Preparation of Novel Super-tough Poly（ethylene terephthalate）Engineering Plastic*

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Abstract: This research focused on a new kind of super-tough engineering plastic based on waste PET bottles chips. The processing technology of this polymer alloy is briefly introduced. This polymer alloy is prepared by low temperature solid-state extrusion and reactive extrusion. Via the reaction among chain extender and PET chips, three-dimension network was formed and the crystal structure in the bottle blowing process was maintained in the new blends. Toughening mechanism was studied, and the relationship between properties and the structure was analyzed.

Key words: PET; impact resistance; engineering plastic; low temperature solid-state extrusion; reactive extrusion; super-toughness
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1 Introduction

Recently, PET product in china has reached 1.2 million tons annually, and it is estimated, in 2005, requirements of PET beverage bottle will exceed 0.6 million tons. Rapidly increasing use of PET bottles results in a large amount of waste PET, which should be recycled in a cost－efficient manner. Traditionally, these PET was depolymerized into monomers, but for technical limits and the high cost, this technology has not been adopted wildly.[1-2]

This research was focused on the low temperature solid-state extrusion and the reactive extrusion of waste PET bottles. Not only the PET waste was re－used, but also a novel engineering plastic is prepared.[3-5]

2 Experimental

2.1 Materials and equipments

Waste PET bottle chips: Zijang Bottle Ltd.（Shanghai）; PC（polycarbonate）: Teijin Ltd（Japan）; Elastomer: Teijin Ltd（Japan）; MDI: Teijin Ltd（Japan）

Twin screw extruder: TSE-35A（Nanjin Ruiya Polymer Machine Ltd, China; Injector: QS-100T（Shanghai Quanshen Polymer Machine Ltd, China）; Drying equipment: MCE（Shanghai Qixin Machine Ltd, China）

2.2 Prepartion of specimen

PC and PET were dried at 120 ℃ for 4h, then pelletized by twin screw extruder, and injected to gain the specimen. In this experiment, chain extender was added in before extruding.

2.3 Characterization

Mechanical properties tests were conducted by WSM-20KN Mechanical properties testing machine produced by Changchun Mechanical Properties Testing Machine Ltd. Standards is as following: Tensile Strength（GB/T1040-1992）; Flexural Strength（GB/T9341-2000）; Charpy Impact Strength（GB/T1043-1993）.

Differential scanning calorimeter（DSC）was performed on NETZSCH DSC PC 200（German）. The process was carried out in the from 23to 300 ℃. The heating rate was 10 ℃/min. The glass transition temperature（T_g）was determined from the temperature diagrams as the temperature corresponding to the upper inflection point or maximum of the curve. The melting point（T_m）and crystallization temperature（T_c）were determined as corresponding to the maximum of the endothermic curve and the minimum of the exothermic curve, respectively.

Scanning electron microscope（SEM）was used to study the morphology of the fracture surface of the specimens via JSM 6100（jeol Ltd）.

The melt flow index（MFI）was tested by SRZ－400C（Changchun Mechanical Properties Testing Machine Ltd）according to standard GB/T3682-2000, at 260 ℃.

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3 Results and discussion

3.1 Low temperature solid-state extrusion

Water contained in PET chips together with the processing temperature are the key problem in this blend system. Water contained in the PET chips can cause the degradation of the PET long chain, and reduce the molecular weight of the blends. Also high processing temperature can cause degradation of polymer. To solve this problem, the PET and PC resins must be dried 4 hours by drying equipment to get rid of the water in the resin.

Properties of the alloy prepared at different processing temperatures are shown in Tab. 1, which proves that higher processing temperature result in poorer mechanical properties.

Tab 1 Properties of PET alloys prepared at different extrusion temperature

Extrusion Temperature/(℃)	100	160	260
Tensile Strength/(MPa)	47.00	44.55	46.01
Elongation at Break/(%)	103.61	42.59	15.86
Flexural Strength/(MPa)	70.66	61.97	65.89
Flexural Modulus/(GPa)	2.15	1.78	1.84
Charpy Impact Strength/(kJ·m^{-2})	20.36	16.17	8.55

In Tab. 1, three processing temperatures are chosen. The reason why we chose these three temperatures can be shown in Figure 1. Figure 1 is the DSC curve of the pure PET resin. From Figure 1, we can see there are three characteristic temperatures (T_g, T_c, T_m).

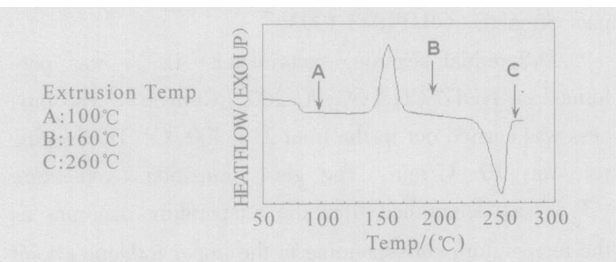

Fig 1 DSC curve of the amorphous PET (Tg: 81℃; Tc: 151℃; Tm: 253℃)

Temperature C (260 ℃) is above T_m. At this temperature, the processing is a melt processing which means all the raw materials were in liquid-state. Temperature B (160 ℃) is between T_c and T_m, temperature A (100 ℃) is between T_g and T_c. At 160 ℃, PET can cold crystallize; at 260 ℃, PET may melt and crystallize again after extrusion; Only at the temperature between T_g and T_c, PET can maintain the crystal structure, which was formed in the former bottle blowing. That is why we call it low temperature solid-state extrusion.

