HIGH-SPEED REACTIVE PROCESSING SYSTEM FOR POLYAMIDE-6 CFRTP MANUFACTURING

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Abstract

In order to manufacture carbon fiber-reinforced polyamide-6 (PA-6) composites, we optimized the reactive processing system. The *in-situ* anionic ring-opening polymerization of ε-caprolactam was utilized with proper catalyst and initiator for PA-6 matrix. The mechanical properties such as tensile strength, inter-laminar shear strength and compressive strength of the produced carbon fiber-reinforced PA-6 composites were measured, which were compared with the corresponding scanning electron microscope (SEM) images to investigate the polymer properties as well as the interfacial interaction between fiber and polymer matrix. Furthermore, kinetics of *in-situ* anionic ring-opening polymerization of ε-caprolactam will be discussed in the viewpoint of increasing manufacturing speed and interfacial bonding between PA-6 matrix and carbon fiber during polymerization.

1. Introduction

Carbon fiber-reinforced plastics (CFRP) are composites materials made of a polymer matrix reinforced with fibers. And they are increasingly used for automotive industries due to high performance and desired light-weight. So far the CFRP has been composed of thermosetting polymer such as epoxy resin. But such thermoset-based composites requires time-consuming curing process which concludes long manufacturing cycle time and high cost of the final product. On the other hand, thermoplastic-based composites do not require the time- and cost-consuming process. Also thermoplastic-based composites can be welded or recycled upon melting, and possibly has higher toughness than thermoset-based composite.

In spite of the advantages of the thermoplastic-based composite, it is hard to apply conventional resin transfer molding (RTM) process, owing to the high viscosity of thermoplastic polymer melts.[1] Therefore, reactive processing has been suggested for the thermoplastic-based composite, where the low viscosity monomer melts instead of polymer melts are injected into fabrics, and the following *in-situ* polymerization enables to produce the thermoplastic-based composites with reasonable cycle time. As the viscosity of the monomer is much lower than that of thermosetting polymer, impregnation time can be much shorter. Also, because processing temperature is below the melting and crystallization temperature of the final polymer, crystallization takes place simultaneously with *in-situ* polymerization, which leads to high degree of crystallinity which concludes high toughness.[2]

In this study, we optimized the reactive processing system for carbon fiber-reinforced polyamide-6 (PA-6) composite. The *in-situ* anionic ring-opening polymerization of ε-caprolactam was utilized with proper catalyst and initiator for PA-6 matrix. The mechanical properties such as tensile strength, inter-laminar shear strength (ILSS) and compressive strength of the produced carbon fiber-reinforced PA-6 composites were measured, which were compared with the corresponding optical microscope (OM) and scanning electron microscope (SEM) images to investigate the polymer properties as well as the interfacial interaction between fiber and polymer matrix. Furthermore, kinetics of *in-situ* anionic ring-opening polymerization of ε-caprolactam for fast manufacturing and strong interfacial interaction formation between PA-6 matrix and carbon fiber during polymerization for high-performance of thermoplastic-based composites will be discussed.

2. Experimental

2.1. Materials

PA-6 used in this study was synthesized *via in-situ* anionic ring-opening polymerization of ε-caprolactam (Sigma-Aldrich. Inc.) with proper catalyst and initiator. The reaction performed at relatively low temperature with high final conversion without by-products within several minutes.[1] TR30 (Mitsubishi Inc. Japan) carbon fiber woven fabric was used as the reinforcement of the composite.

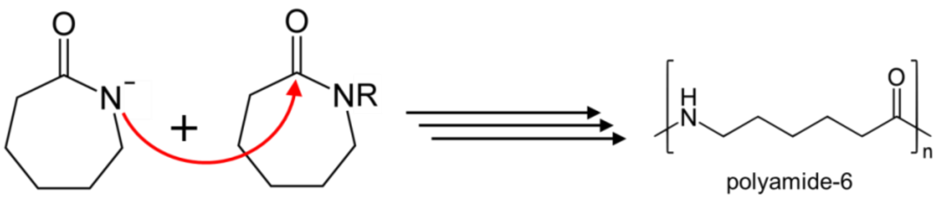

Figure 1. The anionic ring-opening polymerization of ε-caprolactam for PA-6 matrix.

