Recycling of Waste Poly(ethylene terephthalate) into Flame-Retardant Rigid Polyurethane Foams

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ABSTRACT: Waste poly(ethylene terephthalate) (PET) textiles were effectively chemical recycling into flame-retardant rigid polyurethane foams (PUFs). The PET textile wastes were glycolytically depolymerized to bis(2-hydroxyethyl) terephthalate (BHET) by excess ethylene glycol as depolymerizing agent and zinc acetate dihydrate as catalyst. The PUFs were produced from BHET and polymeric methane diphenyl diisocyanate. The structures of BHET and PUFs were identified by FTIR spectra. The limiting oxygen index (LOI) of the PUFs ($\geq 23.27\%$) was higher than that of common PUFs (16–18%), because the aromatic substituent in the depolymerized products improved the flame retardance. To improve the LOI of the PUFs, dimethyl methylphosphonate doped PUFs (DMMP-PUFs) were produced. The LOI of DMMP-PUFs was approached to 27.69% with the increasing of the doped DMMP. The influences of the flame retardant on the foams density, porosity, and compression properties were studied. Furthermore, the influences of foaming agent, catalyst, and flame retardant on the flame retardation were also investigated. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40857.

INTRODUCTION

Because of the excellent thermal and mechanical properties and nontoxic nature, poly(ethylene terephthalate) (PET) is a widely used polymer in the textile industry, electron industry, packaging industry as the fiber, electrical insulating materials, engineering plastics, and blow molding bottles.[1] Although without a direct contamination in the environment, PET is still considered as a noxious material because of substantial contribution in solid waste generation and high resistance to natural degradative assimilation in the environment. Therefore, effectively recycling of PET waste into useful products is a possible way to protect the environment and preserve the natural resources.

The main sources of PET waste for recycling contain manufacturing waste and the postconsumer waste. Theoretically, there are more than 90% of the PET waste could be recycled and reused. The common way of recycling PET waste could be divided into physical and chemical methods. The physical method is to melt, purify, and modify the PET waste and produce them to polyester products again. The chemical method defines as the depolymerization of PET waste into oligomer. Comparing with the physically recycled PET, which could only be formed to degradative products, the chemically recycled PET through depolymerization could be formed to the polymer itself or some other value added products.[2–4]

The methods of the PET depolymerization are hydrolysis, glycolysis, aminolysis, and methanolysis.[5–10] Comparing with other aforementioned methods, glycolysis of PET waste is a convenient method to recycle polymer because of the relative mild reaction conditions and decent yield of oligomer. The main glycolysis products of PET are bis(2-hydroxyethyl) terephthalate (BHET) and terephthalic acid (TPA). How to use the depolymerized oligomer effectively is another important research topic in the field of recycling PET waste. In the recent years, researchers have used the glycolysis products to synthesize kinds of useful products. Kilinc et al. depolymerized PET with ethylene glycol and synthesized the depolymerized products as the PVC secondary plasticizer.[11] Dutt and Soni converted PET waste into polymeric plasticizer with 2-ethyl-1-haxenol and applied it to nitrile rubber and nitrile-PVC blend.[12] Malinconico and coworkers synthesized unsaturated polyester resin from postconsumer PET bottles.[13] Atta et al. recycled PET waste into polyurethane for petroleum sorbent.[14] Shukla et al. synthesized disazo disperse dyestuffs,[4] hydrophobic dyestuffs,[15] and textile auxiliaries[16] from the glycolysis products of PET bottle waste.
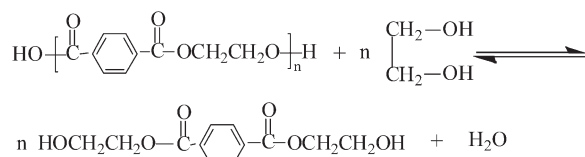
Scheme 1. PET glycolysis with EG.

It is especially worth to mention that, most of the researches recycled the PET from bottles because of the high purity of PET. Few investigations are focus on the recycle of PET fibers and/or textiles because of the influence of the textile dyeing and/or finishing auxiliary on the glycolysis products and the value added products.[17] Actually, the majority of the world's PET production is for synthetic fibers and textiles (in excess of 60%), with bottle production accounting for around 30% of global demand. In the context of PET textile applications, a huge amount of manufacturing and postconsumer PET textile waste generates every year. It inspires us to convert the PET textile waste into useful products. We consider that the depolymerized products (BHET) could be used for the raw materials of producing polyurethane foams (PUFs). Some researches of recycling PET bottle into PUFs are reported. Roy et al. tertiary recycled PET waste into glycolysate with diethylene glycol under the microwave. Then the glycolysate were reacted with adipic acid and sebacic acid to obtain the aromatic oligoesters for the raw materials of polyurethane-polyisocyanurate foams.[14] Atta et al. recycled PET waste with trimethylolpropane or pentaerytheritol. Then the oligomers were reacted with 2,4-toluene diisocyanate to produce PUFs.[18] On the basis of the researches of Atta and Roy, we consider that the purity of depolymerized PET textile (BHET) is suitable for synthesis PUFs.

