

Facilitating transcrystallization of polypropylene/glass fiber composites by imposed shear during injection molding

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Abstract

The transcrystal plays an important role in the enhancement of mechanical and thermal performances for polymer/glass fiber composites. Shear has been found to be a very effective way for the formation of transcrystal. Our purpose of this study was to explore the possibility to obtain the transcrystal in real processing such as injection molding. We will report our recent efforts on exploring the development of microstructure of polypropylene (PP)/glass fiber composite from skin to core in the injection-molded bars obtained by so-called dynamic packing injection molding which imposed oscillatory shear on the melt during solidification stage. A clear-cut shear-facilitated transcrystallization of PP on glass fibers was observed in the injection-molding bar for the first time. We suggested that shear could facilitate the transcrystalline growth through significantly improving the fiber orientation and the interfacial adhesion between fiber and matrix.

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1. Introduction

In recent years, polymer/fiber composites have been intensively investigated in both industrial and academic fields, because they exhibit valuable mechanical and thermal properties when compared with pure polymers. Good adhesion results in efficient stress transfers from the continuous polymer matrix to the dispersed fiber and can increase the ability of the material to absorb energy [1–3], thus improving the mechanical properties of composites.

When a polymer melt is contacting with a foreign surface that can nucleate crystalline growth, the proximity of many nucleation sites on the surface inhibits lateral growth of the resultant spherulites; thus the crystallization develops only in a direction normal to the foreign surface. The development of such a layer has been termed as transcrystal [4]. Several

workers have investigated the intrinsic features of transcrystal and various factors influencing it. The suggested factors influencing transcrystallization are temperature gradients at the interface [4], the wettability and hence, surface energy of foreign surface [5], the chemical composition of surface [6–8], the evolution of volatile products from the nucleant [9], and the crystalline morphology of the nucleating surface [10].

Transcrystallization of polypropylene (PP) at glass fiber (GF) surface was first reported by Gray [11] in 1974, who observed that slight mechanical stress at the PP/GF interface lead to transcrystalline morphology. Misra et al. [12] reported that when glass fibers were intentionally pulled under the hot-stage polarizing microscope, transcrystalline regions developed around fibers, so the shear stresses at the polymer/fiber interface initiated the nucleation. They suggested an interpretation that heterogeneous nucleation at the polymer/fiber interface based solely on the properties of the surfaces.

Single fiber/polymer composites that usually exist as a 'sandwiched' structure are often used for the research of

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transcrystallization [13–15]. Although the transcrystalline kinetics, microscopic details of transcrystallization and their processing condition dependence were well documented, little information about the effect of transcrystalline interphase on the macroscopic performance and the mechanism involved in the semicrystalline polymer-based composite was available. Some studies found that transcrystallization improved interfacial bonding [16] as well as transverse strength of unidirectional composite [17], while Ogata and co-workers [18] proved that the bonding strength was not directly influenced by the formation of transcrystalline layer. The effects of transcrystallization on the interface and properties of composites remain in dispute. It should be mentioned that all these arguments were based on the results of high-heat-resistant semicrystalline thermoplastic resins based composites, such as polyphenylene sulphide (PPS)/fiber composites and polyetheretherketone (PEEK)/fiber composites. For polyolefin/fiber composites, however, there is no report on the effect of transcrystalline interphase on the macroscopic properties because it is difficult to achieve transcrystalline structure in these composites through conventional processing means.

Our recent results suggested that by using polypropylene/glass fiber composites, as an example, shear can not only enhance the fiber orientation, but also enhance the adhesion between the fiber and the matrix [19]. The shear was introduced in our work by so-called dynamic packing injection molding (DPIM), which relies on the application of shear stress field to melt/solid interfaces during the packing stage by means of hydraulically actuated pistons. For the residual GF after extracting PP matrix away, the strong stretching vibration of hydrogen bond characterized by FTIR and the rough surface morphology observed by SEM, approved an increased chemical coupling between the coupling agents and the binding agent was achieved as induced by repeated shear force, thus resulting in an enhanced interaction between the matrix and the fiber [19].

