

IN-SITU POLYMERISATION OF POLYAMIDE 12 FOR THERMOPLASTIC COMPOSITES

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SUMMARY: A major difficulty in processing thermoplastic composites is to achieve cost-effective and high-quality impregnation of the fibre reinforcement by the matrix resin. The aim of this work is to improve impregnation prior to in-situ polymerisation of Polyamide 12 (PA12) by exploiting a very low monomer viscosity ($7 \cdot 10^{-3}$ Pa.s). A Time, Temperature and Transformation (TTT) diagram has been established to map the different events occurring during the PA12 polymerisation. Polymerisation temperatures above as well as below the final polymer melting point (T_m^∞) have been investigated. It was shown that two events occur during polymerisation below T_m^∞ : monomer-polymer phase separation and polymer crystallisation. The polymerisation kinetics of anionic PA12 were studied and the viscosity change during polymerisation was measured to determine how the processing temperature influences the impregnation time. These results define a processing window for composite materials based on in-situ polymerisation of PA12.

KEYWORDS: Polyamide 12 (PA12), Thermoplastic, Polymerisation, Viscosity, TTT diagram.

INTRODUCTION

A good adhesion between the matrix and fibres is usually required to obtain good mechanical properties of a composite. Clearly, prior to adhesion, the fibres and the matrix must be in contact and thus a good impregnation of the fibres by the matrix is important. Thermoplastic resins usually have a high melt viscosity and according to Darcy's law, impregnation can be improved either by using high pressure and a short resin path [1] or by increased permeability. In the current work, the strategy is to impregnate the fibres with a low viscosity polyamide 12 monomer and to then carry out polymerisation in-situ. In

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this way, the processing ease of thermosets and the advantage of thermoplastics (toughness, post-forming, repair, etc.) can be combined.

In-situ polymerisation of PMMA [2], linear PUR [3], PS [4] and PA6 [5-8], have been investigated in previous studies. This paper presents a new polymerisation reaction for PA12 that allows unlimited storage of the reactants. When using this route for composite processing the need for Time - Temperature - Transformation (TTT) diagrams similar to those of thermosets [9] arises. Such TTT diagrams for thermosets provide a framework for understanding the curing process and are used to optimise the cure path and final material properties [10]. In the case of thermoplastics, the diagrams developed in the present work provide a map of the transformations that occur during polymerisation at different temperatures. The influence of the events on the polymerisation kinetics and on the final degree of conversion achieved is also discussed. Time-temperature routes can thus be proposed to exploit in-situ polymerisation with various processing techniques (pultrusion, RIM, rotomoulding).

EXPERIMENTAL

Chemistry

Since the discovery of anionic polymerisation of lactam [11], many pairs of activators and catalysts have been studied. In all studies, the polymerisation was initiated by mixing two monomer batches each containing an activator and a catalyst. In this work, we used a novel liquid system developed by EMS Chemie AG [12] containing both the activator and the catalyst in solution which has the considerable advantage of being able to be stored indefinitely. This liquid system (fig.1) consists of a strong aprotic solvent, a carbodiimide as an activator and Sodium-caprolactam as a catalyst. The activator/catalyst molar ratio is 1/1,5 and the monomer leading to polyamide 12 is ω -Lauro lactam (fig.2).

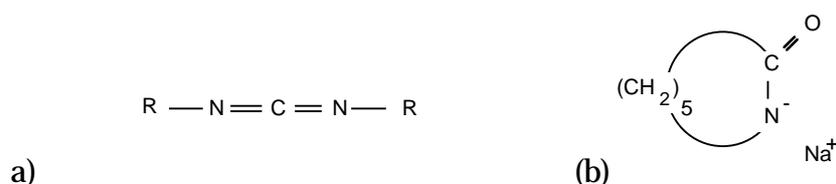


Fig. 1: Liquid system components: (a) Activator: Carbodiimide, (b) Catalyst: Sodium-Caprolactam.

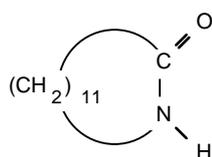


Fig. 2: Monomer: Azacyclotridecan-2-one (L12).

Polymerisation kinetics

The activator and the catalyst were added to the molten monomer just above its melting point and were then cooled down to room temperature in order to stop the reaction. The cold (crystallised) mixture was then sealed in capsules for Differential Scanning Calorimetry (DSC). The polymerisation studied in this work, like every anionic reaction, is sensitive to water and oxygen. Mixing and sealing of the components were thus performed in a dry and oxygen-free glove box atmosphere. The polymerisation exotherms versus time were measured with a differential scanning calorimeter (PERKIN-ELMER DSC-7) and isothermal runs were performed at different temperatures. The reaction rate was calculated by assuming a direct proportionality between the heat flow rate (dH/dt) and the reaction rate ($d\beta/dt$) using ΔH_o (total heat of reaction) as the proportionality constant.

