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A New Way of Strengthening and Toughening for Carbon Fiber Reinforced Polyphenylene Sulfide (CF/PPS) Composites via Matrix Modification

XU Yingkai[1,2], ZHU Shu[1,2*], ZHANG Zhao[1,2], YU Muhuo[1,2], YUAN Xiangkai[1,2]

(1. Key Laboratory of Shanghai City for Lightweight Composites, Shanghai 201620, China; 2. State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University, Shanghai 201620, China)

Abstract: The effect of pressure-induced flow (PIF) processing on the mechanical properties of non-continuous carbon fiber (CF) reinforced polyphenylene sulfide (PPS) composites was investigated. A series of CF/PPS composites under different processing conditions were prepared through PIF-processing. SEM observations showed that the interfaces adhesion between CFs and PPS became stronger and ductile fracture mainly occurred in PPS matrix. This brought to a great increase of both strength and toughness by about 2 folds, when the composites were processed at 240 ℃ and under 263 MPa. The results in differential scanning calorimetry (DSC) and X-ray diffraction (XRD) measurements indicated more regular crystalline structures and orientation of lamellae formed during PIF-processing.

Key words: carbon fiber; polyphenylene sulfide; mechanical properties; crystalline structure

1 Introduction

Owing to the high strength and modulus, thermal stability and precise moldability, polyphenylene sulfide (PPS) is widely applied as high-performance engineering plastics[1,2]. Introducing continuous carbon fiber (CF) into PPS matrix may form CF reinforced PPS (CF/PPS) composites, which have high strength close to or even more than that of metals, but the density is less than a quarter of that of iron[3]. Therefore, these kind of materials attract both military and domestic interests[4,5]. Because the existing yield of continuous CF reinforced plastics seems not able to meet the sharply increasing demand of some industries, *e g*, civil aviation, it is necessary to develop substitutes, such as non-continuous CF reinforced composite materials, which are easier and faster to process and have relatively low cost. However, the strength and toughness of non continuous CF reinforced PPS are not high enough to reach the requirement in civil aviation and some other fields[6-8], and the strengthening and toughening of the composites are essential.

Mechanical properties of CF/PPS composites are mainly determined by two weak points: the interfacial adhesion between fillers and matrix, and the polymeric matrix[9]. Researches on modifications for surfaces of CF have been done to improve the interfacial adhesion and achieved good results[10,11]. There has also been some work on the modification of PPS matrix based on copolymerization or blending with other polymers or inorganic rigid particles[12-14]. However, there are usually conflicts between strengthening and toughening.

In our previous work[15-18], a new way of toughening, pressure-induced flow processing (PIF), was proposed to simultaneously increase the strength, toughness and rigidity of some polymers such as PP, PLA, and ABS. In PIF-processing, materials are heated to a desired temperature higher than T_g and below T_m. Pressure will be loaded to induce solid flow of the materials. During the processing, materials are confined in a channel die so that the plastic deformation would occur in one direction. In PIF-processing, the microstructures of polymers have been adjusted, which leads to the improvement of mechanical performances.

In this paper, we applied this new way of PIF-

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XU Yingkai (徐英凯): E-mail: 253981917@qq.com

*Corresponding author: ZHU Shu(朱姝): Ph D; Assoc. Prof.; E-mail: zhushu@dhu.edu.cn

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processing to enhance strength and toughness of CF/PPS composite materials. The influence of processing conditions, *eg*, temperature and pressure, on the mechanical properties of CF/PPS was investigated. Scanning electron microscopy (SEM), differential scanning calorimetry (DSC) and X-ray diffraction (XRD) were used to study the fractured morphologies and crystalline structures of the composites.

