Reinforced and toughened PP/PS composites prepared by Fused Filament Fabrication (FFF) with in-situ microfibril and shish-kebab structure

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ABSTRACT

In this work, in-situ microfibrillar composites (MFC) of polypropylene (PP)/polystyrene (PS) were produced by Fused Filament Fabrication (FFF) with a self-designed build platform. Due to the high shearing and stretching effect during the FFF process, PS phase underwent a large deformation. A large number of PS microfibrils could be observed in the samples. Meanwhile the molecular chain of PP was also stretched and arranged along the flow direction in the 3D Printing process. Finally, microfibrils, shish-kebab and hybrid shish-kebab crystal structures can be found and they make contributions to the mechanical performance. This work confirms the applicability of semi-crystalline polymer in FFF technology and discusses the development of phase morphology and crystalline morphology during printing. These obtained results will provide new ideas for broadening the amount of available materials and the application fields of FFF samples.

1. Introduction

Additive manufacturing (AM) which is generally known as three-dimensional (3D) printing, has a wide range of applications in the aspect of biomedical [1–3], electronics [4], aerospace engineering [5] and smart materials [6,7]. Fused Filament Fabrication (FFF), commercially known as Fused Deposition Modeling (FDM) is one of the most popular 3D printing technologies with many advantages like high-efficiency operation and high material utilization rate [8,9]. During FFF process, a thermoplastic filament with uniform thickness is used as printing consumable, which is fed into the heated extrusion head and pushed through a heated nozzle later [10,11]. The extruded filament then deposits on the platform. In the meantime, a relative motion between nozzle and printing platform is initiated. Once a layer has been printed, the build platform moves downwards so that the next consecutive layer can be deposited. Layers are repeatedly superimposed, finally the solid part is modeled.

Although FDM technology already has some industrial applications, the main factor that impedes its further development is the material limitation. Nowadays, the most widely used materials are non-crystalline or low crystallinity material like polylactic acid (PLA) [12,13], acrylonitrile butadiene styrene (ABS) [14,15] and Polycarbonate (PC) [16]. Some widely used semi-crystalline materials like polypropylene (PP) and polyethylene (PE) are rarely applied within FFF process due to its severe shrinkage and warpage. Besides the material limitation, the low strength of FFF products also restricts its application as structural parts. Therefore, the development of reinforced composite has attracted tremendous attentions. Researchers used fibers including carbon fibers (CFs) [17], glass fibers (GF) [18] to enhance the mechanical performance of polymer FFF products. The results showed that within printing process, fibers were aligned along the load-bearing direction, that made contribution to the mechanical strength. The improvement of tensile strength can be up to 140% compared with virgin polymer products [19].

It is generally known, the final performance of polymer products depends on the aggregated structure, which is influenced by the process conditions to a largely extend. For semi-crystalline polymers such as PP and PE, when processed under strong shear or stretch field, the molecular chains will align along the flow direction. Their crystal morphology will change from loose spherulite, crystallizing in static condition, into highly compacted shish-kebab structure [20–22]. Because of the outstanding strengthening effect of shish-kebab structure, lots of research works focusing on the ‘self-reinforcement material’ have been investigated [23–27]. Meanwhile, for some polymer blends with...
appropriate blending ratio and viscosity ratio, the strong process field can make the disperse phase deform into fiber and then strengthen the matrix [28,29]. Based on the special processing mechanism, this kind of composites are called as "In-situ microfiber or microfibril composites" (MFC) [30-34]. For MFC, there are some advantages like: easy manufacture, low-energy consumption, high-production efficiency, low wear of processing machinery [35]. During FFF process, the filament undergoes a transition from solid to polymer melt, then solidifies again. Both the shear effect in nozzle and the relative movement between platform and nozzle provide shear and stretch force to the materials. Therefore, for semi-crystalline blending system, if it is possible to prepare FFF products with in-situ microfiber and shish-kebab structure, the mechanical property is expected to improve a lot. Unfortunately, barely research focusing on this topic has been reported as we known.

