Study on Mechanical Properties of Powder Impregnated Glass Fiber Reinforced Poly(phenylene sulphide) by Injection Molding at Various Temperatures

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ABSTRACT: The prepreg of continuous glass fiber reinforced poly(phenylene sulphide) (PPS) was prepared using the powder impregnation technique and cut into the pellets, in which the length of glass fibers was the same as the pellets. After injection molding, the mechanical properties were tested and the effects of the pellet length, fiber content, and thermal treatment on the mechanical properties at different temperatures were studied. It is found that the tensile strength and flexural strength of 6-mm pellet sample are slightly higher than that of 3- and 12-mm pellet samples. The tensile strength, flexural strength, and modulus decrease significantly with increasing the temperature. The notched Izod impact strength at 85°C is higher than both at 25°C and 205°C. At 205°C, the glass fiber reinforced PPS composites can still keep better mechanical properties. When the fiber content ranges from 0 to 50%, the mechanical properties increase with increasing the fiber contents at different temperatures, except the notched Izod impact strength do not further increase at 145 and 205°C with raising the fiber content from 40 to 50%. Thermal treatment could improve the mechanical properties of the composites at higher serving temperature. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 2019–2027, 2010

Key words: glass fiber; poly(phenylene sulphide); powder impregnation; injection molding; mechanical properties; thermal treatment

INTRODUCTION

Ryton was first commercialized by Philips Petroleum (Bartlesville, OK) in 1973 as a trade name of poly(-phenylene sulphide) (PPS). PPS has excellent characteristics, such as high strength and modulus, stiffness, dimensional stability, chemical resistance, electrical properties, flame resistance, and good compactibility. Especially, it has excellent temperature resistance, can be used at 200–240°C for long time. PPS is widely applied in many areas, including electronic, electrical, automotive, aerospace, and mechanical applications. However, its impact toughness is poor. Currently, reinforced modification[1–5] of PPS is one of the key points of the research. After reinforcement, its impact toughness will increase distinctly, and its applications will expand more widely. Fiber reinforcing is very effective, Lin et al.[3] studied the properties of short carbon fiber reinforced PPS, it was found that the Young's modulus increases linearly with increasing volume fractions, whereas strength and fracture toughness increase at first and then peak at a certain volume fraction, and the properties increase nearly two times. After using silane coupling agents to modify the fiber surface, the interlamination shear strength and the flexural strength of the composite were increased further.[6]

Many literatures discuss about the crystallization behaviors and kinetics of PPS composites,[7–12] and heat treatment is a conventional process. For fiber reinforced crystal polymer composites, thermal stress will be formed during their molding processes. Heat treatment can not only relax thermal stress, but also has a certain influence to the crystallization of the polymer composites. Lu et al.[11] studied the effects of heat treatment on the crystal structure and impact strength of PPS and nano-SiO_x/PPS nanocomposites. They found that the molecular weight of heat-treated neat PPS increased by 28% due to the crosslinking reaction that changed its crystal morphology. The Izod impact strength increased by 66% because of crystallinity reduced by 18%.

With rising of the environmental temperature, the molecular motion of the thermoplastic polymer composites is more active, and their strength, modulus, and failure modes of PPS matrix change. PPS is one

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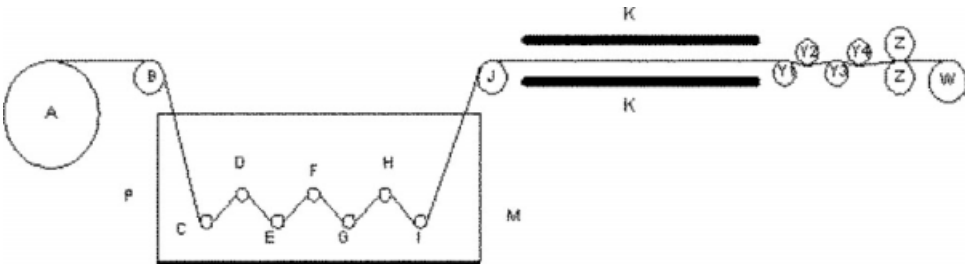

Figure 1 Schematic illustration of powder impregnation process A: glass fiber roving; B, J: guide rollers; C, D, E, F, G, H, I: tension pins; K: heating oven; Y_1, Y_2, Y_3, Y_4: assistant-impregnation pins; Z: compression rollers; W: winding up roller; M: powder bed; P: PPS powder.

of the temperature resistant engineering plastic, and there are few studies focused on the mechanical properties at different temperatures. Park et al.[4] studied the effect of temperatures on the mechanical and morphological properties of PPS/GF composites. Lee et al.[5] studied the mechanical properties and fracture morphologies of PPS/PA66 blends. They found that the impact strength of PPS/PA66 blends increase at all testing temperatures when the nylon66 is more than 30 wt %. Therefore, studying the rule between mechanical properties of PPS/GF composites and different temperatures is necessary.

