

Development of a Polyamide Copolymer Resin Transfer Molding System for Thermoplastic Composites

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SUMMARY:

The present study evaluated a process for fabricating anionically polymerized carbon-fiber reinforced polyamide plaques. Vacuum assisted resin transfer molding (VARTM) was used to impregnate a dry carbon-fiber bed with a low viscosity molten catalyst, activator and monomer mixture. Polymerization occurred in-situ forming a solid thermoplastic polymer matrix composite. Also investigated were the potential benefits or detriments associated with using polyamide copolymers as opposed to homopolymers for the matrix material. The tooling employed were both rigid and semi-rigid matched molds. The entire fabrication process was completed in a matter of minutes. The present investigation showed that the matrix fulfilled the requirements for direct liquid impregnation of fiber-reinforced preforms. The matrix viscosity was low. Once impregnated the melt was solidified in a reasonable amount of time. And the resultant matrix had high enough properties to give good mechanical and physical stability to the composite.

KEYWORDS: anionic polymerization, thermoplastic, copolymer, polyamide

INTRODUCTION

Direct impregnation of fiber-reinforced composites by a liquid matrix allows large, complex, and repeatable parts to be fabricated with low tooling costs and cycle times. As opposed to thermosets, thermoplastic matrices offer the advantages of high impact strengths and the ability to be recycled. Due to high melt viscosities, thermoplastics are generally not used for high volume-fraction resin injected parts. The employment of an activated melt, which polymerizes in-situ, overcomes this problem. The process outlined herein relies on two monomers; caprolactam and laurolactam, which when combined with the activator and catalyst solution form the copolymer polyamide 6/12.

Currently the advanced composite market is dominated by thermoset-based resins. However thermosets have several intrinsic disadvantages that in today's environmentally aware society are becoming increasingly problematic. The two most prevalent problems with thermosets are their inability to be recycled and the harmful emissions that can be produced during processing.

The advantages of VARTM include low tooling costs, the ability to form complex shapes, and the ability to control fiber orientation and volume-fraction. VARTM is suitable however, only for resins with very low viscosity ($\mu \ll 1 \text{ Pa}\cdot\text{s}$). A VARTM copolymer system must satisfy the following 4 criteria: (i) The monomers can be melted under an inert atmosphere. (ii) The monomers, activator, and catalyst can all be mixed thoroughly prior to injection. (iii) The tool must be airtight during impregnation and polymerization. (iv) The tool must be able to maintain a constant temperature for a period of time and then cool down. [1]

The melting temperature of the copolymers examined in this project depends on the polymer ratio and varied between the melt temperatures of PA 12 (178 °C) and PA 6 (220 °C). Because the predominantly PA 6 mixtures have a melt temperature above their polymerization temperature the entire process can be considered isothermal. In industrial terms this means that a mold need not have a temperature cycle. That is to say that the fabrication process can have $T_{\text{injection}} = T_{\text{polymerization}} = T_{\text{demolding}}$. This is advantageous for mass production of parts as the cycle time is not dependent on the molding tool's heat up or cool down rate.

Materials

The problem of thermoplastic material's high melt viscosities can be overcome by using the anionic polymerization processing technique. Anionic polymerization is a quick and clean method of producing polyamide materials. Conversion to high molecular mass polymer is almost instantaneous and does not have any by-products. All that is required is the monomer, a catalyst, an activator and a means to heat and mix them together. EMS Chemie A.G. in Switzerland developed a catalyst and activator solution used in the present study for anionic polymerization. Named GRILONIT, it has a viscosity $< 1 \text{ Pa}\cdot\text{s}$ and can be stored indefinitely in an inert atmosphere. Unlike previous thermoplastic composite matrix systems there is no need for separate pre-blended monomer-catalyst and monomer-activator solutions that slowly polymerize over time.

From a mechanical and physical property standpoint it can be beneficial to mix two monomers, polymerize the mixture, and form a copolymer. The optimal copolymer would take the best properties, applicable to the particular situation, from their respective homopolymers to create a material that is ideally suited to its intended purpose. The monomers discussed here, caprolactam and laurolactam, form PA 6 and PA 12 respectively.