2.2. Sample preparation processes

Pre-treated ε-caprolactam melts in the reactor over 69°C (melting point of ε-caprolactam) with proper catalyst and initiator. The melts injected to pre-heated metal mold equipped in hot press machine with vacuum pressure. As the melts fill the metal molds, in-situ polymerization of PA-6 and impregnation into carbon fiber take place simultaneously.

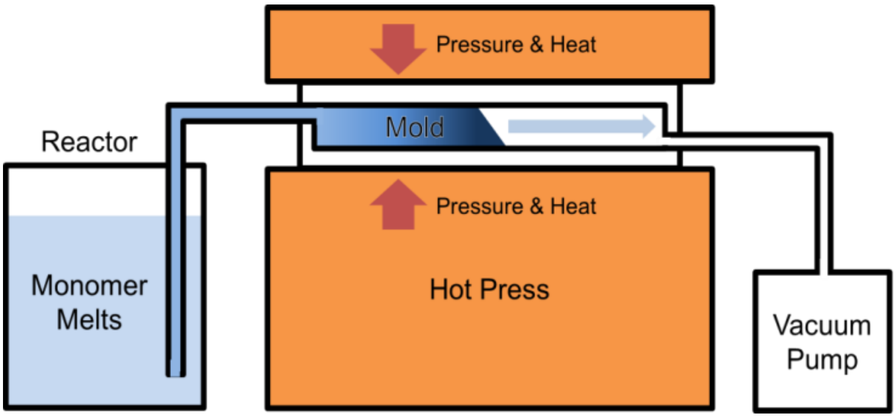

Figure 3. Schematic diagram of the high-speed reactive processing system for PA-6 CFRTP.

2.3. Polymer matrix properties

PA-6 polymer matrix was analyzed in terms of conversion, crystallinity, and molecular weight. The conversion was calculated by measuring sample mass of after/before soxhlet extraction treatment with continuous flow of hot water to extract unreacted materials. Differential scanning calorimeter (DSC) was unutilized to measure melt, crystallization temperatures and crystallinity. Molecular weight of PA-6 polymer was measured by gel permeation chromatography (GPC). Impregnation and interfacial interaction between carbon fiber and PA-6 were analyzed with optical microscopy (OM) and scanning electron microscope (SEM).

2.4. Mechanical properties of the composite

Tensile properties of carbon fiber-reinforced PA-6 composites were analyzed by standard tensile strength testing methods (ASTM D3039) and standard short-beam strength testing methods (ASTM D2344) was conducted to measure inter-laminar shear strength (ILSS). Also compressive properties were investigated based on standard compressive properties testing methods (ASTM D3410).[4-6]

3. Results

3.1. Kinetics of in-situ anionic ring-opening polymerization of ε-caprolactam

Although understanding kinetics of polymerization is beneficial to expect final product properties, it is almost impossible to derive exact kinetic model or directly measure various polymer and composites properties simultaneously because impregnation, polymerization, and crystallization of Polyamide-6 (PA-6) take place at the same time in the reactive processing system. Also the process is too fast to measure with the ex-situ methods. For those reasons, the polymer properties can be predicted by applying the kinetic model with the measured values of temperature or heat flow in the molding process. [3]

3.2. Properties of PA-6 polymer matrix

Carbon fiber-reinforced PA-6 composites were manufactured by the above-mentioned sample preparation process with proper material selection. The ε-caprolactam, which impregnated into carbon fiber, was polymerized into PA-6 and form interfacial interaction with carbon fiber. The polymerized PA-6 was confirmed and evaluated in terms of conversion, crystallinity, and molecular weight. In detail, over 99.5% conversion of the PA-6 was accomplished with 25~50% of crystallinity. Molecular weight of the PA-6 was 30,000~60,000kg/mol.

Table 1. Properties of PA-6 polymer matrix in carbon fiber-reinforced PA-6 composite.

