



REACTIVE STAMP FORMING OF CARBON FIBER/PPA COMPOSITES

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Abstract

The low cost, the excellent mechanical properties, the high temperature stability and the broad chemical resistance are the driving forces for the use of semicrystalline polyphthalamides (PPA) resins as matrix material in structural composites for high temperature applications. Moreover, the combination of features of PPA provides this resin system with the potential to reduce weight at low costs for all types of automotive components including structural parts for fuel, transmission, braking, and engine systems. This paper explains research and development contributions to a new cost-efficient processing method for the use of PPA in continuous-fiber reinforced and highly temperature-resistant composites.

1 Introduction

There is a growing interest in the industry in producing low cost thermoplastic composite parts for structural and high temperature applications. In the automotive industry, for example, big efforts have been already made to reduce weight in non- and semi-structural components. However, reduction of CO₂ and NO_x emissions is today a driving force for further weight reduction in automobiles in combination with improved internal combustion technology and advanced powertrain technologies such as hybrid gasoline/electric and fuel cells [1]. Given that the major gains in powertrain technologies will be realized in the medium-to-long term, weight reduction through new and advanced material applications will be the key element in the short-term [2]. A further weight reduction can also be achieved in structural components and motor parts. However, the use of composites to reduce weight in automotive applications requires special attention not only on material performance but also on material and manufacturing costs: customers

expect a contribution to environmental improvements without additional cost.

In response to this driving force an existing low cost thermoplastic material, polyphthalamide (PPA) PA 6T/6I, with outstanding thermal, mechanical and chemical properties has been processed in this work as matrix material in continuous fiber composites for structural and high temperature applications.

Moreover, in order to attain high impregnation quality of the Fiber reinforcement by the high melt viscosity thermoplastic matrix and in order to achieve cost-effective processing an innovative reactive stamp forming process of PA 6T/6I prepolymers powder coated prepreps was developed.

In this paper the reaction kinetic of PA 6T/6I solid state polymerization (SSP) and the most important variables affecting the SSP reaction were investigated in order to determine the optimum operating conditions and establish a useful process window for the reactive molding.

2 Materials

2.1 Polyphthalamide PA 6T/6I

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), polyesters (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. [3].

2.2 PA 6T/6I Prepolymers

The PPA prepolymers (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. This process is also applicable to the production of other polycondensation polymers. 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 prepolymers (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. The PA 6T/6I precondensates are therefore readily produced especially if compared to cyclic prepolymers. This allows developing an in-situ polymerization process for large manufacturing volume applications with low material costs.

3 Reactive processing

The reactive stamp forming process developed in this work is based on prepreg technologies, reactive processing, and direct stamp forming.

In a first stage, carbon fiber rovings are impregnated with the PA 6T/6I precondensate powder by a powder impregnation technique in order to reduce the flow distance of the low viscosity thermoplastic prepolymer. The powder impregnation process developed in this work utilizes an electrostatic powder spray gun to charge and deposit the PA 6T/6I prepolymers powder onto a continuous carbon fiber tow [4].

In a second stage, the prepolymer powder coated prepregs are heated to the melt temperature

of the prepolymers in a hot press and pressed so that the prepolymers -thank to their low melt viscosity- can easily flow and achieve high wetting and impregnation quality of the fibers. Finally, the temperature is raised to a value between the glass transition and the onset of melting in order to induce the prepolymers to polymerize in solid state and the so formed polymer to crystallize while the entire mass of material is shaped.

4 Experimental methods

Because of their sensitivity to moisture, the PA 6T/6I prepolymers (XE 3733 VK) were dried in a vacuum oven at 80°C and 4 mbar for at least 24 hours before further use. Polymerized samples were prepared at different temperatures and for different times in a hot press under protective atmosphere.

4.2 Rheological characterization

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

4.3 Thermal Characterization

A Perkin Elmer Pyris 1 DSC instrument calibrated using indium was used to study the melting, cold-crystallization and polymerization behaviour of PA 6T/6I prepolymers. All DSC non-isothermal tests were performed from 80° to 350°C at different heating rate under nitrogen atmosphere to prevent high temperature oxidation.

TGA analysis was performed on a Perkin Elmer Pyris 1 TGA under nitrogen atmosphere to study the polymerization behaviour of PPA prepolymers. The PA 6T/6I prepolymers were heated at 30°/min to different polymerization temperatures and held at the polymerization temperatures for different times. The loss of weight (%) was correlated to the loss of the polymerization by-product, i.e. to the progress of the polymerization reaction.

5 Results

The reaction kinetic of PA 6T/6I solid state polymerization (SSP) and the most important variables affecting the SSP reaction were investigated in order to determine the optimum

operating conditions and establish a useful process window for the reactive molding.