In this article, our primary objective is to evaluate the PPS/GF composites for high temperature application, we cut the prepreg of continuous glass fiber reinforced PPS, which was obtained using dry powder impregnation technique[13,14] into a series of pellets for injection molding, then investigate the mechanical properties of injection molding specimens at different temperatures with various glass fiber weight contents. On the other hand, we observe the residual fiber length and preliminary analyze the influence factors of fiber rupture. This will be a significant basis of our further work about long glass fiber reinforced PPS composites.

EXPERIMENTAL

Materials

Continuous untwist glass fiber (2000tex) was supplied by Jushi (Tongxiang, China). Its average diameter was 13 μm, and one fiber bundle had about 6000 filaments. PPS used in our experiments was a commercial grade resin (Deyang, China, PPS-hb (cross), R_m=120 μm).

Preparation of continuous glass fiber reinforced poly(phenylene sulphide) prepreg and pellets

The continuous glass fibers were impregnated with PPS using the powder impregnation process to prepare the impregnated tows, in which the fiber content was controlled between 50–55%.The schematic illustration of powder impregnation process is shown in Figure 1. Glass fiber bundle is spread by tension pins in the PPS powder bed, so that each filament can be coated with powder particles due to Van der Waals force and electrostatic attraction. Then it passes the heating oven and the assistant-impregnation pins, well impregnated by molten resin at a pressure to obtain prepreg.

Prepreg was cut into pellets with different lengths 3 mm, 6 mm, and 12 mm. At the same time pure PPS pellets having the same lengths were prepared with a twin screw extruder (Giant, SJ30, Nanjing, China). The fiber contents can be adjusted by mixing pure PPS and impregnated pellets during injection molding process.

Injection molding

The mixture of pure PPS pellets and impregnated prepreg pellets with various proportions was injection molded with an injection molding machine (YTFX700-H5, Ningbo Yongtai Plastics Machinery, Ningbo, China) to obtain the specimens, which were used for further test. The temperature was maintained at 310, 330, 330, and 330°C from hopper to nozzle, and the mold temperature was room temperature, injection pressure was 75 MPa, backpressure was 1 MPa, packing pressure was 0.5MP, packing time was 60s, injection time was 1.5s, and screw speed was 80r/min.

Testing of fiber weight content

The prepreg or injection molding specimen weighed m_0 was placed in a crucible weighed m and pyrolyzed in a muffle furnace at 650°C until a constant weight m_1, when PPS was burnt off. The fiber content W_f was calculated by

$$W_f = (m_1 - m)/m_0 \times 100\%$$

Observation of fiber length

The residual fibers of injection molding specimen after pyrolysis were placed at a microscope slide,

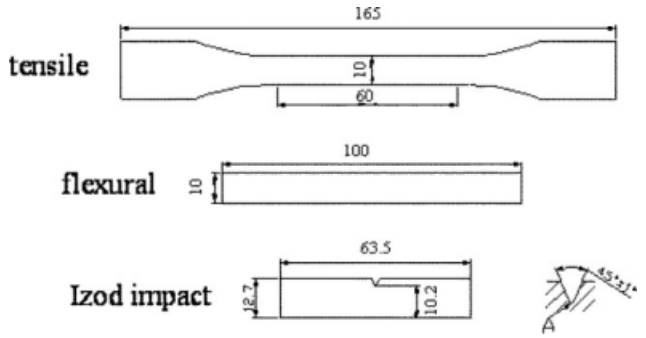

Figure 2 Schematic illustration of specimens.

their length was observed by a Nikon optical microscope (Nikon LV100POL, Tokyo, Japan).

Dynamic mechanical analysis (DMA)

A dynamic mechanical thermal analyzer (TA DMAQ800 New Castle, DE) was used for measuring the temperature-dependant dynamic modulus and loss factor (tanδ). Test was conducted with three-point bending mode, and the support span was 50 mm. The testing temperature ranged from 30 to 220°C at a heating rate of 3°C/min. In this experiment, an oscillation frequency of 1 Hz and a constant strain of 0.03% were used.

Mechanical testing

Tensile properties of PPS composites were measured using a mechanical testing machine (Shenzhen SANS testing machine, CMT4204, Shenzhen, China) according to GB/T 1447 (according to ISO 527-4). The constant crosshead speed was 2 mm/min and the gauge length was 50 mm. All tests were conducted in a thermal cabinet at various temperatures of 25, 85, 145, and 205°C with a 20-min storage time. At least five specimens of each sample were tested, and then the average value was calculated. The flexural testing followed GB/T 1449 (according to ISO 178) with a crosshead speed of 2 mm/min. Notched Izod impact strength was measured using the impact tester (Chengde Testing Machine, XJU-22J, Chengde, China), according to GB/T 1843 (according to ISO 180). Both testing temperatures and storage time were same as the tensile tests. The specific sizes of specimens are shown in Figure 2.

Thermal treatment

Thermal treatment of the specimens was performed at 210°C for 2 h in a circulating air thermostatic chamber.

Thermal analysis

Small fragments weighted about 7 ± 0.8 mg were cut from the specimens and used as the samples for the differential scanning calorimetry (DSC) testing, which was carried out with a Perkin-Elmer Diamond DSC instrument. The samples were heated from room temperature to 320°C at a rate of 10°C/min under N_2 atmosphere.

