



Simultaneous flow enhancement of high-filled polyamide 66/glass fiber composites



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ARTICLE INFO

Article history:

Received 6 March 2017

Received in revised form

16 May 2017

Accepted 13 June 2017

Available online 15 June 2017

Keywords:

Composites

Flow modifiers

Flowability

ABSTRACT

In this work, we investigated the effects of the flow modifier addition on the rheological behavior and mechanical properties of high-filled polyamide 66 composites prepared from melt compounding. The flow modifiers were prepared from various amine monomers and fatty acids, and their structures were analyzed by Fourier transform infrared spectroscopy. The synthesized flow modifiers were added simultaneously during melt compounding. The presence of flow modifiers significantly reduced torque in neat polyamide 66 polymer and glass fiber-reinforced polyamide 66 composites, respectively, while the torque during compounding in composites with glass fiber contents of 50 wt% has decreased by approximately 12% after the addition of 1 phr of hexamethylene *bis*-stearamide indicating the simultaneous enhancement in flowability. The presence of the synthesized flow modifiers in matrix polymers improves flowability of the composites during injection molding without compromising the mechanical properties.

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1. Introduction

Many developed countries have implemented specific policies to reduce greenhouse gas emissions and oil consumption. In order to solve global warming problems, automobile manufacturers have focused on the production of lightweight vehicles with superior driving characteristics and high fuel efficiency [1–4]. Lightweight materials, such as carbon fiber-reinforced plastics (CFRPs) and engineering plastics, have been developed by many automobile companies because they are directly related to the fuel efficiency of vehicles. Although CFRPs possess outstanding mechanical properties, they are mainly used for manufacturing expensive vehicles such as racing cars due to the high costs and processing difficulties [5–9]. However, the high demand for engineering plastics will continue to exist owing to the more strict environmental policies,

and metal replacement materials will be actively developed by many industrial manufacturers.

Polyamide (PA) is an engineering plastic that has been most commonly used in various fields owing to its high crystallinity, good processability, and excellent mechanical properties. Polyamide 66 (PA 66) is one of the aliphatic polyamides that was first invented by W. Carothers in 1935 [10]. It contains twelve C atoms in each repeating unit and can be polymerized by mixing hexamethylenediamine and adipic acid. PA 66 is characterized by enhanced crystallinity, high heat resistance, and good mechanical properties and is currently in high demand as a material for fuel-efficient vehicle parts [11–14]. To enhance mechanical properties of a PA 66 matrix, the addition of various fillers such as glass, carbon, and aramid fibers is required. Among these fillers, glass fibers (GFs) are the most commonly used material because they increase the stiffness and heat resistance of the resulting fiber-reinforced plastics, while their relatively low costs make composite fabrication economically feasible [15].

In order to substitute currently used metals, a significant amount of GF fillers must be added to the PA 66 matrix; however,

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high GF contents may negatively affect composite flowability and often lead to poor dispersion and material rupture, which significantly limit their usage in automotive applications. In addition, the viscosity of a matrix polymer must be low enough to successfully impregnate high GF amounts. Because it is difficult to vary the monomer molecular weight and structure in polymers with high viscosity, special flow modifiers that affect the polymer rheological behavior must be utilized.

In this study, the effects of the flow modifier addition on the rheological and mechanical properties of GF-reinforced PA 66 composites are investigated, and the relationship between the composite mechanical properties and the dispersion and lengths of the added GFs is determined.

2. Experimental

2.1. Materials

The hexamethylenediamine, diethylenetriamine and stearic acid were obtained from Sigma Aldrich and *p*-phenylenediamine was acquired from Tokyo Chemical Industry Co., Ltd. Stabamid 24AE1 plastic supplied by Solvay was used as PA 66 material. A proprietarily surface-treated chopped strand GFs with diameters of 10 μm and lengths of 3 mm for PA matrices were produced by Owens Corning. Prior to melt processing, all materials were dried in a vacuum oven at 80 $^{\circ}\text{C}$ for at least 24 h.

2.2. Synthesis of flow modifiers

Flow modifiers were synthesized from diamine monomers and fatty acids. The diamine monomers were selected to study the effects by alkyl, amine, and phenyl groups during melt processing. Thus, hexamethylenediamine, diethylenetriamine, and *p*-phenylenediamine were used as diamine monomers, while stearic acid was utilized as a fatty acid (the molecular weights and melting points of the used monomers are listed in Table 1). The flow modifier synthesis was conducted using a Dean-Stark apparatus containing a three-neck flask, an agitator, a reflux condenser, and purged with N_2 gas. A diamine monomer and stearic acid were added into the flask at a molar ratio of 1:2, after which the flask was heated to 160 $^{\circ}\text{C}$ accompanied by mechanical stirring at a speed of 100 rpm for about 12 h. During heating, all generated water vapors were removed by the reflux condenser until no traces of water were left in the reaction mixture, which was subsequently transferred onto a wide glass plate and dried in a vacuum oven at room temperature for 12 h. Finally, the completely dried sample was ground by mortar and placed in a glass vial.

