# NEW METHODS TO PRODUCE REINFORCED POLYAMIDE-6 FOR IMPROVED MATERIAL PROPERTIES IN ENGINEERING PLASTIC APPLICATIONS

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## Abstract

Polyamide-6 is widely used in many mechanical applications, also in automotive, replacing more and more traditional materials such as metals, thermosets and elastomers. Good process ability along with outstanding physical properties, also long term stability under tough conditions, and a high value recycling ability make this thermoplastic material also commercial interesting for new demanding machinery parts.

A broad variety of materials is achieved by producing PA-6 “in situ” by anionic polymerisation of Caprolactam, which can be performed on extruders, on RIM machines or in different casting processes. Nano-Clay or Glass fiber reinforced granules, short or long-glass fiber reinforced molded parts, glass-mat reinforced manhole covers or wind turbine blades are some examples of Brüggemann’s AP-Nylon® Material applications, completed by NYRIM®, the wide range impact modified grades.

This paper gives an overview of the new developments in this field we were involved in during the last 2 years

## New developments in processing using anionic polyamide.

The anionic polymerization of caprolactam to polyamide-6 is well known from “casting” of semi-finished products like rods, plates, tubes etc. Also finished products are produced, for instance fuel tanks by in situ polymerization in rotomolding.

NYRIM is an elastomer-polyamide-6 blockcopolymer. Depending the ratio of elastomer to polyamide, NYRIM parts can range from a tough and stiff to a super tough material, even at -40°C. Due to these properties, a variety of finished products is produced. Many of these products are reinforced by hammered or milled fibers from glass or minerals; hollow spheres and woven or non-woven glass mats. An example of a glass mat reinforced NYRIM composite is a manhole cover with a diameter of 1.14 m (40% reinforcement), with a load resistance of 35 metric tons. (Figure 1.)

*Figure 1: Manhole cover*

Cast polyamide-6 and NYRIM products are obtained by mixing a solution of an activator in caprolactam with a solution of an initiator in caprolactam. The mixture is “poured” (casting) or injected (RIM) in a mold. The RIM process can be used for manufacturing of glass mat reinforced composites up to a length of a few meters.

In a joint program with the Technical University of Delft, we are involved in the development of composite windmill wings up to 100 m in length for production of electric energy. Today’s windmill wings are produced from woven glass or carbon fiber mats and thermoset polymers. One of the standard processes for production of the wings is vacuum infusion of a resin-prepolymer into a package of woven mats. The viscosity of the resin-prepolymer (epoxy; unsaturated polyester etc.) allows production of wings up to about 60 m. The service life of windmill wings is about 15 years and after that the wings should be replaced. The recycle ability of the thermoset polymers is very limited and will produce a lot of waste. Polyamide-6 can be fully recycled, for instance as injection molding or extruded product and can even be depolymerized to the monomer caprolactam what can be reused for production of virgin polyamide-6 (from cradle to cradle). Molten (hydrolytic) Polyamide-6 is a very viscous material and cannot be used for (vacuum) injection into a package of glass or carbon fiber mats. The joint program investigates the possibilities of in situ anionic polymerisation of caprolactam in the mold filled with the reinforcing material. After mixing the solutions containing the activator and the initiator, the mixture infused in mold by vacuum. The reactivity of a mixture based on standard activators and initiators is high (viscosity rise within one minute) and from that the dimensions of a composite will be restricted. Especial for the production of large dimension composites we developed a combination of an activator and initiator which exhibits an initiation time (depending on temperature) of 6 to 15 minutes (figure 2.). Since the viscosity of the reaction mixture during the initiation time is low (water-like), injection into the package of reinforcing material is easy and production of large dimensions will be able. Although the program is directed to windmill wings, the data will also be used for developments in production of gas tanks and interior panels for aviation.