Morphological analysis

A scanning electron microscope (SEM; JEOL, JSM-6360LV, Tokyo, Japan) was used to observe the morphology of the fractured surfaces of the tensile specimens. The operating voltage was 15 kV, and the fractured surfaces were coated with gold using ion sputtering machine.

RESULTS AND DISCUSSION

Mechanical properties of composites injection molded with different length pellets at various temperatures

To study the influence of the initial fiber length on the residual fiber length and mechanical properties in our experimental conditions, the prepreg of continuous glass fiber reinforced PPS prepared by powder impregnation process was cut into pellets with different lengths of 3, 6, and 12 mm, in which the glass fiber had the same length as the pellets. The impregnated pellets with different lengths were shown in Figure 3. The mechanical properties at different temperatures were tested after injection molding.

To evaluate the mechanical properties of PPS/GF composites at various temperatures, especially at high temperature, we first performed the dynamic mechanical analysis (DMA) of pure PPS (Fig. 4) to find out the transition temperature of matrix resin. In our experiment, three-point bending mode was employed because Deng et al.[15] reported DMA data

Figure 3 PPS/GF impregated pellets with different length. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

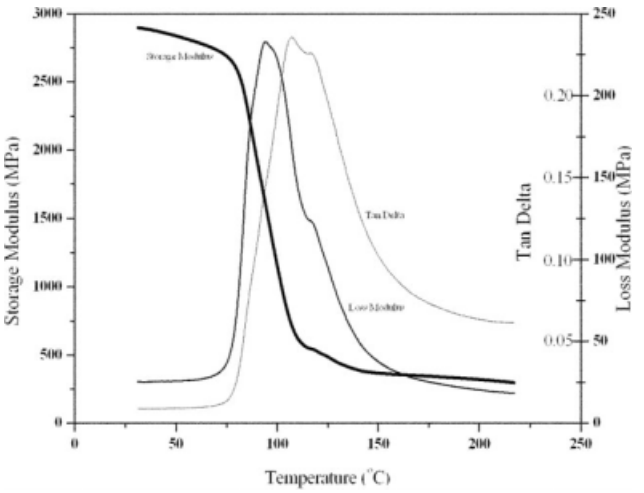

Figure 4 DMA results of pure PPS.

from three-point bending mode were closer to the mechanical testing data than either the single-cantilever or the dual-cantilever modes. As shown in Figure 4, the glass transition temperature (T_g) was considered about 85°C. Meanwhile, the storage modulus showed a rapid decline from 75 to 145°C, which was the glass transition region. After 145°C, it had a gentle decline region until approximately 205°C. According to the DMA results, 25, 85, 145, and 205 °C were chosen for mechanical properties testing temperature.

As shown in Figure 5, the samples injection molded with 6-mm pellets have slightly higher tensile strength, flexural strength, and flexural modulus than 3-mm samples. Moreover, they have the same situation comparing with 12-mm samples, except flexural modulus. For notched Izod impact strength, three kinds of samples are similar and almost have no relationship with the pellet length.

Based on this phenomenon, we calcined the samples after injection molding in the muffle at 650°C until all the PPS were burnt up, and then the left glass fibers were observed using the optical microscope (Fig. 6), simultaneously measuring the residual fiber length and the average length; the distribution is displayed in Figure 7. As shown in Figure 7, the particular residual fiber length is concentrated on 400–600 μm. Generally, the residual fiber length after injection molding is relevant to initial length of the fibers in the pellets. However, during injection molding process, the brittle PPS/GF pellets have ruptured due to the strong shear of screw when plasticizing; furthermore, the strong friction between screw and barrel, the strong shear of high speed flow at nozzle also breaks the fibers; on the other hand, the longer the fiber, the more serious the fracture. Thus, although the impregnated pellets are different, the distribution of fiber length after injection molding is similar between 200 and 600 μm, and the residual length of 6-mm pellet was a little longer.