In this work, we choose polypropylene/polystyrene (PP/PS) blend as 3D printing material, which are widely used in industrial applications. PP is a typical semi crystalline-polymer and PS has better tensile strength than PP, so it has certain strengthening effect to PP matrix. Besides, the shear viscosity of PS and PP is suitable for deformation according to previous research [36,37]. Applying PP within 3D printing is challenging and meaningful. In order to overcome the severe warpage, we design a build platform which has many conical holes. The specific structure and the distribution of conical holes are shown in supporting information. During the printing process, some part of the first layer of deposition would be squeezed into the conical holes. This part of material can act as a fixation, connecting the products tightly with the table and decreasing the warpage. Compared with the material in common straight holes, material in conical holes keeps conical structure after cooling which is more stable and effective. Fig. 1 shows that by using the conical holes, PP is printable. The experimental results indicate that both PS microfiber and shish-kebab structure can be found in FFF products. The fibrous minor phase and super crystalline structures all make contributions to the mechanical strength. The reinforcement of mechanical strength is noteworthy which shows great utilization potentiality in both experimental and industrial field.

2. Experimental

2.1. Material

Polypropylene (trade name T305) was bought from Lanzhou Petroleum Chemical Company. The melt flow rate (MFR) is 2.9 g/10 min (230 °C/2.16 Kg). Polystyrene (trade name 5250) was bought from Taihua Petroleum Chemical Company. The MFR is 7 g/10 min (200 °C/5 Kg).

2.2. Sample preparation

80 wt% PP, 20 wt% PS granules were mixed uniformly by a SHJ-25 co-rotating twin-screw extruder, and the speed of screw was set as 120 rpm and the temperatures were set as 150, 170, 180, 200, 200, 200, 200, 200, 200 and 190 °C from hopper to die, respectively. Granulated plastic pellets were extruded through a single screw extruder. The temperatures were 180 °C, 230 °C, 230 °C and 205 °C from the hopper to the extruder die. The screw rotation speed was fixed at 300 rpm. After the polymer melt came out from the die of the extruder, the filaments were drawn by a take-up device with two squeeze rolls. A cooling water tank was installed between the mold and the take-up device so that the filaments could be sufficiently cooled and shaped. Finally, a wire of Φ 1.75 mm was obtained.

The samples were prepared by a HORI 3D FFF machine (model Z300), the in-house-designed build platform as introduced before was used in all experiments. Both pure PP and PP/PS sample were prepared which named as FP, FC. Some detailed descriptions about the sample size are shown in the Fig. 2. In this study, the internal porosity of part was zero and printing angle was parallel to the x-axis during the entire printing process. In order to study how the shear field in FFF affects the morphology and properties of the polymer blend, we chose three different printing speeds: 60 mm/s, 120 mm/s and 180 mm/s then named samples as: FP1, FP2, FP3, FC1, FC2, FC3 accordingly. After several experiments, the optimum processing parameters were shown as follows: the melting temperature and the printing table temperature were 230 °C and 80 °C, the layer thickness was set as 0.1 mm. Table 1 lists the main parameters of FFF processing of this work. For comparison, compression molded PP, PP/PS samples were also manufactured at 230 °C, and named as CP, CC.

2.3. Characterizations

2.3.1. Capillary rheology measurements

The capillary rheology measurements were carried out by a high-pressure capillary rheometer (RH7D, Malvern Instruments Co., Ltd). The capillary rheology measurements were carried out by a high-pressure capillary rheometer (RH7D, Malvern Instruments Co., Ltd).
Britain). The shear rate ranges from 10 to 1000/s and temperature was set as 230 °C. 20 points’ values were gathered during experiment.

2.3.2. Scanning electron microscope
For the sake of carefully observing two phases morphology, samples were immersed in the xylene at 20 °C for 2 h for etching PS away selectively. To reveal the crystalline morphology of PP matrix clearly, samples were etched chemically by a mixed acid etching solution at 60 °C for 8 h. The solution consisted of sulfuric acid, phosphoric acid, distilled water and potassium permanganate. The volumes for liquid are 20 ml, 8 ml and 2 ml respectively, and the content of potassium permanganate is 1.2 g. The etched surfaces were carefully observed after gold sputtering treatment by a FEI (Nova Nano SEM450) SEM device.

2.3.3. Differential scanning calorimetry
A differential scanning calorimetry (DSC) (TA Q2000) device was used to analyze the thermal behavior of different samples. Samples about 3–8 mg were heated under a dry nitrogen atmosphere, from 30 °C to 200 °C at a heating rate of 10 °C/min. The crystallinity (Xc) of every sample was calculated by the following equation:

\[ X_c = \frac{\Delta H_m}{\Delta H_{m0}} \times 100\% \quad (1) \]

\( \Delta H_m \) can be obtained from the DSC experiment, is the measured value of the fusion enthalpy. \( \Delta H_{m0} \) means the fusion enthalpy of PP completely crystallized and is chosen as 207 J/g in this work. \( \Phi_0 \) represents the mass fraction of PP in the composite.

