

Reactive Extrusion of Recycled Poly(ethylene terephthalate) with Polycarbonate by Addition of Chain Extender

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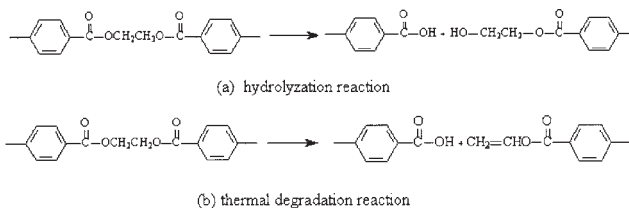
ABSTRACT: Poly(ethylene terephthalate) (PET) resin is one of the most widely used engineering plastic with high performance, but the poor impact strength limits its applications for the notch sensitivity. In this research, toughened PET alloy was prepared by blending recycled PET with polycarbonate (PC) and MDI (methylenediphenyl diisocyanate). Intrinsic viscosity and melt viscosity measurements proved increase of the molecular weights of PET via chain-extending reaction. FTIR and DMA results proved that some PET-PC copolymers were produced and the compatibility of PET phase and PC phase was improved. In addition, the

reaction induced by MDI also affected the crystallization behaviors of PET, as observed from DSC results, and the crystallinity of PET decreased with the increase of MDI content. For all of these effects of MDI of increasing of molecular weight, improving of compatibility, and limiting the crystallization behaviors of PET/PC alloy, the notched-impact strength was greatly improved from 17.3 to 70.5 kJ/m². © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2602–2607, 2007

Key words: poly(ethylene terephthalate) (PET); polycarbonate (PC); reactive extrusion; impact strength; compatibility

INTRODUCTION

Poly(ethylene terephthalate) (PET) has been widely used as soft drink bottles because of its transparency, high chemical resistance, and beneficial barrier properties. Rapid increase in the use of PET bottles results in a large amount of waste PET. It is of great importance to study blending of PET with various polymers^{1–9} so as to convert the recycled PET into high-performance engineering plastic. Polycarbonate (PC) and PET were reported to be partially miscible polymers,^{10–19} and the resulting alloy had properties combining the high impact toughness, good dimensional stability from the PC and excellent solvent resistance from PET. However, simple blending of PET and PC in a mixer will most probably produce a phase-separated PET/PC mixture^{20–23}; attentions have been paid to improve the compatibility between PET and PC. Another key issue in the blending was that molecular weights of PET decreased during the processing because of hydrolytic degradation (a) and thermal degradation (b).



Adding certain chain extenders is an effective way to increase the molecular weights (or melt viscosity) of PET. Some popular chain extenders are dianhydrides, bis(oxazolines), bis(dihydrooxazine), carbodiimides, diepoxides, and diisocyanates. Aharoni et al.²⁴ studied the chain extension reaction of PET with 0.5–2.5 wt % of triphenylphosphite (TPP). Although TPP greatly increased the molecular weight of PET, one drawback was that this reaction also produced diphenylphosphite as byproduct. Inata and Matsumura^{25,26} reported chain extension of recycled PET with addition-type heterocyclic bifunctional compounds such as oxazolines, oxazines, or oxazinones. These compounds reacted with the carboxyl or hydroxyl end group of PET and resulted in chain-extended PET with low carboxyl content. Cardi et al.²⁷ confirmed the chain extension of recycled PET by adding 2,2-bis(2-oxazoline). Haralabakopoulos et al.²⁸ showed that some commercially available cyclic diepoxides were effective in chain extension of PET. Xanthos et al.²⁹ used a diimido-diepoxide compound with low molecular weight and high melting point to reactively modify

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PET, and there was an overall increase in intrinsic and melt viscosities.

In this research, MDI (methylenediphenyl diisocyanate) was used as chain extender to increase the molecular weight of PET. As isocyanate group of MDI can react with hydroxyl and carboxyl end group of PET and PC, it also may improve the compatibility of this blending system.