Chemo-rheology

Viscosities were measured in a dynamic mode at a frequency of 10 [rad/s] at various temperatures on a dynamic mechanical analyser (Rheometric RSA-II). An air-tight experimental apparatus was developed to prevent hydrous and oxygen inhibition, comprising a couette geometry and a friction free sealing joint.

Crystallisation

The differential scanning calorimeter was also used to measure crystallisation during polymerisation. Both polymerisation and crystallisation are exothermic and the two phenomena were deconvoluted [13]. A direct proportionality between the heat flow rate and the crystallisation rate was assumed using the heat of fusion ΔH_f as the proportionality constant (134 J/g [14]). From this crystallisation rate the evolution of the crystallinity was calculated.

The measurements were performed at temperatures within the range of the monomer melting temperature and the final polymer melting temperature.

RESULTS AND DISCUSSIONS

Polymerisation kinetics

Isothermal DSC thermograms are shown in fig. 3, and are plotted as dH/dt versus time. From these curves, the heat evolved in the reaction was determined as the average area under each curve. The corresponding value found is $\Delta H_o = 53 \text{ J/g} \pm 3\%$. This reaction heat is fully consistent with the 53.8 J/g found in a recent study [15]. Previous sources give a reaction exotherm of 66 J/g [16] and 43 J/g [17].

In Figure 4, the degree of conversion is plotted versus time and temperature. It is evident that the major part of the reaction time is required for the final stages of the reaction. These kinetics measurements are used for designing equipment to produce PA12 parts in a short cycle times.

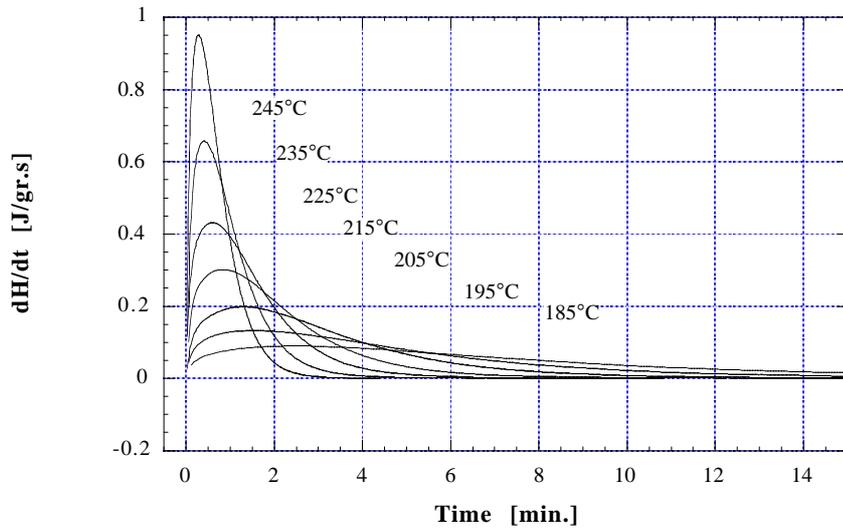


Fig. 3: Heat flow rate versus time with 3% liquid system at different polymerisation temperatures.

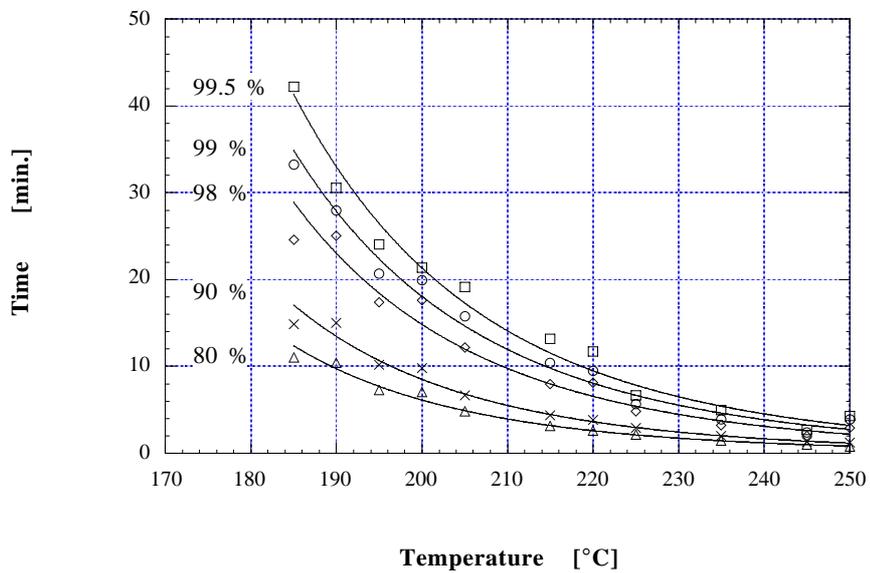


Fig. 4: Conversion degree versus time and temperature with 3% liquid system.

