Characterizations of Fibers Produced from Polypropylene/ Silica Composite

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Abstract

Fumed silica particles filled polypropylene (PP) filament fibers were prepared by melt spin pilot plant. First, virgin PP and silicas(hydrophilic and hydrophobic) were premixed using twin screw extruder to prepare silica containing PP composite resin. Then, the resin composite was again mixed with virgin PP and spun into filaments with various filler loadings in the range of 0.5 - 2.5 wt%. The characterizations of spun composite fibers including crystallization temperature (DSC analysis), polymer orientation (sonic modulus) and the fine structure (XRD) were studied. XRD results showed β-form crystallinity peak in x-ray pattern of fiber drawn with low take-up speed (300 m/min), indicating that infused nano silica was capable of acting as β-form nucleating agent. The crystallization temperatures (Tc) of composite fibers were found to be higher than that of neat fiber, further confirming the nucleating effect of silica filler. However, the presence of silica dispersion resulted in the interference of polymer molecule orientation along a fiber axis as judged by sonic modulus measurement. As a result of hydrophobic silica loading, composite PP fibers exhibited the extent of thermal stability due to the fact that, in addition to a fraction of the heat absorbed by silica particles, extra-heat was required to overcome interfacial adhesion force.

Introduction

Fibers from isotactic polypropylene (iPP) are commonly found in many end-use products due to their advantageous properties such as light weight, resistance to moisture and chemicals, low cost, sufficiency strength and ease in processing. Furthermore, the fiber's properties can be enhanced by melt mixing with particulates and fibrous materials as well as by melt blending with other polymers.[1-5] Nanometer scale particles as nano-sized fillers attract an interest for enhancing the properties of polymeric materials. Particularly, carbon nanotube (CNT)[6-7] and montmorillonite (MMNT)[8-9] have taken a lead as nano-fillers for plastics as well as fibers. Recently, silica has been explored as filler for polymeric materials and it holds a great potential for developing high performance fibers. There are many reports on the usage of silica for improving mechanical properties of polymers. Some articles dealt with silica as filler for polypropylene fibers[10-11], and other articles reported the study of silica addition to polyester and nylon-6 fibers.[12-17]

The surface nature of silica is hydrophilic, but can be hydrophobically modified using organosilane agents. Hydrophobic silica makes it compatible with hydrophobic polymer matrix like PP. In this work, PP/hydrophobic silica composite fibers were prepared. The obtained composites were spun into filaments using Fourne′ pilot plant fiber spinning machine. Characterizations of composite fibers were then performed and discussed.

Materials and Experimental Procedures

Materials

Moplen® HP561R, isotactic polypropylene (iPP) chips with melt flow index of 25 g/10 min at 190°C was kindly provided by HMC Polymers Company (Thailand). Aerosil® R974 (hydrophobic silica) and Aerosil® R200(hydrophilic silica) with an average size of 12 nm. were bought from Degussa AG (Thailand).

Fiber Spinning

Prior to spinning, silica/PP composite resin was prepared by melt blending via twin screw extruder as follows: Weighed AEROSIL and PP were physically mixed with a high speed mixer. The mixture was melt mixed by a twin screw extruder to obtain as-extruded resin containing

