Perspectives for Reactive Molding of PPA as Matrix for High-Performance Composite Materials

Niccolo Pini, Chiara Zaniboni, Stephan Busato, Paolo Ermanni

Center of Structure Technologies, ETH Zurich
Leonhardstrasse 27, LEO B3, CH-8092 Zurich, SWITZERLAND
pini@imes.mavt.ethz.ch

SUMMARY: While Liquid Composite Molding (LCM) technologies for thermoset composites are increasingly used for manufacturing high quality structural components, LCM technologies based on thermoplastic matrices are still in development. Reactive thermoplastic LCM processes are at present applicable only to a few engineering polymers. This work presents perspectives for reactive molding of a high-temperature resistant polyphtalamide (PPA). Thermoanalytical, rheological and optical tests were performed to assess the behavior of low melting PA 6T/6I oligomers with increasing temperature and to monitor the polymerization and crystallisation reactions. The raw oligomeric material first undergoes a solid-liquid phase transition at around 135°C. At this stage its behavior is highly thixothropic and its viscosity around 10^5 mPa·s. At higher temperatures the viscosity of the oligomeric melt decreases further until a high temperature crystallisation process occurs at about 180°C. Polymerization starts at about 220°C and ends at 290°C. During the reaction the polymer crystallises as soon as it is formed with an achievable degree of crystallinity considerably higher than that of melt-crystallised samples. In accordance with the results, a viable processing technology based on powder impregnated intermediate materials is proposed.

KEYWORDS: PPA, reactive molding, oligomers, *in-situ* polymerization, powder impregnation.

INTRODUCTION

The potential of composite materials for lightweight structures is nowadays broadly recognised and exploited, even though several drawbacks prevent their more widespread adoption in modern technologies [1,2]. State-of-the-art high-performance thermoset composites show low damage tolerance and out-of-plane toughness [2], two factors limiting their application in safety critical parts. Furthermore their temperature resistance is mostly poor. From these points of view high-performance thermoplastic composites perform clearly better, but they require complex processing routes, which make them expensive and inadequate for geometrically complex parts [1,2].

The problems in processing thermoplastic composites arise mostly from their high viscosity in the molten state [2,3], which antagonizes the impregnation of the fiber bed. The processing window is usually quite narrow excluding a further viscosity reduction by temperature increase without degradation. A viscosity reduction could be achieved by using solvents, which however would have to be removed after impregnation.

A more recent approach consists in performing *in-situ* polymerization of precursor materials [3,4], in principle similar to the curing of thermoset resins. Low molecular species – monomers or oligomers – with low melt viscosity impregnate the fiber bed, then react after impregnation to form a polymer.

Because of the often delicate polymerization conditions, not many thermoplastic polymers can be *in-situ* polymerized. So far the following systems have been commercially promoted: Laurinlactam monomers producing PA12 (EMS Chemie, Switzerland) [3], "Fulcrum" producing TPUR (Dow Plastics, USA), CBT oligomers producing PBT (Cyclics Corp., USA) [4]. These processes yield well-known engineering thermoplastics, thus reducing the innovation potential and commercial impact of the *in-situ* technologies. In order to achieve a breakthrough for the latter, a reactive system delivering a high-performance polymer is needed.

Polyphtalamides (PPA) fill in the gap between engineering polymers and high-performance polymers such as polyphenylenesulfide (PPS) and polyetheretherketone (PEEK). PA 6T/6I is a cocondensation product of terephtalic and isophtalic acids with hexamethylenediamine with outstanding thermal properties: its melting point T_m is around 325°C, while its glass transition temperature T_g is 138°C. The heat deflection temperature HDT at 1.8 MPa is as high as 120°C [5].

The production process of PA 6T/6I at EMS Chemie involves a pre-condensation step, in which monomers condensate to oligomers (up to 10 repeating units). In a second step these oligomers condensate further to a polymer under loss of a small amount of water, making them potentially applicable in LCM processes.

The aim of this work is to study the suitability of these oligomers for LCM processes by characterising them from a thermal (DSC, TGA) and rheological point of view. Furthermore, optical analysis is performed in order to assess the polymer's microstructure.

