

# Effect of Cryogenic Treatment on Micro-structure and Properties of Different Polymer Materials

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**Abstract.** In order to improve the mechanical properties of the polymer materials, three kinds of samples with the same size were manufactured by the 3D printing equipment. And the materials were polycarbonate, ABS and polypropylene, respectively. After -190°C+8h cryogenic treatment, the mechanical properties such as wear resistance and hardness were tested and the functional groups and internal molecule chain changes were observed by Fourier transform infrared spectrometer. The results showed that the mechanical properties of polymer materials can be improved effectively after the cryogenic treatment. Compared with the untreated samples, the hardness of the PC, ABS and PP samples increased by 27.6%, 10.8% and 20.3% respectively. Among the three materials, the wear resistance of ABS material was improved obviously.

## 1 Introduction

3D printing technology, known as additive manufacturing technology, is a manufacturing method based on three-dimensional models, making the adhesive materials stack layer by layer in the principle of discretion and accumulation. As an advanced manufacturing technology, 3D printing provides a new method of manufacturing materials and structures. And it is an important complement to the traditional manufacturing technology system<sup>[1]</sup>.

At present Fused Deposition Modeling (FDM) has been widely applied in the field of science, education and family<sup>[2]</sup>. The thermoplastic polymer materials such as Polycarbonate (PC), Acrylonitrile - Butadiene - Styrene (ABS) and Polypropylene (PP) are used as the raw materials in this kind of technology. By the means of hot extrusion, the material is ordered stacked under the control of computer and finally the three-dimensional parts are obtained<sup>[3]</sup>. The 3D printed parts must have adequate mechanical strength, stiffness and wear resistance to ensure the durability of the final product<sup>[4]</sup>. Therefore, improving the performance of printed materials is the prerequisite for the universal application of 3D printed parts.

Cryogenic treatment is a kind of special heat treatment method. It usually refers to the cold treatment of raw materials in the environment of -190°C to -230°C, so as to improve the microstructure and properties of the materials<sup>[5]</sup>. Related studies showed that cryogenic treatment can improve the mechanical properties such as hardness and wear resistance of metal materials<sup>[6]</sup>, mainly

due to the elimination of residual austenite and the initiation of nucleation sites for the subsequent precipitation of large number of very fine carbide particles<sup>[7]</sup>. However, the effect of cryogenic treatment on the properties of polymer materials need to be further explored<sup>[8]</sup>.

In this paper, the three samples of different materials were produced by the technology of FDM. The samples were placed in -190 °C environment for 8h and then cooled to room temperature. The cryogenic treatment and untreated specimens were tested for wear resistance, hardness and Fourier transform infrared spectroscopy (FT-IR) to investigate the effects of cryogenic treatment on the properties of different polymer materials.

## 2 Experimental

The samples were tested by standards (GB/T 228.1-2010) of polymer materials mechanical performance, which were printed by rapid prototyping machines. The material of the the sample was PC, ABS and PP.

The samples of 150mm×4mm×20mm were drawn by 3D software<sup>[9]</sup>. Each of the three materials was divided into four groups and placed in SLX-80 cryogenic treatment box at -190 °C for 8h, respectively.

The wear resistance of the samples were tested by the MP-2B grinding and polishing machine (Laizhou Experimental Instrument Manufacturing Co., Ltd.) and electronic scales. The samples were exerted pressure of 1N and rotating at the speed of 500r/min with a 200-mesh electrostatic sand-grained alumina sand paper for 3min. The hardness of samples were tested by the HR-150A

Rockwell hardness taster. The German company Brook Vertex 70 Fourier infrared spectrometer scans range from 400cm<sup>-1</sup> to 4000cm<sup>-1</sup> and the resolution of is 1 cm<sup>-1</sup>, which was used to detect the change of the functional group and molecular chains.

### 3 Results and discussion

#### 3.1 Mechanical properties

##### 3.1.1 Wear resistance

The changes of the qualities of the samples were tested by the wear experiments for 3 min and listed in Table 1. It can be seen from the table that the wear resistance of the three materials is improved after the cryogenic treatment, especially the material of ABS. The cryogenic treatment can effectively improve the wear resistance of polymer materials with the poor properties. It is because the increased crystallinity can promote the interaction between molecules and the arrangement of material molecular chain tighter and more sequential as a whole.