silica particles of 5.61 wt% (measured by TGA). The obtained blend chip was subsequently re-mixed with virgin PP at the various ratios in the hopper of Fourne′ pilot plant fiber spinning machine (Figure 1). After that, the mixed pellet was fed into the spinning machine comprsing a spinneret with 36 nozzles of 0.32 mm diameter to produce filament fibers. In this experiment, a series of filament fibers containing 0.5, 1.0, 2.5 wt% silica were spun using Fourne′ pilot plant fiber spinning machine. For a typical example, the calculated amount of as-extruded resin was physically mixed with virgin PP prior to feeding into the spinning machine's extruder where barrel zone temperatures were set at 210, 220 and 230°C for extruder zones 1, 2, and 3, respectively. Fibers with take-up speeds of 300, 500 and 1100 m/min were produced in this experiment.
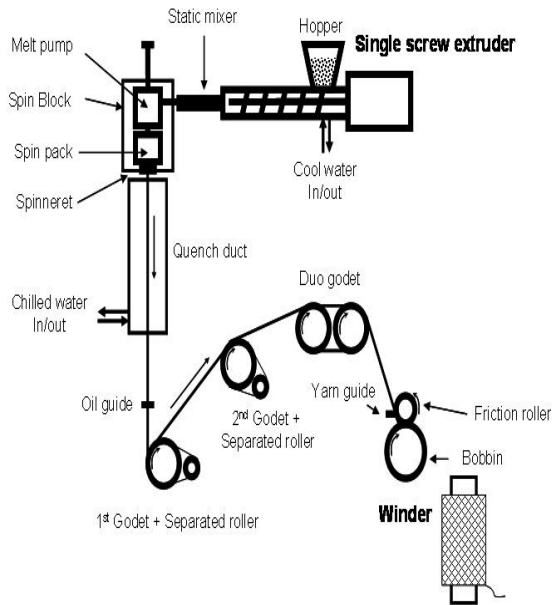
Figure 1. Schematic Diagram of Fourne′ pilot plant fiber spinning machine
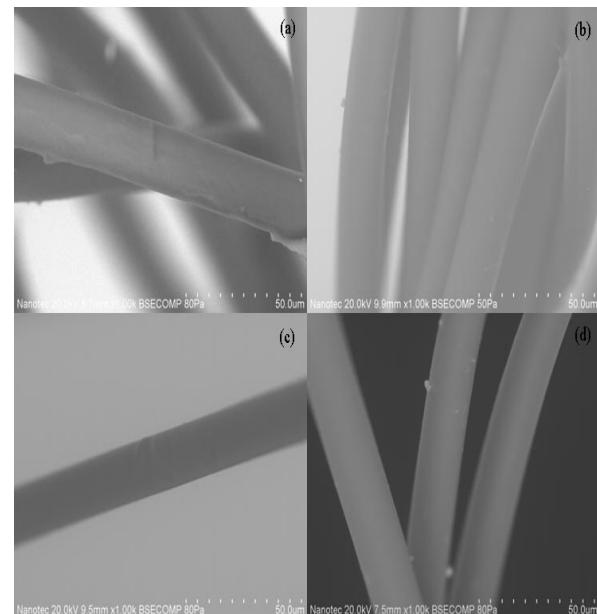
Characterizations

The fiber morphology was examined using Hitachi S-3400N environmental scanning electron microscope (ESEM) with energy dispersive spectrometer. XRD patterns of the fiber samples were achieved using Bruker - D8 Advance model with CuKα radiation at the wave length of 1.5 Å. The diffraction spectrogram was recorded in 2θ (2 theta) ranging from 10 to 50°C. TGA analysis was performed with a TGA/SDTA851ᵉ Mettler Toledo thermal analyzer. The results were acquired with a heating rate of 10°C/min from 50 to 600°C under nitrogen gas at constant flow rate of 20 ml/min. Differential scanning calorimetry

(DSC 200 F3 from NETZSCH) was performed to obtain the crystallization temperature. Sonic modulus technique with Dynamic Modulus Tester PPM-5R, Lawson-Hemphill Company, was employed to determine molecular orientation along the fiber axis.

Results and Discussion

Fiber Morphology

Figures 2 and 3 shows the SEM images of the fiber's morphology of neat PP and silica/PP filaments. In general, the filament surfaces are smooth. When focusing on the fiber cross-sectional cut, the images of infused silica/PP composite fibers reveal information on the dispersion of silica particles in PP matrix. As seen, an increase in percent silica loading leads to an increase in silica particle density as well as agglomeration problem. These results indicate that, at low percent silica loading, shear force applied during spinning seems to be effective enough to disaggregate the silica agglomerate. However, the opposite holds true for composite fibers with higher silica loading (2.5 wt %), indicating that the shear force failed to overcome cohesion force among agglomerate particles. As a result, the range beyond 2.5 wt% silica loading is excluded from this study since it is likely that the composite fibers contain mostly a population of micro-sized particles, which is not preferable for fiber processing as well as assessment of fiber's properties.

Figure 2. Fiber surface morphology (a) neat PP (b) 0.5 wt% SiO_2/PP (c) 1.0 wt% SiO_2/PP (d) 2.5 wt% SiO_2/PP

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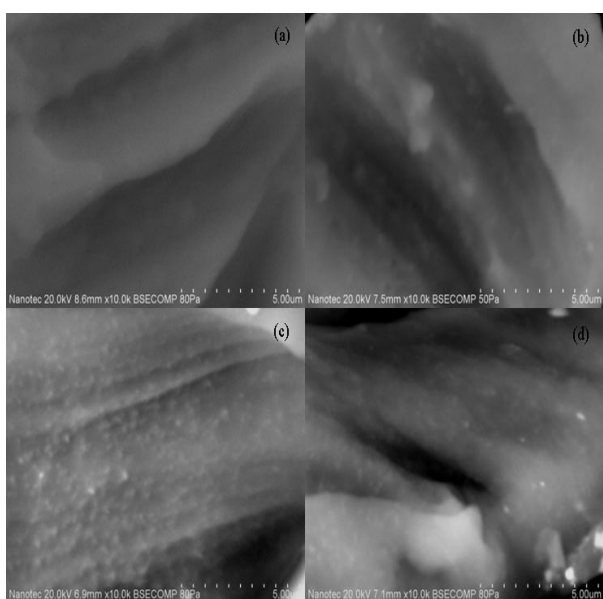
Figure 3. Cross sectional view of (a) neat PP fiber, (b) 0.5 wt% SiO$_2$/PP fiber (c) 1.0 wt% SiO$_2$/PP fiber(d) 2.5 wt% SiO$_2$/PP fiber

