EFFECTS OF EXTRUDER TEMPERATURE AND SCREW SPEED ON THERMAL PROPERTIES OF GLASS FIBER REINFORCED POLYAMIDE 6 COMPOSITES THROUGHOUT THE DIRECT LONG-FIBER REINFORCED THERMOPLASTICS PROCESS

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Abstract

This study investigates the effects of extruder temperature and screw speed on the thermal properties of glass fiber reinforced polyamide 6 (PA6) composites throughout the direct long-fiber reinforced thermoplastic (D-LFT) process. Thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC) analyses were performed on samples taken from different locations along the D-LFT process. TGA results showed that the low screw speed of the extruders increased apparent activation energy of the final product. Non-isothermal DSC crystallization analysis revealed no substantial changes to the material’s degree of crystallinity with the variations in extruder temperature and screw speed; however, isothermal DSC crystallization analysis showed that the low screw speed of the extruders increased crystallization half-time of the final product.

Introduction

The direct long-fiber reinforced thermoplastic (D-LFT) process, depicted in Figure 1, is a one-stop manufacturing process starting from raw materials to a final product, and includes various types of equipment. The process is summarized as follows: dried polymer pellets are fed into the first twin-screw extruder to melt them. A film die, which is attached to the end of the first extruder, transfers the molten plastic into the second extruder. The plastic is briefly introduced to atmospheric conditions at a molten state as it flows from the film die into the second extruder. The molten plastic is then combined with continuous fibers in the second extruder. The plastificate is ejected from the second extruder onto a conveyor, where it is cut into an appropriate shot size using a shear cutter. Finally, the plastificate is transferred to a compression molding machine to shape and solidify the plastificate into the final part.

Polyamide 6 (PA6) is a good candidate as polymer matrix in the D-LFT process because it has high toughness over a large range of temperatures, good impact and abrasion resistance, lubricity, and resistance to organic solvents [1]. Despite their wide range of excellent properties, polyamides are susceptible to degradation during processing [1]–[6]. When PA6 is used in the D-LFT process, PA6 has the potential to undergo thermal [1], [7], mechanical [8], and thermo-oxidative [1], [9] degradation. As mentioned above, the D-LFT process includes tandem twin-screw extruders (i.e., the first and second extruders), which are the main components of the D-LFT process. The control of these extruders dictates productivity and properties of products. Therefore, it is important to understand how process parameters of the tandem twin-screw extruders in the D-LFT process influence material properties of PA6-based composite materials. In this study, glass fiber reinforced PA6 composites were produced through the D-LFT process by changing barrel temperatures and screw speeds of the first and second twin-screw extruders. Apparent activation energy for decomposition, and crystallization behavior of the materials were characterized as a function of locations in the D-LFT process line.

Experimental Procedure

Materials and fabrication of composites

PA6 (Ultramid® 8202 HS, supplied in the form of pellets, BASF) was used as the matrix. The glass fiber (StarRov® 886 RXN, provided in the form of rovings, Johns Manville) was used as the reinforcement. The PA6 was first dried in a dryer (LUXOR S 120, Motan Colotronic) at a set temperature of 80 °C for 16 hours. The PA6 was combined with 30 wt % of the glass fibers using an industry-scale Dieffenbacher D-LFT line at the Fraunhofer Project Centre for Composites Research in University of Western Ontario. The D-LFT line includes a dryer, two extruders, a conveyer, and a 2,500-ton hydraulic
press (DCP-U 2500/2200, Dieffenbacher). The two extruders are a compounding twin screw extruder (ZSE-60HP-28D, Leistritz), named the first extruder, and a mixing twin screw extruder (ZSG-75 P-17D, Leistritz), named the second extruder, the screws of which have a diameter of 60 mm and 75 mm, respectively, and a length to diameter ratio of 28 and 17, respectively. Conveyer belt temperature was set to 260 °C. For the hydraulic press, mold temperature was set to 120 °C, and force applied to plastificates was set to 5,000 kN for 30 seconds.

The barrel temperature and screw speed of the two extruders were varied in this study. In the standard condition experiments, the temperature of both extruders was 280 °C, and the screw speeds of the first and second extruders were 80 rpm and 50 rpm, respectively. To study effects of barrel temperature, the barrel temperature of both extruders was changed to 270 °C or 290 °C. To examine effects of screw speed, the screw speeds of the first and second extruders were decreased, respectively, to 40 rpm and 25 rpm, or the screw speeds were increased, respectively, to 161 rpm and 100 rpm. Since the volume of material filled in the extruders was kept constant, the change of the screw speeds accompanied the change in flow rate of material from the second extruder: 102 kg/h for the standard condition, 51 kg/h for the low screw speed setting, and 205 kg/h for the high screw speed setting.