**Table 1.** Test of wear resistance of different materials.

Experimental group	Weight before experiment (g)	Weight after experiment (g)	Loss of weight (g)	Proportion (%)
Untreated PC	4.1789	4.1690	0.0099	0.24
-190°C for 8h PC	3.3038	3.3017	0.0021	0.06
Untreated ABS	2.4574	2.4257	0.0317	1.29
-190°C for 8h ABS	2.7795	2.7631	0.0164	0.59
Untreated PP	2.4586	2.4479	0.0107	0.43
-190°C for 8h PP	2.7194	2.7181	0.0013	0.05

##### 3.1.2 Hardness

The hardness changes of the materials after cryogenic treatment were tested by Rockwell hardness tester. The surface of the samples were dotted repeatedly to eliminate the influence of extreme value. The results are shown in Table 2.

After cryogenic treatment, the hardness of the three kinds of materials increased by 27.6%, 10.8% and 20.3%, respectively. It can be seen that after the cryogenic treatment, the hardness of the three materials has been improved a lot. To some extent, this is because the development of the cryogenic treatment eliminated part of the residual stress.

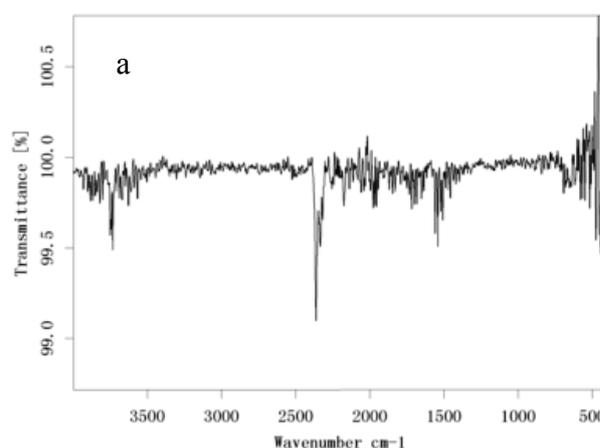
**Table 2.** Test of hardness of different materials.