X-ray Analysis

X-ray patterns of neat PP fibers and infused silica/PP fibers are shown in Figure 4 and Figure 5. At low spinning speed (300 m/min), the broad peak of monoclinic crystalline (α-form), which is indicative of poor crystallinity, is observed in all cases. This form is characteristic for a low orientation of polypropylene. An increase in spinning speed leads to an appearance of β-form crystallinity which reaches the strongest intensity with fully drawn fiber (spinning speed of 1100 m/min). In case of silica infused PP fiber, β-form crystallinity appears in the x-ray pattern of fiber drawn with low take-up speed (300 m/min), indicating that infused nano silica is capable of acting as β-form nucleating agent for isotactic PP.[18] However, at high take-up speed, the β-form crystallinity peak is found noticed to be identical to that of fully drawn neat PP, implying that take-up speed plays a dominant role in a gain in fiber crystallinity due to an increasing molecular orientation along the fiber axis. At the high speed stage, silica filler seems to lose its influence. It could be said that fiber take-up at high speed results in fully drawn fiber with optimum molecular orientation which unnecessarily requires filler's nucleation action.

Thermogravimetric Analyzer (TGA)

The TGA was performed to evaluate thermal stability of the fibers as well as particle-matrix interaction. Figure 6 shows TGA thermograms of neat fiber and silica filled fibers. The onset temperatures of degradation are given in Table 1. The neat fiber starts to decompose at 416°C. When compared to the neat fiber, the hydrophobic silica (R972) filled fibers begin to decompose at a relatively higher temperature of ca 430°C and, in similar manner, their degradation temperatures recorded at 50% residual weight are found to be above the temperature of 455°C. In this scenario, the reason for an additional increase in onset temperature is
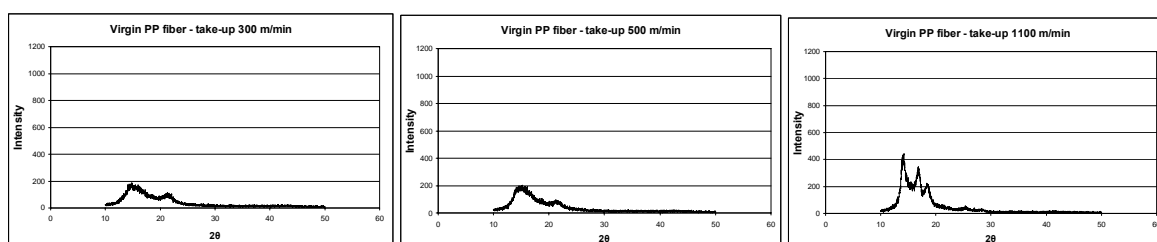

Figure 4. XRD patterns of virgin PP fibers drawn at take-up speeds of 300, 500, and 1100 m/min
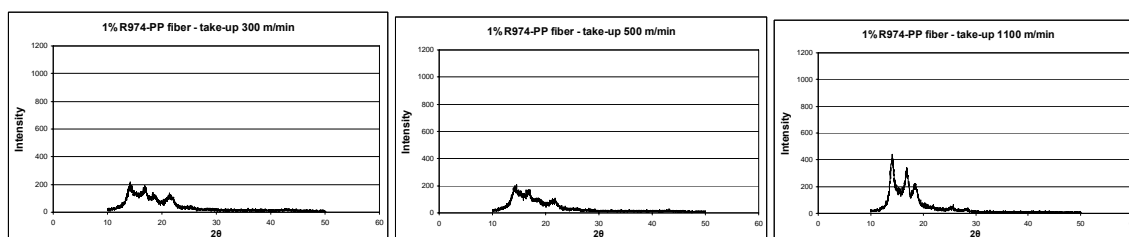
Figure 5. XRD patterns of PP/hydrophobic silica composite drawn at take-up speeds of 300, 500 and 1100 m/min