Samples were collected from three locations along the D-LFT process line: (a) as received (i.e., virgin PA6), (b) directly after the first extruder (taken from the waterfall film die), and (c) a compressed plaque. A schematic indicating the points of sample collection along the process can be seen in Figure 1.

Thermogravimetric analysis

Decomposition kinetics of both the polymer and composite samples were investigated using a thermogravimetric analyzer (TGA) (SDT Q600, TA Instruments). Mass of samples was 8.5 mg (±0.5 mg). The temperature profile of the TGA analysis conducted was as follows: (1) heating ramp of 20 °C/min from room temperature to 250 °C, (2) isothermal for 5 minutes to ensure homogeneous temperature distribution in the cell, and (3) temperature ramp from 250 °C to 500 °C using one of the following heating rates: 1, 2, 5, or 10 °C/min. Flowing nitrogen was used as a purge gas at a flow rate of 100 mL/min. The decomposition kinetics of the PA matrix were analyzed using the Ozawa/Flynn/Wall (O/F/W) method [10]. The experimentation and calculation follow ASTM E1641-15 [11]. The degree of conversion, α, of the sample was calculated by

\[ \alpha = \left( \frac{M_o - M_t}{M_o - M_f} \right) \times 100 \]  

where \( M_o \), \( M_t \), and \( M_f \) are, respectively, the mass at the beginning of the decomposition profile, the corresponding mass at the decomposition level being calculated (e.g. mass when 20% decomposed), and the final mass after decomposition. In this study, \( \alpha \) values of 5, 10, 15, 20, 40, and 60% were selected to investigate effects of \( \alpha \) on apparent activation energy for decomposition. Apparent activation energy \( E_a \) was calculated by

\[ E_a = -\left( \frac{R}{b} \right) \log[\beta] / \Delta \left( \frac{1}{T} \right) \]  

where \( R \) is the gas constant (8.31 J mol⁻¹K⁻¹), \( b \) is the logarithm of the approximation derivative, \( \beta \) is the heating rate (K/min), and \( T \) is temperature (K).

Differential scanning calorimetry

Non-isothermal and isothermal crystallization behaviours of the materials were studied using a differential scanning calorimeter (DSC) (Q200, TA Instruments). Temperature and heat-of-fusion were calibrated using sapphire and indium, respectively. A nitrogen purge gas with a flow rate of 50 mL/min was used. Mass of samples was 8.5 mg (±0.5 mg) in both non-isothermal and isothermal measurements. In non-isothermal crystallization measurements, a sample was first heated to 270 °C at 10 °C/min and held at that temperature for 5 minutes to erase the thermal history in the collected sample. The sample was then cooled to 20 °C at 10 °C/min and held at that temperature for 5 minutes. Lastly, the sample was reheated to 270 °C at 10 °C/min. The degree of crystallinity \( X_c \) of the sample was calculated from the second DSC heating curve and the following equation:

\[ X_c = \frac{\Delta H_m}{\Delta H_f(1 - W_f)} \times 100\% \]  

where \( \Delta H_m \) is enthalpy of fusion; \( \Delta H_f \) is enthalpy of fusion of fully crystalline PA6, which is taken to be 230 J/g [12]; and \( W_f \) is the weight fraction of fiber.

In the isothermal crystallization measurements, a sample was first heated to 270 °C at 10 °C/min and held at that temperature for 5 minutes to erase the thermal history of the collected sample. Then, the sample was cooled to the isothermal temperature of 200 °C at 50 °C/min and held at that temperature for 30 minutes to allow the sample to fully crystallize. Using the isothermal DSC curves, relative degree of crystallinity \( X_{rel} \) was calculated as follows:

\[ X_{rel} = \frac{\int_0^t \frac{dH(t)}{dt} \, dt}{\int_0^\infty \frac{dH(t)}{dt} \, dt} \]  

where the isothermal DSC curve is integrated between \( t = 0 \) and \( t \), and divided by the overall crystallization area.

The crystallization kinetics were analyzed using the Avrami equation. According to the Avrami model [13],
the relative degree of crystallinity $X_{rel}$ is described as follows:

$$X_{rel}(t) = 1 - \exp(-kt^n)$$

where $n$ is the Avrami exponent that depends on the nucleation mechanism and growth geometry of crystals, $k$ is the crystallization rate constant that involves both nucleation and growth rate parameters, and $t$ is time.