2.3. Composite preparation

Specimens for mechanical property testing were prepared using a SM Platek TEK30 twin-screw extruder (with a diameter of 32 mm and length to diameter ratio of 40) operated at a barrel temperature of 250–280 $^{\circ}\text{C}$ and screw speed of 300 rpm. The ratio of PA 66 and glass fiber is 1:1 and the content of the flow modifier is 1 phr. The obtained pellets were dry-mixed with various amounts of GFs

followed by Pro80mc injection molding machine (Dongshin hydraulics). The temperature of the feed zone was set to 290 $^{\circ}\text{C}$, while the mold temperature was maintained at 120 $^{\circ}\text{C}$.

2.4. Sample characterization

A Fourier transform infrared spectroscopy (FTIR) analysis was conducted with a Vertex80v (Bruker) spectrometer for powder flow modifiers over a scanning range of 650–4000 cm^{-1} . The morphology of the produced composites was studied using a Mira 3 LMU FEG (Tescan) scanning electron microscope (SEM) operated at an accelerating voltage of 20 kV. The obtained SEM specimens were polished by Ilion II Model 697 (Gatan) prior to the SEM observations. Capillary extrusion experiments were performed using a Rheograph25 (Gottfert) instrument at a temperature of 280 $^{\circ}\text{C}$, capillary diameter of 1 mm, and die length to diameter ratio of 30. In order to measure the GF length, the polymer was burned off from the injection-molded samples inside a furnace at 550 $^{\circ}\text{C}$ for 5 h. The resulting GFs were dispersed in an aqueous solution containing small contents of surfactant to reduce surface tension. A small amount of the fiber-containing solution was placed on a glass slide using a pipette and studied by Eclipse 50i POL (Nikon) optical microscopy (OM). The analysis of the scanned OM images was performed by using the SigmaScan Pro software. Tensile testing and flexural testing of the obtained samples were performed by using an Instron 4482 universal testing machine (UTM). Tensile test was conducted in accordance with the ISO 527 standard at a crosshead speed of 5 mm/min, while flexural test was performed in accordance with the ISO 178 standard at a crosshead speed of 2 mm/min. Notched impact test was conducted using a Tinius Olsen 92T Izod impact machine following the ISO 75 standard procedure. Torque and flowability measurements were conducted using an Xplore[®] micro compounder and injection molding machine at a barrel temperature of 280 $^{\circ}\text{C}$, screw speed of 80 rpm, and injection pressure of 6 bar. A custom-made spiral mold (with 5 mm \times 3 mm \times 590mm) was used to determine the flowability of PA 66 and composites.

3. Results and discussion

3.1. Characteristics of the flow modifiers

The FTIR spectra of the synthesized flow modifiers are shown in Fig. 1. The peak at 3500–3300 cm^{-1} corresponds to the $-\text{NH}$ stretching of diamine monomers, while the peak at 1540 cm^{-1} can be assigned to the $-\text{CONH}-$ bending of the flow modifiers. Since the reactivity of the diamine monomers towards fatty acids can be characterized by a ratio between the intensities of these two peaks, the obtained FTIR results indicate that the flow modifiers have been successfully synthesized in this study from various diamine monomers and stearic acid [16,17].

3.2. Morphology

The SEM images of the cross-sections of the PA 66/GF composites with GF contents of 30 wt% are shown in Fig. 2. Fig. 2(b) and (c) show that the morphologies of the HMBS- and PBS-containing composites are characterized by better dispersion of the GFs inside the polymer matrix compared to that for the non-modified control sample as shown in Fig. 2(a). The presence of the flow modifiers has promoted the dispersion of the GFs in PA 66 due to the improved flowability and prevented their agglomeration. The obtained morphological results revealed the excellent dispersion properties of the added GFs, which should have led to a more effective filler reinforcement of the polymer matrix.

Table 1
Molecular weights and melting points of the monomers utilized in this study.

Monomer	M_w (g/mol)	T_m ($^{\circ}\text{C}$)
Hexamethylenediamine	116.2	42
Diethylenetriamine	103.17	–39
<i>p</i> -Phenylenediamine	108.14	147
Stearic acid	284.48	69.3

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