

REACTIVELY PROCESSED POLYAMIDE-6 STRUCTURAL COMPOSITES FOR AUTOMOTIVE APPLICATIONS

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Abstract

Over the last decade, a lot of material and process developments using thermoplastic composites such as LFT, D-LFT and GMT were implemented into automotive applications. Most of them were suitable for high volume semi-structural parts. Small to mid-size volume production cannot economically be realized with these processes due to the high tooling and equipment costs. Anionic Polyamide-6 (APA-6) offers an alternative that allows economic production of structural parts as well as to fulfill the European regulations for recycling. It will be demonstrated that the properties of reactively processed APA-6 are superior to its melt processed counterparts.

The reactive processing (vacuum infusion, RTM) of glass fabric reinforced APA-6 is being developed to increase product size/thickness and level of integration of thermoplastic composite parts. The process uses a monomer melt with a water-like viscosity to impregnate a dry fiber pre-form. A catalyst system initiates polymerization at temperatures in the range of 150-180°C, which is well below the melting and crystallization point of the final polyamide-6 (PA-6) polymer. As a consequence, solid highly crystalline PA-6 is formed. The simultaneous occurrence of polymerization and crystallization leads to a stiffness far greater than injection molded PA-6 and a strength that even exceeds the strength of PA-6 nano-composites. This in combination with the fact that reactive processing offers the possibility of tailoring the fiber-to-matrix interface clearly shows the potential for this high-performance material.

This paper will highlight the potential of this material and process for high-performance structural automotive parts.

Introduction

Anionic polyamide-6 (APA-6) is a reactive thermoplastic resin for the manufacturing of polyamide-6 parts. At temperatures between 150 to 180°C, the caprolactam monomer polymerizes within minutes into solid, highly crystalline polyamide-6 (PA-6) with a high molecular weight. Whereas the polymerization temperature can be used to tailor the polymer properties [1], the type and amount of activator and initiator provide the necessary control of the polymerization rate [2].

Fast reacting systems (figure 1) have already proven itself for rapid manufacturing of PA-6 parts with or without particle/short fiber reinforcement through casting [3], (reinforced) reaction injection molding (R)RIM [4, 5] and rotational molding [6]. The water-like viscosity of the resin (10 mPa·s) allows filling of large complex moulds or multi-cavity moulds in short time followed by a polymerization steps of only a few minutes after which the parts can be demolded hot.

Recent advances in initiator-activator chemistry have led to the development of an APA-6 resin with a long initiation time followed by a rapid polymerization step (figure 1). This system is ideally suitable for infusion of textile fiber reinforced composites for structural automotive parts through infusion processes, which require relatively longer mould filling times, such as structural reaction injection molding (SRIM) [7], resin transfer molding (RTM) [8] or vacuum infusion [9].

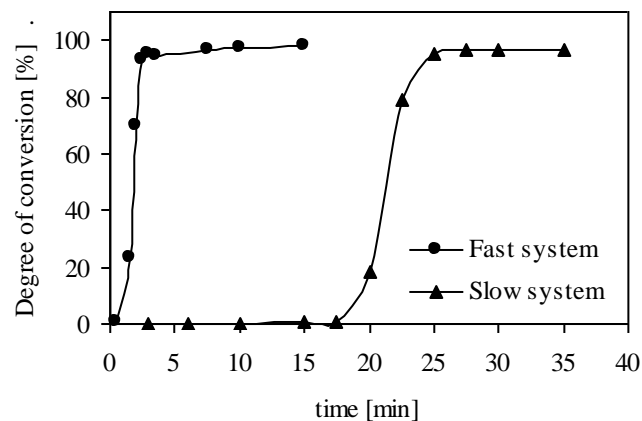


Figure 1: Conversion-time relations for a commonly used fast reacting system and the newly developed slow reacting system, polymerized at 150 °C.

The above mentioned reactive APA-6 infusion process allows manufacturing of very large structural and semi-structural parts for automotive and non-automotive applications including interior, exterior and under-the-hood applications. By tailoring the process conditions, structural steel parts can be substituted by composites. Besides reducing the tooling cost tremendously, mechanical properties increase due to the high crystalline material and the warpage will be reduced due to the process conditions used. APA-6 allows reducing the total cost of production. Especially for lower volume parts, APA-6 is the process of choice. Therefore, this technology forms an important addition to common PA-6 melt processes such as injection molding, LFT, GMT and SMC in obtaining a so-called all PA-6 car.

After the experimental section the polymer and composite properties of APA-6 are discussed and it will be demonstrated that the properties of reactively processed PA-6 are superior to its melt processed counterparts.