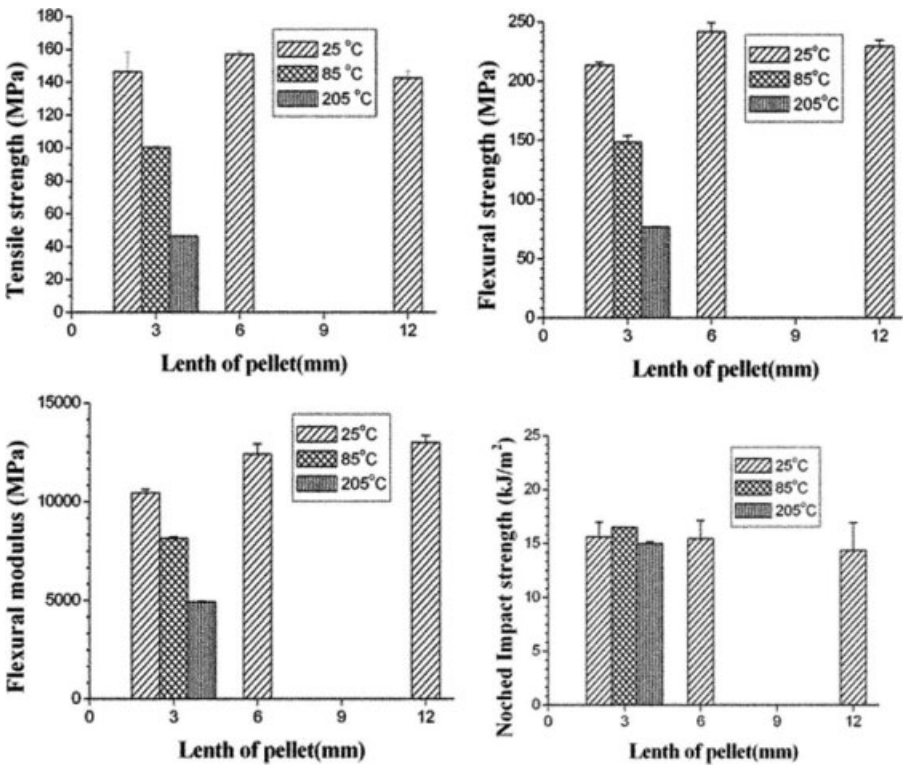

Figure 5 Mechanical properties of injection molding PPS/GF composites vs. length of impregated pellets at various temperatures (glass fiber content is 40 wt %).

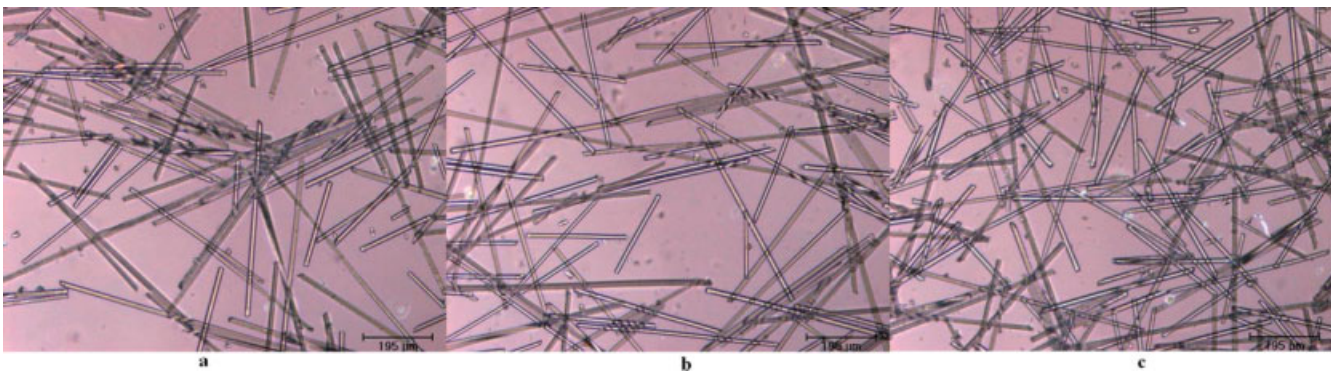

Figure 6 Residual fiber length of PPS/GF impregated pellets after injection molding: (a) 3 mm; (b) 6 mm; (c) 12 mm. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Thus, the tensile strength, flexural strength, and flexural modulus of 6-mm pellet composites showed higher values than other pellets.

In Figure 5, for the 3-mm pellets, the tensile strength, flexural strength, and flexural modulus are 146.35 MPa, 213.43 MPa, and 10,438 MPa at 25°C, respectively, and decrease significantly with the increase of temperature. This phenomenon is based on the molecular motion of PPS, which is more active with the increasing of the molecular volume when the temperature rises, similar to other thermoplastic polymers. Therefore, the chains interaction