2.3.4. Mechanical strength test
For tensile strength test, the dumbbell bars were prepared in standard shape. Before the impact strength tests, a 45° V-shape notch (depth of 2 mm) was made using a XJUD-5.5(Chengde, China) Izod machine at 25 °C. The experiments were carried out at room temperature, by an Instron testing machine (model 5967) and the tensile speed of across head is 50 mm/min. To control the error of the mechanical strength, the value of every results was all calculated as an average of five samples.

2.3.5. X-ray measurement
The synchrotron X-ray experiments were carried out on the in the Shanghai Synchrotron Radiation Facility (SSRF) BL16B1 beamline, Shanghai, China. The wavelength of X-ray was 0.124 nm and the size of the rectangle-shaped beam was 0.5 × 0.8 mm². The rectangular beam was perpendicular to the XZ plane of samples. For the WAXD and SAXS tests, the distance between the sample and detector was 102 and 1850 mm, accordingly. For the detection of images, A MAR CCD X-ray detector (MARUSA) was applied and having a resolution of 2048 × 2048 pixels. In addition, the orientations of lamellar crystals of different FFF samples were calculated by the Hermans orientation function. And the average orientation for a set of planes was calculated mathematically using the equation:

\[ f = \frac{3 \cos^2 \phi - 1}{2} \]

\( \cos [2] \phi \) is the orientation factor and is defined as:

\[ \cos^2 \phi = \frac{\int_{-\infty}^{\infty} I(\phi) \cos^2 \phi \sin \phi d\phi}{\int_{-\infty}^{\infty} I(\phi) \sin \phi d\phi} \]

\( \phi \) is the azimuthal angle and \( I(\phi) \) is the scattered intensity along the angle \( \phi \). Having a value of 0 signifies the random orientation. And a value of −0.5 or 1 respectively means that the reflection plane is perpendicular (\( \phi = 90^\circ \)) or parallel (\( \phi = 0^\circ \)) to the reference direction.

3. Results and discussion

3.1. The rheological behavior
Some detail information about the rheological behavior is shown in Fig. 3. Fig. 3(a) is the apparent viscosity change over a range of shear rates. Because of the increased chain orientation and the reduction of the chain entanglement density, all samples show typical shear thinning behavior when the shear rate increases. It is not difficult to speculate that the stronger shearing and stretching field in FFF process would cause severe shear thinning phenomenon. Comparing with PP, the viscosity of PP/PS is lower in the whole shear range. During FFF printing, lower viscosity would benefit the adhesion between neighbor filaments so the printing effect of PP/PS would be better than PP in this respect.

According to other researchers’ work [36,37], the viscosity ratio (disperse phase/continuous phase) of two phases has strong effect on the morphology structure. A ratio at 0.5 < \( \eta_1/\eta_0 \) < 1 would be favorable for disperse phase deformation and fibrous structure maintain. When \( \eta_1/\eta_0 > 1.5 \), it is hard to find fibrous phase because when the ratio reaches some extent, the adhesive and drag force of matrix are too weak to make disperse phase deforming into fibers. In this FFF experiment, the shear rates of three different printing speeds are estimated at range of 100–300/s according to Gilmer, Eric L’s results [38]. Fig. 3(b) gives us the viscosity ratio of PS/PP, the ratio is between 0.6 and 0.68 when the shear rate is 100–300/s, which proves the capacity for PS to form microfiber during FFF processing.

3.2. Phase morphology
Clearly phase morphologies of FFF PP (FP) and PP/PS (FC) at three printing speeds are shown in Fig. 4. The observation plane is parallel to the XZ plane as Fig. 2 shows. The PS phase was etched, for sake of observing the phase morphology more precisely, then the phase morphologies of it could be exposed and presented. For FP samples, the white lines are the adhesive traces of nearby filaments and some defects exist obviously. Compared with FP samples, concaves with large draw ratio could be found in all FC samples which means the microfiber could be prepared by FFF, that is also consistent with the rheological result. Furthermore, it is worth noting that the fibers’ orientation degree and uniformity improve with increasing printing speeds. When the printing speed is 180 mm/s, the composites show best in-situ fiber-forming effect.

