

AN ELECTROSTATIC POWDER SPRAY PROCESS FOR MANUFACTURING POLYPHTHALAMIDE HIGH PERFORMANCE COMPOSITE

Chiara Zaniboni¹, Paolo Ermanni²

¹ *Centre of Structure Technologies, ETH Zurich, Leonhardstrasse 27, LEO B3, CH-8092 ZURICH, SWITZERLAND: Corresponding Author's e-mail: czaniboni@ethz.ch*

² *Centre of Structure Technologies
ETH Zurich, Leonhardstrasse 27, LEO B3, CH-8092 ZURICH, SWITZERLAND:
permanni@ethz.ch*

ABSTRACT: The powder impregnation of carbon fiber rovings with low viscosity PA6T/6I polyphthalamide oligomers for the reactive moulding of unidirectional fibre-reinforced thermoplastic composites for high temperature applications was investigated. In order to impregnate the continuous carbon fiber tow with the PA6T/6I oligomer powder an electrostatic powder spray impregnation technique was developed and the material system was characterized. The most pertinent material parameters were determined to establish their influence on the desired powder impregnated prepreg. The oligomers undergo a nonreversible cold crystallization process on heating. The time and temperature interval of this solid state transformation is very sensitive to the applied force field. The definition of a suitable process window with respect to the external forces is necessary to avoid cold crystallization and to effectively impregnate the fibers.

KEYWORDS: Thermoplastic matrix composites, PPA, oligomers, cold crystallization, powder impregnation, reactive processing, in-situ polymerization.

INTRODUCTION

There is a growing interest in the industry in producing high quality thermoplastic composite parts for structural and high temperature applications. In response to this driving force an innovative stamp forming process with a reactive thermoplastic material system is currently being researched and developed aimed at cost-effective processing polyphthalamide PA 6T/6I in the field of continuous-fiber high temperature resistant composites.

Semi-crystalline polyphthalamides (PPA) are semi aromatic high performance engineering thermoplastics that bridge the cost-performance gap between traditional engineering thermoplastics such as polycarbonate (PC), polyamides (PA), polyester (PET, PBT), acetals (POM) and higher-cost specialty polymers such as liquid crystal polymers (LCP), polyphenylene sulfide (PPS) and polyetherimide (PEI). PPA resins and in particular copolyamides based on hexamethylenediamine, terephthalic acid and isophthalic acid (PA 6T/6I) have excellent mechanical properties (e.g. strength, stiffness, fatigue, creep resistance)

over a broad temperature range. PA 6T/6I resin features an excellent stiffness-to-cost ratio and a high strength-to-weight ratio, both of which are superior relative to PBT, PPS, PEI, PET and PA 6,6. Its thermal performance is exceeded only by polyetheretherketone (PEEK) and some LCPs. PA 6T/6I resin has lower moisture absorption than PA 6,6, and its broad chemical resistance is exceeded only by few more costly specialty polymers. This combination of features provides PA 6T/6I resin with the potential to reduce weight, cut costs, and deliver long service life for all types of automotive components, including parts for fuel, transmission, braking, and engine systems [1].

This paper discusses the impregnation of carbon fibers with the low viscosity PA 6T/6I oligomer powder. The most pertinent material parameters were determined to establish their influence on the desired powder impregnated prepreg. The oligomers undergo a nonreversible cold crystallization process on heating. The time and temperature interval of this solid state transformation is very sensitive to the applied force field. The definition of a suitable process window with respect to the external forces is necessary to avoid cold crystallization and to effectively impregnate the fibers.

EXPERIMENTAL

Material

The PPA oligomers (PA 6T/6I, XE 3733 VK) utilized in this work are the intermediates in a two-stage method developed by EMS-CHEMIE AG for the production of partially aromatic polyamides. Because of the typically very high structure-dictated melting viscosities of such polyphthalamides, the polycondensation with a single-stage batch process must be stopped at a very early stage to enable discharging the melt from the autoclaves and processing it into granular material. Limiting the average molecular weight of these polymers to comparatively low values has a very negative effect on their mechanical properties. In order to overcome these problems, the production process of PA 6T/6I at EMS-CHEMIE involves a continuous process for the production of precondensates (prepolymers), in which monomers condensate to oligomers (up to 10 repeating units). In a final reaction stage the precondensates are melt polymerized in a double-or single-screw extruder into high-molecular weight polyphthalamide [2]. The low cost PA 6T/6I precondensates are readily produced especially if compared to cyclic oligomers and allow the development of an in-situ polymerization process for large manufacturing volume applications and reduced production costs [3].