EXPERIMENTAL

Materials and sample preparation

Recycled PET bottle flakes were provided by Zijang Bottle Co. (Shanghai, China), intrinsic viscosity (IV) = 0.65 dL/g; PC was supplied by Teijin Co. (Japan), IV = 0.70 dL/g. MDI (methylenediphenyl diisocyanate) was supplied by Japan Polyamide Incorporation (Japan). Some elastomers, stabilizers, and processing aids were also added in the blends. No other additives were used to catalyze transesterification between PET and PC, because certain extent of transesterification would decrease molecular weight of PET.

Before blending, PC and PET were dried at 120°C in a vacuum oven for at least 4 h. Blends were prepared in a TSE-35A twin-screw extruder ($L/D = 45$, Nanjin Ruiya Polymer Machine Co., China) at a temperature range of 100–240°C and a screw speed of 100 rpm. The extrudates were pelletized at die exit, dried, and injection molded into standard dumbbell tensile specimens (150 mm gauge length, 10 mm width, and 4 mm thickness) and rectangular bars (80 mm length, 10 mm width, and 4 mm thickness) by a QS-100T injection-molding machine produced by Shanghai Quansheng Polymer Machine Co. (China). The barrel temperature of injection-molding machine was kept at 240°C, and the mold temperature at 40°C. The rectangular bars were subsequently used to izod-notched impact testing. A 45° V-notch (depth = 0.8 mm) was machined midway on one side of the bar with a slow speed to avoid plastic deformation. Finally, specimens with the same weight ratio of PET and PC (70/30) but containing different amounts of MDI (0–1.1 wt %) were prepared.

Characterization

Viscosity measurements were carried out in a mixture of phenol and dichloroethane (60:40 by volume) using an Ubbelohde dilution viscometer. The intrinsic viscosity (η) was determined by extrapolation using the Huggins equation.

The melt flow rate (MFR) was tested by SRZ-400C made by Changchun Mechanical Properties Testing

Machine (R.P.R.), according to Chinese standard GB/T3682–2000, at 260°C.

Attenuated total reflection (ATR) FTIR spectra were performed by using a Bruker Vector 22 instrument in the range of 700–4000 cm^{-1} . The specimens were etched in chloroform to remove PC before being investigated.

Loss modulus (E'') and its temperature dependence of the alloy were determined by a Japan UBM dynamic mechanical analyzer. DMA test was conducted with the heating rate of 3°C/min and frequency of 11 Hz in the temperature range of 30 to 200°C using the compression-molded plate specimen with the thickness of 2.5 mm.

Differential scanning calorimetry (DSC) was performed on NETZSCH DSC PC 200 (Germany) in the temperature range of 23–300°C. The heating rate was 10°C/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.

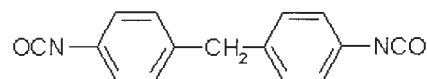
A Jeol JSM-35CF Scanning electron microscope (SEM) was used to study the morphology of the fracture surface of the specimens. The specimens were impact fractured at ambient temperature, and the fractured surface was gold-coated with a thickness of 0.3 μm .

Mechanical property tests were conducted by WSM-20KN Mechanical properties testing machine produced by Changchun Mechanical Properties Testing Machine Ltd. according to the Chinese standard (GB/T1040–1992) for tensile strength and elongation at break, GB/T9341–2000 for the flexural strength and flexural modulus, and GB/T1043–1993 for izod impact strength.

RESULTS AND DISCUSSION

Chain-extending reaction

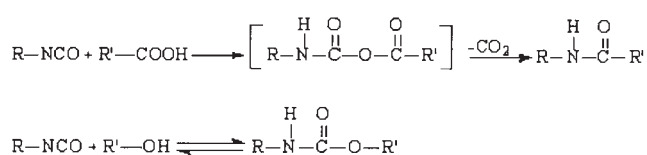
MDI is a kind of diisocyanate used widely in producing polyamide (its molecular formula is shown below).