In this work, we will show clear-cut evidence that the prolonged shear function during melt solidification stage would prominently facilitate transcrystallization of PP on glass fibers in the injection-molded bar, instead of in a ‘sandwiched’ single fiber/polymer composites. Meanwhile, the reasons for facilitating transcrystalline growth were ascribed to shear-induced orientation of GF and enhanced interfacial adhesion between matrix and fiber. This provides us with a good base for the future investigation on the effect of transcrystalline interphase on the macroscopic properties of PP/GF composites. Our preliminary results indeed indicate that transcrystallization of PP on glass fibers would be one of the reasons for increases in the tensile strength and the onset degradation temperature.

2. Experimental

2.1. Materials

A commercially available isotactic PP was purchased from Shihezi Petroleum Chemical Co. (Xinjiang, China) and used as the basal polymer. The melt flow index (MFI) of PP is 2.64 g/10 min (230 °C and 2.16 kg load). PP-MA (MA

content = 0.9 wt%, MFI = 6.74 g/10 min) in which anhydride group is randomly grafted on a PP backbone was supplied by Chenguang Co. (Sichuan, China) and used as a binding agent. Long glass fiber (GF E-glass, EC11-2400, Beijing FRP Research and Design Institute, China) was used as the reinforcement agent. The manufacturer has treated the glass fiber with silane coupling agent before selling. And the adsorption of coupling agent on the raw GF surface has been confirmed by FTIR in our past work [19].

2.2. Preparation of PP/glass fiber composites

The PP/GF composites with fixed GF content (30 wt%) and PP-MA content (10 wt%) were melt-mixed in a TSSJ-2S co-rotating twin-screw extruder. The temperature of the extruder was maintained at 160, 190, 210, 210 and 195 °C from hopper to die and the screw speed was about 110 rpm. After a conventional extrusion step, the PP/GF composites were molded through dynamic packing injection molding (DPIM). The schematic representation of this equipment and the test sample dimension are shown in Fig. 1. The main feature is that after the melt is injected into the mold, the sample is forced to move repeatedly in a chamber by two pistons that move reversibly with the same frequency as the solidification progressively occurs from the mold wall to the core part. The detailed experiment procedure has been described in Ref. [20]. We also carried out injection molding under static packing by using the same processing parameters but without shearing for comparison purpose. The sample obtained by dynamic packing injection molding is called dynamic sample, while the sample obtained by static packing injection molding is called static sample. The processing parameters are listed in Table 1. Shear rate was about 10 s^{-1} calculated from the geometry of mold.

2.3. SEM experiment

The samples were cryogenically fractured in liquid nitrogen by bending. After the surface was coated with gold powder, the orientation of the fiber and its adhesion with PP matrix

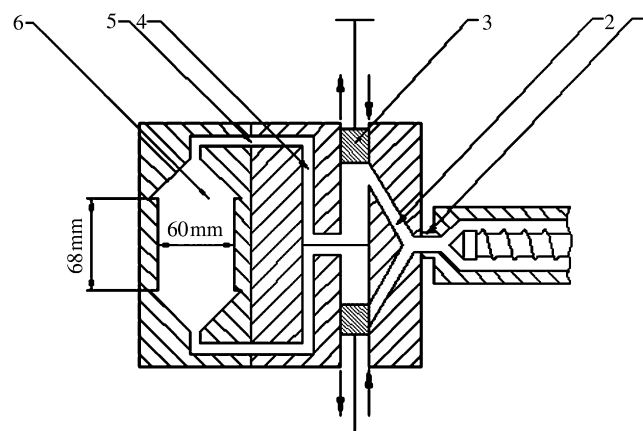


Fig. 1. The schematic representation of dynamic packing injection molding: (1) nozzle, (2) sprue, (3) piston, (4) runner, (5) connector, (6) sample.