The as-received amorphous prepolymers undergo cold crystallization upon heating, at a temperature between the glass transition temperature and the offset of the SSP reaction. The cold-crystallization behavior observed for PA 6T/6I prepolymers arise probably 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 [5].

The optimum crystallization of the prepolymers is an important step to produce high molecular weight PA 6T/6I polymers by SSP. Zimmerman [6,7] suggested that the end groups were excluded from the crystalline region of the prepolymer, i.e. they are not present as isolated defects in crystallites. Thus, the concentration of each end group in the solid polymer is many times higher than the concentration that would be present in a completely noncrystalline polymer at the same temperature. Moreover, the end groups exist in regions of relatively high mobility which we commonly think of as amorphous. The equilibrium in the amorphous regions is the same as for a completely amorphous or molten polymer at the same temperature [8].

The SSP reaction is carried out on the low molecular weight semicrystalline PA 6T/6I prepolymers at different temperature between 220° and 305°C, i.e. below their melting point.

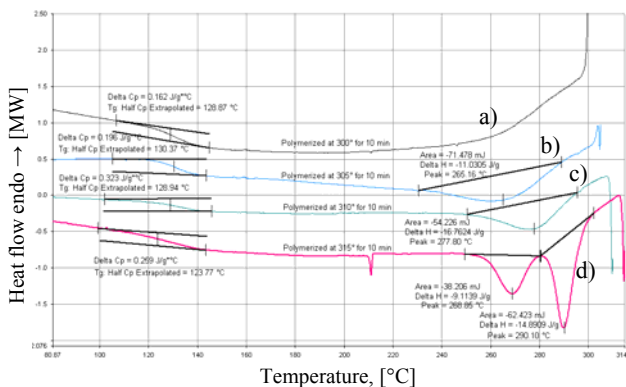


Fig. 1. DSC thermograms obtained by cooling polymer samples from different polymerization temperatures: a) 300°C for 10 min; b) 305°C for 10 min; c) 310°C for 10 min; d) 315°C for 10 min. Cooling rate 10°/min.

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The SSP reaction was characterized by the crystallization temperature (T_{CC}) on cooling from the polymerization temperature at 10°C/min, as shown in Figure 1 and 2.

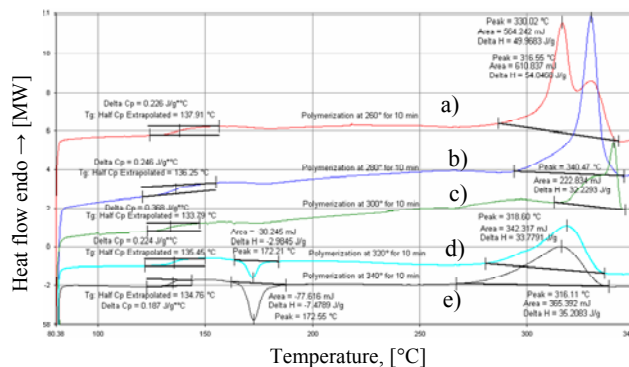


Fig. 2. DSC thermograms obtained by heating polymer samples previously polymerized at different temperatures: a) 260°C for 10 min; b) 290°C for 10 min; c) 300°C for 10 min; d) 320°C for 10 min; e) 340°C for 10 min. Heating rate 10°C/min.

Of particular interest was the crystallization behavior of the samples solid state polymerized upon heating to 300°C under nitrogen for ten minutes, a temperature close to the polymer melting temperature. The absence of crystallization temperature on cooling from the SSP reaction of the above mentioned polymer indicates that the SSP reaction probably proceeds in the amorphous region of the cold crystallized prepolymers, i.e. the chains grow via the reaction between the chain ends of the prepolymers that are already ordered in different lamella. Due to the above mentioned short chain lengths and the low level of entanglements of the PA 6T/6I prepolymers chain, bigger crystals with fewer defects are expected especially if compared with high molecular weight polymers [9]. The polymerization reaction can occur between molecules of the same or adjacent lamella. The reaction between prepolymer chains within one lamella leads to a folded polymer lamella. The reaction between prepolymers chains in adjacent lamellae leads to more tie molecules and therefore to a reduction of the overall SSP rate during the later stages [9]. In any case, the force of attraction between the chains in the well-ordered depths of the crystal is greater than at the surface, so that thicker crystals have higher melting point [10]. This could

explain the higher melting temperatures of the samples polymerized in solid state compared to melt temperatures of samples melt polymerized, as shown in Figure 2.