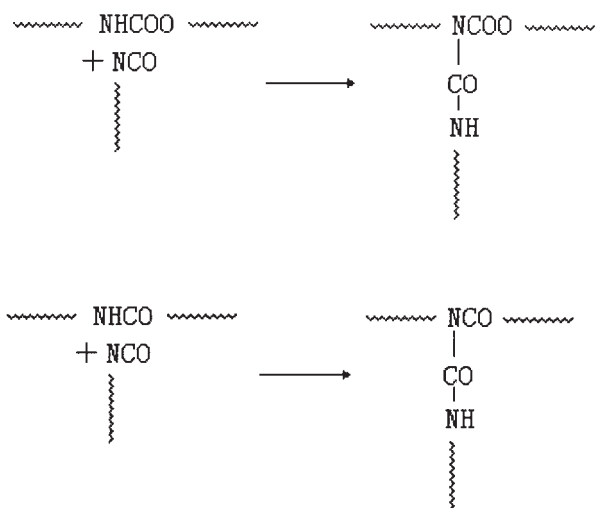
In this blending system, its isocyanate group ($-\text{NCO}$) also can react with hydroxy and carboxyl end group of PET and PC.

TABLE I
Intrinsic Viscosity (η) and Melt Flow Rate (MFR) of the Alloys with Different MDI Contents

MDI content (wt %)	Intrinsic viscosity [η] (dL/g)	Melt flow rate (MFR) (g/min)
0	0.67	13.52
0.1	0.70	10.14
0.3	0.74	5.92
0.5	0.75	4.02
0.7	0.85	3.89
0.9	0.92	2.05
1.1	—	1.82



But if the reaction proceeds for long enough time or MDI was over added excessively, the product will be crosslinked like the progress of producing polyamide because of the extraordinary activity of isocyanate group. Residual isocyanate group can react with the hydrogen of urethane or amide groups to form allophanate or urea.



The crosslinked structure will affect the ductility of the blend; hence, the chain extending reaction should be controlled within a certain extent. In this research we fixed processing parameter on extruding time of components staying in twin-screw extruder, and paid more attention to the effect of MDI content on reactive degree. The effect of MDI content on MFR and intrinsic viscosity (IV) of the alloy is listed in Table I. Table I shows that the intrinsic and melt viscosities of the alloy increased with the increasing content of MDI, which proved that the chain-extending reaction in-

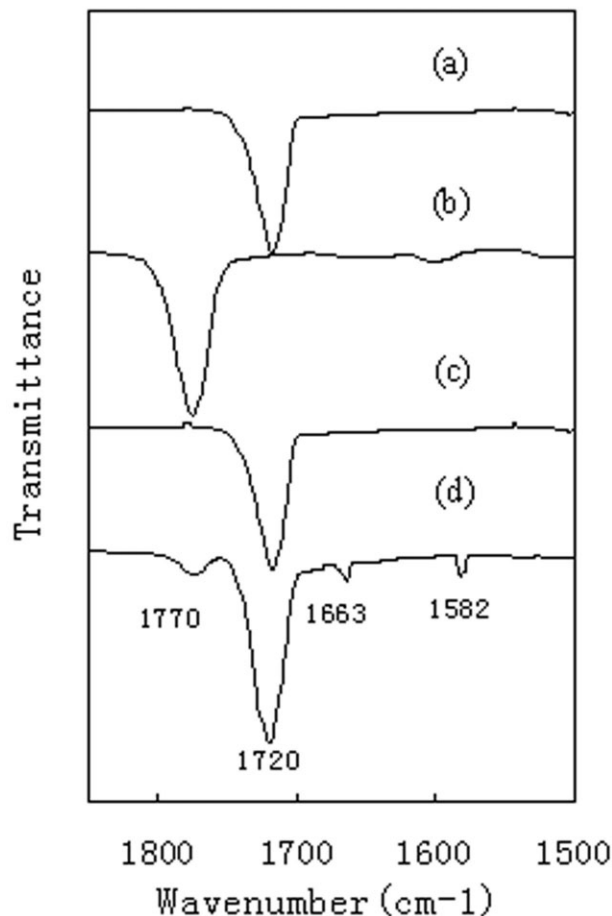


Figure 1 FTIR spectra of bulk PET and PET alloys. (a) bulk PET, (b) bulk PC, (c) the alloy without MDI, and (d) the alloy with MDI added (0.9 wt %).

creased the molecular weight of the alloy. There was no description about IV of the specimen when MDI content is 1.1%, because this specimen cannot be completely dissolved in the mixing solvent of phenol and dichloroethane, which suggests that the alloy was crosslinked when MDI content exceeded 1.1%.