In this article, we provided a method to recycle PET textiles into flame-retardant rigid PUFs. The waste PET textiles were depolymerized to BHET and synthesized as the flame-retardant rigid PUFs in the presence of polymeric methane diphenyl diisocyanate, foaming agent, catalyst, and flame retardant. The flame-retardant rigid PUFs could be used as thermal insulation wall materials, packing materials, and so on. This method could be applied in recycling PET waste from films, bottles or fibers as well as textiles.

EXPERIMENTAL

Materials
Waste PET textiles were obtained from Bosideng Downwear, Ltd (Jiangsu, China), which were cut into pieces of ~5 mm^2 surface area. The cutted-textiles were washed with water and acetone successively, and then dried at 80°C for 8 h until the weight of cutted-textiles were invariable.

Ethylene glycol (EG), zinc acetate dihydrate, silicone oil, Tin(II)bis(2-ethylhexanoate), dimethyl methylphosphonate (DMMP), all of CP grade, were purchased from Sinopharm Chemical Reagent, Ltd. (Shanghai, China). Polymeric methane diphenyl diisocyanate (PMDI, NCO content 31.2%), was purchased from Juyou Chemical Reagent, Ltd. (Xiamen, China). Distilled water was used as a blowing agent.

Glycolysis of PET
A 500 mL four-necked round-bottom glass flask equipped with a thermometer, a reflux condenser, a nitrogen catheter and a magnetic stirrer was used for the glycolysis experiments. Fifty grams of PET wastes were degraded using excess of EG (3 times weight of PET) in the presence of zinc acetate dihydrate as a transesterification catalyst. The glycolysis reactions (Scheme 1) were processed at 196–200°C under nitrogen atmosphere for 4 h. The glycolysis products were purified through repeated crystallization to get 82% yield of BHET. The hydroxyl values (HV) 423.5 mg KOH/g were determined by acetylarion of samples dissolved in pyridine by acetic anhydride, followed by back titration of excess reagent with 1 N sodium hydroxide solution.[19] The acid values (AV) 0.12 mg KOH/g were determined by titration of samples dissolved in prydinc with 0.1 N potassium hydroxide solutions.[20]

Synthesis of Flame-Retardant Rigid Polyurethane Foams
The flame-retardant rigid PUFs were prepared by one-step and free-rise method with the chemical compositions showed in Table I. Distilled water, tin(II) bis(2-ethylhexanoate), silicone oil, and DMMP were used as the foaming agent, catalyst, stabilizer, and flame retardant, respectively. All of the materials, except PMDI, were mixed in a beaker with mechanical stirring at the speed of 1000 rpm. To confirm the completion of the reaction, excess PMDI (NCO/OH = 1.1 : 1, in molar ratio) was added into the beaker and stirred for 10 s.[21] The mixture was immediately poured into an open mold (ϕ 60 × 100 mm^3) to produce free-rise foam in 2–10 s. A series of reactions occurred while the foams were produced[22]: (1) the addition polymerization of PMDI and BHET (Scheme 2a); (2) the reaction of PMDI and water to generate the unstable intermediate carbamic acid, and the decomposition to amine and carbon dioxide (Scheme 2b), the mixture expanded dozens of times in several seconds; (3) the side reaction of amine and PMDI to generate biuret diisocyanate (Scheme 2c). Then, the foams were kept in an oven at 60°C for 24 h, to complete the polymerization reaction. The test samples were cut from the cured foams and rubbed with fine emery papers.

Characterization
Fourier-transform infrared (FTIR) spectra of BHET and PU foams were obtained on a Nicolet Nexus-470 IR Spectrometers (Thermo Nicolet, USA) with KBr as a reference material. The scanning range was 650–4000 cm^{-1} and the resolution was 1 cm^{-1}.
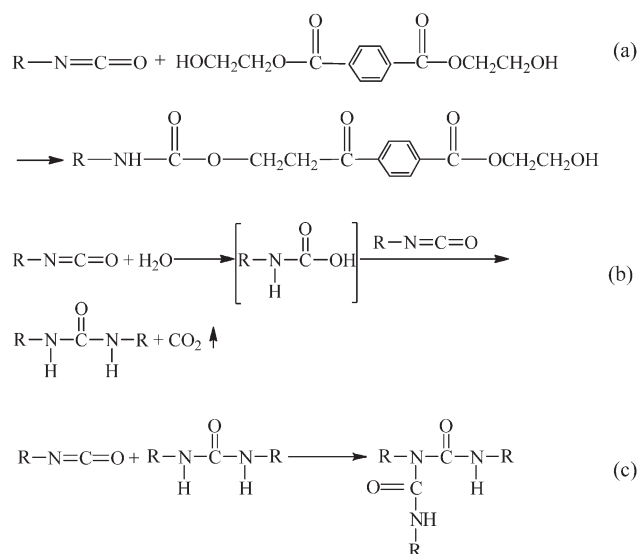
Morphology of PUFs was observed by using a DMC-TZ7 digital camera (Panasonic Corporation, Japan) and a Zoom 645 optical microscope (Maidisen Trument, Nanjing, China).