3.3. The crystalline structure and thermal behavior
On account of limited researches about semi-crystalline material FFF parts, the crystalline structure and their influence on final property have been barely reported before. Here, the crystalline structures of samples with different printing speeds are shown in Fig. 5. For all FP samples, typical shish-kebab structure could be found. In addition, the lamella arrangement became more and more dense and regular with increasing printing speed. For FC samples, PS phase was dragged into fibers as

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Materials</th>
<th>Temperature/ °C (nozzle – plate)</th>
<th>Nozzle dimension/ mm</th>
<th>Layer thickness/ mm</th>
<th>Printing speed/ mm/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>FP1</td>
<td>PP</td>
<td>230–80</td>
<td>0.8 mm</td>
<td>0.1 mm</td>
<td>60</td>
</tr>
<tr>
<td>FP2</td>
<td>PP</td>
<td>230–80</td>
<td>0.8 mm</td>
<td>0.1 mm</td>
<td>120</td>
</tr>
<tr>
<td>FP3</td>
<td>PP</td>
<td>230–80</td>
<td>0.8 mm</td>
<td>0.1 mm</td>
<td>180</td>
</tr>
<tr>
<td>FC1</td>
<td>PP/PS</td>
<td>230–80</td>
<td>0.8 mm</td>
<td>0.1 mm</td>
<td>60</td>
</tr>
<tr>
<td>FC2</td>
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<td>0.1 mm</td>
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<td>0.8 mm</td>
<td>0.1 mm</td>
<td>180</td>
</tr>
</tbody>
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shown in Fig. 4, beyond that, highly oriented kebab structure could be found in the surrounding area of PS microfibers, showing hybrid shish-kebab structure. As is widely known, this kind of super crystalline structures has big application in self-strengthening field \cite{39-41}, their influence on the mechanical property of FFF products would be discussed later.

2D-WAXD experiment was used for characterizing the structure more deeply and find more information about crystal orientation. In Fig. 6, the diffraction patterns consist of several diffraction rings were shown, which is associated with different lattice planes, including (110), (040), (130), (−131) \cite{42}. In this work, the (040) diffraction ring was chosen for calculating the degree of orientation (f) in the two-dimensional pattern. And the calculated results are also labeled in the right bottom corner for each sample. It is evident that the arc like diffraction signal can be found in all samples which also can prove the existence of highly oriented structure. When the speed is 60 mm/s, the orientation degree is relative lower, but when the speed reaches 120 mm/s or 180 mm/s, the orientation degree keeps at a very high level (more than 0.9).

The DSC melting curves of PP samples and PP/PS samples prepared...
by compression molding and FFF are presented in Fig. 7, where crystallinity ($X_c$) and melting temperature ($T_m$) are labeled above the curves. It is distinct that the $X_c$ improves after adding PS when comparing (a) with (b), this kind of phenomenon is called heterogeneous nucleation. Because PS phase can work as the heterogeneous nucleating agents, the crystallization ability for PP increases accordingly. When the printing speed increases, the $X_c$ has a slight increasement. As is well-known, the flow field helps polymer chains arrange into one direction, so more polymer chains will trend to fold and arrange into crystalline region, which makes contribution to the improvement of crystallinity.

3.4. Mechanical properties

As mentioned above, it is crucial to improve the mechanical property for FFF products. Compared with compression molding samples, the mechanical strength of FFF samples is always lower because of the voids and bonding defects [10]. In Fig. 8(a) the tensile strength of CP is higher than all FP samples. After adding PS, there are some different trends. First, adding PS impairs the tensile strength of PP in compression molding but benefits FFF samples. For CC, the week interfacial strength of two immiscible polymers leads to worse stress transfer. However, because of the existence of PS in-situ microfiber and interfacial crystalline structure in FFF samples, the strengthening effect can overcome the defect after adding PS. The tensile strength of FC3 is 43.6% higher than CC. Second, when the printing speed increases, the difference within FP samples is not apparent but shows distinct rise in FC. Previous results show that the uniformity of PS microfiber and the density of PP lamella increase with speed increasement accordingly. So that’s why the tensile strength increases 13.6% from FC1 to FC3. Fig. 8(b) shows the stress-strain curves of test samples. Both two compression molded samples have a pretty low elongation at break. For FFF samples, the filament can slip, debond with surrounding filaments and rupture individually which make contribution to the energy dissipation during test. The photograph of fractured FFF sample is shown in supporting information.