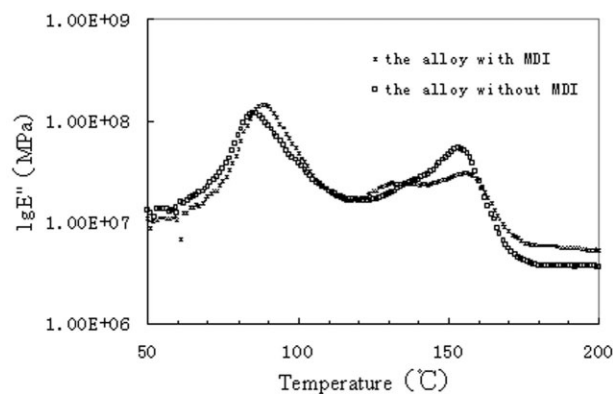


Figure 2 Loss modulus (E'') and its temperature dependence of the alloy with MDI added and without MDI.

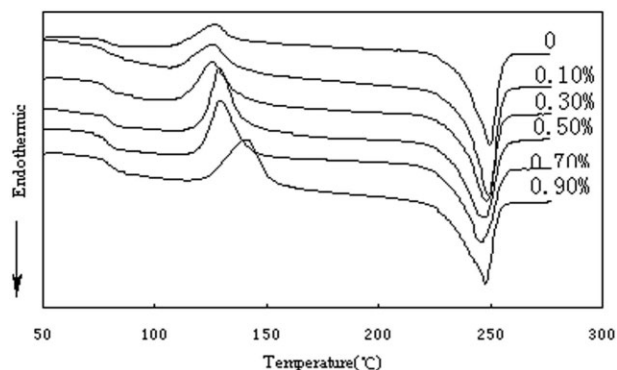


Figure 3 DSC curves of PET alloys with different MDI content.

More details about the reaction are shown in the FTIR spectra of the specimen in Figure 1. Before being characterized by FTIR, the blend specimens were etched by chloroform to remove PC. From Figure 1, the curve of the alloy without MDI (spectrum (c)) was similar to the one of the bulk PET (spectrum (a)), and the peak 1720 cm^{-1} arose from $\text{C}=\text{O}$ stretching of PET. It suggested that there was no chemical bond between PET and PC in this alloy because PC was easily removed by being soaked in the solvent. In other words, there is no reaction such as transesterification between PET and PC in this low temperature blending condition. But the curve of the alloy containing MDI showed distinct differences from the former ones. Two peaks around 1663 and 1582 cm^{-1} due to amide ($-\text{NH}-\text{CO}-$) group were found. It proved that the chain-extending reaction induced by MDI happened, as the amide groups were the outcome of reaction between isocyanate group (in MDI) and carboxyl group (in PET or PC). Torres et al.³⁰ reported hydroxyl end groups of PET could preferentially react with NCO groups of MDI. But based on Figure 1(d), we can not quantify by infrared analysis the characteristic peak of urethane groups ($1690\text{--}1740\text{ cm}^{-1}$), because there were two broad peaks located at 1720 and 1770 cm^{-1} .

In addition, the peak around 1770 cm^{-1} appearing in Figure 1(d) was due to $\text{C}=\text{O}$ stretching of PC [like the bulk PC in Fig. 1(b)]. It can be concluded that some PC chains were connected with PET. In other words, some PET-PC copolymers were made when PET and PC were blended with MDI.

Effect of MDI on compatibility of the system

As PET and PC are partly miscible polymers, simple blending probably produces phase-separated morphology, which leads to low mechanical properties. As a third component with active group, MDI can react with both end groups of PET and PC, and it can improve compatibility between PET and PC.

Examining glass transition temperatures of two components with different compositions approaching or detaching is an effective way to study the compatibility of blends. DSC and DMA are always used to investigate the glass transition temperature in this field. As observed by DSC on this blending system, the cold-crystallization exotherm of PET and the glass transition temperature of PC are adjacent in the curve; so it is hard to discern the glass transition temperature of PC. But there is not such limitation for DMA curves; the loss modulus peaks can indicate the glass transition temperatures legibly without the effect of PET crystallization behavior.