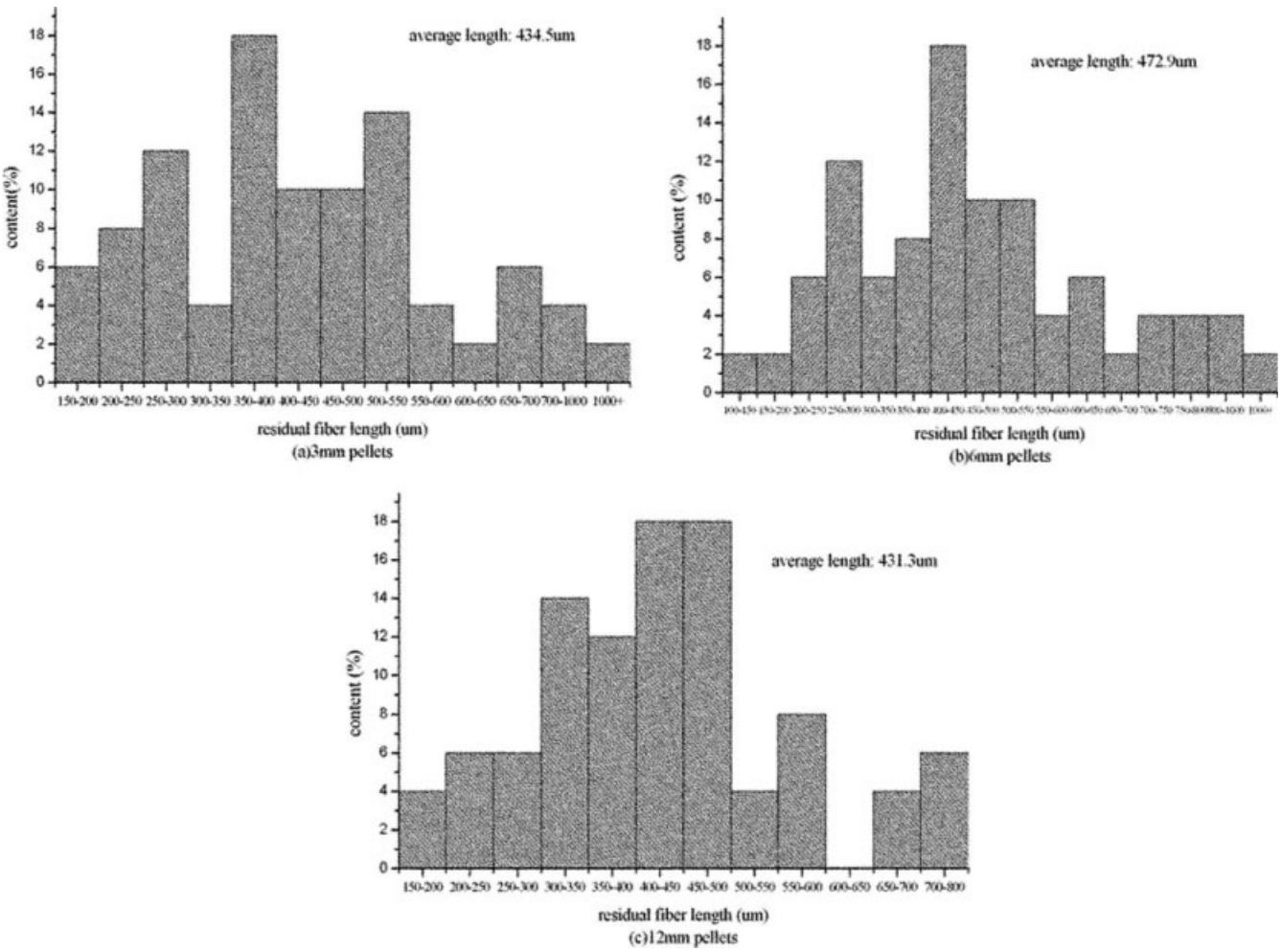

Figure 7 The particular residual fiber length and average length after injection molding: (a) 3-mm pellets; (b) 6-mm pellets; (c) 12-mm pellets.

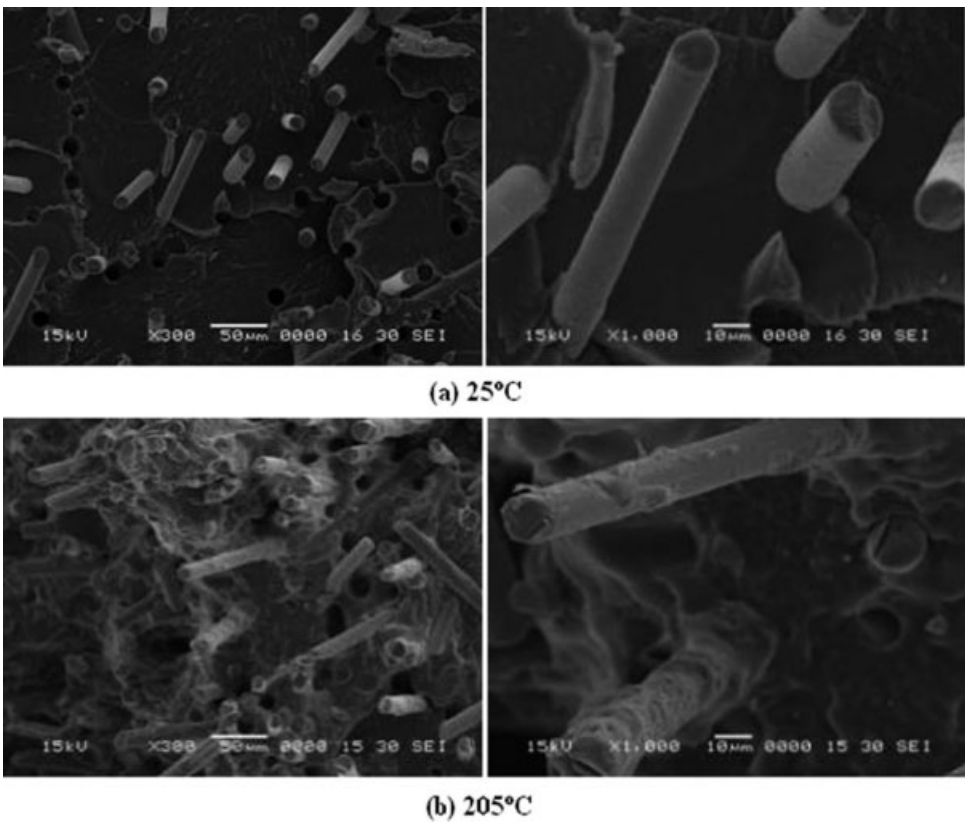

Figure 8 SEM micrographs of tensile fractured surface of PPS/ 20 wt % GF composites at various temperatures.