2 Experimental

2.1 Materials and sample preparation

CF/PPS material was procured from Guangzhou Jin Zhenghong Plastic Company Limited, which contained 30wt% CF. The density was 1.35(g/cm^3). The metal mold was heated to the desired temperatures, T_{PIF}, and loaded under pressures, P_{PIF}, for 5 min. T_{PIF} is higher than T_g and lower than T_m of PPS. After cooling to room temperature, the pressures were released from the samples. The symbols LD, FD, and CD represent the loading direction, flowing direction and constraint direction, respectively.

2.2 Characterizations

Tensile properties were carried out according to ASTM D3039, using a universal testing machine (Instron 5985) with a crosshead speed of 72 mm/min. Toughness was determined from the integral areas of tensile stress-strain curves. Ten parallel tests had been carried out to calculate an average value as a result. The morphologies of fractural surfaces for CF/PPS composites were observed on SEM (HITACHI S-300N). The electron acceleration voltage was 10 kV. The crystalline structures were studied with DSC (TA/Q20) at a heating rate of 5 ℃/min and XRD (D/Max-2550 PC).

3 Results and discussion

3.1 Mechanical properties of composites

Tensile strength and toughness for CF/PPS with PIF-processing are shown in Fig.1. After matrix modification by PIF-processing at 240 ℃ (Fig.1(a)), tensile strength first increased with the shift of loading pressure, PPIF. But when PPIF was larger than about 263 MPa, the increase of strength tended to be gentle or even decreased. Stress-strain curves exhibited that elongation at break also grew except for the sample processed under high P_{PIF} of 704 MPa, as shown in the