Experimental

Processing

Brüggolen C20 was used as activator and Brüggolen C1 as initiator for the anionic polymerization of the AP-caprolactam monomer into AP Nylon[®] (Brüggemann Chemical, Germany). A special designed lab-scale mixing unit (Mini Mixing Unit “MMU-TU Delft”, Bronk Industrial b.v., The Netherlands) is used to prepare two liquid material formulations at 110°C under a nitrogen atmosphere: a monomer/activator-mixture in tank A and a monomer/initiator-mixture in tank B, see figure 2. The two material feeds are mixed in a heated static mixer (110°C, 1:1 ratio) and dispensed into a heated (110°C) buffer vessel with nitrogen protective environment. Prior to infusion the reactive mixture is degassed at 10 mbar for 5 minutes.

To manufacture neat APA-6 panels (250 x 250 x 2 mm), a stainless steel infusion mould was used together with a 3 mm thick stainless steel cover plate (not shown). Homogeneous heating of the mould was obtained by placing it in a vertically placed hot flat platen press. A silicon tube connected the resin inlet of the mould with the buffer vessel and the resin outlet with a vacuum pump. Infusion from bottom to top is necessary to prevent entrapment of air. Additionally, a resin trap and a cold trap were placed directly after the mould to protect the vacuum pump.

To manufacture APA-6 composites (figure 2), a balanced and symmetrical laminate consisting of 12 plies (19 x 20 cm) of E-glass fabrics (8-harness satin weave) was built up on top of a 3 mm thick steel plate with Teflon top coating. The lay-up was bagged using a polyimide film (Upilex, UBE, Japan) and a heat resistant sealant tape (SM-5142, Schnee-Morehead, USA). The bagged lay-up was heated (170°C) in the previously mentioned press. A pressure control system was used to precisely set the infusion and curing pressure at 250 mbar (absolute pressure in the mould). After 60 minutes, demolding took place resulting in a 2.7 mm thick composite with a fiber volume content of 50%.



Figure 2: Infusion equipment. Left: Mini Mixing Unit “MMU-TU Delft”, center: bagged fiber lay-up, right: resin trap and vacuum pump with cold trap.

Details on the manufacturing of the injection molded PA-6, the PA-6 nano-composites and the textile fiber reinforced melt processed PA-6 composites can be found in one of our previous publications [10].

Analysis

Crystallinity and polymer melting points were measured on a Perkin-Elmer DSC-7, whereas the degree of conversion was measured according to a method presented in [1]. Densities were determined by submersion (ASTM D792) and the fiber content of the composites by thermal cleaning at 565°C. Tensile testing of the neat polymer (ISO 527-2) was performed on a Zwick 1455 universal testing machine equipped with a 10kN force cell. Mechanical testing of the composites was conducted on a Zwick-Roell Z250 25 tons machine equipped with extensometers. The following mechanical tests were performed: tension (ISO 527), compression (ISO 14126), and $\pm 45^\circ$ shear (ISO 14129). Samples were tested dry and after conditioning in a Weiss SB11/300-40 climate chamber (ISO 1110).

Properties of Neat APA-6

This section discusses the properties of neat APA-6 manufactured at two different mould temperatures (150 and 170°C) in comparison with common injection molded PA-6 and a PA-6 nano-composite. Being a semi-crystalline thermoplastic material that is prone to water absorption, both the effect of temperature and moisture absorption on the polymer properties is assessed.

Figures 3 to 5 show the tensile properties as a function of the environmental temperature. For all polyamides, the gradual reduction in strength and stiffness when crossing the glass transition temperature (62-69°C) can be seen. As expected, the PA-6 nano-composite has the highest modulus. The reinforcing effect of the nano-particles is clear and is explained in [11]. APA-6 ($T_{\text{mould}} = 150^\circ\text{C}$) has the second highest modulus due to the significantly higher degree of crystallinity compared to the other polyamides and is also the least ductile. The fact that the maximum strength of APA-6 outperforms even the PA-6 nano-composite is most likely caused by its morphology. Initial crystallization takes place at temperatures approximately 150-160°C, and as a consequence, crystal nuclei are plentiful and the final size of the spherulites is relatively small. Combining this with the high molecular weight of APA-6 [1], one can expect that a single polymer chain is part of many of these small spherulites, which leads to a polymer morphology in which small spherulites are connected by a well-developed network of tie-molecules. Another way to interpret figure 3 and 4 is that APA-6 shows equal performance as PA-6 but at a 50 to 80°C higher temperature, which clearly demonstrates the higher temperature resistance.

The figures also show that when increasing the mould temperature to 170°C, a lower degree of crystallinity is obtained (table I), which results in a more ductile and less stiff polymer. This clearly demonstrates that the mould temperature can be used to tailor the polymer properties. Another way to increase the ductility (but with a lower penalty on the Young's modulus) is to use the rubber modified version of APA-6, called NyRIM[®], which can be processed in exactly the same way.