Polymer Properties	Values
Conversion (%)	> 99.5
Crystallinity (%)	20~50
Molecular weight (kg/mol)	30~60

3.3. Impregnation and interfacial interaction

Impregnation/interfacial interaction between carbon fiber and polymer matrix were analyzed with optical microscopy (OM) and scanning electron microscopy (SEM) images before and after fracture test. It was confirmed that polymer matrix is well-impregnated into carbon fiber and interfacial interaction was formed between carbon fiber and polymer matrix during reactive processing. And similar results was obtained when we analyzed CFRTP having sizing material treated carbon fiber.

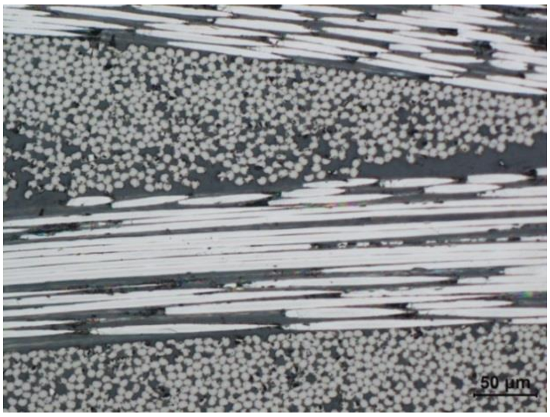

Figure 5. OM image of the produced CFRTP.

3.4. Mechanical properties of the CFRTP

The mechanical properties of produced CFRTP were measured by using the above-mentioned standard testing methods. The young's modulus, tensile strength, inter-laminar shear strength (ILSS), and compressive strength were measured by the mechanical tests. For a carbon fiber-reinforced PA-6 composites (3.2mm thickness, 36% fiber volume fraction), tensile modulus is 67.1 GPa, tensile strength is 641 MPa, inter-laminar shear strength is 42.5 MPa, and compressive strength is 237.7 MPa as represented in Table 2.

Table 2. Mechanical properties of the produced thermoplastic CFRTP.

Mechanical properties	Values	Testing Methods
Tensile modulus (GPa)	67.1	ASTM D3039 [4]
Tensile strength (MPa)	641	ASTM D3039 [4]
Inter-laminar shear strength (MPa)	42.5	ASTM D2344 [5]
Compressive strength (MPa)	237.7	ASTM D3410 [6]

4. Conclusions

In this study, our research team developed the reactive processing system for PA-6 CFRTP. The *in-situ* anionic ring-opening polymerization of ε-caprolactam was utilized for PA-6 matrix synthesis. The properties of PA-6 polymer matrix, mechanical properties, and impregnation and interfacial interaction of the CFRP are investigated.

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References

[1] Rijswijk, K. V., Bersee, H. E. N. "Reactive processing of textile fiber-reinforced thermoplastic composites – An overview", Composites: Part A, 38(3)(2007): 666-681

[2] Rijswijk, K. V., Geenen, A. A. V., Bersee, H. E. N. "Textile fiber-reinforced anionic polyamide-6 composites. Part I: The vacuum infusion process", Composites: Part A, 40(1)(2009): 1-10

[3] Russo, S.; Maniscalco, S.; Moretti, P.; Ricco, L. Journal of polymer Science, Part A: Polymer Chemistry 2013, 51, 4474

[4] ASTM Standard D2344, 2014, "Standard Test Method for Tensile Properties of Polymer Matrix Composite Materials" ASTM International, West Conshohocken, PA, 2014, DOI:10.1520/D3039_D3039M-14, www.astm.org.

[5] ASTM Standard D3039, 2013, "Standard Test Method for Short-Beam Strength of Polymer Matrix Composite Materials and Their Laminates" ASTM International, West Conshohocken, PA, 2013, DOI:10.1520/D2344_D2344M-13, www.astm.org.

[6] ASTM Standard D3410, 2008, " Standard Test Method for Compressive Properties of Polymer Matrix Composite Materials with Unsupported Gage Section by Shear Loading" ASTM International, West Conshohocken, PA, 2008, DOI: 10.1520/D3410_D3410M-03R08, www.astm.org.