Phase diagram

The diagram of temperature, time and transformation for the PA12 polymerisation shown in Figure 5 was constructed from isothermal measurements. PA12 is a semi-crystalline polymer and its monomer is fully crystalline. The final melting point of the polymer (T_m^∞) and the melting point of the monomer (T_m^0) which is also the initial melting point of the polymer are indicated by horizontal white dotted lines (174° and 150°C respectively).

The successive isoconversion lines are represented by the solid white curves. A phase separation of the polymer and its monomer occurs at 10% to 30% of conversion. This data was obtained by measurement of turbidity at equilibrium [18].

Below the melting point of the monomer, no reaction can occur and consequently the isoconversion lines have a discontinuous slope change. Below the final polymer melting point, crystallisation due to polymerisation takes place. Indeed, the polymerised fraction can start to crystallise whereas the monomer remains molten. The curves on the right of the diagram represent degrees of crystallinity of 10%, 30% and 50%. Competition between the polymerisation rate and the crystallisation rate occurs. The polymerisation rate increases with temperature whereas the crystallisation rate decreases. At low temperatures, where the induction time of crystallisation is short, crystallisation and polymerisation occur at the same time.

Crystallisation has two effects on the polymerisation. The first effect is a strong decrease in the reaction rate. The isoconversion lines in Figure 5 (meanwhile the logarithmic scale) are extended to longer times when they overlap crystallisation. This polymerisation rate decrease can be explained by the fact that some active centres are caught in crystalline regions and that the overall reactivity is thus decreased. The domain morphology results in a mixture of diffusion and reaction controlled mechanisms.

The second effect of crystallisation on polymerisation is the increase in the final conversion degree. Indeed, the crystal fraction is not involved in the polymer-monomer equilibrium [19], and as only the polymerised fraction can crystallise, the final concentration of monomer is shifted to a lower content.

In order to work with short cycle time, it would be preferable to avoid the polymerisation rate decrease due to crystallisation. This can be performed by working above the final melting point of the polymer or by having a rapid polymerisation as compared to crystallisation. However, it has to be kept in mind that thermoplastics have to be cooled for demolding and that an increase in the polymerisation temperature is also an increase in the cycle time due to the cooling.

The reaction exotherm can be exploited in order to reach a higher temperature than the mould temperature. In the case of polyamide 12, the reaction in fully adiabatic conditions leads to an increase of 20°C only. It is however much higher with PA6.

For the polyamide 12, the diagram deals with melting temperatures rather than with T_g . No vitrification has been observed because the final glass transition (T_g^∞) is below the monomer melting point (T_m^0) and because no polymerisation takes place below the monomer melting point. Vitrification would take place when the glass transition of the polymer reaches the polymerisation temperature. It should be possible to observe vitrification during polymerisation of PA4 and PA3 from pyrrolidone and propiolactam respectively. Indeed, their final glass transition (T_g^∞) is above the lowest possible polymerisation temperature, which is the monomer melting point, T_m^0 .

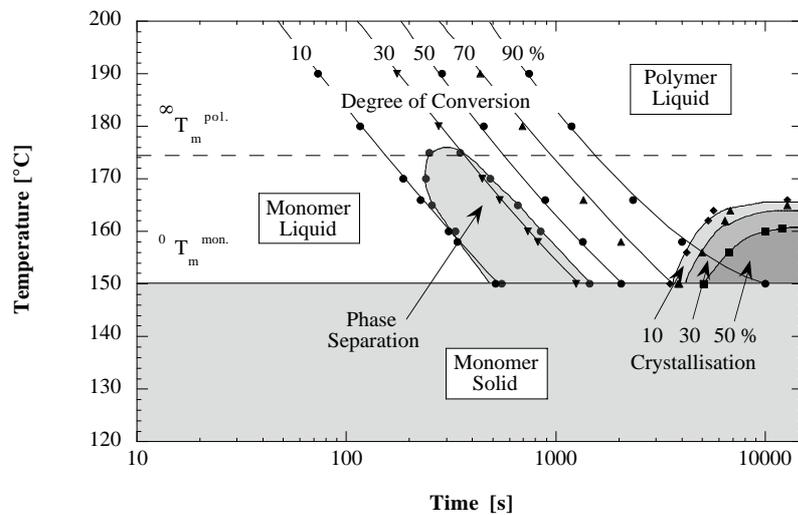


Fig. 5: Isoconversions and phase transformations versus time and temperature during the polymerisation. The horizontal lines show the melting point of the monomer (150°C) and of the polymer (174°C).

