Influence of additives on polycarbonate/acrylonitrile-butadiene-styrene blending for fused deposition modeling

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Abstract. This study aimed to investigate the use of polycarbonate (PC), acrylonitrile-butadiene-styrene (ABS), PC/ABS/maleinized acrylonitrile-butadiene-styrene copolymer (ABS-g-MAH) composite, PC/ABS/methyl methacrylate-butadiene-styrene (MBS) composite, and PC/ABS/organic montmorillonite composite for fused deposition modeling experiments and compare their mechanical properties. The tensile test results of specimens printed with different orientations revealed that PC/ABS compatibilized by 7% MBS exhibited the highest tensile elongation of the samples built in a horizontal orientation. Moreover, PC/ABS compatibilized by 6% ABS-g-MAH showed the greatest tensile strength between the three composite specimens printed with horizontal orientations. The notch impact test results revealed that PC/ABS/ABS-g-MAH and PC/ABS/MBS composite specimens printed with horizontal and vertical orientations were much stronger than the other systems.

1. Introduction

Three-dimensional (3D) printing, also known as the additive manufacturing method, has attracted wide attention and is increasingly used in medical treatment, education, manufacturing, and so on [1, 2]. Compared with the traditional manufacturing molding methods, 3D printing offers a new option for pattern design and final product manufacturing. In the automobile industry, 3D printing can help design pneumatic models, cylinders, and other interiors without the need of developing molds. Developers can find problems through static analysis and real vehicle installation of 3D printed parts, and then communicate with structural design engineers to optimize parts of the structural design, improve the strength and manufacturability of parts, simplify part structures, verify technical structure feasibility, and improve product maturity [3]. 3D printing can not only break through the design constraints of products and shorten the product development cycle but also significantly reduce costs.

Fused deposition molding (FDM) [4-6] is the most commonly used desktop 3D printer that relies on the process of melting and extruding a polymer filament from a nozzle and depositing it on a platform layer by layer until the preset model is created. The preset model is designed by computer-aided design. In addition to the properties of the molded material, the strengths of FDM-printed parts depend to a large extent on the choice of molding parameters, such as the raster angle, layer thickness, air gap, orientation, and other similar parameters. Mohamed et al. [7] studied the effects of different printing parameters on the dynamic mechanical properties of polycarbonate/acrylonitrile-butadiene-styrene (PC/ABS) composite. They found that the storage modulus, loss modulus, and mechanical damping of FDM-molded parts were promoted by an increase in the layer thickness. Moreover, if the air gap was reduced, the dynamic mechanical properties of the molded parts were enhanced. The raster angle had less of an
influence on the performance of the products. Durgun et al. [8] investigated the FDM process for improving the mechanical properties. They confirmed that the orientation had a more important influence than the raster angle on surface roughness. When the specimens were built with a raster angle of 0° in the horizontal direction, optimal mechanical properties and surface roughness with the optimum production time and cost were exhibited.

Materials used for FDM are thermoplastic polymers that can withstand multiple melt molding processes. During the FDM printing process, the material goes through high-temperature melting and rapid cooling to solidify, which has higher performance requirements for the material, such as crystallinity, dimensional stability, and forming warpage, such that limited materials can be used in FDM [9, 10]. Moreover, to be able to print a variety of different materials, the specifications of the printer are also more detailed because the maximum temperature that the printer nozzle can reach is higher than the melting point of the material. Theoretically, materials that can be used for FDM mainly include PC, ABS, polylactic acid (PLA), polyvinyl alcohol, polyamide (PA), and polyetheretherketone (PEEK) [11]. However, due to the high melting points of materials, such as PC and PEEK, only printers produced by a few manufacturers can satisfy the printing temperature. Currently, most FDM printers on the market are designed for PLA \( (T_m = 170^\circ C - 220^\circ C) \). The highest temperature that the nozzle can reach is 250°C, which makes it difficult to meet the printing temperature of PC \( (T_m = 240 - 270^\circ C) \).

To develop better materials for selective use in 3D printing, the development of polymer composite by mixing or blending of different polymers is necessary. PC and ABS materials are excellent thermoplastic engineering plastics. The PC matrix has good heat resistance, dimensional stability, and mechanical properties, but it also has disadvantages such as poor processing fluidity and notch sensitivity [12]. The ABS material has good processability and anti-notch impact sensitivity, and can make up for the shortcomings of PC [13]. Additionally, the melting point of ABS \( (T_m = 210^\circ C - 230^\circ C) \) is lower than that of PC. Blending PC and ABS to obtain a PC/ABS composite can not only reduce the extrusion temperature of PC to facilitate its application to FDM but also improve the processing fluidity and notch sensitivity of PC. Hence, the preparation of a PC/ABS composite filament that can be adapted to FDM printing is an excellent extension of the material range for FDM.

