Processing Window for Vacuum Infusion of Fiber-Reinforced Anionic Polyamide-6

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SUMMARY: In order to manufacture durable wind turbine blades for offshore application in a sustainable way, Delft University of Technology is currently developing vacuum infusion technology for reactive processing of thermoplastic composites. This paper presents a processing window for Anionic Polyamide-6 (APA-6), a reactive thermoplastic system produced by DSM Fiber Intermediates. Injection times, polymerization rates and degree of conversion for various processing temperatures and resin formulations are determined.

KEYWORDS: anionic polyamide-6, thermoplastic composites, vacuum infusion, processing window, viscosity, degree of conversion.

INTRODUCTION

Following international agreements on reduction of CO_2-emission, the Dutch government has formulated the ambitious target to have 6,000 Megawatt wind power installed offshore in 2020. A knowledge program is initiated by the WE@SEA foundation (Wind Energy at Sea), which reflects the combined effort of public and private interest towards realizing this target. In the next decades, more than 1,000 turbines need to be installed in the North Sea. The two main requirements formulated by WE@SEA for the 3,000 blades to be constructed are durability and sustainability. The blades should be more fatigue resistant to increase the current lifetime of 20 years and to reduce preventive and corrective maintenance visits, which are currently required 4 to 6 times a year, costing 7 to 12 k€ per visit. In the light of producing green energy, effort is put in the development of economic and environmental friendly manufacturing processes, procedures for installation and dismantling, and the destruction and re-use of materials.
Delft University of Technology is currently developing a process for manufacturing large thermoplastic composite (TPC) blades. Due to the higher toughness of the matrix, TPC potentially offer a higher resistance to fatigue than their thermoset counterpart currently applied, such as fiber-reinforced epoxies and vinylesters. In addition, TPC can be remolded upon melting, opening the door for re-use of the blade material. In order to produce blades with lengths in excess of 50 meter, the currently most widely applied manufacturing process for turbine blades, vacuum infusion, is maintained. This process utilizes a low viscosity resin that is injected in a mold with pre-placed fibers, followed by a curing step. Since the viscosity of thermoplastic polymer melts is too high, reactive processing is required: a low viscosity monomer melt is injected between the fibers, followed by in situ polymerization of the thermoplastic matrix.

This paper presents a processing window for processing of Anionic Polyamide-6 (APA-6), a reactive thermoplastic system produced by DSM Fiber Intermediates. Injection times, polymerization rates and degree of conversion for various processing temperatures and resin formulations are determined.

EXPERIMENTAL

Chemistry

Polyamide-6 (APA-6) was obtained through anionic polymerization of ε-Caprolactam. The lactam monomer was molten (T_m = 79 °C) and mixed with the activator (Hexamethylene Diisocyanate) and the catalyst (Caprolactam Magnesium Bromide), all supplied by DSM Fiber Intermediates [1]. By heating up this mixture to 130-180 °C, polymerization is completed within 30 minutes. Polymerization time can be adjusted between 2 to 60^+ minutes, by changing the amount and type of activator and catalyst. In general, activator and catalyst are added in a 1:1 ratio of 0.6 mol%. This is referred to as a 1-1 formulation. In this paper, various x-y formulations are used (e.g. 2-1 refers to the addition of 1.2 mol% activator and 0.6 mol% catalyst).

Rheology

Viscosities were measured in a Bohlin V88 concentric cylinder viscometer (speed = 6, spindle type 6) for various resin formulations at various temperatures. An experimental setup with Nitrogen supply provided a water and oxygen free environment for polymerization. Repeated measurements demonstrated the consistency of this test. After injection, viscosities were measured continuously up to a value of 1 Pa·s. From past experiences, this value is regarded as the upper limit for the injection window.