Figure 2 show the DSC scan of different samples polymerized for ten minutes under nitrogen at different polymerization temperatures. Three samples were polymerized in the solid state at 260°, 280° and 300°C respectively, and the other two samples were polymerized in melt phase at 320° and 340°C respectively. The results of the DSC analysis clearly show higher and sharper melting peak for the solid state polymerized sample especially if compared with the broad melting peak of melt polymerized samples. In the latter case, the morphology, the size and perfection of the crystalline domains are also significantly affected by the rate at which a sample is cooled from the melt: this is also evident from the existence of cold-crystallization peak that appear on heating the samples. On the contrary, in SSP the lamella are already formed during cold crystallization of the prepolymers and we can supposed that the rate of cooling has no influence over the overall degree of crystallinity. Moreover, the reduced mobility of high molecular weight chains formed during melt polymerization compared to short chain prepolymers leads to crystalline domain with a distribution of fold periods and hence melting temperatures. The size and degree of perfection of the polymer crystals are also correlated with the regularity of the polymer structure, for example with the degree of branching. As we will show later, high SSP polymerization or melt polymerization temperatures, combined with high residence times, encourage side reaction leading to a three dimensional network formation (table 1).

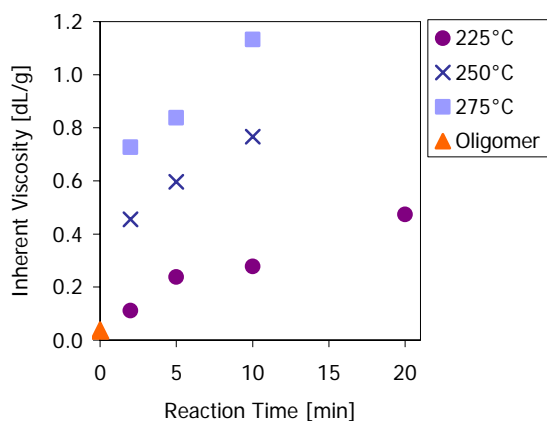


Fig. 3. Effect of the reaction temperature on the inherent viscosity of PA 6T/6I SSP for different times. Solution concentration of 0.3 g/dL in 98% sulphuric acid at 25°C.

The reaction temperature is probably the most important factor in SSP of semicrystalline PA 6T/6I prepolymers, as show in Figure 3. The inherent viscosity of the polymerized prepolymers was measured for different polymerization temperatures demonstrating the progress of the PA 6T/6I SSP.

At low SSP temperatures the chain building reactions are slow compared to polymerization in the melt, probably because of the reduced mobility of the reacting species, and the slow diffusion of the by-products. On the other hand, high SSP polymerization or melt polymerization temperatures, combined with high residence times, encourage thermal degradation and undesirable side reaction. The side reactions can lead to three-dimensional network formation (table 1), can drastically impair the quality of the end PA 6T/6I product, and therefore have to be avoided.

Table1. Inherent viscosity of samples polymerized at different temperatures for different times. Solution concentration of 0.3 g/dL in 98% sulphuric acid at 25°C.

Temperature [° C]	Time [min]			
	2	5	10	20
225	0.118	0.245	0.285	0.480
250	0.462	0.603	0.774	
275	0.734	0.846	1.141	*
300	0.743	*	*	
325	0.811	*	*	
350	0.7		*	

* Insoluble; only swelling.

The progress of the polymerization reaction was assessed by TGA analysis in order to determine the amount of water formed during the reaction, as shown in Figure 4. The prepolymers weight loss and therefore the progress of PA 6T/6I polymerization increases very rapidly during the first ten minutes and then slows down for all polymerization temperatures. The temperature is the most important factor in polymerization rate but also in side-reactions. However it may be noted that the final weight loss at 290° is higher than at 300°. Probably at 300° the prepolymers are very close to their melting temperatures and partial melting may occur with reduced by-product diffusion and particle

agglomeration.

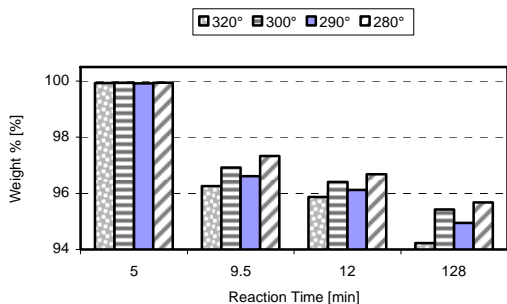


Fig. 4. Prepolymers polymerization reaction at different temperatures and for different times

It is generally accepted that the SSP proceeds by stepwise reaction in the amorphous phase of the semicrystalline polymer [9]. Thus, in semicrystalline PA 6T/6I prepolymers the rapid increase in polymerization rate during the initial stages of SSP could be due to availability of a large number of end groups in the amorphous phase. The Figure 5 shows the progress of the SSP reaction as mentioned by TGA analysis upon heating the sample to 290°C and holding it for ten minutes at the SSP temperature. The prepolymers were sieved to obtain particle size of 100 μm and different total sample weights were investigated.