Table 1
Processing parameters in dynamic packing injection molding

Parameters	Values
Injection pressure	90 MPa
Injection speed	80 cm ³ /s
Oscillating packing pressure	4 MPa
Oscillating frequency	1.0 Hz
Holding time	~3 min
Melt temperature	200 °C
Mold temperature	Room temperature (about 25 °C)

were studied by SEM instrument, JSM-5900LV, operating at 20 kV. And samples were also etched by a complex solution of KMnO₄, H₃PO₄ and H₂SO₄ [21] to observe the crystal morphology, particularly, the transcrystal of PP on glass fibers.

3. Results and discussions

3.1. Transcrystalline growth in single glass fiber/PP composite

Transcrystalline of PP on glass fiber was often investigated in single fiber/PP composite by polarized optical microscopy (POM) [16,22]. In literature, fibers were embedded in the middle of two thin PP films, and then the single fiber/polymer systems were melted in a hot stage and rapidly cooled to anticipative crystalline temperature after pulling fibers using force [23]. It was obvious that the shear stresses at the polymer/fiber interface initiated the nucleation. We also carried out POM experiment on the single glass fiber/PP composites to find out the good condition for the formation of transcrystalline structure. Shear was found to play a key role on the transcrystallization of PP on glass fiber. Without shear (pull and push the fiber in the PP melt before crystallization), the transcrystalline structure can be hardly observed disregarding crystallization temperature, cooling rate, and addition of compatibilizer (PP-MA), but spherulites are there in the bulk, as shown in Fig. 2a. However, only a simple shear (pull the fiber slowly only one or two times) could result in an obvious transcrystalline phase around the glass fiber, as shown in Fig. 2b. Therefore it is possible to achieve the transcrystallization of PP on glass fiber in real processing if a shear is applied or there exists relative movement between the fiber and the

matrix during solidification (crystallization). Dynamic packing injection molding may provide us such opportunity to validate this assumption.

3.2. Formation of transcrystalline structure in real processing

Macroscopically, the main feature of dynamic samples of PP/GF composites is the shear-induced morphologies with core in the center, oriented zone surrounding the core and the skin layer in the cross-section areas of the samples. Fig. 3 shows the crystalline morphology of the dynamic sample after being etched. One observes stacked lamellar which are arranged perpendicular to the fiber direction, indicating really the formation of transcrystal in the skin layer and the shear layer, as shown in Fig. 3a and b (viewed along shear flow direction) and Fig. 3d (viewed perpendicular to the shear flow direction). Transcrystallization is seen to develop only in a direction normal to the fiber surface, because the nucleation occurs with a sufficiently high density along the fiber surface. As shown in Fig. 3c, no perfect transcrystal but some individual crystals and primary nuclei are observed around the glass fibers in the core due to weak shear effect or adequate disorientation of fibers and PP macromolecules. In contrast, only spherulitic morphology in the bulk is observed for static sample, no matter in the intermediate region or in the center region, as shown in Fig. 4. It is valuable noting that the crystalline morphology of the core in the dynamic sample is apparently different to that in the static sample through comparing Fig. 3c and Fig. 4b, indicating that shear can promote the nucleation ability of PP on GF surface. So the transcrystalline structure seems to easily grow in the dynamic sample that solidified and cooled under the oscillatory shear function. The effect of transcrystalline interphase on the macroscopic properties of PP/GF composites can be ascertained by comparing the tensile strength and degradation temperature between dynamic and static samples. We found in our previous work that a very limited increase of tensile strength was observed for static samples, but an obvious increase of tensile strength and the onset degradation temperature was seen for dynamic samples [19]. For example, the tensile strength is about 43 MPa for static sample, but for dynamic sample it becomes to 58 MPa. We also inspected the thermal stability of