Tenax 5N21 carbon-fiber woven into a 2/2-twill fabric was used for all reinforced processing and testing. The density of the carbon-fiber was 1770 kg/m^3 . The weight of the fabric was 440 g/m^2 . The 2/2 twill fabric used in the present study was quite drapeable unlike most thermoplastic pre-pregs, which tend to be stiff and "boardy." A desktop heated composite tool was designed and used to create both reinforced and un-reinforced plates. Plates were also

created on an industrial-sized, double daylight, hydraulic composite press. Both employed matched rigid molds.

It was found through testing un-reinforced samples that PA 6 had the most suitable mechanical properties for a composite matrix. PA 6 was also found to process more readily as its monomer precursor had a lower melt temperature and lower viscosity than PA 12. Polyamide 6 has one great drawback however, its moisture absorption. Immersed in water it can absorb up to 9.5% by weight in moisture. This can lead to dimensional changes, mechanical and physical property changes, internal stresses, and in the case of a composites, delamination. Polycaprolactam based composites are therefore suitable only for applications where moisture absorption and dimensional stability are not of critical importance. [2]

Anionically Polymerized Lactam Composite Injection Process

The entire polymerization process in terms of composite fabrication is quite straightforward. It can be broken down into three main stages, which consist of the mixing, the injection, and the polymerization. The mixing stage begins by placing measured amounts of monomers consecutively into a conical flask and melting the mixture in an oil bath. The melting temperature of caprolactam is 69 °C and that of lauro lactam is 151 °C. A temperature of 175 °C was chosen.

This was done so that the melt would not polymerize during the mixing process, but when injected the by placing temperature would only need to be raised by a few degrees in order to accelerate the polymerization process. After the caprolactam / lauro lactam mixture has been thoroughly melted and mixed, the injection portion of the process is ready to begin.

During the injection the GRILONIT is added to the co-monomer melt and the entire mixture is stirred for approximately 30-60 seconds depending on volume. As the melt enters the mold and wets the fibers the pressure must be monitored carefully to ensure laminar flow. If the flow is turbulent it creates voids in the finished composite structure that can cause stress concentrations or act as crack initiators.

When enough of the mixture has flowed through the fiber bed into the outlet trap, the inlet and outlet are sealed. The temperature of the mold is raised to the polymerization temperature. The panels outlined in this study were polymerized at 200°C for 20 minutes. Higher temperatures accelerate polymerization. Figure 1 illustrates a schematic of the APLC process.