Degree of conversion

The degree of conversion (X) of the polymerization of APA-6 in heated reaction tubes was determined for various resin formulations at various temperatures. At regular time intervals, polymerization was terminated by quenching the closed tubes in ice water. Samples were grinded, weighed (m_{tot}) and refluxed overnight in demineralized water. After filtering and rinsing, samples were weighed again (m_{pol}). Whereas the Caprolactam monomer dissolves easily in water, the APA-6 polymer does not. The degree of conversion was determined according to Eqn. 1.

$$X = \frac{m_{pol}}{m_{tot}} \cdot 100\% \qquad (1)$$

RESULTS AND DISCUSSION

Rheology

Viscosity-time relations are presented in Fig. 1, for 1-1 and 2-2 formulations polymerized at 140, 150 and 160 °C (T_{pol}). It can be seen that less time is required to reach the 1 Pa·s limit for a higher polymerization temperature. The same can be concluded for the addition of more activator and catalyst. The viscosity remains extremely low (< 0.1 Pa·s) during most of the injection time, which facilitates fiber wetting and increases the flow rate of the resin through the fibers. Upon reaching the 1 Pa·s limit, the spindle with the polymerizing Caprolactam was removed from the setup and quenched in liquid Nitrogen. Determination of the degree of conversion correlated the 1 Pa·s viscosity limit to a 10 % conversion limit.

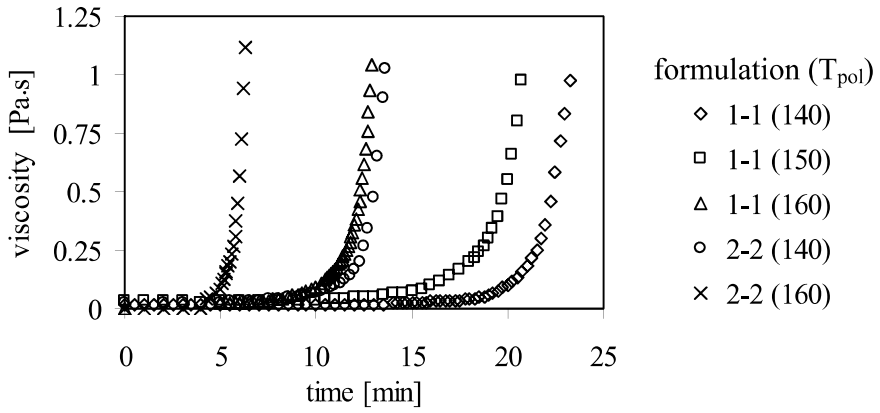

Fig. 1 Viscosity-time relations for anionic polymerization of Polyamide-6

Degree of conversion

Fig. 2 shows the degree of conversion in time for 1-1 and 2-2 formulations polymerized between 130 and 180 °C. As expected, higher polymerization temperatures and the addition of more activator and catalyst increase the polymerization rate. For the 1-1 formulation, polymerization at 130 °C is extremely slow. This can be explained by the semi-crystalline nature of APA-6. During formation of APA-6, which takes place well below its melting point (T_m = 220 °C), polymerization and crystallization occur as two competitive processes. At 130 °C, crystallization is the more dominant process and reactive sites can become trapped in the crystals very easily. As a result, polymerization is slowed down or even halted [2].

Final degree of conversion

The parameters changed not only influence the rate of polymerization, but also the final degree of conversion and hence the material properties. Residual Caprolactam acts as plasticizing agent for the APA-6 matrix for conversions below 95% [2]. Moreover, leftover Caprolactam will either diffuse to the product surface, making the product tacky and unpaintable, or in case of

composites it might diffuse to the fiber surface where it can significantly weaken the fiber-matrix interface. The final degree of conversion obtained in this study (conversion after 45 minutes) was determined for various formulations at a polymerization temperature of 140 °C, Table 1. Conversions obtained correspond to values found in literature [3]. It can be seen that increasing the amount of catalyst reduces the final degree of conversion, whereas the addition of more activator has no effect. The reason for this is that for every catalyst molecule added a MgBr cation is introduced, whose positive charge needs to be compensated for by a Caprolactam anion throughout the polymerization. Caprolactam left over to compensate for the cations is inevitable and determines the maximum obtainable degree of conversion, in other words a conversion of 100% is not achievable [4]. In literature, conversions of 98 % and higher have been reported for various activator/catalyst combinations [5]. Additional Caprolactam in the final product is caused by other phenomena (processing conditions, pollutions, …) and should be kept to a minimum.