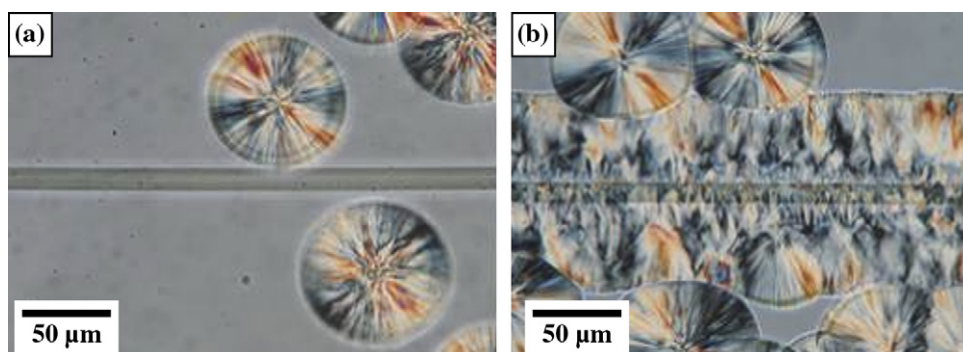


Fig. 2. POM experiment on the single glass fiber/PP composites (a) without shear, (b) with shear.

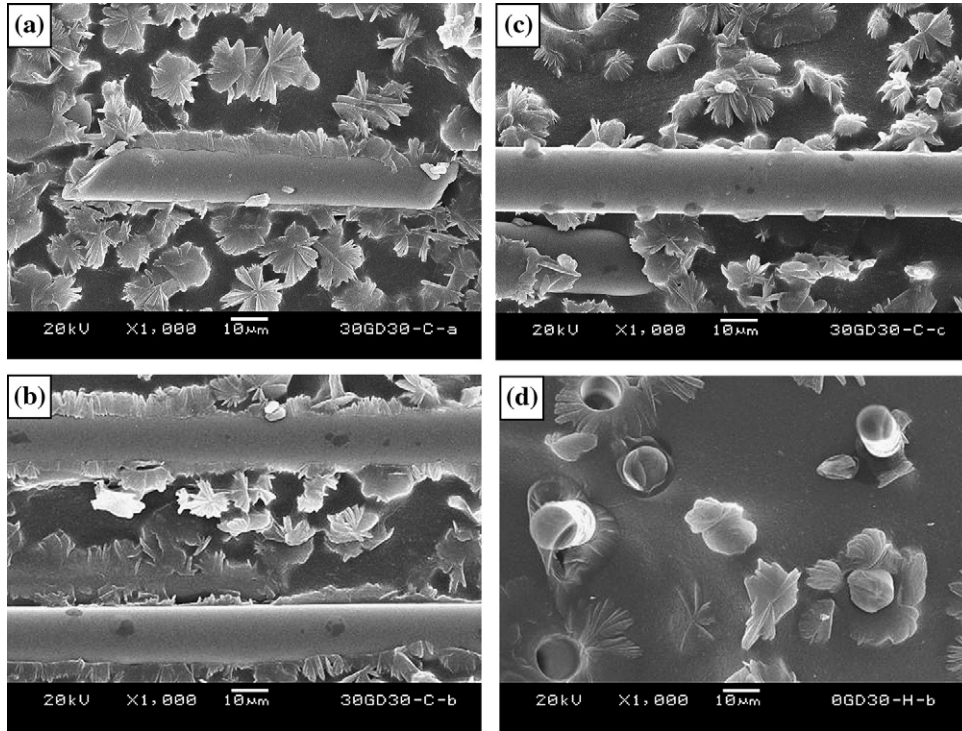


Fig. 3. SEM micrographs represent the transcrystallization at PP/GF interfaces in dynamic sample along shear flow direction at: (a) skin, (b) shear layer, (c) core, and (d) shear layer but viewed perpendicular to the shear flow direction.