2. Experimental procedure

Three composites were produced using PC and ABS as matrix materials at a proportion of 70:30. The matrix materials were loaded with 6 wt.% maleinized acrylonitrile-butadiene-styrene copolymer (ABS-g-MAH; Dongyuan County Haoheng Plastic Factory, 9906B, China), 7 wt.% methacrylate-butadiene-styrene (MBS; Dow, MB880, America), and 3 wt.% organic montmorillonite (OMMT; Zhejiang Fenghong New Material Co., Ltd., industrial grade, China). As shown in table 1. Composites were produced as particles using a twin-screw extruder with the same extrusion parameters. The temperature profile was set as \( T_1 = 225^\circ C, T_2 = 240^\circ C, T_3 = 240^\circ C, T_4 = 245^\circ C, T_5 = 245^\circ C, \) and \( T_6 = 220^\circ C \). In addition, the mechanical properties of the three composites were compared with those of PC particles provided by Covestro Co., LTD, China.

| Matrix material | Additives (wt.%) |
|-----------------|-----------------|
|                 | ABS-g-MAH | MBS | OMMT |
| PC              | 0         | 0   | 0     |
| ABS             | 0         | 0   | 0     |
| PC/ABS          | 6         | 0   | 0     |
| PC/ABS          | 0         | 7   | 0     |
| PC/ABS          | 0         | 0   | 3     |

Next, each of the three composite materials was extruded through a single-screw extruder and removed to form a filament with a diameter of 1.75 mm. The formation of the filament was realized by the joint action of the single-screw extruder and the tractor. The process parameters are shown in table 2. Then, the filament was printed into the national standard samples in an FDM machine. The FDM
parameters are shown in table 3. Except the tensile specimens that were printed with a vertical orientation, all specimens were printed with horizontal (H), vertical (V), and perpendicular (P) orientations according to ISO 527, ISO 180, and ISO 178, respectively, as shown in figure 1.

**Table 2.** Molding parameters of PC/ABS composite filaments.

| Extrusion temperature | Traction condition |
|-----------------------|-------------------|
| Feeding section       | Compression section | Homogenization section | Cooling water temperature | Extrusion speed | Traction speed |
| 215ºC                 | 230ºC              | 225ºC                  | 55ºC                     | 800 rpm         | 580 rpm        |

**Table 3.** FDM parameters of PC/ABS composite filaments.

| Printing speed | Nozzle temperature | Platform temperature | Layer sickness |
|----------------|--------------------|----------------------|---------------|
| 30 mm·s⁻¹      | 230–240ºC          | 90ºC                 | 2 mm          |

**Figure 1.** Diagram of specimen orientations.

**Figure 2.** Difference in tensile strength and elongation between the horizontal and vertical test samples. I, PC material; II, ABS material; III, PC/ABS/ABS-g-MAH composite; IV, PC/ABS/MBS composite; and V, PC/ABS/OMMT composite.

All matrix materials and composite samples were tested to determine their mechanical properties. Tensile strength and flexural strength were tested using an Instron 5960 universal testing machine (Instron, MA, USA). The tensile test specimens were tested at a speed of 20 mm/min at room temperature. Figure 2 shows the tensile properties for the three material systems. The samples were tested for notch impact strength on an impact testing machine after a 2-mm notch was milled on a notch sampler. The notch impact strengths of the three composites are also shown in figure 3.
Figure 3. Notch impact test results of horizontally, vertically, and perpendicularly printed samples. I, PC material; II, ABS material; III, PC/ABS/ABS-g-MAH composite; IV, PC/ABS/MBS composite; and V, PC/ABS/OMMT composite.

The fractured surfaces of the composite samples after notch impact tests were observed using a scanning electron microscope (SEM) from JEOL (JSM-5510LV, Japan). The samples were first placed in an ion sputtering instrument to plate them with a layer of gold, and then the samples were placed on the platform of the SEM to observe the microscopic appearance of the fractured surface.