EXPERIMENTAL

PA 6T/6I oligomers (XE 3733 VK) were kindly donated by EMS Chemie, Domat-Ems, Switzerland. Because of their sensitivity to moisture, the oligomers were dried at 80°C and 4 mbar for at least 24 hours before polymerization.

Thermal Analysis

DSC analysis was performed on a Perkin Elmer DSC 7 with nitrogen as purge gas in order to prevent high-temperature oxidation. Powder samples were tested in the temperature range from 80°C to 350°C with different thermal profiles in order to assess the progress of the polymerization reaction.

TGA Analysis was performed on a Perkin Elmer Pyris 1 TGA in nitrogen atmosphere from 80°C to 600°C at a heating rate of 10°C/min.

Rheological Analysis

The oligomer powder was pressed to pills with 20 mm diameter at 145°C and 160 MPa. The viscosity of the oligomers was measured on a plate-plate Paar Physica UDS 200 rheometer at different constant temperatures.

Optical Analysis

The microstructure of the polymer was observed by optical analysis of thin sections (microtome Leica RM2155 and optical microscope Leica RX DMA). Cryo-fracture was performed on polymerized samples and the fracture surface observed with a Scanning Electronic Microscope (SEM).

RESULTS AND DISCUSSION

Thermal Analysis

A typical DSC temperature scan from 80°C to 350°C at 10°C/min is shown in Fig. 1. In the heating curve (upper curve) four peaks can be clearly identified.

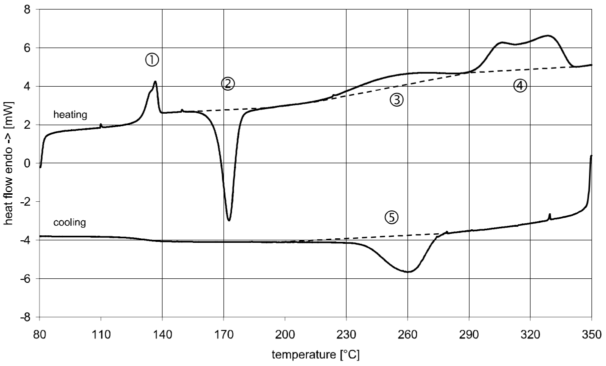

Fig. 1 DSC scan at 10°C/min under nitrogen of the oligomers XE 3733 VK.

Peak 1 at about 133°C represents the endothermal melting peak of the oligomers. Its enthalpy strongly depends on the sample history, which affects the degree of crystallinity of the sample.
Between 135°C and 170°C the sample is in a molten state. At peak 2 the oligomers undergo a high temperature crystallisation. Oligomers are short chain molecules: in the solid state their mobility is strongly reduced but in the melt they can easily rearrange and crystallise in a paraffin-like structure (fully extended chain crystals) without any entanglement between the chains. The stability of this configuration is further increased in the case of polyamides, which can form hydrogen bonds between the chains. Peak 2 could also be interpreted as a first polymerization step, but the narrow peak is more typical for crystallisation processes and TGA analysis does not show evidence of volatile reaction by-products at this temperature, which would be expected in case of a polycondensation.

Between 220°C and 290°C peak 3 can be identified as a broad endothermal peak. This peak is the superposition of three processes, namely polycondensation, crystallisation of the formed polymer and evaporation of the reaction by-product water. At 290°C the oligomers have completely reacted. The polymer crystallises as soon as it is formed: the temperature range of peak 3 corresponds namely to the temperature range where the crystallisation driving force is very large, as can be deduced from the position of crystallisation peak 5.

Peak 4 between 290°C and 340°C is a broad double melting peak of the polymer. This broad melting range mirrors the broad crystallisation range between 215°C and 290°C.

In the cooling curve (lower curve in Fig. 1) only one crystallisation peak from the melt can be identified between 290°C and about 220°C.

TGA experiments under nitrogen at 10°C/min showed that up to 200°C no volatile by-products are emitted. Therefore, DSC peaks 1 and 2 are no polycondensation peaks. Between 220°C and 290°C about 3.5 wt% water is released, due to the polycondensation reaction taking place in correspondence to DSC peak 3.