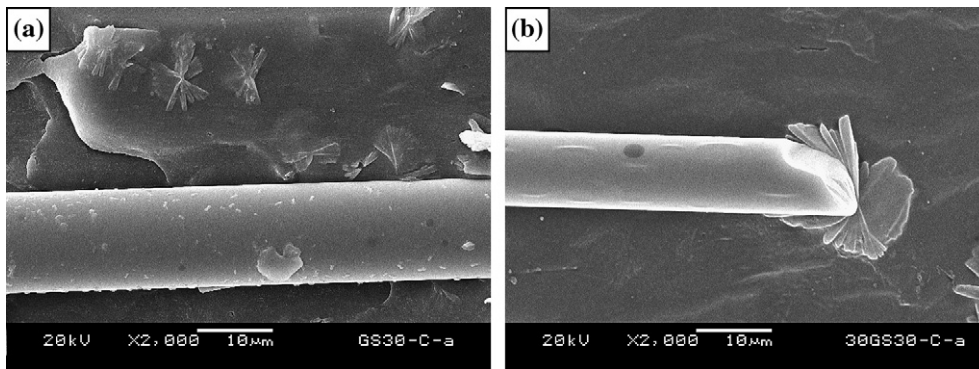


Fig. 4. SEM micrographs of PP/GF in static sample along shear flow direction at: (a) intermediate region, (b) center region.

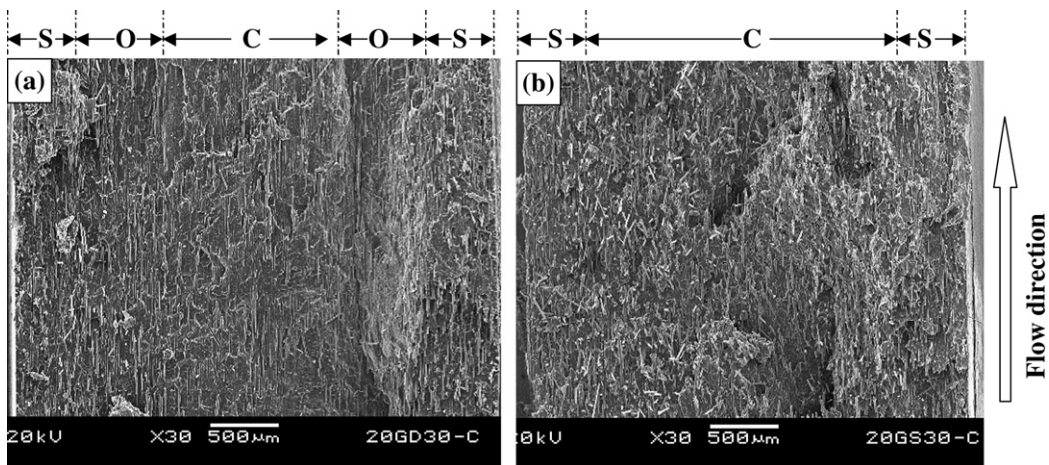


Fig. 5. SEM micrographs represent the dispersion and orientation of fibers along the flow direction at low magnification (a) dynamic one and (b) static one. The positions of skin (S), shear layer (O) and core (C) are indicated directly on the micrographs.