Powder impregnation and reactive processing

The reactive stamp forming process is based on prepreg technologies, reactive processing, and direct stamp forming. In a first stage, carbon fiber rovings are impregnated with the PPA precondensat powder by powder impregnation technique in order to reduce the distance to flow of the low viscosity thermoplastic prepolymer.

The powder impregnation process developed in this work utilize an electrostatic powder spray gun to charge and deposit the PA 6T/6I oligomers powder onto a continuous carbon fiber tow [4] A schematic of the electrostatic spray impregnation process is shown in Figure 1. The process uses a bi-directional fiber tensioner to maintain constant tension in the fiber tow. A pneumatic fiber spreader spreads the fibers, just prior to coating the fibers. An ITWGema EASY 1-L powder coating equipment is used to coat the spread carbon fibers with the

oligomeric powder. The coated fibers are then passed through an infrared heater to melt and adhere the powder to the fibers. The towpreg is then wound onto a take-up mandrel.

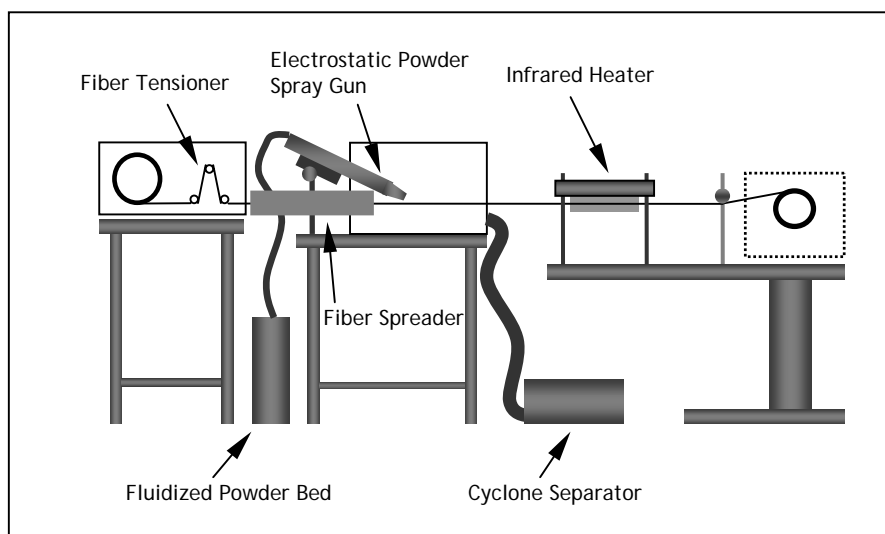


Figure 1. Schematic of electrostatic powder spray impregnation process

In a second stage, the oligomer powder coated prepregs are heated to the melt temperature of the oligomers in a hot press and pressed so that the oligomers, thank to their low melt viscosity, can easily flow and achieve high wetting and impregnation quality of the fibers. Finally, the temperature is raised between the glass transition and the onset of melting in order to induce the oligomers to polymerize in solid state and the so formed polymer to crystallize while the entire mass of material is shaped.

Rheological characterization

Solution Viscosity

Solution viscosity measurements of oligomers were carried out at concentrations of 0.1 g/dL, 0.3 g/dL, 0.5 g/dL and 0.7 g/dL in 98% sulphuric acid in a Paar Physica MC 300 rheometer using Couette geometry. The intrinsic viscosity $[\eta]$ of oligomers was calculated from the reduced viscosity η_{sp}/c by extrapolation to zero concentration.

Complex Viscosity

The complex viscosity of the PPA oligomers was investigated with a Paar Physica UDS200 rheometer in a parallel plate configuration. All measurements were carried out under nitrogen atmosphere to prevent degradation or absorption of moisture. The oligomer powder was pressed to pills of 20 mm diameter with pressure of 160 MPa and 1 MPa at 140°C.