Low temperature solid-state extrusion not only can avoid losing molecular weight of PET, but also the former crystal structure was maintained in our alloy materials. All these improved properties of the alloy, which is shown in Tab. 1.

3.2 Reactive extrusion

MDI is a kind of diisocyanate, whose isocyano group (—NCO) can react with hydroxy group (OH) and carboxyl (COOH) of PET and PC. The reaction take place among PET and MDI, or PC and MDI, the molecular weight will be enlarged. Also those reactions take place among PET and PC can improve compatibility of the alloy. So MDI act as not only extender but also compatilizer.

Fig. 2 is MFI of different alloy. The lower MFI means higher molecular weight. Fig. 2 and Tab. 2 show that the higher molecular weight, the better mechanical properties. Especially the charpy impact strength, the alloy with MDI is three times higher than the one without MDI and reaches 65.81 kJ/m^2. That is why we call it super-tough engineering plastic.

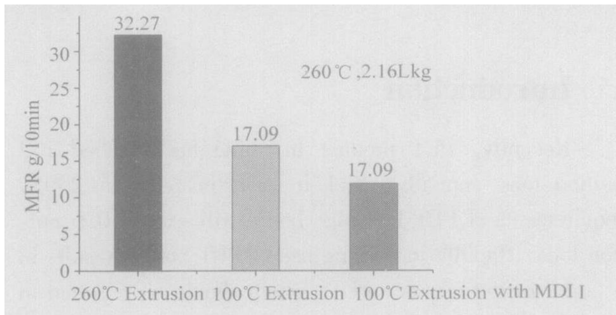

Fig 2 MFI of different alloy

Tab 2 Mechanical properties of PET alloy

Mechanical properties	A	B
Tensile Strength/(MPa)	47.02	43.63
Elongation at Break/(%)	114.28	120.09
Flexural Strength/(MPa)	60.80	67.39
Charpy Impact Strength/(kJ·m^{-2})	18.84	65.81

3.3 Toughening mechanism

SEM images of the fracture surface of the specimens are show in Fig. 3 and Fig. 4.

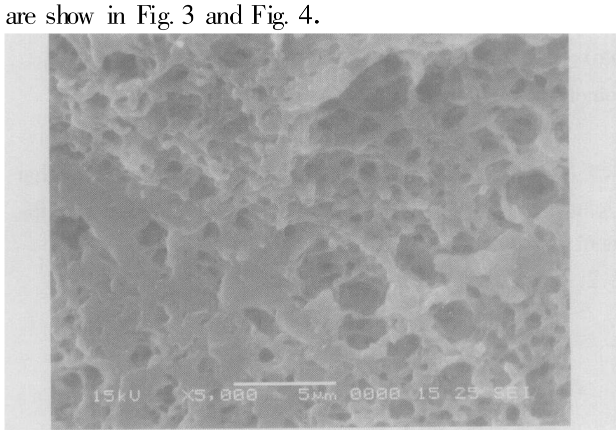

Fig 3 SEM of the alloy without MDI

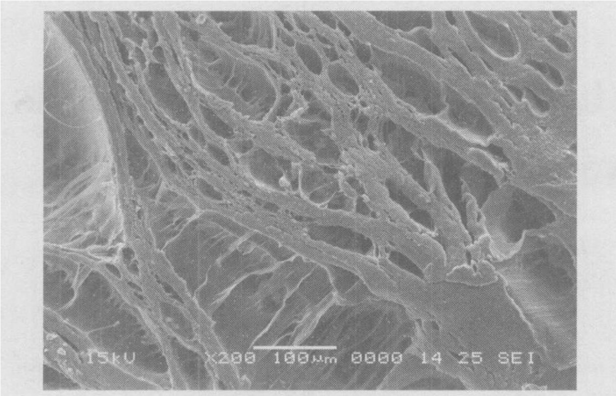

Fig 4　SEM of the alloy with MDI

Fig. 3 is the surface of the sample without MDI, and Fig. 4 is the sample with MDI. Fig. 3 shows the character of brittle fracture; otherwise Fig. 4 shows the character of ductile fracture. Furthermore, the one with MDI (Figure 4) shows that the structure of three-dimension network was formed, so the polymer alloy performs super-toughness.

In addition to the network structure, maintaining PET bottle's crystal structure and adding ealstomer are also contribute to toughness of the polymer alloy.

3.4　Application

With metal-like ductility, this polymer alloy can be processed in ambient temperature by extrusion, impact forging and molding. It will not break after tacked with a nail, and the fastness can be compared with that of the wood.

This alloy can be used in building materials, mobile phone shell and other industrial goods such as automobile accessory.

4　Conclusion

This research is based on waste PET bottles chips. By low temperature solid-state extrusion and reactive extrusion, a new kind of super-tough engineering plastic is prepared. Low temperature solid-state extrusion can avoid degradation of molecular weight and maintain the bottle-blowing crystal structure of PET. Reactive extrusion can enlarge the molecular weight, improve the compatibility of the blend and eventually benefit to form network structure. Because of the excellent properties, this polymer alloy can be widely used in many kinds of ways.

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新型 PET 超韧性工程塑料的制备

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摘　要：此项工作集中于基于回收 PET 瓶的高韧性工程塑料的研究。简要介绍了该聚合物合金的加工过程，其主要工艺是通过低温固相挤出和反应挤出制备。借助扩链剂与 PET 的反应，形成该材料的三维网络结构，同时保留吹瓶加工时的有序结构。研究了该聚合物合金材料的增韧机理，并分析其性能与结构的关系。

关键词：PET；抗冲击性能；工程塑料；低温固相挤出；反应挤出；超韧性
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