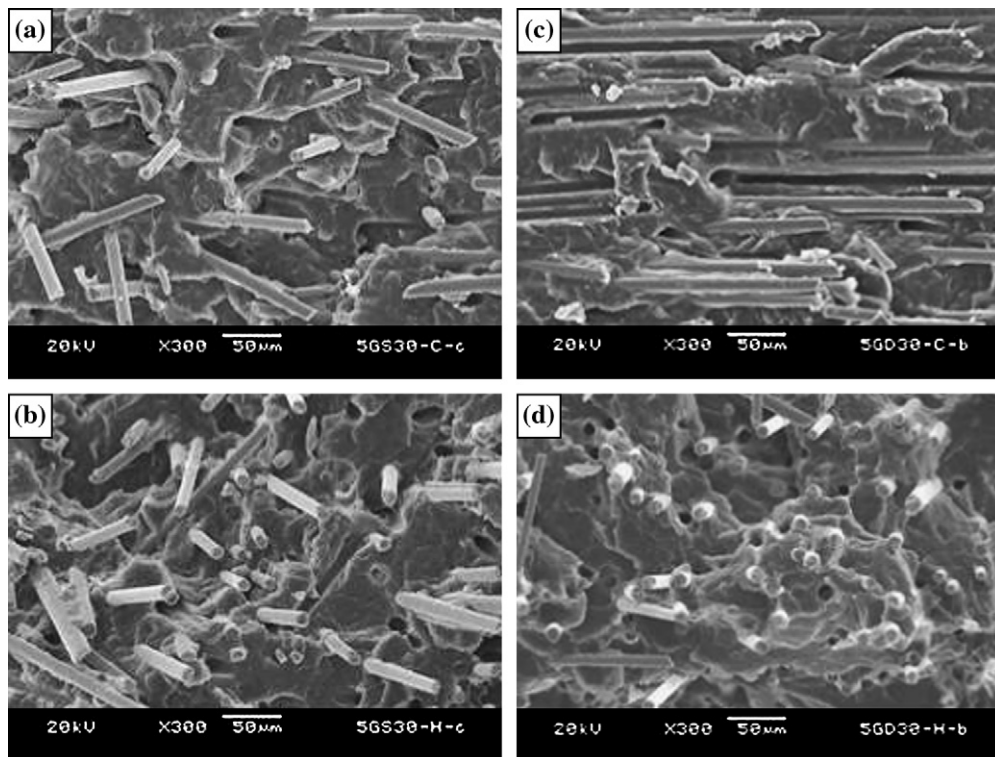


Fig. 6. SEM micrographs represent the orientation of fibers in the core region of static sample: (a) viewed along the flow direction, (b) viewed perpendicular to the flow direction. And the orientation of fibers in the shear layer of dynamic sample: (c) viewed along the flow direction, (d) viewed perpendicular to the flow direction.

composites with a Perkin–Elmer TGA7 instrument on a temperature range from 40 to 600 °C. The onset degradation temperature seen was only 270 °C at the core, but 310 °C at the skin, for static sample, but for dynamic sample, a shift of the onset degradation temperature to 290 °C at core, and to 330 °C at the skin, was observed. But, at this moment, it cannot be absolutely concluded that the formation of transcrystallites is the only cause for the improvement of performance. More experimental data are necessary for clearly describing the relation between macroscopic properties and transcrystallization. The improvement of performance, at least, is contributed from both the transcrystalline interphase and fiber orientation. Future work is needed to separate the effect of transcrystalline interphase and fiber orientation on the macroscopic properties of PP/GF composites.

Transcrystallization is induced by the preferential heterogeneous nucleation at interfaces. The prerequisite for transcrystallization is the presence of a high density of active nuclei on the substrate/fiber interface. The closely packed nuclei hinder the full extension of spherulites, which are then forced to grow in one direction, namely perpendicular to the substrate/fiber interface [4,24]. Shear has been found to be a very effective way for the formation of transcrystallization [25–27]. In our study, transcrystallization grown along the fiber is expected to be due to the preferential orientation of fiber parallel to the shear flow direction and the enhanced interfacial adhesion for the dynamic sample, particularly under the effect of prolonged shear function during melt solidification, as shown below.

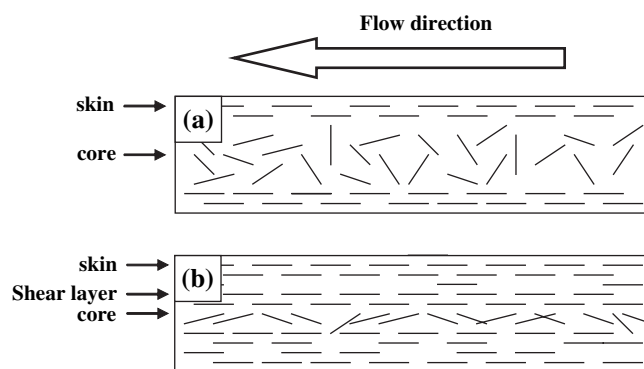


Fig. 7. The fiber orientation across the sample thickness is schematically represented in (a) static sample and (b) dynamic sample.