Thermal Characterization

A Perkin Elmer Pyris 1 DSC instrument calibrated using indium was used to study the melting, cold-crystallization and polymerization behaviour of PPA oligomers. All DSC non-isothermal tests were performed from 80° to 350°C at a constant heating rate of 10°C/min under nitrogen atmosphere to prevent high temperature oxidation.

RESULTS AND DISCUSSION

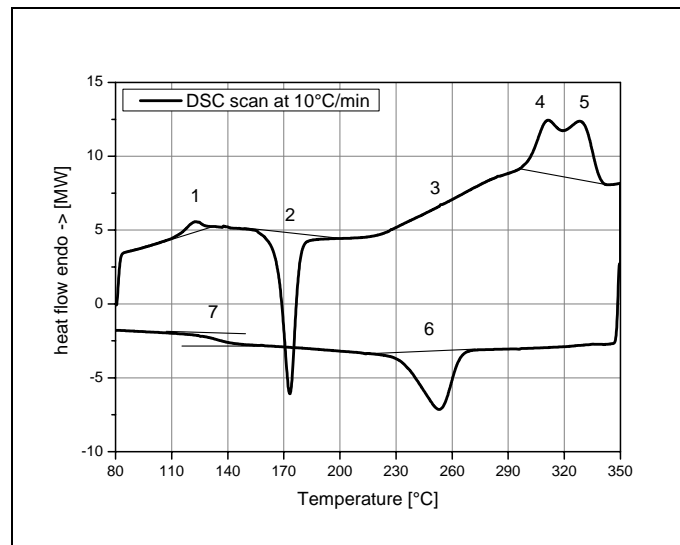


Fig. 2. DSC temperatures scan of PA 6T/6I precondensates from 80°C to 350°C at 10°C/min:
a) upper curve is the heating curve b) lower curve is the cooling curve

A typical DSC temperature scan of PA 6T/6I precondensates from 80°C to 350°C at 10°C/min is shown in Fig. 1. The as-received oligomers show seven distinct transitions in the heating (upper curve) and cooling curve (lower curve). Peak 1 represent a glass transition (T_g) step with a strong pronounced enthalpy relaxation [6] where the oligomers undergo softening. The peak temperature and enthalpy are strongly dependent on the thermal history of the sample. On further heating from the glass transition the oligomers are brought to crystallize (peak 2). The cold-crystallization behaviour observed for PA 6T/6I oligomers arises from the short chain lengths and low level of entanglements of the molecules: in the solid state the mobility of the short chain molecules is strongly reduced but above glass transition temperature they can easily rearrange and crystallise in a paraffin-like structure (fully extended chain crystals). The stability of this configuration is further increased in the case of polyamides, which can form hydrogen bonds between the chains [7]. Between 220°C and 305°C peak 3 can be identified as a broad endothermal peak where polycondensation and evaporation of the reaction by-product water take place. Peak 4 between 305°C and 345°C is a double melting peak of the formed polymer. In the cooling curve (lower curve in figure 1) one crystallization peak form the melt can be identified between 280°C and about 210°C and one glass transition temperature at 130°C of the final polymer.

Powder impregnation process window

Cold-crystallization of the low molecular weight PA 6T/6I oligomers was found to be very rapid as shown in figure 3 from the cold-crystallization half time. At a temperature lower than 155°C 50% of crystallization is attained in a time scale of several minutes, while above 155° the half time decreases to seconds. At 180° the oligomers are fully crystalline after few seconds. The cold crystallization of PA 6T/6I oligomers is not a reversible process: once the oligomers are crystallized, they can not be remelted. The powder impregnation process has, therefore, to occur at a temperature lower than 155° in order to fully impregnate the fibers and to avoid cold crystallization.