weakens, the strength and modulus reduce. Below T_g, PPS is at glassy plateau, the molecular chains are frozen and the molecular free volume is a constant value. Only molecule expansion happens with the increasing of temperature at this state. When the temperature reaches T_g, the molecular chains begin to motion. Above T_g, the molecular free volume also expand, so the molecular motion is more active. Therefore, the strength and modulus has a rapid decline during glass transition region. It was in accordance with the result of DMA. Moreover, the contracting forces of resin acting on fibers (the heat stress formed by shrinkage of both matrix and fibers during cooling consolidate process) also decrease due to the large difference in thermal expansion coefficient between glass fiber and PPS, so the interfacial bonding strength reacting on strength and modulus of composites reduced.

Figure 8 shows the SEM micrographs of the tensile fractured surface of PPS/glass fiber composites at different temperatures. In Figure 8(a), matrix resin presents brittle fracture. Little resin adheres to the surface of fibers pulled out from the PPS matrix and many voids are residual on the fractured surface at 25°C. The interfacial debonding is obvious. From Figure 8(b), we can see that PPS matrix shows plastic deformation and yield phenomenon at 205°C. The surface of fibers pulled out from matrix is covered with more resin. It indicates that the cohesive strength between matrixes decreases rapidly and is lower than the interfacial bonding strength at 205°C.

When external load is applied, impact energy can be absorbed by different modes, such as matrix deformation and fracture, fiber fracture, fiber-matrix debonding, and fiber pull-out. In this case, the energy absorption based on matrix deformation increases, but that based on fiber pull-out reduces when the temperature rises, because the resin volume expansion makes the contracting forces of resin acting on fibers drop, especially above the T_g of PPS. As remarked above, the absorbed energy by means of matrix deformation increases significantly at 85°C but the decrease in the absorption energy by means of fiber pull-out is not obvious. However, the rapid decrease based on fiber pull-out mode gets the run upon 205°C and therefore the notched Izod impact strength at 85°C is higher than both at 25°C and 205°C, it does not increase with the temperature rising.

At 205°C, the glass fiber-reinforced PPS composites still have better mechanical properties when compared with common thermoplastic composites. It is indicated that the PPS composites have excellent thermal resistant when used as structure materials.

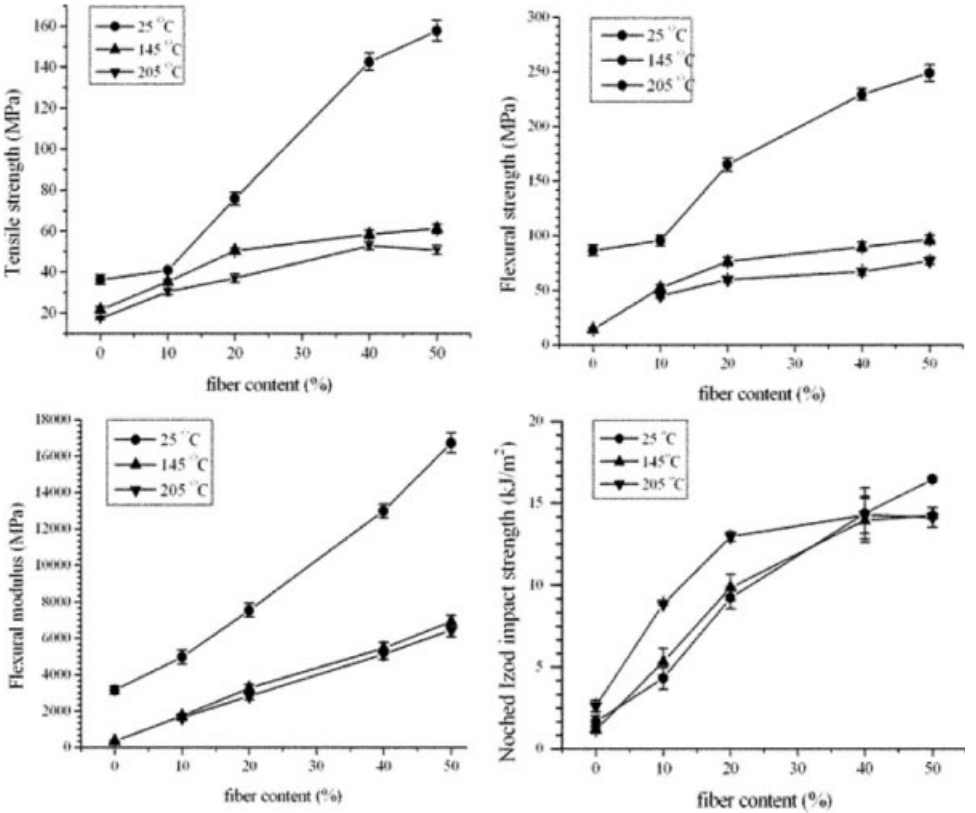

Figure 9 Mechanical properties versus glass fiber weight contents of PPS/GF composites at different temperatures (the length of impregated pellet is 12 mm).