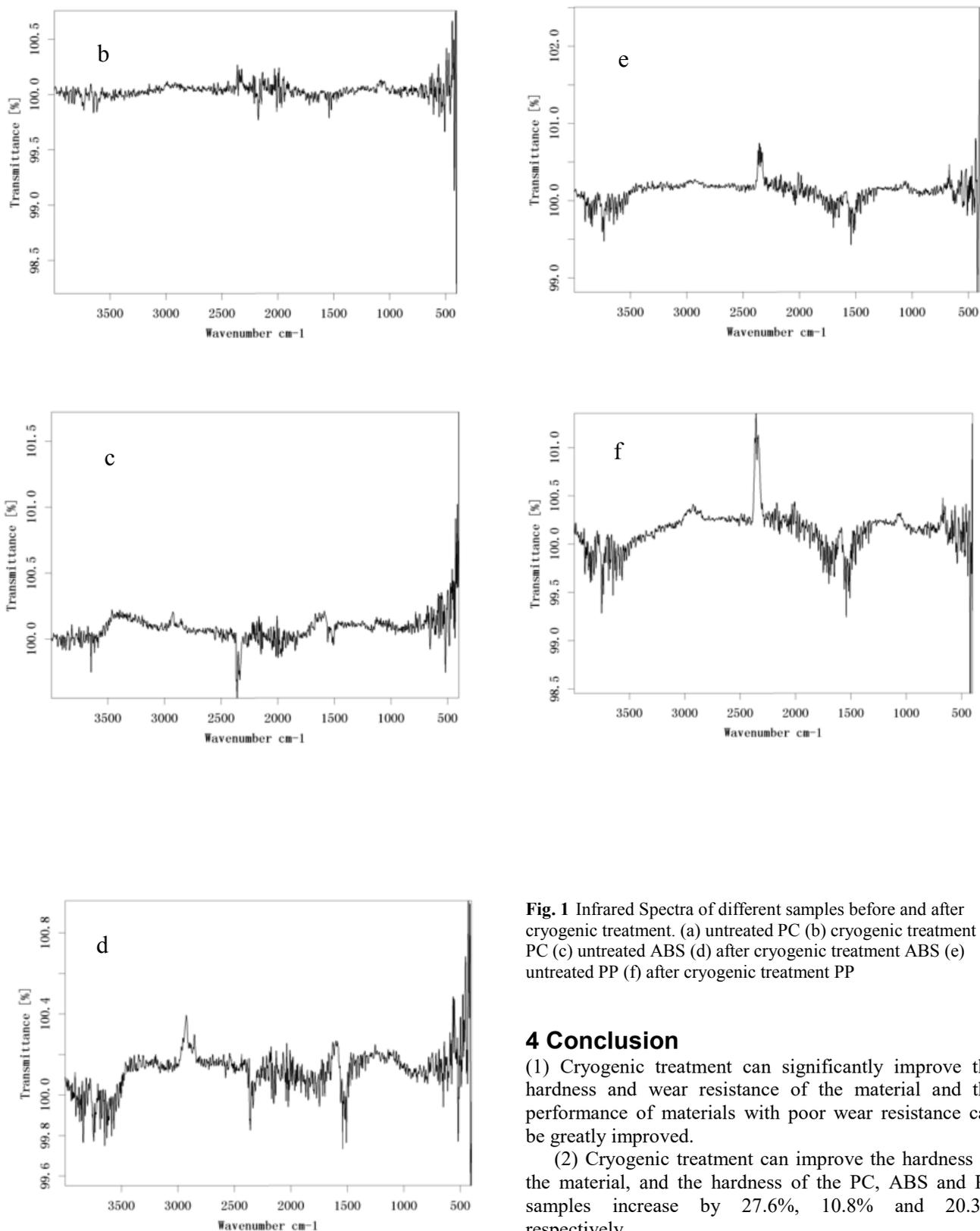
Experimental group	PC	ABS	PP
Untreated sample dot1	77	76.2	79
Untreated sample dot2	76	76.3	80
Untreated sample dot3	76	77	79
-190°C for 8h sample dot1	79.5	77	81.2
-190°C for 8h sample dot2	78	77.5	80.5
-190°C for 8h sample dot3	78	77.5	81.2

#### 3.2 Fourier transform infrared spectroscopy

The samples were characterized by Fourier transform infrared spectroscopy (Vertex 70) to observe the change of their functional groups [10]. The infrared spectra of the three kinds of materials are shown in Fig. 1.

There are three peaks near 1600, 1500 and 1450cm<sup>-1</sup>, especially the first two zone is an important feature of the aromatic ring belt. As is shown in Fig.1, the peaks were produced by the stretch vibration of the aromatic ring skeleton C=C. The area of 1900-2500cm<sup>-1</sup> is the cumulative double bond stretching vibration region, while the carboxyl may be at 3600cm<sup>-1</sup>. After cryogenic treatment, the infrared transmittance spectrum of the three materials showed an increase in the peak transmissivity, indicating a decrease in absorption, which caused the properties of the functional groups weakened, the molecular chain length increased and the crystallinity increased [11-13]. And the arrangement of material molecular chain became more ordered, the stability got enhanced and the relevant mechanical properties were improved.





**Fig. 1** Infrared Spectra of different samples before and after cryogenic treatment. (a) untreated PC (b) cryogenic treatment PC (c) untreated ABS (d) after cryogenic treatment ABS (e) untreated PP (f) after cryogenic treatment PP

#### 4 Conclusion

(1) Cryogenic treatment can significantly improve the hardness and wear resistance of the material and the performance of materials with poor wear resistance can be greatly improved.

(2) Cryogenic treatment can improve the hardness of the material, and the hardness of the PC, ABS and PP samples increase by 27.6%, 10.8% and 20.3% respectively.

(3) After cryogenic treatment, the properties of functional groups are weakened, the length of molecular chain is increased, the crystallinity is increased, the arrangement is more orderly, and the stability of the material itself is enhanced, which can contribute to the promotion of its application

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