It is interesting to note that the melting enthalpy of the *in-situ* polymerized PA 6T/6I (ΔH^m=54.1 J/g) is about 33% higher than that of the melt-crystallised polymer (ΔH^m=40.7 J/g). This implies that the crystallinity of *in-situ* polymerized PA 6T/6I is 33% higher than that of the melt-crystallised polymer.

Heating of the oligomers only to 290°C followed by cooling to 80°C (Fig. 2) showed complete absence of any peaks in the cooling curve, thus implying that the oligomers reacted completely during the heating phase. On second heating of the *in-situ* synthesised polymer to 350°C only the melting peak between 305°C and 330°C can be observed.

These findings open up new opportunities to process PPA directly into a solid phase at lower than melting temperatures.

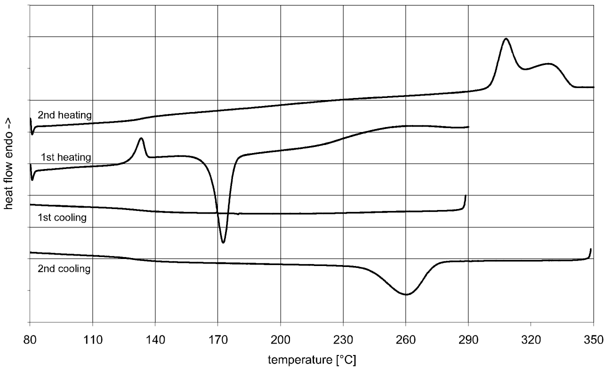

Fig. 2 DSC scan at 10°C/min under nitrogen of the oligomers XE 3733 VK. First heating to 290°C, then cooling to 80°C. Second heating to 350°C and cooling to 80°C.

Rheological Analysis

During processing the viscosity of the oligomers changes by several orders of magnitude. As expected, both viscosity and pot life of the material strongly decrease with increasing temperature (Fig. 3). Furthermore molten samples showed a pronounced shear thinning behavior, which causes the low viscosity to be evident only at higher shear rates.

The lowest observed viscosity of about 50 Pa·s at 180°C is still too high to allow injection of the oligomers in Resin Transfer Molding-like processes, but it is one order of magnitude lower than that of thermoplastic melts, so ensuring a more efficient fiber impregnation.

Optical Analysis

The polymer's microstructure was presumed to be of a spherulitic type. However, microscopical analysis of thin sections under polarised light did not unsheathe single overstructures like spherulites but only a smeared cluster of optically active crystals.

SEM analysis of cryo-fractured samples delivered pictures of fracture surfaces typical for brittle semi-crystalline polymers. A cellular structure could be identified on the surface with a cell width in the order of 0.1 μm, which could be the prints of the very single crystals.

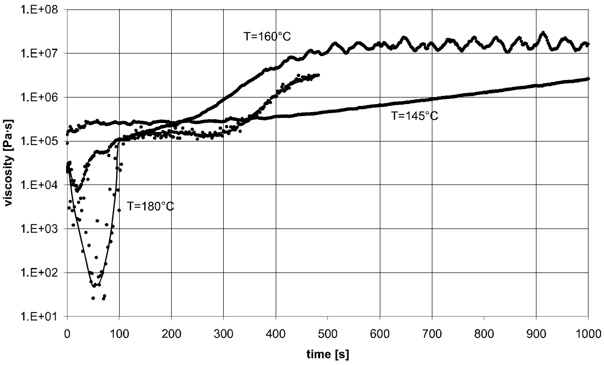

Fig. 3 Oligomer viscosity as function of dwelling time at three constant temperatures: 145°C, 160°C and 180°C (shear rate D = 20 s^{-1}).

CONCLUSIONS

The investigations presented open up a new way to process high-performance composites materials with PPA matrix. The unique thermal and rheological properties of the studied oligomers allow the manufacturing of oligomer powder impregnated reactive intermediate materials. The low viscosity of the molten oligomers can be fully exploited during the forming step, so that a faster – according to Darcy's Law – fiber impregnation can take place. After impregnation with the molten oligomers the temperature has to be increased up to the polymerization temperature, which is lower than the melting point of the polymer. After polymerization the part can be theoretically directly demolded. This processing route is expected to reduce cycle time, tooling and energy costs and deliver at the same time a high-temperature resistant high-performance composite material with an excellent price-performance ratio.

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