that extra energy is required to break down adhesion force at polymer-silica interface. Therefore, the interfacial interaction plays an important role in degradation of polymer nanocomposites. In case of good interfacial interaction, particles are capable of restricting the movement of a polymer chain, making the scission of a polymer chain harder at lower temperature. As a consequence, the degradation temperature of the nanocomposite shifts to higher temperature.[19] In contrast, the 1 wt% hydrophilic silica (A200) filled fiber exhibits a marginal increase in the decomposition temperature compared to neat fiber as a result of poorer hydrophilic particle-hydrophobic matrix interaction. These results provide indicative information on the relationship between interfacial interaction and degradation temperature. Above 0.5 wt% hydrophobic silica content, there is an insignificant difference in degradation temperature, indicating further silica loading plays no part in increasing the onset temperature of degradation. As seen in SEM images, micro-sized particles are observed in fibers with silica loading above 1 wt%. Micro-sized fillers are prone to exhibit poor adhesion to polymer matrix due to their relatively small surface area. As a result, the effect of their presence on the degradation temperature is minuscule.
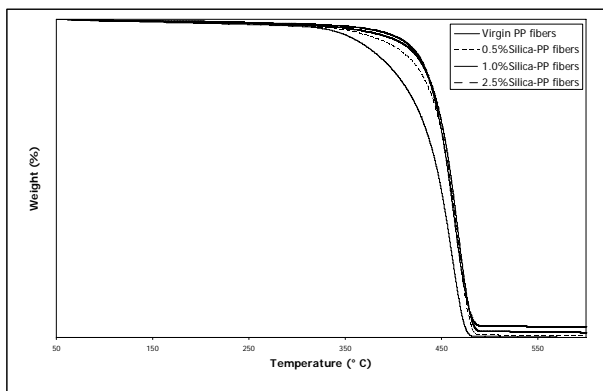

Figure 6. TGA thermograms of neat fiber and silica filled fibers

Table 1. The onset Degradation Temperatures of Composite Fibers

| SiO$_2$ (wt%)	On-set Temp. (°C)	Temp. at 50% weight loss (°C)
0	416.20	446.33
0.5(R972)	436.94	457.33
1.0	438.53	459.33
1.0(Aerosil 200)	417.53	459.33

Differential Scanning Calorimetry (DSC) Analysis

DSC curves of the composite fibers are shown in Figure 7 – Figure 8 and their crystallization temperatures (T$_c$) obtained from DSC curves are plotted as shown in Figure 9. Tc values of virgin polypropylene fibers appear at 113.59°C, 113.39°C, and 118.09°C for spinning speeds of 300, 500, and 1100 m/min, respectively. An increase in Tc values with an increase in spinning speed is related to an increase in PP crystalline orientation along fiber axis which is induced by spinning speed. The Tc values for the composite fibers are found to be higher than the value of neat PP fibers. At spinning speed of 300, 500, and 1100 m/min, for example, PP fibers filled with hydrophobic silica loadings of 1.0 wt% have Tc values of 115.79°C , 116.99°C, and 117.70°C, respectively, indicating that the crystallization of PP occurred more rapidly when compared to neat fiber in accompany with release of latent heat. As the crystallization behavior of infused silica fiber is found to be affected by the presence of silica dispersion, the result proves that silica particles play a nucleating role in inducing a faster crystallization process.[20-21] The figure demonstrates that hydrophobic silica tends to induce a slightly faster crystallization process of PP than the hydrophilic silica counterpart. It can be said that the interaction of hydrophobic silica with PP matrix has higher capacities as compared to silica. This finding leads to the conclusion that, apart from the speed of spinning, change in degree of molecular orientation could arise from interactions between the filler and fiber polymer matrix.
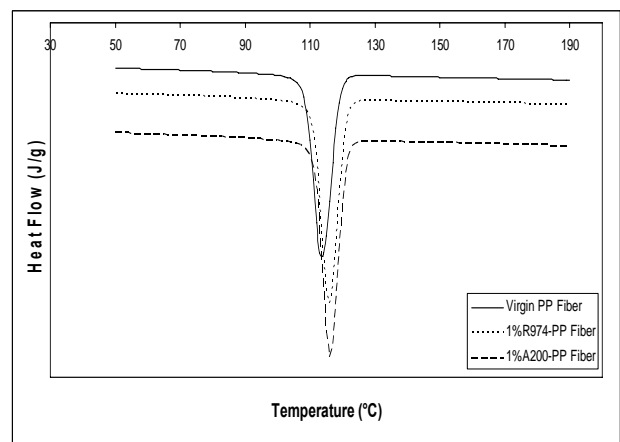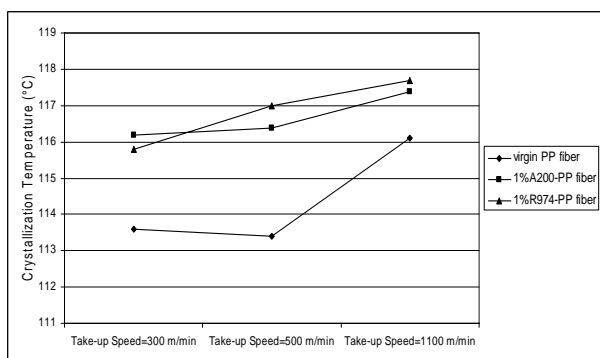