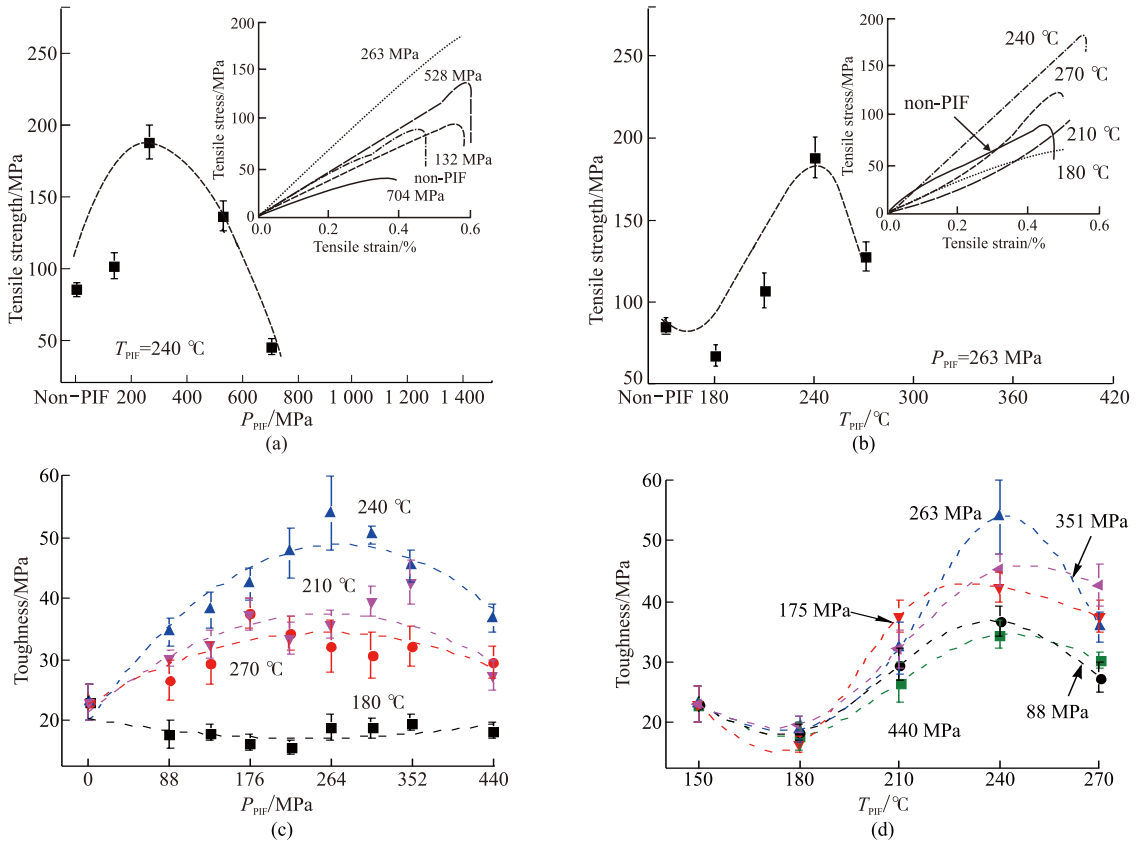

Fig.1 Tensile strength and stress-strain curves for CF/PPS with and without PIF-processing at different P_{PIF} (a) and under different T_{PIF} (b); toughness (calculated as integral area under stress-strain curves) for CF/PPS with and without PIF-processing at different P_{PIF} (c) and under different T_{PIF} (d)

embedded figure in Fig.1(a).

Effect of different T_{PIF} on the tensile strength for CF/PPS was investigated and the results are shown in Fig.1(b). When processed at 180 ℃, modification of PIF-processing showed a negative impact on tensile strength. However, the strength boosted if T_{PIF} was not below 210 ℃. Maximum increase occurred at a T_{PIF} of about 240 ℃, at which the tensile strength of CF/PPS with PIF-processing reached 187.7 MPa, showing a enhancement of 120% (the average tensile strength for CF/PPS without PIF-processing was 85.4 MPa).

Figs.1(c) and 1(d) exhibited the static toughness, which was calculated as integral area under stress-strain curves, for CF/PPS with PIF-processing at different T_{PIF} and under different P_{PIF}. Generally, larger toughness can be observed at higher T_{PIF} or P_{PIF}, but when T_{PIF} was less than 180 ℃ or more than 240 ℃, as well as P_{PIF} was more than 263-351 MPa, the toughness reached a plateau or decreased. Maximum toughness, 53.9 MPa, which was more than double of the original one, 22.9 MPa, occurred when T_{PIF} was 240 ℃ and P_{PIF} was 263 MPa. These results showed that the strength and toughness for CF/PPS with PIF-processing were simultaneously and markedly improved. This phenomenon did not often occur in the modification of composites containing polymeric matrix, when increase of toughness seemed likely to take the cost of strength[19].

3.2 Morphologies of fractured surfaces for CF/PPS

Fig.2 exhibits SEM observations of fractured surfaces in varied directions of CF/PPS composites without and with PIF-processing. In non-PIF samples (Fig.2(a)), rather neat and smooth surfaces of pull-out CFs were demonstrated, indicating separations happened between CFs and PPS matrix during fracture and relatively weak interfaces existed between the reinforcements and matrix. On the other hand, the fractured surface of PPS matrix was relatively flat, showing a mechanism of brittle fracture. After PIF-processing (as shown in Figs.2(b), 2(c), and 2(d)), the surfaces of CFs were rougher than that in non-PIF samples, showing that more PPS matrix was adhered to CFs when fracture occurred. This implies stronger connections between CFs and PPS. More interesting phenomenon lies in the fractured surface of PPS matrix. Different from the flat one in non-PIF materials, much more rugged surfaces with lots of gullies (see the arrow) were seen in three directions for the CF/PPS composites with PIF-processing. Deformation of PPS matrix can be clearly seen, indicating a mechanism of ductile fracture within the matrix. We assume that boost of tensile strength is ascribed to the increase of interface adhesion between CFs and PPS, while the shift of toughness comes from the change of the fracturing mechanism for PPS matrix. However, what caused this change is still unknown at this stage and needs further study.