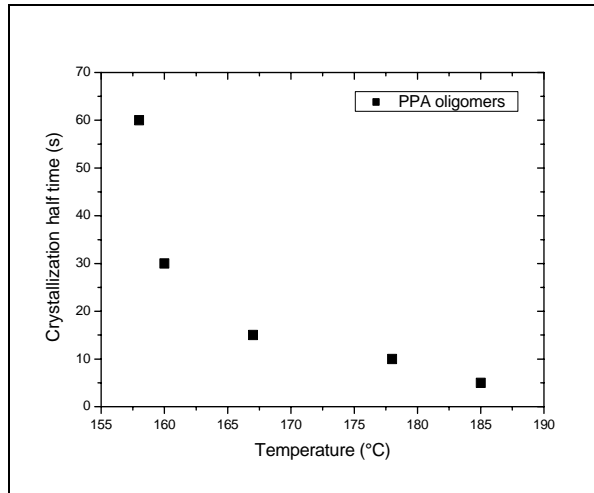


Fig. 3. Crystallization half-time of PA 6T/6I oligomers

The intrinsic viscosity of short chain PA 6T/6I oligomers was found to be very low with $[\eta] = 0.07$ dl/g, especially if compared, for example, to low molecular weight PET and PEN oligomers with $[\eta] = 0.2$ dl/g [8]. The low molecular weight oligomers begin to soften at 135°C, but they were found to melt only under shear force. In order to measure the complex viscosity at 140°C the oligomer powder was pressed to pills of 20 mm diameter under two different pressures. The complex viscosity values $[\eta^*]$ of the oligomer powder pills (pressed at 140°C with 160 MPa pressure) measured as a function of time at 140°C are very high, $[\eta^*] > 10^4$ Pa·s, as shown in Figure 4. On the other hand, complex viscosity of oligomer powder pills pressed at 140°C with pressure of 1 MPa show much lower values, $[\eta^*] > 10^2$. Further investigations were carried out to study the effect of pressure on the cold crystallization process with a torsional resonance rheometer.

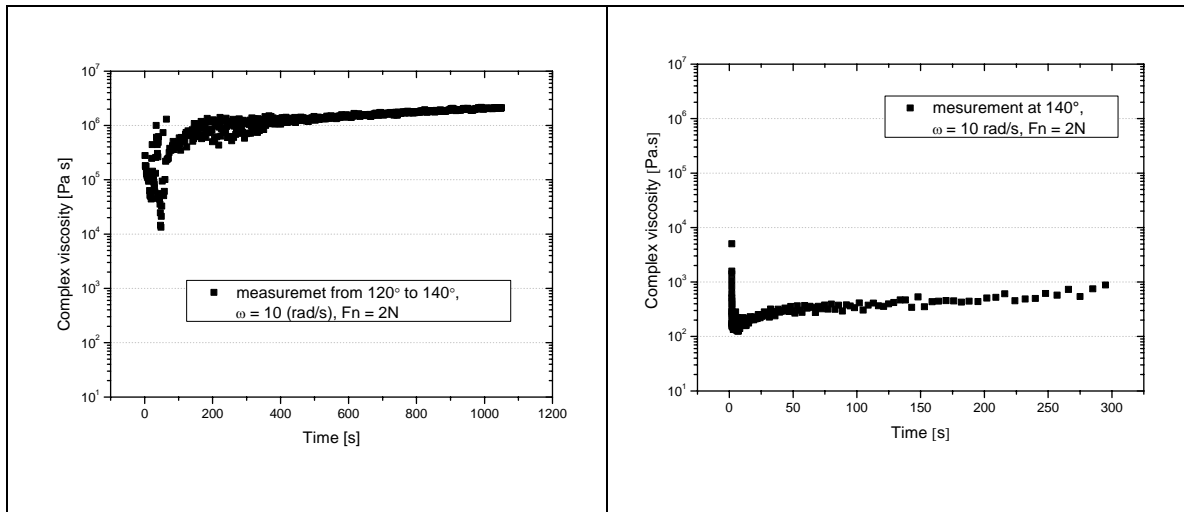


Figure 4. Complex viscosity values versus time for PPA oligomer powder sample pressed at 140°C with different pressure.

The time and temperature interval of cold crystallization was found very sensitive to the applied pressure force: increased applied pressure induces the PPA oligomers to crystallize at lower temperature and with increased crystallization rate [9].