3. Results and discussion

3.1. Mechanical properties of printed samples

3.1.1. Tensile tests. Figure 2 summarizes the results of the strength and elongation tests for all the material systems tested for samples manufactured in both the horizontal and perpendicular printing directions. From the data for the horizontal strength of the different material systems, the strength of the PC sample was the highest. Moreover, PC samples printed in the H-orientation had better elongation. However, compared with PC, the ABS samples had inferior tensile strength and elongation, but the ABS system printed in the P-orientation had a preferable tensile strength. Interestingly, the three composite systems all had better tensile strengths in the P-orientation compared with the PC system. This was because the ABS component melted and bonded to the upper layer better at a melt printing temperature of 220°C–230°C. The adhesion between the layers was high, which increased the tensile strengths of the samples. Some systems with H-orientation printing revealed better tensile strength, while other systems showed worse tensile properties. This phenomenon might be due to the uniformity of different composite filaments and the properties of the composite itself. However, it also illustrated the immaturity of the current FDM technology. The performance of FDM products was affected by not only the properties of the printing materials but also the FDM process parameters. The performance differences of FDM samples were influenced by different process parameters and external environments, such as the oxygen content. As shown in figures 2(a) and 2(b), the PC/ABS/MBS composite printed in the H-orientation had both good tensile strength and elongation. Compared with the other two composites, the tensile properties of the PC/ABS/MBS composite were improved.
3.1.2. Notch impact tests. Figure 3 shows the notch impact strengths for all material systems. The notch impact strengths of the PC material printed in all three orientations were found to be much lower, consistent with the great notch sensitivity of the PCs. Many studies indicated that the blending of PC and ABS polymers could significantly decrease the notch impact sensitivity of PC. Figure 3 shows that although the notch impact strength of ABS was not very high, the notch impact strength of PC/ABS composite was greatly increased by the effects of ABS-g-MAH and MBS compatibilizers. The notch impact strength of the PC/ABS/OMMT composite was even lower than that of the PC material in any printing orientation. The OMMT was inserted into the polymer matrix of PC and ABS in a layer-shaped structure. The effective bonding between OMMT and the PC/ABS matrix was destroyed when the samples were notched by the milling cutter, resulting in defects at the notch and lowering of the notch impact strength of the PC/ABS/OMMT composite. Due to the specifics of the P-orientation printing, the notch impact strengths of all samples were very low.

3.2. Fractography of printed samples

3.2.1. H-orientation. Figure 4 shows the fractography of the composites printed in the H-orientation. The printed samples of PC/ABS/ABS-g-MAH and PC/ABS/MBS composites were regularly deposited and arranged neatly, and the cross-deposition of the filaments between the sample layers could be clearly seen. Shrinkage of the deposition filaments was observed in the fractured cross-section of the PC/ABS/ABS-g-MAH composite due to the force of the pendulum bob exerted on the specimen. The PC/ABS/MBS composite was closely bonded, but the deposition filaments were pressed into flat shapes rather than retaining their original cylindrical shapes. No obvious boundary was found between the layer and the fractured layer of PC/ABS/OMMT composite samples, and the adhesion of adjacent filaments in the same layer was also not obvious. This might be because the deposition temperature was too high for extruding the filament. The filament had great melt fluidity under high-temperature heating, such that the extrusion rate of the filament was much higher than the movement of the nozzle in the horizontal direction, resulting in accumulation.

![Figure 4](image-url)

**Figure 4.** SEM images of the fractures of the samples printed in the H-orientation: low magnification. (a) PC/ABS/ABS-g-MAH, (b) PC/ABS/MBS, and (c) PC/ABS/OMMT.

![Figure 5](image-url)

**Figure 5.** SEM images of the fractures of the samples printed in the H-orientation: high magnification. (a) PC/ABS/ABS-g-MAH, (b) PC/ABS/MBS, and (c) PC/ABS/OMMT.

Figure 5 shows the microscopic morphology of the natural impact sections of the three composites
at high magnification. The compactness of the PC/ABS/ABS-g-MAH composite sample was the highest, and the microstructure of the deposited filament was almost solid. The PC/ABS/MBS composite showed ductility at the impact fracture surface, but micropores appeared on the fracture. The PC/ABS/OMMT composite contained a larger number of micropores, and the compactness of the deposited sample was lower. Apparently, the presence of micropores led to a low-density sample, which affected the notch impact strength.