Figure 7. DSC heating curve for virgin PP fiber, 1 wt% A200-PP fiber and 1 wt% R974-PP fiber, (spinning speed of 300 m/min

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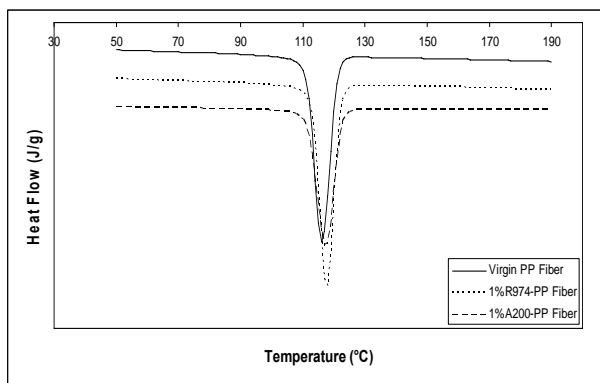
Figure 8. DSC cooling curve for virgin PP fiber, 1%A200-PP fiber and 1%R974-PP fiber, spinning speed of 1100 m/min)

Figure 9. Crystallization temperatures (Tc) of various PP fibers

Fiber Molecular Orientation

Sonic modulus technique was used to determine molecular orientation along fiber axis. The transit time of pulse sound was employed to calculate the sonic modulus according to the equation 1. The sonic modulus value (E) is proportional to the molecular orientation in the fiber axis direction.

is observed that the sonic modulus of neat PP fiber is slightly higher than that of composite fibers. The results indicate that the relatively decreased polymer chain orientation found in case of composite fibers is likely due to the molecular orientation interference caused by the presence of silica dispersion. Therefore, the addition of silica particle into PP fiber may affect the fiber's mechanical properties, particularly the fiber elongation.
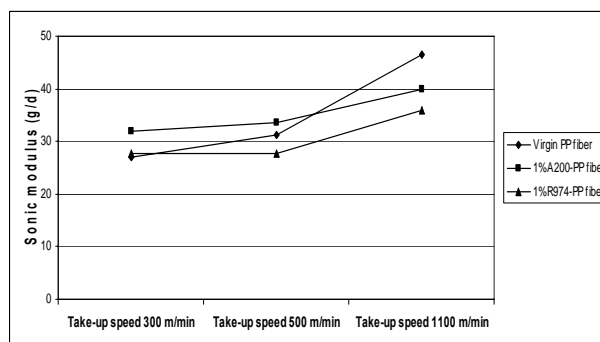
Figure 10. Sonic modulus of neat PP fiber, 1 wt% hydrophilic silica/PP fiber and 1 wt% hydrophobic silica/PP fiber drawn at various spinning speeds

Conclusions

The silica loading in PP led to a nucleation effect on the polymer crystallization process, resulting in β-form crystallinity appearing in PP fibers drawn at low spinning speed. The crystallization temperature (Tc) of silica filled composite fiber was found to be higher than those of virgin PP fiber. This implied that a faster cooling rate would be obtained, producing a faster processing time (when operating at low take-up speed). However, the polymer chain orientation in fiber axis direction was interfered by the presence of silica particles. Thermal stability of PP fibers could be improved when filled with hydrophobic silica in comparison with hydrophilic silica.

$$C = \frac{\text{Distance (centimeters) x}10^{-5}}{\text{Transit time (microseconds) x }10^{-6}}$$

$E = C^2K = C^2 11.3 =$ sound velocity(km/sec)
$K =$ a constant conversion factor $= 11.3$
$E =$ Young's modulus of elasticity (grams/denier)

The results of sonic modulus values are presented in Figure 10. The sonic modulus value increases with an increase in spinning speed, indicating polymer orientation along fiber axis due to an increase in drawing force. When considering the spun fibers taken at 1100 m/min, it

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