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Spinning and Characterization of Silica/Polypropylene Nanocomposite Fibers

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Introduction

Isotactic polypropylene (iPP) fibers are found in many end-use products thanks to their advantageous properties such as light weight, resistance to moisture and chemicals, low cost, sufficient strength and ease in processing. Furthermore, iPP’s properties can be enhanced by melt-mixing with particulates and fibrous materials as well as by melt blending with other polymers [1-5].

Recently, polymeric nanocomposites which contain nano-sized particles at a much lower loading ratio than conventional fillers have been focused, they offer enhanced mechanical properties and thermal properties when compared to conventional composites. Nano-sized particles, particularly, carbon nanotube (CNT) [6-7] and montmorillonite (MMMT) [8-9] have taken a lead as the novel nano-fillers for plastics as well as fibers due to their high aspect ratio. Recently silica has been widely investigated for polymer matrices and held a great potential for developing nanocomposites. Particularly, fumed silica has been received considerable interest. Fumed silica is a monosilicate particle which is synthesized by hydrolysis of chlorosilane in an oxygen-hydrogen gas flame. It is amorphous silicon dioxide which is claimed to be non-toxic when compared to crystalline silica. There are many reports on the usage of silica for enhancing mechanical properties of polymer. Some articles dealt with silica as filler for polypropylene fiber [10-11].

The scope of this experiment was to prepare nanocomposite polypropylene fibers in order to improve properties of isotactic polypropylene fiber, particularly its modification behavior, mechanical and surface properties. To achieve these improvements, nanosized silica must be fully dispersed throughout and connected to the iPP matrix. In this study, solution mixing was adopted to investigate the particle dispersability. iPP and silica/iPP nanocomposite resins were spun into fibers including free-drawn monofilament and heat-drawn monofilament. Then, characterizations of nanocomposite fibers were performed and discussed.
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Abstract: The preparation of nanocomposite resins by solution (toluene) mixing was conducted, aiming at disaggregating silica agglomerates down into primary nanoparticles. The obtained nanocomposite resin was spun into monofilament fibers using ThermoHaake\textregistered single screw extruder. The characterizations including morphological analyses (SEM and AFM) and crystallization profile (DSC). AFM images revealed that silica particles having nanoscale sizes were evenly distributed on the surface. The presence of silica nanoparticles resulted at higher crystallization temperature (Tc) of the nanocomposite fiber when compared to those of neat fiber. As a result, the shrinkage resistance of the nanocomposite fibers was significantly improved due to an effective reinforcement. The surface hydrophobicity of the nanocomposite fibers was found higher than neat fiber due to an increase in surface roughness arising from the presence of nanoparticles on the surface.

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Isotactic polypropylene (iPP) fibers are found in many end-use products thanks to their advantageous properties such as light weight, resistance to moisture and chemicals, low cost, sufficient strength and ease in processing. Furthermore, PP's properties can be enhanced by melt mixing with particulates and fibrous materials as well as by melt blending with other polymers [1-5]. Recently, polymer nanocomposites which contain nano-sized particles at a much lower loading ratio than conventional fillers have been focused, they offer enhanced mechanical properties and thermal properties when compared to conventional composites. Nano-sized particles, particularly, carbon nanotube (CNT) [6-7] and montmorillonite (MMNT) [8-9] have taken a lead as the novel nano-fillers for plastics as well as fibers due to their high aspect ratio. Recently silica has been widely investigated for polymeric materials and held a great potential for developing nanocomposites. Particularly, fumed silica has been received considerable interest. Fumed silica is a nanoscale particle which is synthesized by hydrolysis of chlorosilane in an oxygen-hydrogen gas flame. It is amorphous silicon dioxide which is claimed to be non-toxic when compared to crystalline silica. There are many reports on the usage of silica for enhancing mechanical properties of polymer. Some articles dealt with silica as filler for polypropylene fiber [10-11].

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Experimental

Materials

Moplen® (isotactic polypropylene) chip with melt flow index of 25.8 g/10 min at 190 °C was purchased from HMC Polymers Co., Ltd (Thailand) and ground into powder by THL Industry Co., Ltd (Thailand). AEROSIL® R974 (hydrophobic silica with an average size of primary particles of 12 nm and BET surface area of 170±20 m²/g) were provided from Degussa AG (Thailand). A commercial-grade toluene was obtained from a local supplier.

Preparation of PP/Silica Nanocomposite Resins

Weighed AEROSIL® R 974 was suspended in a beaker containing toluene and sonicated at 80 °C for one and a half hour. PP powder was added to the mixture and heated to 140 °C for 30 minutes. Then toluene was allowed to evaporate and the resultant nanocomposite resin was ground. In this case, PP/hydrophobic silica nanocomposite resins loaded with 0.25, 0.5, 0.75, and 1.0 wt% AEROSIL, were prepared.