Eq. (5) can be transformed into the double-logarithmic form,

$$\log[-\ln(1 - X_{rel}(t))] = \log k + n \log t$$

The parameters $n$ (slope) and $k$ (intercept) were determined by plotting $\log[-\ln(1 - X_{rel}(t))]$ against $\log t$. The crystallization half time $t_{1/2}$, which is defined as the time from crystallization onset until 50% completion, was calculated as follows:

$$t_{1/2} = \left(\frac{\ln 2}{k}\right)^{\frac{1}{n}}$$

Results and Discussion

Thermal decomposition

Figure 2 shows apparent activation energy $E_a$ of first extruder samples (Figure 2a) and compressed plaque samples (Figure 2b) processed under different extruder temperatures (i.e., a standard temperature of 280 °C, a lower temperature of 270 °C, and a higher temperature of 290 °C). It can be seen that $E_a$ decreases with increasing $\alpha$ (i.e. the percent of total decomposed material), whereas $E_a$ increases farther along the process, that is, the virgin samples < the first extruder samples < the compressed plaque samples. A possible explanation for the increase of $E_a$ is that the content of char generated in the materials increased along the D-LFT process. It was reported that the presence of char can influence apparent activation energy [9], [15].

When samples processed at different extruder temperature are compared, the standard sample (medium temperature) showed the highest $E_a$ at the end of the first extruder (Figure 2a), but the sample with the high extruder temperature had the highest $E_a$ after the press (Figure 2b). The increase of extruder temperature may have promoted char formation in the material. Further research into the causing mechanisms of this increase is required.

Figure 3 shows $E_a$ of first extruder samples (Figure 3a) and compressed plaque samples (Figure 3b) processed under different screw speeds (i.e., standard screw speeds of 80 rpm for the first extruder and 50 rpm for the second extruder, lower screw speeds of 40 rpm and 25 rpm, and higher screw speeds of 161 rpm and 100 rpm). When samples processed at different screw speeds are compared, all the samples showed almost the same $E_a$ in the range of low conversion at the end of the first extruder (see Figure 3a), but the sample with the low screw speed had the highest $E_a$ after the press (see Figure 3b). The higher $E_a$ of the sample with the low screw speed may be due to increased amount of char. As mentioned above, the flow rate of material with the low screw speed is the lowest, which means it took the longest time to deliver material from the exit of the second extruder to the shear cutter on the conveyer, where material is exposed to the atmosphere. The longest exposure time to the atmosphere may have facilitated char formation in the material.

Crystallization

The thermal properties obtained from the DSC cooling and heating curves are summarized in Table 1, which includes crystallization peak temperature ($T_c$), enthalpy of crystallization ($\Delta H_c$), melting peak temperatures ($T_{m1}$, $T_{m2}$), enthalpy of fusion ($\Delta H_m$) and degree of crystallinity ($X_c$). Two melting peaks ($T_{m1}$ and $T_{m2}$, where $T_{m1} < T_{m2}$) were observed on the DSC heating curves, which are associated with a difference in melting temperatures between the two phases present in the morphology (α and γ) of PA6 [16]–[18]. Table 1 suggests that the increase of extruder temperature decreased the crystallization peak temperature of the first extruder samples but little changed the crystallization peak temperature of the compressed plaque samples. On the other hand, the samples with the low screw speed had the lowest crystallization peak temperature at the ends of both the first extruder and press. The table also suggests that the change of extruder temperature or screw speed had little effect on the two melting peaks and degree of crystallinity.

Figure 4 shows crystallization half-time from samples processed under different extruder temperatures (Figure 4a) and different screw speeds (Figure 4b). Crystallization half-time was decreased farther along the process, that is, the virgin samples > the first extruder samples > the compressed plaque samples. The decrease in the first extruder samples was possibly due to the decrease occurring in the molecular weight [19]. The decrease of crystallization half-time in the compressed plaque samples was possibly a result of the slight decrease in the molecular weight of PA6 and/or the incorporation of glass fibers in the second extruder. Fibers when introduced to a polymer can act as heterogeneous nucleating agents (NA) during crystallization [17], [20], [21]. If the fibers do act in such a way, they may have provided nucleation sites for crystal growth and decreased the time required for crystallization.

When samples processed at different extruder temperature are compared (Figure 4a), the sample with the high extruder temperature showed the longest crystallization half-time at the end of the first extruder. The increase of extruder temperature may have decreased the mechanical shear acting on PA6 in the first extruder, thus minimizing reduction of molecular weight of PA6.
However, after the press, the change of extruder temperature had little effect on the crystallization half-time. The fiber incorporation may have been more influential on the crystallization half-time than the change of extruder temperature.

When samples processed at different screw speeds are compared (Figure 4b), the sample with the low screw speed showed the longest crystallization half-time at the end of the first extruder. The decrease of screw speed may have decreased the mechanical shear acting on PA6 in the first extruder, thus minimizing reduction of molecular weight of PA6. After the press, the trend was maintained even though fibers were added to PA6. The decrease of screw speed may have minimized further reduction in molecular weight of PA6.