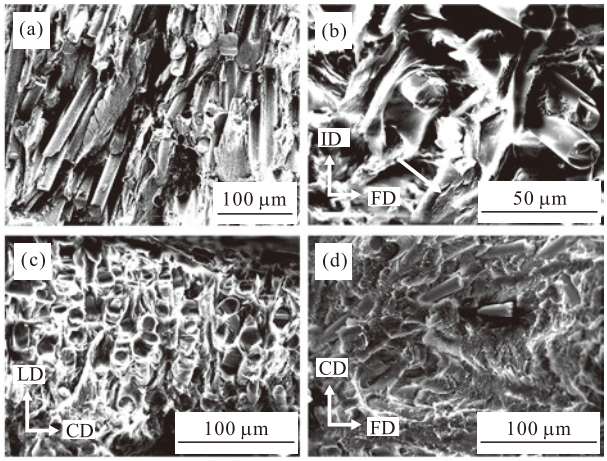

Fig.2 SEM images of fractured surfaces for CF/PPS samples: (a) without PIF-processing, (b), (c), and (d) with PIF-processing at 240 ℃ and under 263 MPa

3.3 Crystal structures of PPS matrix

In order to understand the reason for the

Table 1 Melting temperature and crystallinity for CF/PPS composites derived from Fig.3 using value of ΔH_f^0 proposed by TenCate of 150.4 J/g [20]

T_{PIF} /℃	P_{PIF} /MPa	T_m /℃	T_{onset} /℃	ΔH_f/(J·g^{-1})	Crystallinity/%
Non-PIF	Non-PIF	278.2	244.3	42.46	40.3
180	263	279.3	253.1	46.48	44.1
210	263	280.5	261.2	45.42	43.1
250	263	280.6	263.2	43.68	41.5
270	263	280.4	257.5	44.32	42.1
250	132	280.3	263.1	43.25	41.1
250	263	280.6	263.2	43.68	41.5
250	528	281.2	253.6	49.35	46.9

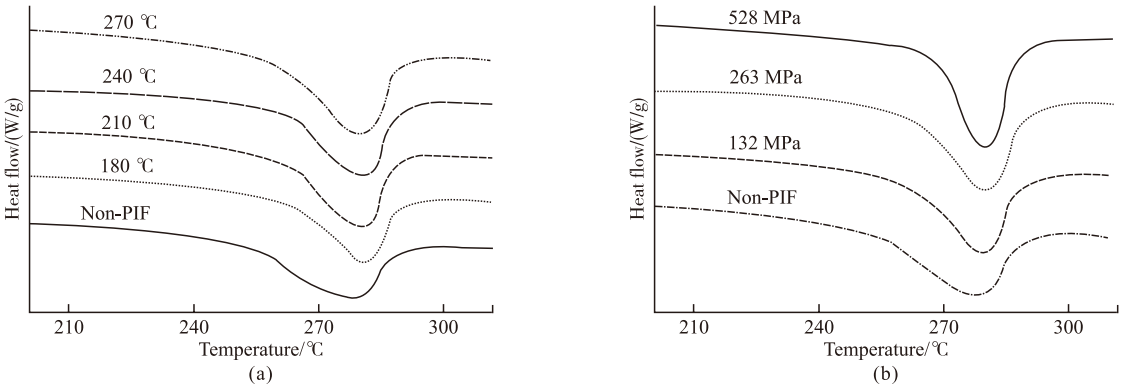

Fig.3 DSC traces of CF/PPS composites without and with PIF-processing: (a) at different T_{PIF} and under 263 MPa; (b) at 240 ℃ and under different P_{PIF}