Next, AROSIL® R 974 (1 wt% based on PP) in toluene was cooked in an autoclave at 140 °C for one hour. The autoclave was removed and left standing for several hours to reduce the pressure. Then toluene - PP solution was added to the silica dispersion. The mixture was stirred in a hot bath for 30 minutes. The toluene was dried out to evaporate in the tray for at least 2 days. 1 wt% silica/PP nanocomposite resin as a white sheet was obtained and ground into powder prior to spinning.

Spinning of Monofilament Fiber from Toluene Mixed Nanocomposite Resins

ThermoHaake® single screw extruder was employed for spinning fibers. The composite resin was fed into the hopper. Spinning conditions for free-fall monofilament fiber were set: screw speed : 4 rpm, temperatures of extruder zone 1 (170 °C), zone 2 (180 °C), and zone 3 (190 °C) throughput : 0.42 g/min. The monofilament fiber was heat drawn to obtain a drawn monofilament fiber of draw ratio of 2 using the conditions as follow: 1st godet speed: 25 m/min heater temperature: 110°C 2nd godet speed: 51 m/min winding speed: 50 m/min die hole diameter: 0.5 mm.

Characterizations

Fiber morphology was examined using JEOL JSM-6510 scanning electron microscope with accelerating voltage: 5 KV, working distance: 10 mm and magnification: 1,000-3,000X. AFM images were taken by SEIKO Instruments (SPA 400 model). DSC measurement was performed using DSC 200 F3 from NETZSCH. A sample was heated from 30 to 200 °C with a heating rate of 10 °C/min and kept for 5 min to eliminate the thermal history. Then, the sample was cooled down to 30 °C at a cooling rate of 10 °C/min under nitrogen gas at constant flow rate of 20 ml/min. From heating scan the on-set temperature, the melting temperature (Tm) and heat of fusion (ΔHf) of the fibers were measured. The crystallinity of the samples was calculated using ΔHf of 170 J/g for 100% crystalline iPP [10]. From cooling scan, the crystallization point (Tc) was measured. Tensile measurements of fiber were performed via a Instron® tensile tester 5569 model with gauge length of 25 mm at a crosshead speed of 20 mm/min. Hot air shrinkage and hot water shrinkage of nanocomposite fibers were determined in a hot air oven at 110°C for 30 min and in boiling water for 30 min, respectively. The average percent shrinkages obtained from 5 specimens. Contact angle measurement was conducted using Data Physics model PSL 250.
Results and discussion

Morphological analyses of monofilament fibers

SEM images of fiber surface and bulk are shown in Fig. 1. The monofilaments exhibited very smooth fiber surfaces with no detection of silica particles. It can be said that toluene solvent combined with sonication can disperse the cluster of hydrophobic silica better than the shear stress. SEM images of PP bulk revealed, in a similar manner, no evidence of the silica agglomerate. Therefore, sonicated silica and autoclaved silica uniformly dispersed in the bulk of the fiber as well as on the surface. AFM images of fiber surfaces are shown in Fig. 2. The images reveal an incorporation of silica nanoparticles leads to apparent surface modification. The result shows that silica particles are predominantly present on the fiber surface spun from the autoclave mixed nanocomposite. This indicates that high pressure mixing could produce an even distribution of nanoparticles within the bulk of the fiber and on the surface. To a less extent, solvent mixing by ultrasonication results in relatively uneven distribution of nanoparticles, judged from lesser presence of nanoparticles on the fiber surface.

Fig. 1 SEM images of fiber surface and fiber bulk

Fig. 2 AFM images of neat PP fiber surface, sonicated SiO$_2$/PP fiber surface and autoclaved SiO$_2$/PP fiber surface.

Crystallization behavior investigations

DSC cooling curves of the nanocomposite fibers are shown in Fig. 3 and their DSC data are presented in Table 1. Ta values of neat PP fiber (free-fall), sonicated 1 wt% silica/PP fiber (free-fall), and autoclaved 1 wt% silica/PP fiber (free-fall) appear at 113.5 °C, 115.1 °C and 118.3 °C, respectively. Neat PP has Ta value of 113.5 °C which is a typical Ta value for iPP. An increase in Ta value of PP above 113.5 °C can be found only when loading with a nucleating agent such as the case of nanocomposite. The silica/PP fiber with autoclaved 1 wt% exhibits the highest crystallization rate followed by sonicated 1 wt% silica/PP fiber (free-fall). The high crystallization rate reflects that the state of nanoscale dispersion was achieved.

