves a superior fit to kinetic data. The veracity of this model was later verified by Russo et al. [13] as part of a series of works on the system.

$$\frac{\partial \beta}{\partial t} = (k_1 + k_2 \beta^m)(1-\beta)^n \tag{1}$$

$$k_i = A_i \times \exp\left(\frac{-Ea_i}{RT}\right) \tag{2}$$

All of these models were developed through thermal studies, whereby the (quasi-) adiabatic temperature rise is recorded and correlated to the rate of reaction by way of the reaction exotherm. This approach begins to break down where other, irreducible, thermal phenomena occur simultaneously (such as crystallisation, evaporation, or significant side reactions). When considering the manufacture of

parts (especially composites), it is advantageous to conduct the injection and reaction below the melting point of the final polymer to avoid a time consuming cooling and solidification step. Thus it is desirable to polymerise and crystallise simultaneously in the interest of reducing the cycle time. Additionally, Davé et al. [3,4] suggested that side reactions that may occur later into the polymerisation process (at high conversions and temperatures), leading to undesirable chain branching and cross-linking, obstructing quality crystal formation. This in turn leads to a higher γ/α crystalline ratio and an associated reduction in polymer mechanical properties.

Crystallisation of polyamide-6 is typically modelled through use of the Avrami model [8,14] (Eqs. (3) and (4)). In the reactive system however, an additional complication exists in the effect of the growth of polymer chains and the consumption of solvent (monomer) as the reaction progresses. Both of these effects (low molecular weight, and high solvent concentration) result in a reduction of stability of the crystal form leading to a lower crystallisation temperature and a lower equilibrium concentration of crystals. Counter to this, however, is the improved polymer chain mobility associated with both effects – meaning that once crystallisation is energetically preferred, crystallisation may occur more rapidly than would be otherwise expected. Secondary crystallisation also occurs in this system, though is not expected to be as pertinent to the modelling and final polymer properties. This secondary stage is not included in the Avrami model (the Johnson-Mehl-Avrami-Kolmogorov Equation (JMAK)).

$$\alpha(t) = 1 - \exp\left[-\left(\frac{t}{t_0}\right)^{n_c}\right] \tag{3}$$

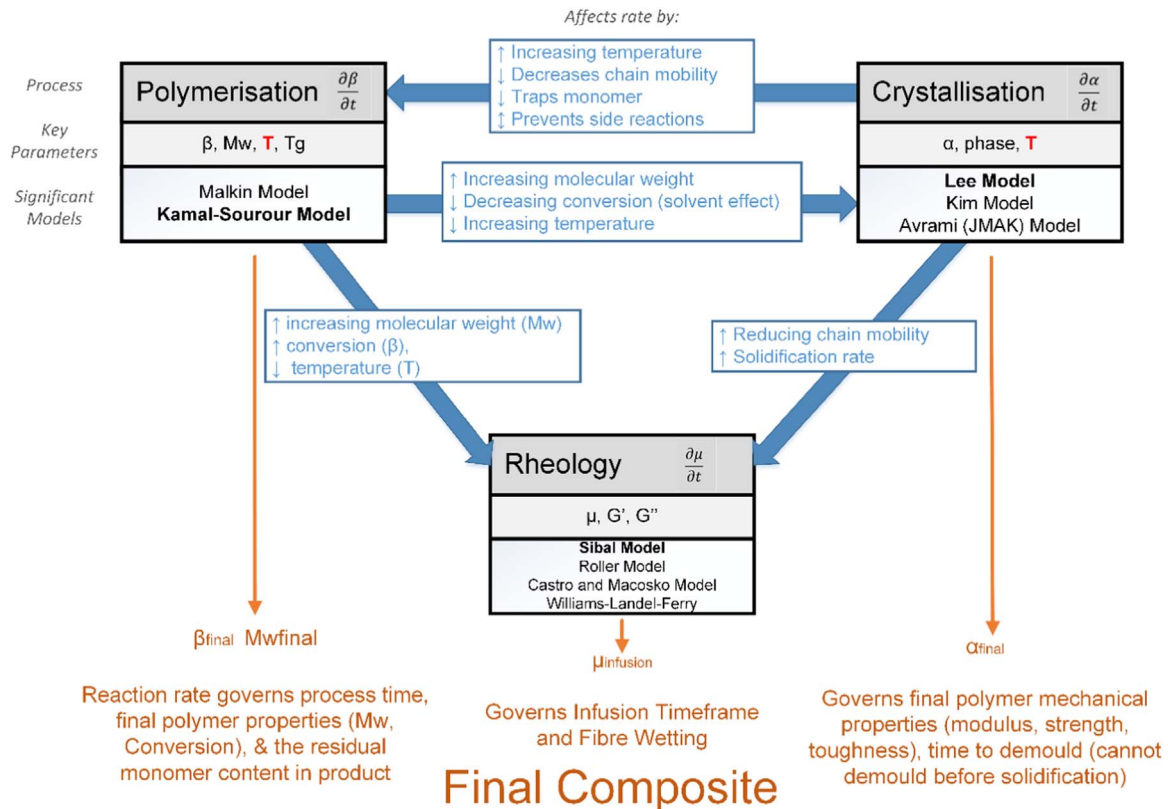


Fig. 1. Summary figure on the interactions between polymerisation, crystallisation, and rheology in the Anionically Polymerised Polyamide-6 System (APA6). The figure includes the key parameters for each process, the processes effects on each other, and the ultimate effect they have on composite properties and manufacture. Also given are the key models for each process, bold are those addressed in this communication. α , β , and μ refer to the crystallinity percentage, conversion percentage, and viscosity respectively. T is the part temperature and Tg is the glass transition temperature of the polymer. Mw is the molecular weight of the polymer. G' and G'' refer to the storage modulus and the loss modulus respectively giving the complex viscosity. Phase refers to the orientation of the polymer chains in the final part, typically either in an α , γ , or amorphous arrangement [5]. Not included here is the effects of process parameters such as temperature, fibre, geometry, and catalyst selection.

Download English Version:

<https://daneshyari.com/en/article/7857582>

Download Persian Version:

<https://daneshyari.com/article/7857582>

[Daneshyari.com](https://daneshyari.com)