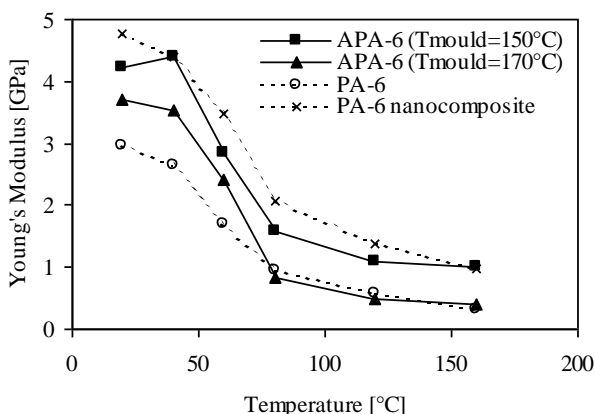


Figure 3: Young's modulus at various temperatures.

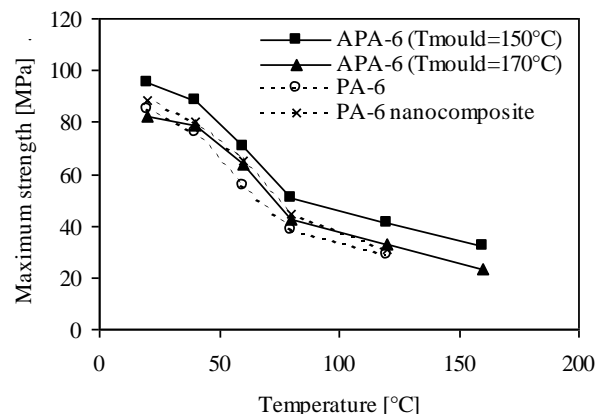


Figure 4: Maximum strength at various temperatures.

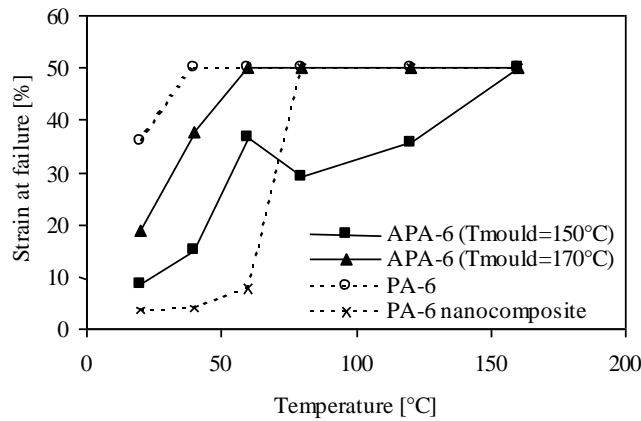


Figure 5: Strain at failure at various temperatures. (Tests were stopped at a maximum of 50% strain).

Table I: Physical properties of the polyamides

	APA-6 ($T_{\text{mould}}=150^{\circ}\text{C}$)	APA-6 ($T_{\text{mould}}=170^{\circ}\text{C}$)	PA-6	PA-6 nano-composite
Degree of conversion [%]	98	96	100	100
Degree of crystallinity [%]	45	36	37	35
Melting point [$^{\circ}\text{C}$]	218	212	220	220
Density [g/cm^3]	1.17	1.16	1.12	1.18

Figure 6, 7 and 8 show the tensile properties at various moisture contents. The PA-6 nano-composite has the highest modulus for all moisture contents, APA-6 ($T_{\text{mould}} = 150^{\circ}\text{C}$), however, comes close and has a higher strength. PA-6 and low crystalline APA-6 ($T_{\text{mould}} = 170^{\circ}\text{C}$) show a more or less equal performance.

The encircled data-points in figure 6 originate from samples that were all conditioned at 23°C -50%RH. It can be seen that APA-6 manufactured at 150°C absorbs less moisture and consequently, in the same environmental conditions, a much higher modulus (2.1 vs. 1.3 GPa) is obtained compared to PA-6.

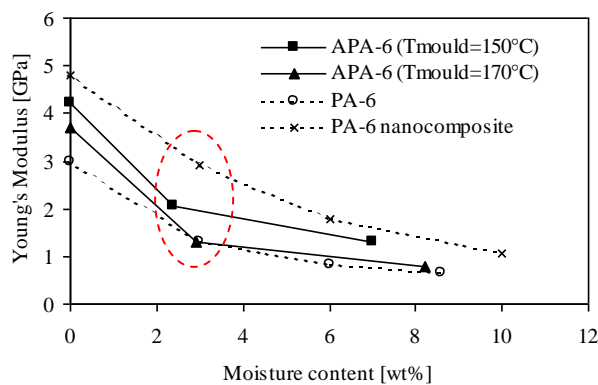


Figure 6: Young's modulus at 23°C for various moisture contents.