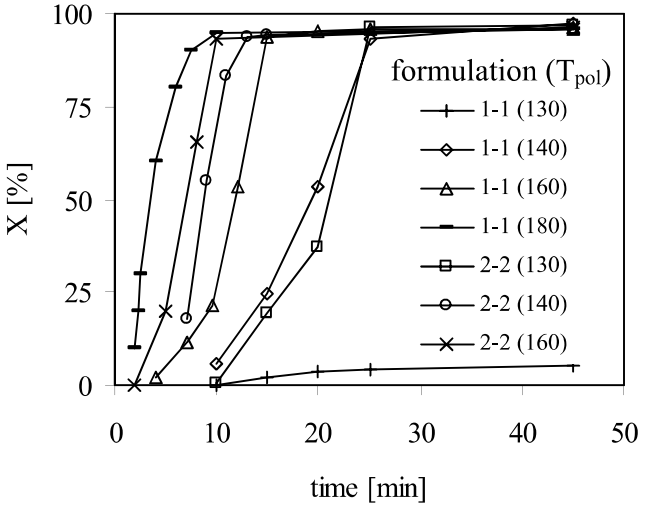

Fig. 2 Degree of conversion-time relations for anionic polymerization of Polyamide-6

Table 1 Final degree of conversion at a polymerization temperature of 140 °C

Formulation	Final degree of conversion [%]
1-1	97
2-1	97
5-1	97
1-2	94
2-2	94
1-5	93
5-5	93

Processing windows

For both the 1-1 and 2-2 formulation a processing window for various polymerization temperatures is constructed, see Fig. 3. A degree of conversion of 10 %, which correlates to a viscosity of 1 Pa·s, determines the end of the injection window. In the rheology experiments, the time to reach 10 % conversion appeared to be longer than in the experiments with the reaction tubes quenched in liquid Nitrogen. The explanation for this is that a single rheology test requires more reactive mixture (450 ml vs. 30 ml in a reaction tube). Consequently, heating up the material takes longer and polymerization is delayed. It can be concluded that part thickness is also an important parameter in constructing the processing window. The processing windows presented make use of the results obtained from the reaction tube tests and, therefore, are more

representative for manufacturing of thin walled composites. After 95 % conversion, the product can be demolded. It can be clearly seen that by adding more catalyst, the polymerization is much faster up to a degree of conversion of 90%. However, compensating for the higher concentration of cations takes its toll in terms of a longer processing time to reach 95% conversion.

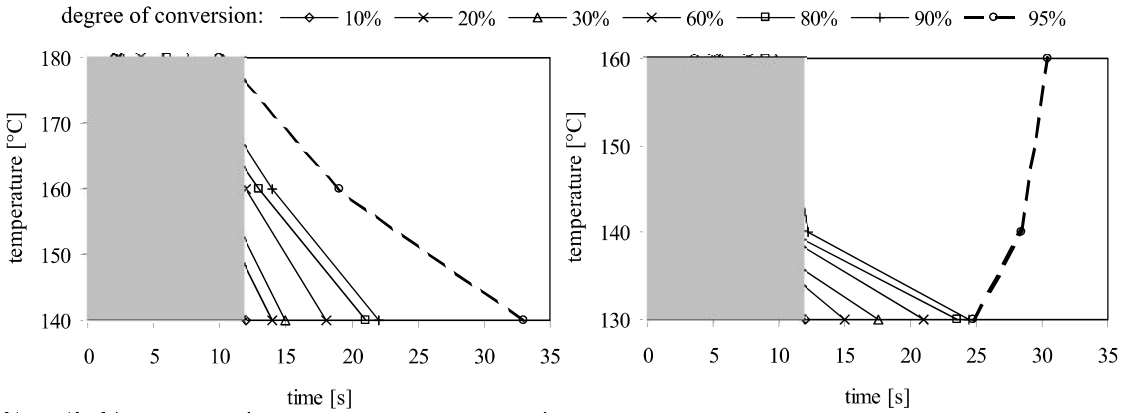

Fig. 3 Vacuum infusion processing windows for 1-1 (left) and 2-2 (right) formulations of Anionic Polyamide-6. Gray area represents the injection window, dotted line indicates demolding time.

CONCLUSIONS

A processing window for vacuum infusion of fiber reinforced Anionic Polyamide-6 was constructed for two resin formulations. Time to complete infusion and time to demold are indicated. Addition of more catalyst reduces the final degree of conversion, due to compensation for the higher number of metal cations present. This compensation also causes the polymerization process to slow down significantly above conversions higher than 90%. It was shown that besides resin formulation and polymerization also the part thickness has a strong influence on the processing window.

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