Spherulite crystal images are revealed by SEM analysis. Figure 4 shows SEM surface images of free-fall and drawn fibers taken at 3000X. The large spherulite crystal can be obviously seen on the surface of neat free-fall fiber. Then, the trend of decreasing crystal size as percent silica loading increases is observed. Since the free-fall fiber describes the spun fiber obtained by the only gravity force, change in the crystal size is likely to be affected by the presence of silica loading. Subsequent heat drawing of free-fall fibers was carried-out. As seen, spherulite size of heat-drawn neat fiber is altered with a decrease in growth.

Mechanical Properties of Nanocomposite Fibers

An improvement of tensile strength could be achieved with an incorporation of silica nanoparticles (fig. 5). The tensile strength values of nanocomposite fibers containing 0, 0.25, 0.5, 0.75, 1.0 wt% silica, and autoclaved 1 wt% silica are about 79.25, 110.65, 85.58, 100.45, 88.70, and 107.12 MPa, respectively. The corresponding % elongation values are 427.64, 932.05, 304.60, 574.22, 529.73 and 794.76, respectively. It should be noted that control PP fiber (toluene fiber) exhibits a sharp decrease in tensile strength when compared to neat PP fiber (179.27 MPa). This indicates that
toluene combined with heat and ultrasonication treatments to some extent degrade the polypropylene chain molecule. An incorporation of silica nanoparticles provides a positive effect on tensile strength improvement despite its very low aspect ratio. It is likely that the notable improvement in tensile strength of nanocomposite fibers is related to the existence of silica nanoparticles, producing significant reinforcement effect.

Fig. 3 DSC cooling curve for neat PP free-fall fiber, toluene PP free-fall fiber, 0.25 to 1.0 wt% silica/PP free-fall fiber (sonication) and 1.0 wt% silica/PP free-fall fiber (autoclave)

Fig. 4 SEM surface images (3000X) of free-fall fibers of neat PP (a), PP-toluene (control) (b), sonicated 0.25 wt%SiO₂/PP (c), sonicated 0.5wt% SiO₂/PP (d), sonicated 0.75wt% SiO₂/PP (e), sonicated 1.0wt% SiO₂/PP (f) and autoclaved 1.0wt% SiO₂/PP(g) (scale bar = 5 μm)

**Fiber shrinkage**

From the table 2, the shrinkage resistance of nanocomposite fibers is improved by the presence of silica loading the higher the silica content the lower the % shrinkage. In case of autoclaved 1 wt% silica/PP nanocomposite fiber where the % shrinkages are found as low as 6.80% and 4.60% for hot air shrinkage and water boiling shrinkage, respectively. The autoclaved treated silica was extremely fine and evenly distributed in the polymer matrix, producing an effective reinforcement. Moreover, the fiber samples were immersed into liquid nitrogen in order to study the effect of low temperature environment. From SEM pictures, the results shown in Fig. 6 clearly illustrate that silica/PP
nanocomposite fibers are stiffer than control PP fiber. The fiber stiffness caused by the silica nanoparticles restricts the movement of polymer molecule, resulting in a sharp cut without the distorted behavior as seen in case of neat fiber.

Table 1 DSC data of SiO$_2$/PP nanocomposite fibers

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Melt. Temp. (onset) (°C)</th>
<th>Melt. Temp. (peak) (°C)</th>
<th>Heat of Fusion (J/mg)</th>
<th>Crystallinity (%)</th>
<th>Crystallization Temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PP (free-fall)</td>
<td>159.0</td>
<td>167.5</td>
<td>72.27</td>
<td>42.51</td>
<td>113.1</td>
</tr>
<tr>
<td>Toluene PP (free-fall)</td>
<td>160.9</td>
<td>167.0</td>
<td>71.53</td>
<td>42.08</td>
<td>113.5</td>
</tr>
<tr>
<td>Sonicated 0.50% SiO$_2$/PP</td>
<td>159.2</td>
<td>167.3</td>
<td>77.26</td>
<td>45.45</td>
<td>114.9</td>
</tr>
<tr>
<td>Sonicated 1.0% SiO$_2$/PP</td>
<td>160.0</td>
<td>167.9</td>
<td>66.81</td>
<td>39.30</td>
<td>115.1</td>
</tr>
<tr>
<td>Autoclaved 1.0% SiO$_2$/PP</td>
<td>158.5</td>
<td>169.7</td>
<td>72.33</td>
<td>42.55</td>
<td>118.3</td>
</tr>
<tr>
<td>Neat PP (drawn)</td>
<td>155.5</td>
<td>165.1</td>
<td>75.69</td>
<td>44.52</td>
<td>114.6</td>
</tr>
<tr>
<td>Toluene PP (drawn)</td>
<td>155.6</td>
<td>165.6</td>
<td>71.92</td>
<td>42.31</td>
<td>115.8</td>
</tr>
<tr>
<td>Sonicated 0.50% SiO$_2$/PP</td>
<td>157.0</td>
<td>166.5</td>
<td>75.91</td>
<td>44.65</td>
<td>117.4</td>
</tr>
<tr>
<td>Sonicated 1.0% SiO$_2$/PP</td>
<td>155.9</td>
<td>166.7</td>
<td>66.75</td>
<td>39.26</td>
<td>117.6</td>
</tr>
<tr>
<td>Autoclaved 1.0% SiO$_2$/PP</td>
<td>155.0</td>
<td>166.2</td>
<td>68.37</td>
<td>40.22</td>
<td>118.4</td>
</tr>
</tbody>
</table>