PP as one of the most widely used polymers has wonderful comprehensive chemical and physical properties, however, the fracture toughness is dissatisfactory especially at under a high load of stress or low environment temperature. The toughening of IPP has been a hot issue for a long time [43–45]. Fig. 9 exhibits the impact strength of test samples. There are three points needs to be paid attention to. First of all, the FFF samples have better performance than compression samples. Just as the fractured samples depicting in Fig. 9(b), FC sample shows an incomplete fracture morphology. Magnified figure gives more information that there are two kinds of failure: filament fracture and interlayer failure. The multiple energy dissipation ways will support samples with better toughness which is consistent with the results of elongation at break. Secondly, increasing printing speed is beneficial to toughness for both FP and FC. The value increases by 200% for FP3 compared with FP1. In rheological behavior part, the viscosity drops when shear rate increases that means the viscosity would also drop when printing rate increases. Low viscosity would help melted filaments adhere each other better so the connection between filaments is improved. Third, the toughening of PS is obvious. The impact strength of FC3 reaches 55.96 kJ/m$^2$ which is 1.63 times to FP3. Compared with CP, the impact strength of FC3 increases by 18.6 times. Just like mentioned before, the existence of PS microfiber and shish-kebab structure can be very useful to improve mechanical strength. And the elevation in toughness is outstanding.

3.5. The morphology evolution of PP/PS during FFF process

Previous result already shows the phase morphology and crystal structure of FFF samples by different methods. But the transformation and development process are still veiled. By observing samples at different stages, describing the morphology evolution process is available. Fig. 10 is the schematic illustration, which shows composite at three stages: as filament, melting extrusion and deposition on platform. The SAXS patterns of relevant samples are presented and SEM photos are shown in supporting information. Due to the relatively weak extruding and shearing effect in filament making process, some PS droplets would slightly deform and finally the filament is composed of elliptical PS.
phase and PP spherulite like (a) in the figure. During the stage two, the filament is heated and then extruded from nozzle which also has a dragging and shearing effect. Therefore, the deformation of PS further increases, more and more PS droplets exist as microfibers, like (b). After stage 3, the filament deposits on the platform and the SEM photo shows large difference. Not only uniform PS microfibers, but also tightly arrangement shish-kebab and hybrid shish-kebab structures can be observed, illustrated as (c). From SAXS pattern, there also exists strong streaks at equatorial and meridional direction that represent the shish-kebab structure. The deposited material can be regarded as semi-melt which withstands a push-and-pull force along the deposition direction. This process can provide a strong external force and determines the final morphology of composites. When printing speed improved, the dragging effect would become more intense. Combining the effect of microfiber and orientated crystal structure, the mechanical performance of FFF processed PP/PS samples becomes excellent.

4. Conclusion

This work discussed the morphology development of PP/PS blend during FFF, mainly focused on the phase morphology and crystal structure. Due to the strong shearing and pulling forces during FFF process, the PS phase can deform into fiber and orient along the deposition direction. After etching, the shish-kebab and hybrid shish-kebab structures can be found in the FFF products. The semi-crystal material like PP has been barely applied in FFF previously and the researches about crystal structure was also limited. In this work, both PS fiber and strengthening crystalline structure made contributions to the mechanical properties. Beyond that, when printing speed increased, the advantage became more evident. This work broadens the amount of available material for FFF and provides a new direction for strengthening, which is meaningful to the future application of FFF technology.
Declaration of competing InterestCOI

We wish to draw the attention of the Editor to the following facts which may be considered as potential conflicts of interest and to significant financial contributions to this work. We wish to confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work with which may have influenced its outcome.

We confirm that the manuscript has been read and approved by all named authors and that there are no other persons who satisfied the criteria for authorship but are not listed. We further confirm that the order of authors listed in the manuscript has been approved by all of us.

We confirm that we have given due consideration to the protection of intellectual property associated with this work and that there are no impediments to publication, including the timing of publication, with respect to intellectual property. In so doing we confirm that we have followed the regulations of our institutions concerning intellectual property.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jpolym.2019.121971.

References