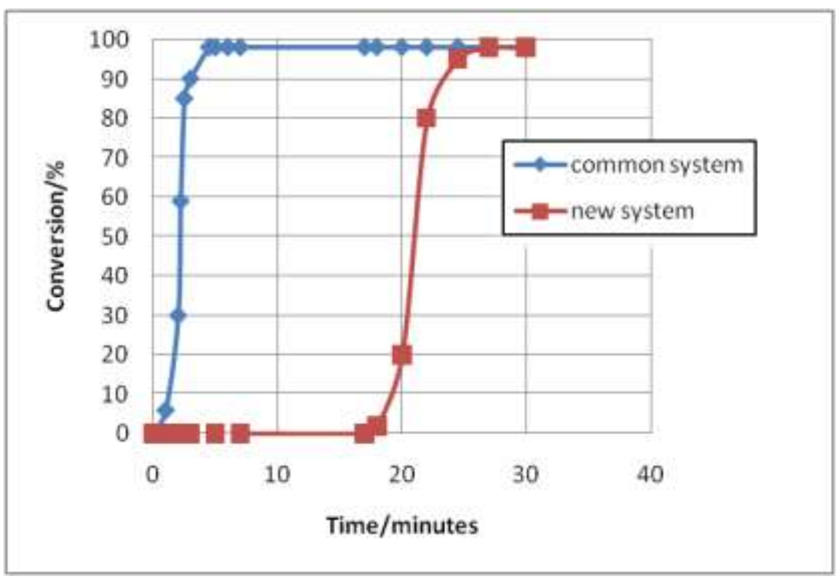


*Figure 2: Anionic polymerization using new system with initiation time*

The polymerization of caprolactam to polyamide-6 (composites) in extruders is investigated in a joint program with the Institut für Kunststoff Verarbeitung of the RWTH Aachen. The advantages of in situ production of polyamdie-6 in an extruder are several:

- Polymerisation and compounding can be accomplished in one step: cost savings
- Due to short residence times (small volume of extruder), fast grade changes are possible with only minor losses of materials (compared to continuous hydrolytic poly volumes 25-150 ton per reactor)
- Good wetting of fiber rovings
- Standard glass reinforcement
- Glass fiber reinforcing of (very) high molecular weight polyamide (impossible by compounding)
- Perfect dispersion and exfoliation of Nano-Clays
- Compared to hydrolytic polyamide-6, anionic polyamide-6 is more melt-stable.

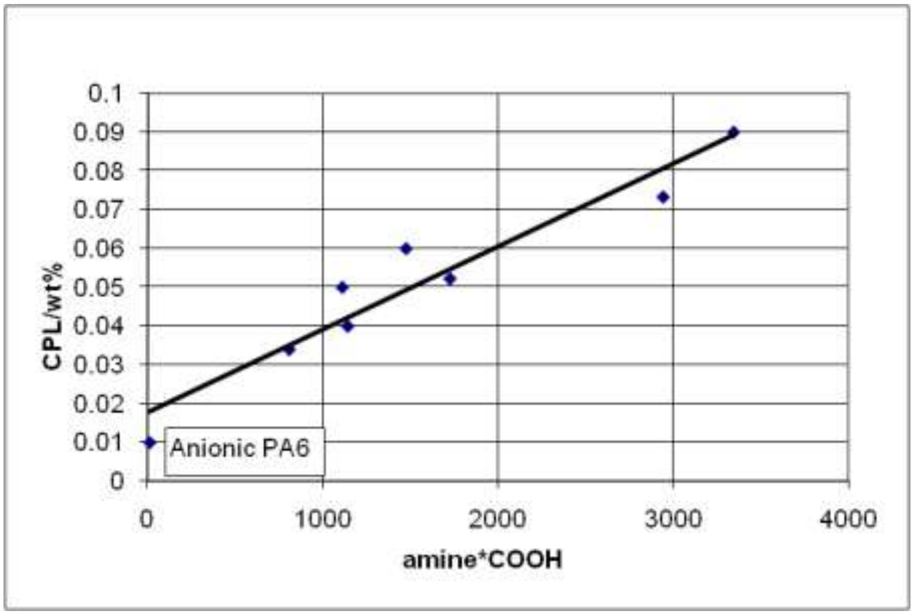


*Figure 3: Evolution of caprolactam during melt processing for 3 minutes at 265°C.*

The processes of casting, reaction injection molding (RIM) and vacuum infusion described above are all performed at 140-170°C, temperatures below the melting point of the resulting polyamide-6 (220°C). The articles produced are semi-finished (which will be brought into shape by mechanical tooling) or finished products. The molecular weight of the polyamide-6 in the semi finished products is usually high and the polymer is branched/cross linked thus imparting hardness and stiffness. However, the products of the anionic polymerization in extruders will mainly be (filled) granules which will be melt-processed to obtain the final products. To control the molecular weight of the polyamide-6 produced, a new combination of an activator and initiator was developed which results in a linear, non-branched polyamide-6. The molecular weight of the products is fully controlled (Figure 3.) and can range from low viscous injection molding grade (RV sulfuric acid 2.2) to very high molecular weight extrusion grade.