3.2.2. V-orientation. All breakage of the filament occurred on the impact fracture of samples printed in the V-orientation because the deposition direction of the filament was 45° in the interior structure of the sample. Compared with the samples printed in the H-orientation, the deposition direction of each layer of the filament was at an angle of 45° to the fracture surface. Thus, more filaments were impact-broken by the pendulum, but the resistance was greater, so that the impact strength was higher. The fractured filaments in the micromorphology confirmed that the notch impact strengths of the V-orientation-printed samples of each composite were better than those printed in the H-orientation (figure 6). However, the deposition effects of each composite filament for samples printed in the V-orientation were similar to those printed in the H-orientation. The samples of PC/ABS/ABS-g-MAH and PC/ABS/MBS composites were regular, and the PC/ABS/MBS composite filaments were bonded more tightly in the monolayer. The deposition effect of the PC/ABS/OMMT composite was similar to that of the H-orientation-printed samples, and it was difficult to distinguish obvious layer-to-layer boundaries.

Figure 6. SEM images of the fractures of the samples printed in the V-orientation: low magnification. (a) PC/ABS/ABS-g-MAH, (b) PC/ABS/MBS, and (c) PC/ABS/OMMT.

Figure 7 shows the microscopic morphology of the V-orientation printed composite at high magnification. The impact fracture surface of the PC/ABS/MBS composite in figure 7(b) shows a certain impact toughness. An obvious pit was observed as shown in figure 6(c), which might be because the OMMT was not completely inserted into the PC and ABS polymer chains in a sheet structure. Some incompletely distributed OMMT was embedded in the PC/ABS composite in the form of particles. Thus, samples had stress concentration points, such that the notch impact strength of the PC/ABS/OMMT-printed samples was much lower.

Figure 7. SEM images of the fractures of the samples printed in the V-orientation: high magnification. (a) PC/ABS/ABS-g-MAH, (b) PC/ABS/MBS, and (c) PC/ABS/OMMT.

3.2.3. P-orientation. Figure 8 shows the microscopic morphology of the natural impact section of the
three composites printed in the P-orientation at low magnification. Obviously, as the fractures of the P-orientation-printed samples were breaks between layers, the orientation of the nozzle-extruded filament on one layer was clearly observed, especially for the PC/ABS/ABS-g-MAH composite and PC/ABS/MBS composite. The PC/ABS/ABS-g-MAH composite had a tighter bond between the filaments in a layer. The PC/ABS/MBS composite was more closely bonded between adjacent layers, such that when it was impacted, the separation between the layers led to the destruction of the monolayer filament.

![Figure 8. SEM images of the fractures of samples printed in the P-orientation: low magnification. (a) PC/ABS/ABS-g-MAH, (b) PC/ABS/MBS, and (c) PC/ABS/OMMT.](image1)

The impact fracture surface of the P-orientation-printed samples was the separation between the layers. The microscopic morphology of the layer-to-layer separation was clearly observed. Figures 5 and 7 show the microscopic topography of the fracture of the deposited filament at high magnification, but figure 9 shows the morphology of the peeling between different layers of the deposited sample. The cross-section of the impact fracture surface was found to be rough, as shown in figure 9.

![Figure 9. SEM images of the fractures of the samples printed in the P-orientation: high magnification. (a) PC/ABS/ABS-g-MAH, (b) PC/ABS/MBS, and (c) PC/ABS/OMMT.](image2)

4. Conclusions

The addition of compatibilizers to PC/ABS composite affects the mechanical properties and molding properties of the filament. These systems are PC/ABS with 6% ABS-g-MAH, PC/ABS with 7% MBS, and PC/ABS with 3% OMMT. The notch impact strengths of all three systems greatly improved, and a good tensile strength was maintained. Especially for the PC/ABS/MBS system, the fractography of the notch impact samples was rough and complex, and the notch impact strength of the composite was even higher than that of pure ABS. The PC/ABS/MBS composite was characterized by both high strength and high toughness, but the melt fluidity was slightly poor.

The three composite systems were made into filaments and printed as samples with three different orientations. The ABS component provided great dimensional stability to the composite filament, such that the diameters of the composites could be better maintained at approximately 1.75 mm when made into filaments. The mechanical properties of the samples printed with a perpendicular orientation were poorer than the properties of those printed with horizontal and vertical orientations because of the specifications of the molding method. As the horizontally and vertically printed samples were printed
layer by layer, when the samples were subjected to a force, the effect of the multilayers greatly increased the mechanical strength, especially the notch impact strength. However, the PC/ABS/OMMT composite had a lower notch impact strength due to the properties of the nano-reinforced materials and the influence of the notch preparation.

Acknowledgment
This study was performed with the support of Guangdong Key Laboratory of Enterprise of 3D Printing Polymer and Composite Materials (No. 2018B030323001).

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