Mechanical properties of composites with different fiber weight contents at various temperatures

Figure 9 shows the mechanical properties of PPS/GF composites at different temperatures. The result has similar rules with Hern-Jin Park's research.[7] First, we can see when the fiber content ranges from 0 to 50 wt %, the tensile and flexural properties increase with increasing of the fiber contents at different temperatures. But at the same fiber content, the tensile strength, flexural strength, and flexural modulus show a decrease trend with raising the temperature, because of the lessened molecular interactions and the low interfacial bonding strength; moreover, Figure 4 shows that the storage modulus reduced rapidly with temperature rising from 75 to 145°C, but had a gentle decline from 145 to 205°C. Figure 9 also shows similar phenomenon, the value at 25°C was much higher than the other two, but the value of 145°C was only a little higher than 205°C. On the other hand, the mechanical properties of glass fiber were considered constant due to only 20-min storage time in a thermal cabinet. Therefore, according to composites mixing law, the mechanical properties of PPS/GF composites significantly decreased from room temperature to 145°C but slightly changed when temperature further rose to 205°C.

In this case, it is also found that the notched Izod impact strength reveals a general trend of increase with increasing the fiber content at various temperatures when the fiber content range from 0 to 40 wt %. With increasing the fiber content, although the absorbed energy due to matrix deformation decreases, the absorbed energy by means of interfacial debonding and fiber pull-out increase more significantly. However, at the temperature above the T_g, the improvement of the impact strength is not as obvious as at the room temperature when the fiber content reaches 40–50 wt %. As mentioned earlier, the reason is that although the fiber number increases, the ability of absorbing energy by single filament pull-out and interfacial debonding decreases at higher temperature, and therefore the increase by means of interfacial debonding and fiber pull-out reaches equilibrium with the decrease due to the matrix deformation.

Effects of thermal treatment on mechanical properties

The mechanical properties of PPS/GF composites, before and after thermal treatment at 210°C for 2 h, were tested at different temperatures, shown in Figure 10. It is found that the tensile strength, flexural

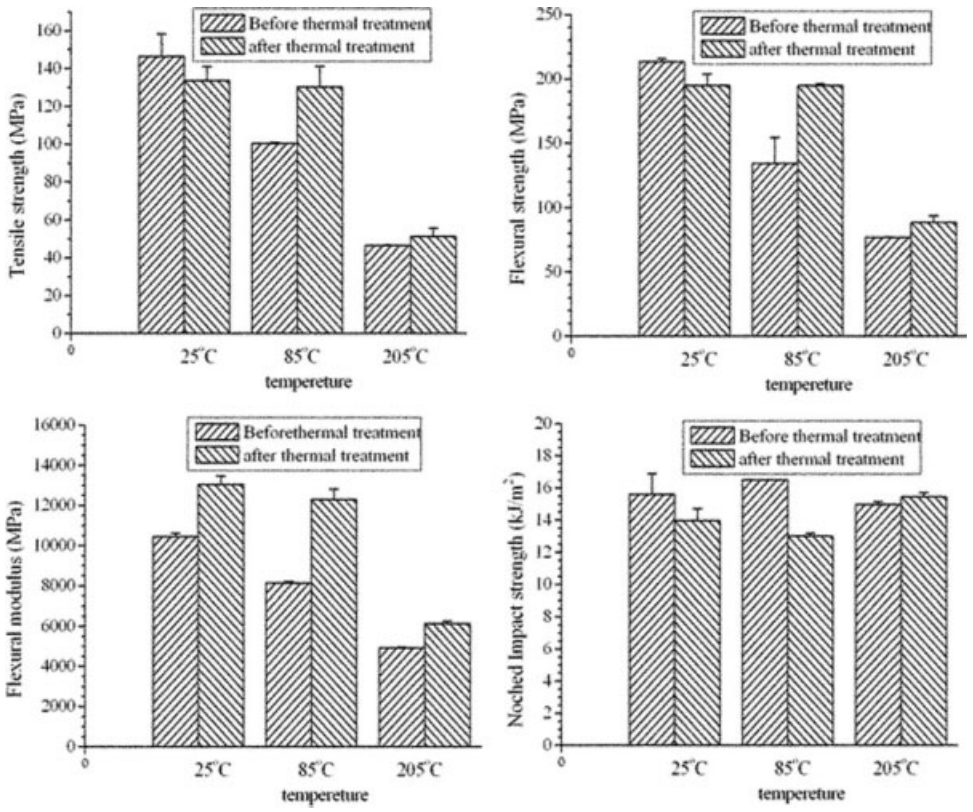

Figure 10 Effect of thermal treatment on mechanical properties at various temperatures (the length of impregated pellet is 3 mm and the fiber content is 40 wt %).

strength, and impact strength all decrease at 25°C, but the flexural modulus enhances after thermal treated. However, the results at higher temperature are different. At 85°C, the tensile strength, flexural strength, and flexural modulus improves, but the impact strength decreases. At 205°C, all the tensile strength, flexural strength, flexural modulus and impact strength are improved. It shows that the thermal treatment can improve the mechanical properties of GF/PPS composites at higher serving temperature.