Conclusions

Effects of the extruder temperature and screw speed on the thermal properties of glass fiber reinforced PA6 were studied at three locations within the D-LFT process. TGA results showed that the compressed plaque sample processed with the high extruder temperature had the highest apparent activation energy among the samples with different extruder temperatures. Also, the compressed plaque sample processed with the low screw speed exhibited the highest apparent activation energy among the samples with different screw speeds. Non-isothermal DSC crystallization analysis revealed no substantial changes to the material’s degree of crystallinity with the change of extruder temperature or screw speed. Isothermal DSC crystallization analysis showed that the compressed plaque samples had almost constant crystallization half-time regardless of variations in the extruder temperature, but the compressed plaque samples processed with the low screw speed exhibited the longest crystallization half-time among the samples subject to different screw speeds.

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References

Figure 1 Schematic of D-LFT process with indicated locations for sample collection.

Figure 2 Apparent activation energy throughout decomposition of (a) first extruder samples and (b) compressed plaque samples processed under different extruder temperatures.

Figure 3 Apparent activation energy throughout decomposition of (a) first extruder samples and (b) compressed plaque samples processed under different screw speeds.
Table 1  Non-isothermal crystallization data of materials collected from the three locations within the D-LFT process.

<table>
<thead>
<tr>
<th>Process Location</th>
<th>Process Condition</th>
<th>$T_c$ (ºC)</th>
<th>$\Delta H_c$ (J/g)</th>
<th>$T_{m1}$ (ºC)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$X_c$ (%)</th>
</tr>
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<tbody>
<tr>
<td>Virgin</td>
<td>Standard Condition</td>
<td>180.3</td>
<td>61.5 (0.2)</td>
<td>211.1 (0.6)</td>
<td>221.9 (0.2)</td>
<td>65.7 (2.0)</td>
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<td></td>
<td>Low Extruder Temperature</td>
<td>188.0</td>
<td>65.6 (1.4)</td>
<td>214.5 (0.9)</td>
<td>221.0 (0.1)</td>
<td>70.5 (2.2)</td>
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<tr>
<td></td>
<td>High Extruder Temperature</td>
<td>185.7</td>
<td>65.3 (0.9)</td>
<td>213.5 (0.3)</td>
<td>221.1 (0.2)</td>
<td>69.4 (2.0)</td>
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<tr>
<td></td>
<td>Low Screw Speed</td>
<td>184.5</td>
<td>63.1 (1.1)</td>
<td>213.0 (0.2)</td>
<td>221.0 (0.2)</td>
<td>67.6 (4.3)</td>
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<tr>
<td></td>
<td>High Screw Speed</td>
<td>186.7</td>
<td>63.6 (0.9)</td>
<td>213.8 (0.3)</td>
<td>220.9 (0.1)</td>
<td>69.1 (2.0)</td>
</tr>
<tr>
<td>First Extruder</td>
<td>Standard Condition</td>
<td>190.2</td>
<td>41.2 (0.9)</td>
<td>215.3 (0.2)</td>
<td>220.6 (0.2)</td>
<td>48.7 (3.8)</td>
</tr>
<tr>
<td></td>
<td>Low Extruder Temperature</td>
<td>190.4</td>
<td>44.7 (1.1)</td>
<td>216.0 (0.6)</td>
<td>220.4 (0.2)</td>
<td>49.0 (2.8)</td>
</tr>
<tr>
<td></td>
<td>High Extruder Temperature</td>
<td>190.1</td>
<td>42.6 (2.9)</td>
<td>215.4 (0.1)</td>
<td>221.0 (1.0)</td>
<td>46.0 (2.5)</td>
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<tr>
<td>Compressed</td>
<td>Standard Condition</td>
<td>188.0</td>
<td>43.8 (1.8)</td>
<td>215.1 (0.9)</td>
<td>221.7 (0.9)</td>
<td>46.7 (2.6)</td>
</tr>
<tr>
<td>Plaque</td>
<td>Low Screw Speed</td>
<td>189.0</td>
<td>43.8 (0.5)</td>
<td>216.3 (0.1)</td>
<td>220.4 (0.1)</td>
<td>48.7 (1.2)</td>
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<tr>
<td></td>
<td>High Screw Speed</td>
<td>190.9</td>
<td>43.8 (0.5)</td>
<td>216.3 (0.1)</td>
<td>220.4 (0.1)</td>
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</tr>
</tbody>
</table>

Figure 4 Crystallization half-time of first extruder and compressed plaque samples processed under different (a) extruder temperatures and (b) screw speeds.