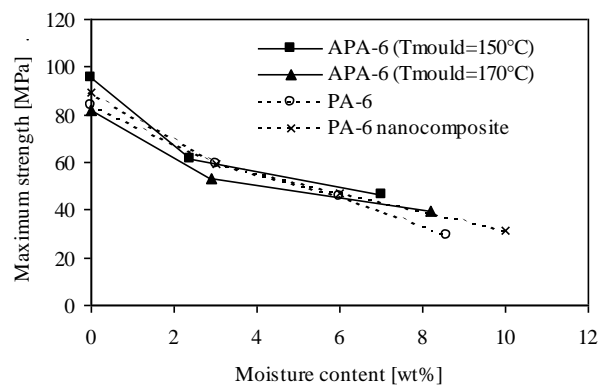


Figure 7: Maximum strength at 23°C for various moisture contents.

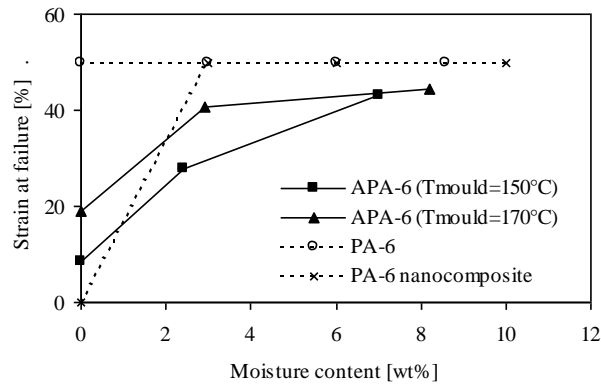


Figure 8: Strain at failure at 23 °C for various moisture contents. (Tests were stopped at a maximum of 50% strain).

Properties of APA-6 Composites

Table II shows that in dry as molded conditions (DAM), the infused APA-6 composite outperforms the melt processed PA-6 counterpart in all tests performed, which is most likely caused by a higher degree of crystallinity, see table III. Upon moisture conditioning, however, the PA-6 composites perform slightly better. The APA-6 composites are more affected by conditioning due to the higher void content (table III) and the hygroscopic nature of residual monomer (conversion is only 95%). Although the selected fiber sizing is known to yield a strong bond with the PA-6 matrix during melt processing, this is no guarantee that during reactive processing the same will happen.

Current research efforts of the consortium consisting of the Delft University of Technology, Brüggemann Chemical, Bronk Industrial and Johns Manville, aim at developing a more compatible fiber sizing. It is expected that improved chemical compatibility will further improve the APA-6 composite properties by increasing the conversion and the fiber-to-matrix interface strength, whereas improved processing characteristics of the fibers will reduce the void content. The final remark is made that with the described process already composites with a fiber volume content of 50% of up to 2cm have been manufactured, which demonstrates the potential for manufacturing structural automotive parts, see figure 9.

Table II: Mechanical properties of polyamide composites

Matrix material	DAM		23°C -50%RH	
	APA-6	PA-6	APA-6	PA-6
Mechanical property				
Compressive Strength [MPa]	473	390	290	314
Compressive Modulus [GPa]	26	25	23	23
Compressive Strain [%]	1.9	1.5	1.3	0.9
Tensile Strength [MPa]	495	456	430	450
Tensile Modulus [GPa]	26	26	23	24
Tensile Strain [%]	2.4	2.5	2.0	2.0
Shear Strength [MPa]	127	117	105	100
Shear Modulus [GPa]	4.1	3.7	1.9	1.7

Table III: Physical properties of polyamide composites

Physical property	APA-6 composite	PA-6 composite
Thickness [mm]	2.8	2.7
Density [g/cm ³]	1.8	1.9
Fiber Volume Content [%]	50	51
Void Content [%]	3.0	1.3
Melting point [°C]	217	220
Degree of Conversion [%]	95	100
Degree of Crystallinity [%]	35	33



Figure 9: A 2cm thick vacuum infused APA-6 composite.

Conclusions

Reactive processing of anionic polyamide-6 (APA-6) was discussed for manufacturing of structural automotive composite parts. APA-6 outperforms melt processed PA-6 in terms of modulus and strength, and shows increased temperature and moisture resistance. Despite the superior behavior of the reactively processed polymer is, the APA-6 composites only perform better than their melt processed PA-6 counterpart in dry conditions. The properties of APA-6 composites are strongly reduced when moisture conditioned. It is expected that sizing optimization will increase the composite properties. APA-6 allows producing parts with structural reinforcements such as fabrics that cannot be easily molded using standard processes. The low viscosity during processing allows thorough impregnation of continuous reinforcements. It was also demonstrated that infusion processes can be used to manufacture thicker structural composite parts than is currently possible with melt processing and that the processing temperature can be used to tailor the polymer properties.

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