The crystallization features of PPS/glass fiber composites before and after thermal treatment were studied using DSC measurement. The results are given in Figure 11, and the melting temperature (T_m), heat of fusion (ΔH_m), and crystallinity (X_c) are given in Table I, accepting 121 J/g as the melt enthalpy of the 100% crystalline PPS[16] (H_f). Double endothermal peaks were observed after thermal treatment, as described by Kenney[9] and Karger-Kosis.[17] The crystallinity of the composites changes from 34.06% to 38.06%. The crystallinity of the composite (X_c) was calculated by the following equation:

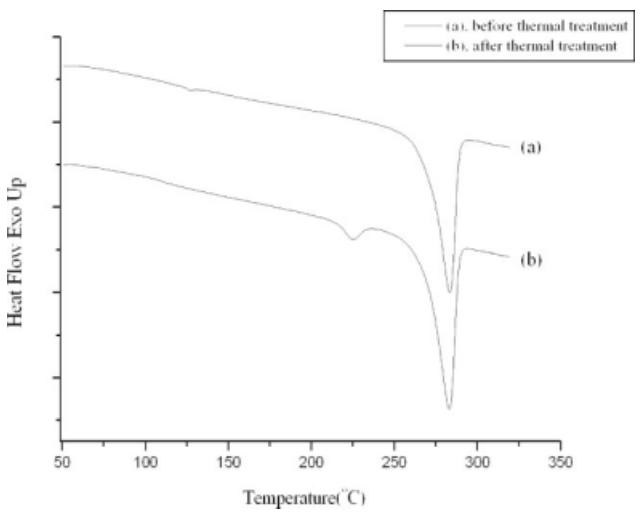

Figure 11 Differential scanning calorimetry (DSC) analysis of PPS/40 wt % GF composites: (a) before thermal treatment; (b) after thermal treatment.

TABLE I
Effect of Thermal Treatment on the Thermal Properties from DSC Analysis

Sample	T_m(°C)	ΔH_m(J/g)	X_c (%)
PPS-40 wt % GF before thermal treatment	283.47	24.73	34.06
PPS-40 wt % GF after thermal treatment	283.21	27.63	38.06

$$X_c = \frac{\Delta H_m}{H_f(1-\alpha)}$$

where α is the fiber weight content.

When the composites were heat-treated at 210°C, the molecule chains of PPS can arrange regularly and recrystalline; on the other hand, the residual thermal stress forming during the molding process can be effectively released. During the injection molding, PPS melt covers on the fiber surface under high pressure, and then contracting force occurs due to the melt shrinkage, which is benefit to make sliding of the PPS over the fiber more difficult. After the thermal treatment at 210°C for 2 h, the contracting force is released, that diminishes the interfacial bond strength and the ability of stress transfer through the interface. So the tensile, flexural, and impact strength diminish at 25°C. The increase of the crystallinity also makes the impact strength decrease but the flexural modulus enhance.

When testing the mechanical properties of composites at 85 and 205°C, the specimens were stored in a thermal cabinet for 20 min, which was similar to the thermal treatment, relaxing the contracting forces. Due to the increase in the crystallinity during thermal treatment, the tensile, flexural strength, and flexural modulus of samples, after thermal treatment improve to some extent. At 85°C, the impact strength declines due to the increase of the crystallinity. However, at 205°C the deformation ability of the amorphous region becomes bigger, the failure and deformation occur firstly in the amorphous region when applied the external load. Thus, the impact strength does not decrease.

CONCLUSION

After injection molding, the distribution of fiber length is similar between 200–600 μm, though the length of the impregated pellets are different. The tensile strength and flexural strength of 6-mm pellet sample are slightly higher than that of 3- and 12-mm pellet samples. For notched Izod impact strength, three kinds of samples are similar and almost have no relationship with the pellet length.

Tensile strength, flexural strength, and modulus decrease significantly with increasing the temperature. The notched Izod impact strength at 85°C is higher than both at 25 and 205°C, it does not increase with the temperature rising. At 205°C, the glass fiber reinforced PPS composites still keep better mechanical properties, indicating that the PPS composites have excellent thermal resistant.

When the fiber content ranges from 0 to 50 wt %, the tensile and flexural properties increase with increasing the fiber content at different temperatures. At the same fiber content, the tensile strength, flexural strength, and flexural modulus show a decrease trend with raising the temperature. The notched Izod impact strength has a similar trend as the tensile and flexural properties when the fiber content changes from 0 to 40 wt %, but not further increasing at 145 and 205°C with raising the fiber content to 50 wt %.

All the tensile and flexural strength and modulus increase at 85 and 205°C after thermal treatment at 210°C for 2 h, whereas the tensile and flexural strength diminish to some extent at 25°C. The thermal treatment results in the decrease in the impact strength at various temperatures.

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