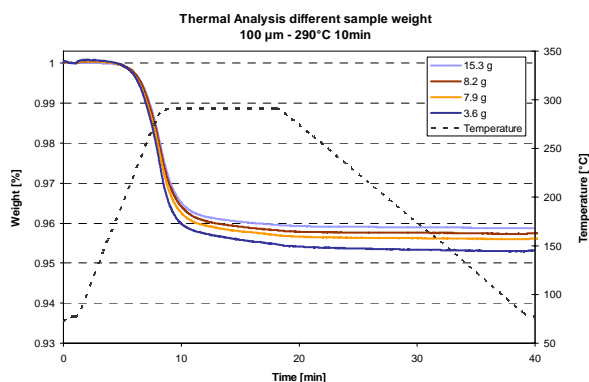


Fig. 5. TGA of prepolymers heated to 290°C and held for ten minutes; constant powder particle size (100 μm), different powder sample weights.

One might expect that the rate of SSP would be many times faster than in a melt polymerization at the same temperature because of the concentration of ends in the noncrystalline regions. However, the activation energies for diffusion of ends in the solid polymer are higher and the diffusion coefficient of the reaction by-product, i.e. water, is lower. Assuming that the diffusion of the condensate in the reaction solid and that the diffusion of the condensate from the solid to the surrounding

atmosphere as the rate-determining steps in SSP of PA 6T/6I prepolymers, the reduction of the progress of the SSP reaction with increasing sample weights would be explained

The effect of the by-product diffusion on the SSP is evident by varying the reacting particle size keeping the total powder sample weight constant. The graph in Figure 6 shows the progress of the SSP reaction by weighting the reacting powder with TGA analysis upon heating to 290°C and holding the different samples for ten minutes at the SSP temperature. The prepolymers were sieved to obtain different particle size (50, 100 and 250μm) but the total sample weights were held constant.

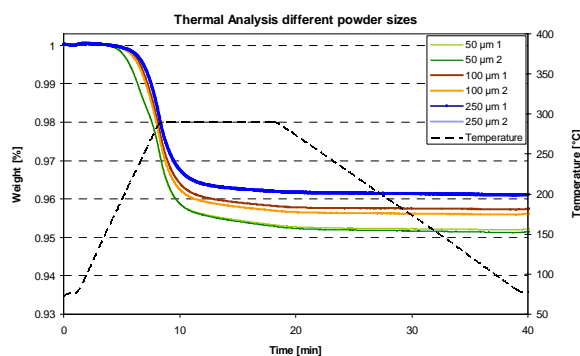


Fig. 6. Prepolymers SSP reaction at 290°C for ten minutes with constant powder sample weight but with different powder particle size.

It is generally accepted that smaller prepolymer particles can lead to an increased SSP rate [8], as observed in the different PA 6T/6I prepolymers powder of constant weight but of different particle sizes (Figure 6). This is due to the shorter diffusion distance and the larger particle surface area per unit volume. Moreover, the progress of the SSP is found to increase when the diameter of prepolymer particles decreases, indicating that diffusion of the by-product through the solid polymer is rate-controlling.

6 Conclusions

High molecular weight PA 6T/6I can be produced by solid state polymerization of PA 6T/6I precondensate without catalyst and at lower reacting temperature with a consistent reduction of energy consumption and tooling costs. Additionally, the low reacting temperature of PA 6T/6I SSP restrains side reactions and thermal degradation of the resulting polymer leading to increased degree of

polymerization and to improved quality of the end product. The polymerization reaction, usually slow in SSP compared to melt phase polymerization, was found for PA 6T/6I prepolymers to proceed in a few minutes (Figure 1), and the reaction temperature has emerged as the most important parameter of SSP advancement.

Polymerization, crystallization, consolidation and shaping of the final part can occur simultaneously under ideal isothermal condition with a consistent reduction of processing time.

During polycondensation reaction the PA 6T/6I short prepolymer chains combine to form a longer chain with the release of a small molecule by-product, i.e. water. A prerequisite to obtain a PA 6T/6I polymer product of high molecular weight (MW) consists in removing the condensate to prevent depolymerization, thereby shifting the reaction equilibrium to the final polymer. Fortunately in polyamides the equilibrium constant is two or three order of magnitude larger than other polycondensation polymer, and thus a much higher by-product concentration can be tolerated and the removal requirements are much less severe [11].

7 References

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