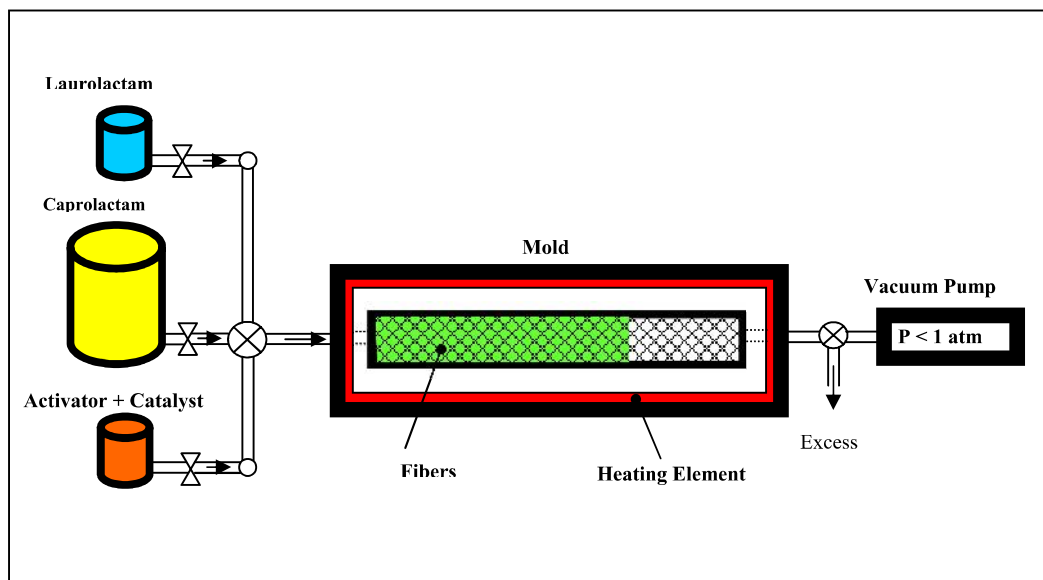


Figure 1 VARTM APLC Process

RESULTS

Mechanical and physical tests were carried out at the National University of Ireland, Galway and the Composites Testing Lab Ltd. Galway, Ireland. Tensile and flexural composite samples at 60% volume fraction were tested according to ASTM standards. The results of the tests are detailed in Tables 1 and 2. Values in parentheses are percentage standard deviations.

Table 1 Tensile and Flexural Testing

Material	Tensile		Flexural	
	<i>E (Gpa)</i>	<i>Strength (MPa)</i>	<i>E (GPa)</i>	<i>Strength (MPa)</i>
PA 12	56.3 (1.3)	768.0 (3.7)	49.11 (7.1)	404.8 (5.1)
90/10 PA 6/12	55.0 (3.0)	684.5 (1.3)	52.00 (4.4)	478.4 (4.7)
95/5 PA 6/12	62.3 (3.3)	773.8 (2.6)	52.93 (7.6)	400.6 (3.7)

Table 2 Anionically Polymerized Polyamide Moisture Absorption Properties

Material	Equilibrium (50% Rel. Humidity)	24 Hr. Immersion	2 Hour Immersion @ 100 °C
PA 12	0.30 (3.3)	0.17 (5.9)	0.65 (3.1)
90/10 PA6/12	0.61 (6.6)	1.02 (6.9)	3.14 (3.5)
95/5 PA6/12	0.56 (3.6)	0.88 (2.3)	2.76 (2.9)
PA 6	0.53 (7.5)	0.68 (4.4)	2.06 (5.8)

While all of the materials exhibited good moisture absorption performance throughout the tests, the trends between them were somewhat unexpected. The results showed that the addition of

lauro lactam to a caprolactam melt actually increased the moisture absorption. This would suggest that in the present study there are no benefits, in terms of moisture performance, in using a copolymer as opposed to a homopolymer.

CONCLUSIONS

Anionic polymerization using the GRILONIT system proved to be a quick, clean, and reliable method of producing polyamide 6, polyamide 12, and polyamide 6/12. Both the polymers and copolymers exhibited good tensile and flexural strengths as well as relatively low moisture absorption. The composites fabricated in this project were impregnated using low pressure (< 1 bar). The plate manufacturing cycle time was also low. The wetting of the fiber bed (injection time) took as little as 10 seconds. Polymerization time, in this case, was 20 minutes. Higher temperatures accelerate the polymerization process leading to even shorter cycle times.

Thermoplastic composite materials have considerable potential for the composite industry. Their ability to be recycled and their improved toughness offer distinct advantages over their thermoset counterparts. Other benefits such as vastly reduced cycle times, ease of storage, and ease of handling, create the potential for mass production. Traditionally it has not been easy to mold thermoplastic-reinforced composites due to the high viscosity of the matrix material. High temperatures and pressures were required to fully impregnate the fiber beds. Thermoplastic liquid composite molding proved to be virtually impossible. The employment of an activated monomer melt eliminates the problems associated with high viscosity. Applications of the current system include automotive parts. These can involve structural parts for cars such as bumpers, hoods, as well as interior components such as dashboards and panelling. APLC's could also be formed into sandwich structures, which could then make up self-supporting exterior panels on busses, trucks, and other large automotives.

In conclusion, the anionic polymerization of polyamide copolymers as a matrix for advanced composites proved to be successful. The VARTM processing method was a simple and effective way of impregnating a carbon-fiber bed. The resulting composite materials exhibited good mechanical and physical properties thereby creating a potential for effective use in a variety of diverse applications.

REFERENCES

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