3.3. Fiber orientation and interfacial adhesion in PP/GF composites

In our work, SEM was employed as an easy and simple method to assess the fiber orientation and dispersion. As an overall review of fiber dispersion and orientation, as shown in Fig. 5, the SEM fractured surfaces of PP/glass fiber composites with low magnification were investigated. For dynamic sample, through exerting only 1.0 Hz oscillatory shear on the composites during cooling, the majority of fiber is aligned parallel to the flow direction across sample thickness. For static sample, it is observed that the fibers are aligned parallel to the flow direction only in the skin area. For more detailed information, the

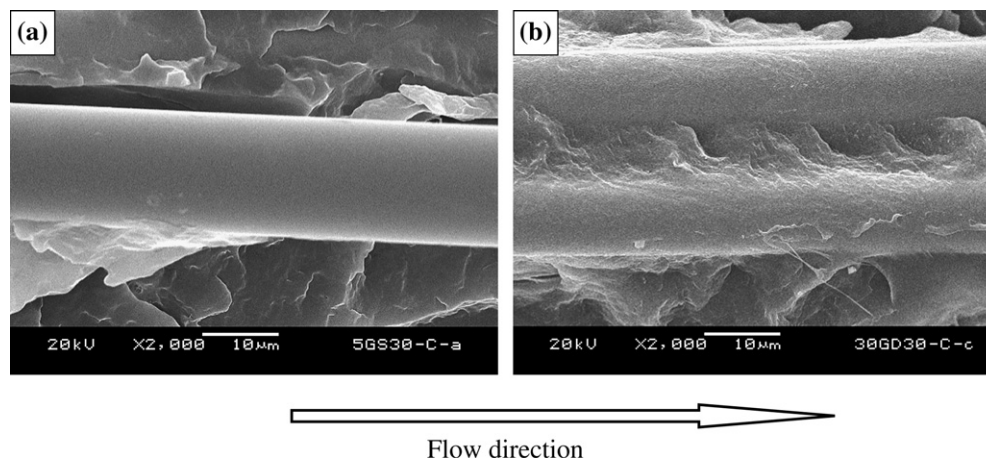


Fig. 8. SEM micrographs represent the interfacial adhesion between fiber and PP matrix: (a) static sample, (b) dynamic sample.

SEM photographs with a higher magnification are shown in Fig. 6. Not much fiber orientation is seen for static sample, however, for dynamic sample, one observes highly oriented fibers no matter viewed along the flow direction or perpendicular to the flow direction. The fiber orientation across the sample thickness can be schematically represented in Fig. 7.

To see clearly the interfacial adhesion between PP and GF, the SEM photographs with the same magnification are shown in Fig. 8. One observes a smooth surface of fibers and weak adhesion between PP matrix and fiber in the static sample even though the coupling agent and binding agent are used. For dynamic sample, however, an obviously enhanced adhesion between fiber and the matrix is observed. As viewed along the flow direction in Fig. 8b, the fiber is embedded into the matrix, instead of separated from the matrix. In this case, the destruction is more likely to occur in the matrix rather than at the interface. Furthermore, after extraction of PP matrix by boiling xylene, a smooth surface of fiber was obtained for static sample, whereas, a rough surface of fiber was observed for dynamic sample [19]. The rough surface was most likely caused by the matrix pieces remaining on fiber, indicating a shear-induced strong interaction between matrix and fiber in the dynamic sample.

4. Conclusions

By comparing the static and dynamic samples, the effect of shear on the fiber orientation and interfacial adhesion can be clearly demonstrated. More importantly, shear is found to play a key role in the transcrystallization of PP/GF composites obtained by injection molding. By imposing the prolonged shear function on melts during solidification stage, we have successfully achieved, for the first time, a clear-cut shear-facilitated transcrystallization of PP on glass fibers in practical processing, instead of in a “sandwiched” single fiber/polymer composite. This shear-facilitated transcrystallization has been attributed to the enhanced orientation of GF and interaction of matrix/fiber. A future work is needed to separate the effect of transcrystalline interphase and fiber orientation on the macroscopic properties of PP/GF composites.

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