This behaviour could be explained by the increase of orientation of the short oligomer molecules with increasing applied pressure. Pressure could give rise to a more ordered structure as in the case of drawing and cold crystallization in poly(ethylene terephthalate)

fibers [10]. The oligomer segments are shorter than the macromolecules and therefore easier to orient with pressure. The ordered segments are easily arranged into the crystal lattice, making the onset and the end temperature of oligomer crystallization shift to lower values. In other words, the orientation of amorphous phase promotes a substantial increase in crystallization rate.

The low viscosity of the PPA oligomers could not be measured do to the necessity of press the oligomer powder to pills for the rheological measurements. The applied pressure induced partial crystallization of the oligomers that surely affected the measured viscosity values. The low oligomer viscosity was proved during impregnation of the prepregs and has to be taken into account in order not to excessively impregnate the fibers and to maintain the flexibility of the prepreg.

Conclusions

Low molecular weight PPA oligomers begin to soften at 135°C but melt only under shear force. On further heating the oligomers undergo a non-reversible cold crystallization process. This solid state transformation was found to be very rapid: above 155°C crystallization half time of the material is only few seconds. Therefore, an efficient powder impregnation process has to occur at a temperature lower than 155°C in order to preimpregnate the fibers and to avoid solid state transformation. The time and temperature interval of cold crystallization is very sensitive to the applied pressure force: increased applied pressure induces the PPA oligomers to crystallize at lower temperature and with increased crystallization rate. Finally, the very low viscosity of the PPA oligomers was not proved do to the necessity of press the oligomer powder to pills for the rheological measurements. The low oligomer viscosity was proved during impregnation of the prepregs and has to be taken into account in order not to excessively impregnate the fibers and to maintain the flexibility of the prepreg.

ACKNOWLEDGEMENTS

The authors are grateful to GEBERT RÜF STIFTUNG for the financial support and would like to thank EMS Chemie for supplying the PA 6T/6I oligomers, ITWGema for supplying the EASY 1-L powder coating equipment.

REFERENCES

1. H.P. Schmeer, "Polyphthalamid", *Kautschuk.Gummi Kunststoffe*, Vol. 46, Nr. 10/93, 1993, pp. 799-804.
2. EMS-Inventa AG, U.S. Patent 5,708,125, 1998.
3. Weixia Yan, KeQing Han, LiuLiang Qin, MuHuo Yu, "Study on Long Fiber-Reinforced Thermoplastic Composites Prepared by In Situ Solid-State Polycondensation", *Journal of Applied Polymer Science*, Vol. 91, 2004, pp. 3959–3965.
4. K. Ramani, D. E. Woolard, M. S. Duvall, "An Electrostatic Powder Spray Process for Manufacturing Thermoplastic Composites", *Polymer Composites*, December 1995, Vol.16, No.6.

5. H. G. Kim, R.E. Robertson, “A New Approach for Estimating the Recrystallization Rate and Equilibrium Melting Temperature”, *Journal of Polymer Science: Part B: Polymer Physics*, Vol. 36, 133–141 (1998).
6. N. Pini, C. Zaniboni, S. Busato, P. Ermanni, “Perspectives for Reactive Molding of PPA Matrix for High-Performance Composite Materials”, FPCM7 2004.
7. S. Affolter, A. Ritter., M. Schmid, “Interlaboratory Tests on Polymers by Differential Scanning Calorimetry (DSC): Determination of Glass Transition Temperature (T_g)”, *Macromol. Mater. Eng.*, 286 (2001), 605-610.
8. K. Yao, W. Ray, “Modeling and analysis of new processes for polyester and nylon production”, *AIChE*, J 47 (2) (2001), 401-412.
9. C. Zaniboni, N. Pini, S. Busato, P. Ermanni, “Reactive Processing of Polyphthalamide as Temperature Resistant Matrix for High Performance Composite Materials”, *Theplac 2005*, Lecce, Italy.
10. Supaphol, P.; Apiwanthanakorn, N. “Nonisothermal Cold-Crystallization Kinetics of Poly(Trimethylene Terephthalate)”, *Journal of Polymer Science: Part B: Polymer Physics*, Vol. 42, 4151–4163 (2004).