Chemo-rheology

An essential parameter to control, in reactive processing, is the viscosity increase. It is important to determine a maximum usable time that exists to impregnate the fibres since the viscosity increases as polymerisation progresses. This usable time must be compared with the time needed for processing. The usable time depends on the reaction kinetics and thus on the temperature, whereas the time needed depends on pressure, on fibre permeability and on the path length that the resin has to cover. Isoviscosity curves are represented in Figure 6 versus time and temperature. The measurements have been done isothermally. The curve at 1 [Pa·s] allows usable impregnation time versus temperature to be determined, if we estimate that impregnation should be finished when the viscosity reaches 1 [Pa·s].

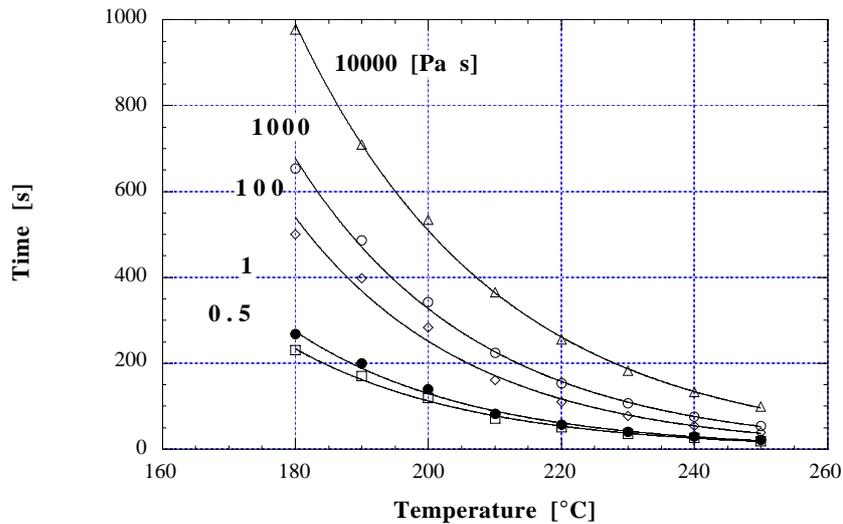


Fig. 6: Isoviscosity curves versus reaction time and reaction temperature. Available impregnation times can be read on the 1 [Pa·s] curve.

The use of the Time-Temperature-Transformation diagram

Thermoplastic Time-Temperature-Transformation diagrams allows the full potential of in-situ polymerisation to be used in various processing routes. The potential applications of these thermoplastic diagrams are not strictly the same as those for thermosets [10], since the transformations encountered are different. They may, however, have a similar effect; thus the crystallisation of thermoplastics greatly decreases the reaction rate, just as vitrification does in thermosets. It should be noted that vitrification is to all effects instantaneous, whereas crystallisation has an induction time and a crystallisation rate which are influenced by temperature. During processing, the reaction exotherm should be controlled by crystallisation in the same way as vitrification in thermosets[10].

Complete polymerisation can be achieved above and below the final polymer melting temperature (T_m^∞). Systems below T_m^∞ have been studied by Wichterle [19] with PA6. Full polymerisation (maximum equilibrium degree of conversion) was obtained even in cases were crystallisation started before the end of polymerisation. Although the temperature increased due to the reaction exotherm and the crystallisation exotherm, the polymerisation temperature stayed below T_m^∞ . Rapid polymerisation can be obtained above or below the final melting temperature, if the reaction is completed before crystallisation starts.

Using a processing temperature lower than the polymer melting temperature could improve the processability of certain thermoplastics presently having a poor final degree of conversion. Indeed, it has been established that the crystalline fraction of the polymer being formed, does not participate in the polymer-monomer equilibrium [19]. Thus, the association of crystallisation and polymerisation can shift the residual monomer content to lower values. The monomer melting point limits the lowest polymerisation temperature. In opposition to thermosets where the crosslink density can be controlled, a full degree of conversion is needed for thermoplastics, because the residual monomer will diffuse to surfaces of the parts. It is thus impossible to control the final properties by the degree of conversion and the reaction temperatures. However, the final properties can be controlled by the cooling rate. Indeed

crystallisation not only appears during polymerisation but also along the cooling path. The informations on cooling, needed to design the whole processing route are missing on TTT diagrams, nevertheless from preliminary results the PA12 crystallinity is not strongly influenced.

CONCLUSION

A thermoplastic Time-Temperature-Transformation diagram was established for PA12. Subsequently, different paths were viewed to process PA12 composites in function of reaction time and temperature as well as in function of the different events occurring during polymerisation. Results will permit the construction of process windows and will allow the development of pultrusion, resin transfer moulding and rotomoulding using PA12 in-situ polymerisation.

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