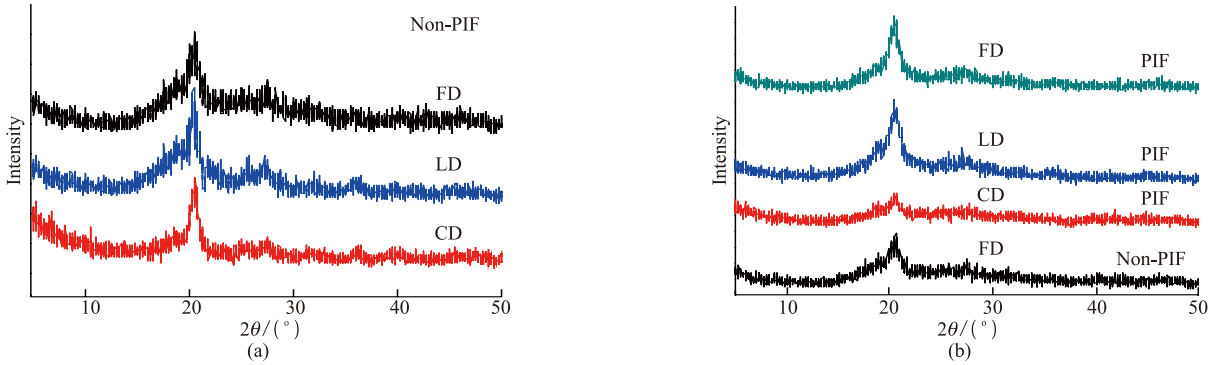

Fig.4 XRD Patterns of CF/PPS composites: (a) without PIF-processing; (b) with PIF-processing at 240 ℃ and under 263 MPa. FD, LD, and CD implies the directions of irradiation of X-ray

conversion of fracturing mechanism for PPS matrix from the brittle to the ductile, DSC and XRD measurements were conducted to learn the evolution of crystal structures of PPS matrix with PIF-processing.

Figs.3(a) and 3(b) demonstrate the DSC traces of CFF/PP composites prepared at different T_{PIF} and under different P_{PIF}, respectively. Corresponding data are shown in Table 1. With the change of condition parameters in PIF-processing, only a slight increase was found at melting temperatures, T_m, suggesting that the thickness of lamellae did not vary during the processing. Onset temperatures of melting, T_{onset}, shifted to higher temperatures. Double peaks of melting process for non-PIF samples turned to exhibit single and smooth peaks in the composites with PIF-processing. Both of these phenomena imply that more regular crystalline structures have been formed during PIF-processing. There was very little difference lying in crystallinities for most samples processed at different T_{PIF} and under different P_{PIF}, except for the ones below 210 ℃ and those under 528 MPa.

Patterns in XRD measurements for CF/PPS composites are shown in Fig.4. FD, LD, and CD imply the directions of irradiation of X-ray. The main peak in each pattern was at about 20.57°, corresponding to 200 and 111 faces[20]. It is seen that the peak position did not vary with the direction of irradiation in both non-PIF and PIF-processed samples, indicating that the crystal type did not change. As can be seen in Fig.4(a), the intensities of this peak were almost the same when the directions of X-ray irradiation changed. However, after PIF-processing, the intensity of peak became varied when the incident X-ray was in different directions (Fig.4(b)). Relatively stronger peaks could be observed when X-ray was irradiated a long FD and LD, while very weak peak was detected when X-ray was parallel to CD. This means that orientations of lamellae occurred during PIF-processing, as the *c*-axis turned along FD.

4 Conclusions

Both of strength and toughness for CF/PPS were simultaneously and markedly improved after PIF-processing. T_{PIF} and P_{PIF} showed strong impact on the mechanical performances of the composites. When the samples were processed at 240 ℃ and under 263 MPa, the strength and toughness were more than double of the original ones.

When fracture occurred, the surfaces of pull-out CFs became rougher, showing that more PPS matrix was adhered to CFs. On the fractured surfaces of PPS

matrix, much more rugged morphologies with lots of gullies, as well as the deformation of polymer, could be seen in CF/PPS composites with PIF-processing. Changes of fractured morphologies and fracturing mechanisms of PPS may be attributed to more regular crystalline structures and orientation of lamellae formed during PIF-processing.

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