DMA results of two specimens with the same composition of PET and PC (MDI content = 0 or 0.9%) are shown in Figure 2. Two loss modulus peaks, referring to glass transition temperatures of PET (84.3°C) and PC (154.5°C), respectively, can be found in the curve of the alloy without MDI. As the alloy with MDI, the glass transition temperature of PET moves to the higher temperature to 91.2°C because of the increase of molecular weight caused by chain-extending reaction. On the other hand, when a fraction of MDI reacted between PET and PC, which could create some PET-PC copolymers, the loss modulus peak of PC turned broad (there was a third peak at 130°C due to T_g of PET-PC copolymers). As these two glass transi-

TABLE II
DSC Data of PET Alloys with Different MDI Contents.

MDI (wt %)	T_g ($^\circ\text{C}$)	T_c ($^\circ\text{C}$)	ΔH_c (J/g)	T_m ($^\circ\text{C}$)	ΔH_m (J/g)	Crystallinity ^a (wt %)
0	76.5	126.9	10.87	249.7	33.58	22.4
0.1	78.5	125.5	12.77	248.7	40.31	27.1
0.3	78.4	125.5	18.68	248.3	35.06	16.1
0.5	79.8	129.3	24.53	247.1	37.71	13.0
0.7	79.3	129.6	21.81	246.1	35.10	13.1
0.9	80.4	140.6	22.54	248.2	34.88	12.1

^a Crystallinity = $(\Delta H_m - \Delta H_c)/k\Delta H_m^* \times 100\%$, where $\Delta H_m^* = 144.664\text{ J/g}$, is the melt enthalpy for 100% crystallized PET, k is the weight proportion of PET in the alloy (70%).

TABLE III
The Mechanical Properties of the Alloys with Different MDI Contents

Property	MDI content						
	0	0.1	0.3	0.5	0.7	0.9	1.1
Tensile strength (MPa)	50.11	51.31	49.62	53.64	52.44	48.67	43.35
Elongation at break (%)	235.32	221.50	202.71	200.64	201.85	180.67	120.25
Flexural strength (MPa)	75.23	76.21	73.54	69.30	72.64	75.27	68.58
Flexural modulus (GPa)	2.15	2.17	2.20	2.35	2.20	2.30	1.92
Unnotched impact strength (MPa)	48.56	NB	NB	NB	NB	NB	42.62

NB, not broken.

tion temperatures approach together, conclusion could be drawn that compatibility of PET and PC had been improved by adding MDI.

Effect of MDI on crystallization behaviors of PET

The mechanical properties of alloys are related with the crystallization behaviors of crystal component, and it was reported³¹ that increasing crystallization rate and crystallinity would lower the ductility of PET blends.

DSC curves of PET alloys extruded with different MDI content are shown in Figure 3 and the relevant data are compiled in Table II. From Figure 3, it is found that the glass transition temperature and crystallization temperature of PET change regularly with the MDI content. With the MDI content increasing, both T_g and T_c moved toward higher temperatures (T_g 's were from 76.5 to 80.5°C, T_c 's were from 126.9 to 140.6°C). In an opposite way, a decrease of crystallinity of PET was observed (from 22.4% to 12.1%).

When MDI was introduced in this blending system, on the one hand, the chain-extending reaction among PET would make the molecular weight of PET increase; on the other hand, the reaction between PET and PC restricted movements of PET chains. As the

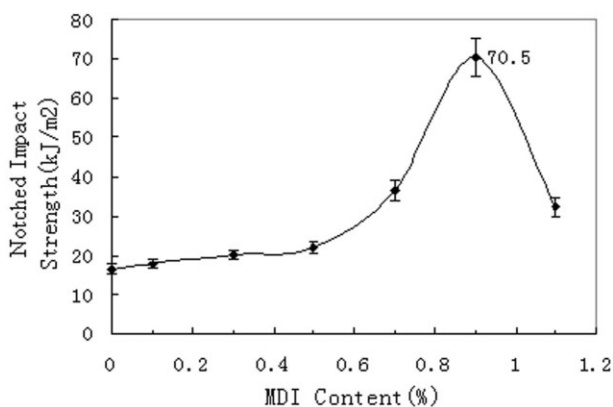


Figure 4 Effect of the MDI contents on impact strength of the alloy.

mobility of PET chains decreased, PET was more difficult to crystallize than that without MDI, and its cold crystallization temperature increased together with decrease of the crystallinity.