Table 2 Percent shrinkages of neat fiber, toluene PP fiber and SiO$_2$/PP nanocomposite fibers

<table>
<thead>
<tr>
<th>Fiber</th>
<th>% shrinkage (hot air)</th>
<th>% Shrinkage (boiling water)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat Fiber</td>
<td>13.20</td>
<td>7.20</td>
</tr>
<tr>
<td>Toluene Fiber</td>
<td>11.20</td>
<td>8.40</td>
</tr>
<tr>
<td>0.25%SiO$_2$/PP Fiber</td>
<td>11.80</td>
<td>7.60</td>
</tr>
<tr>
<td>0.50%SiO$_2$/PP Fiber</td>
<td>12.00</td>
<td>7.00</td>
</tr>
<tr>
<td>0.75%SiO$_2$/PP Fiber</td>
<td>11.60</td>
<td>7.60</td>
</tr>
<tr>
<td>1.0%SiO$_2$/PP Fiber</td>
<td>10.80</td>
<td>7.60</td>
</tr>
<tr>
<td>1.0%SiO$_2$/PP Fiber (autoclave)</td>
<td>6.80</td>
<td>4.60</td>
</tr>
</tbody>
</table>

Contact angle measurement of the nanocomposite fibers

Surface property of the nanocomposite fibers was observed by contact angle measurement using Data Physics model PSL 250. It should be noted that water contact angle measurement on fiber sample was difficult. Instead, the contact angle measurement was measured on flat film sample prepared by compressing the nanocomposite fiber. 20 measurements were recorded and averaged. Contact angles of toluene PP fiber, sonicated 0.5 wt% silica/PP fiber, sonicated 1 wt% silica/PP fiber and autoclaved 1 wt% silica/PP fiber are 86.99°, 97.83°, 98.76°, and 101.16°, respectively. The additional increase in surface hydrophobicity is believed to be involved with an incorporation of silica nanoparticles. From Fig. 7 (water contact angle), the autoclaved silica/PP fiber when compared to sonicated mixed silica/PP fiber possesses a relatively higher contact angle which is governed by the predominant silica particles present on the fiber surface as revealed by the AFM image. From these results, it is assured that autoclave mixing was the most effectiveness in disaggregating the silica agglomerate, resulting in even particle distribution. As a result, the surface and bulk properties of the resultant nanocomposite fiber were successfully modified.
Fig. 5 Tensile strength and Percent elongation at break of SiO$_2$/PP free-fall monofilament fibers

Fig. 6 SEM images of liquid nitrogen treated nanocomposite fibers (scale bar = 200 μm)

Fig. 7 Water contact angle of SiO$_2$/PP films prepared by compressing free-fall monofilament fibers.

Conclusions

This work has demonstrated that the silica dispersion at nanoscale level played a determining role in altering the fine structure and properties of PP matrix. The autoclaved silica loading into PP fiber combined with low speed spinning rate led to the nucleation effect on polymer crystallization process. The crystallization temperature (Tc) of silica filled nanocomposite fiber was found higher than those of neat PP fiber, implying that the faster cooling rate would be obtained (when operating at low spinning speed). An improvement of tensile strength could be achieved with an incorporation of silica nanoparticles due to the reinforcement effect of the nanoparticle. Interestingly, the shrinkage resistance of nanocomposite fibers was improved by the presence of silica nanoparticle, enhancing its thermal stability. Moreover, the presence of nanoparticles on the fiber surface led to the modification of fiber surface property. The results demonstrated that surface hydrophobicity of the nanocomposite fiber tended to increase due to an increase in fiber surface roughness.

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