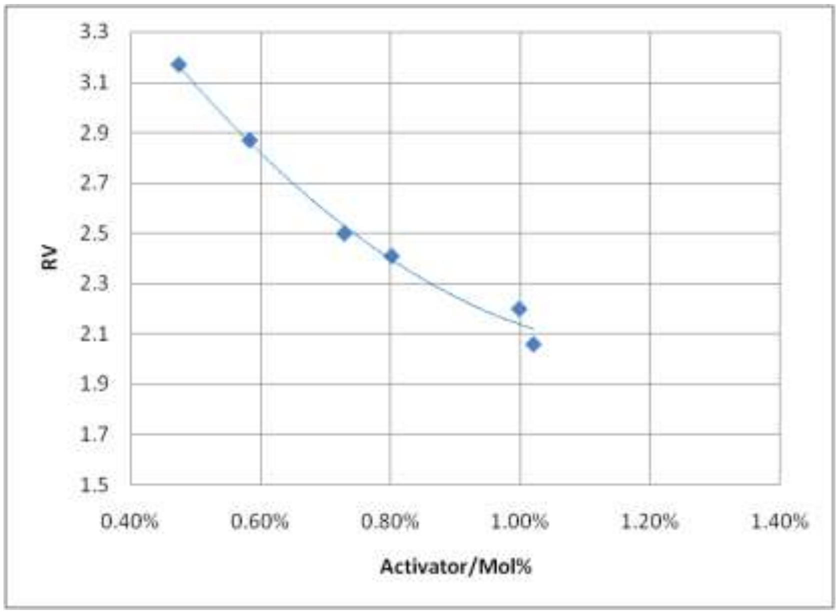


*Figure 3: Molecular weight (RV) of anionic polyamide using new Activator/Initiator system*

Besides by the concentration of activator, we developed an in process chain regulator (modifier) what allows control over the molecular weight of the polymer at constant activator concentration (Figure 4.). In the extrusion process, the polymerization is started first and the modifier is added to the extruder at a point were the polymerization has come to equilibrium.

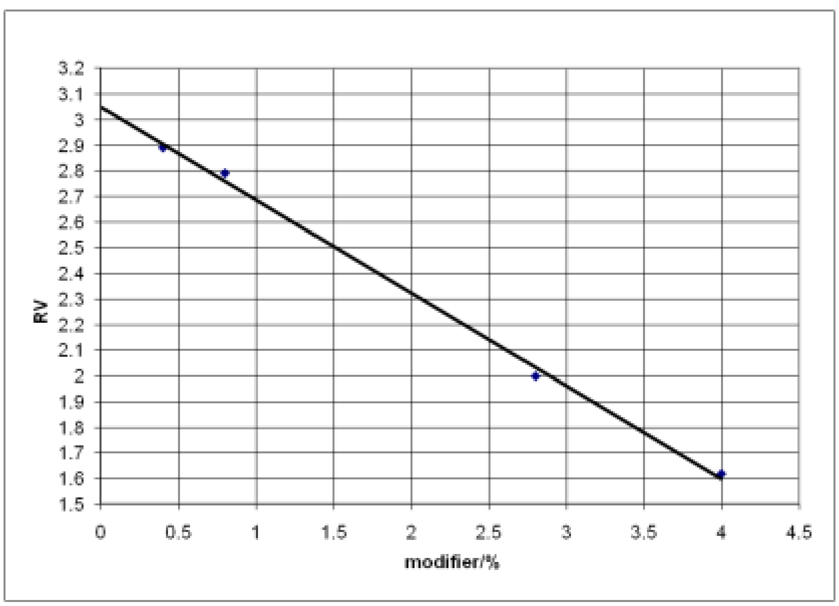


*Figure 4: Molecular weight controlled by new modifier*

The main part of the joint project is directed to Nano-Clay reinforced injection molding grades (GE funding) with promising results. Besides that, the possibilities for production of long glass fiber reinforced polyamide-6 granules are under investigation. The sizing on standard glass for reinforcement of hydrolytic polyamides is not compatible with the anionic chemistry for polymerization of lactams to polyamides. Investigations for sized glass for use in the anionic polymerization process are performed by Johns Manville with promising results.

## Summary and Next Steps

The developments on composites obtained by injection molding; vacuum infusion and reactive extrusion were described. At the moment we are in the middle of the projects for the windmill blades and reactive extrusion for obtaining clay nano-compounds and long glass fiber filled polyamide. The results so far show:

- The development of anionic polymerization system with extended initiation times allowing (vacuum) injection of parts with large dimensions
- The possibility of producing linear, molecular weight regulated polyamide in an extruder.
- A good connection between glass roving and polymer matrix can be obtained by a new developed glass-sizing.

Developments in the projects will go on and based on the data so far a number of customers have showing interest in using the systems.

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