Mechanical properties of PET/PC alloy

Table III shows the mechanical properties of the alloys with different MDI contents, and the effect of MDI content on notched impact strength is shown in Figure

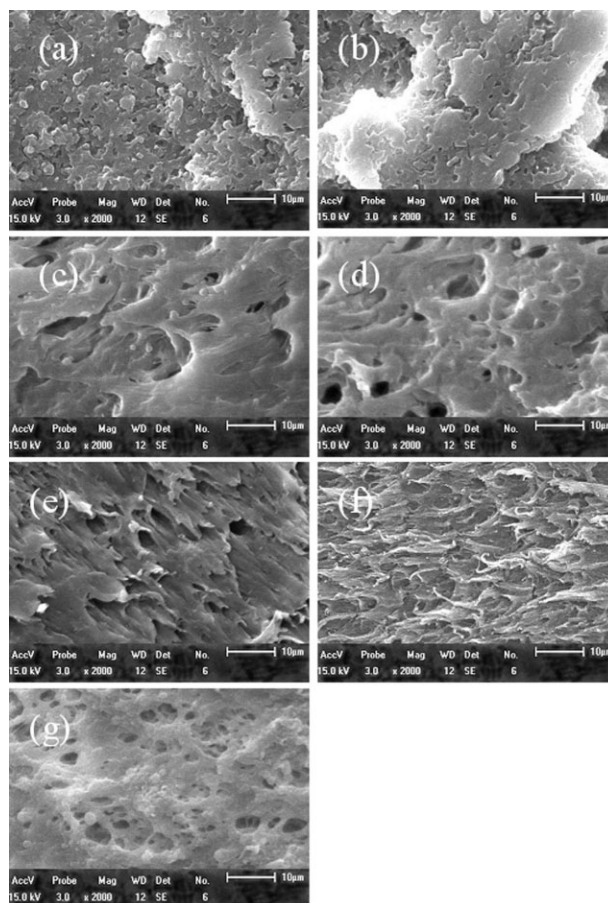


Figure 5 SEM images of impact-fractured surfaces of the alloy with different content of MDI (a) 0%, (b) 0.1%, (c) 0.3%, (d) 0.5%, (e) 0.7%, (f) 0.9%, and (g) 1.1%.

4. There are not so much differences between the alloy with or without MDI in tensile and flexural properties; only when MDI reached excessive content ($>0.9\%$), such properties had decreased to some extent.

The effect of MDI on notched impact strength is obvious. From Figure 4, all specimens with MDI show higher notched impact strength than those without MDI, especially the one with MDI content of 0.9% reached the maximum (70.5 Mpa), which suggested that the toughness of the alloy was strikingly improved on adding MDI.

Figure 5 shows the SEM impact-fractured surface images of the alloy with different MDI contents. Brittle–ductile (B–D) transition of the PET/PC alloy can be observed. The alloy without MDI clearly showed separated phase [Fig. 5(a)] and displays a brittle surface. With MDI fed, the compatibility between PET was improved and the dispersed phase size had been reduced [Fig. 5(b)]. With MDI content increasing, the fracture began to display cavitation [Fig. 5(c,d)] and matrix shear yielding [Fig. 5(e,f)]. The alloy with 0.9% MDI showed full extent of matrix yielding, and its impact strength value was the largest one among all the samples. But when the content reached 1.1% , the impacting property decreased to some extent because of its crosslinked structure.

CONCLUSIONS

The PET/PC alloy is prepared by reactive extrusion of recycled PET with PC by addition of chain-extender: MDI. By adding MDI, the molecular weights of components increased and the compatibility between PET and PC has been improved. So it can be considered that MDI acted both as chain extender and as compatibilizer in this blending system. In addition, MDI also affected crystallization behaviors of PET. The alloy's mechanical property had been improved, for example, the notched impact strength was up to 407.5% from 17.3 to 70.5 kJ/m^2 .

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