Table I. Formulation of Lame-Retardant Rigid Polyurethane Foams

Component	Parts by weight[a]
BHET	100.0
PMDI	133.0
Silicone oil	3.0
Distilled water	3.0–6.5
Catalyst	2.5–6.5
DMMP	0.0[b], 5.0–18.0

[a] Parts per hundred of BHET by weight.
[b] Part of DMMP at zero means PU foam without DMMP.

Scheme 2. Synthesis of PU foams with PMDI and BHET.
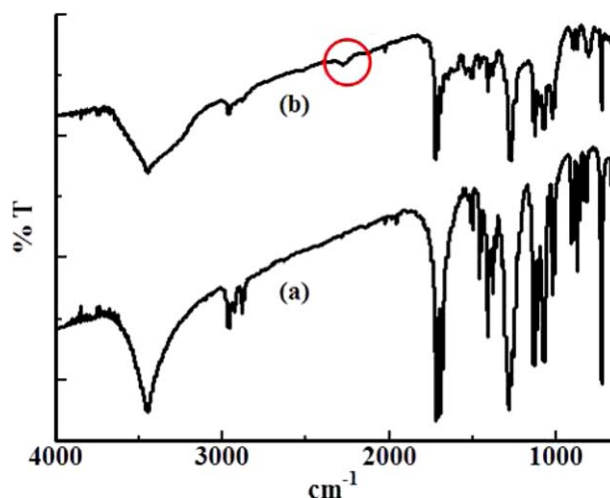

Figure 1. FTIR of (a) BHET and (b) PU foams. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Density and porosity of PUFs were detected by a TW-300 Y porous solids density meter (Xiongfa, Xiamen, China). All samples were cut to remove the outer layer and waterproofing treated. The density and porosity of each sample was defined as the average value of five parallel samples.

Compressive strength (CS) and compressive displacement (CD) of different samples were measured using a 3385H electronic tensile machine (Instron, USA). The size of the PUFs was $50 \times 50 \times 25$ mm^3, and the strain rate was fixed at 2.5 mm/min. The average strength of five specimens per sample is reported.

The limiting oxygen index (LOI) of the PUFs were detected through a JF-3 oxygen index apparatus (Jiangning analytical instrument factory, Nanjing, China) by ASTM D2863-00. Each sample ($90 \times 40 \times 10$ mm^3, length $\times$ width $\times$ thickness) was supported by a sample holder. An oxygen and nitrogen gas mixture is supplied to the burning chamber at a flow rate of 17.5 L min^{-1} equivalents to 40 ± 4 mm s^{-1} at STP.[23] Then, the top of the sample was ignited by a propane gas igniter producing a flame of 25 mm in height. The LOI defined as the minimal volume fraction of oxygen in a slowly rising gaseous atmosphere that will sustain the candle-like burning of a stick of polymer. The LOI of each sample was defined as the average value of five parallel samples. Before the sample test, the equipment was calibrated to ensure accuracy of results.

RESULTS AND DISCUSSION

FTIR Spectroscopy of BHET and PU Foams
The structural formulae of BHET and PUFs were showed in Schemes 1 and 2. Both compounds showed three sharp absorption peaks in the IR regions of 1610–1370 cm^{-1} due to benzene ring groups (Figure 1): two absorption peaks were appeared at 1500–1450 cm^{-1}, the other peak was showed around 1300 cm^{-1}. The absorption bands due to the —OH group showed at 3400–3230 cm^{-1} demonstrated the completely depolymerization of PET to BHET. The absorption peak at 2275–2225 cm^{-1} related to the —NCO group was showed in Figure 1(b). The addition polymerization of PMDI and BHET could be verified.

Morphology of PU Foams
Morphology of the PUFs was observed in the parallel direction to the blowing. Figure 2 showed the micrographs of cellular structures in the cores of the PUFs. The shape of the cells was approximately spherical. Some rupture of the cell structure could be observed. The cell diameter was around 200–440 μm with an ∼20 μm wall thickness.

Density and Porosity
Density of the foam is a very important physical property, which has great influence on the mechanical properties of the PUFs such as CS and thermal conductivity. The foam density mainly depends on the amount of blowing agent.[24] When other components of foams are constant, the increasing amount of blowing agent generates large volume of carbon dioxide (CO_2), which leads to the decrease of foam density and increase of foam porosity. On the other hand, the rigidity of foam is usually enhanced with the increase of blowing agent. This enhancement is due to the increase of hard phase of biuret diisocyanate.
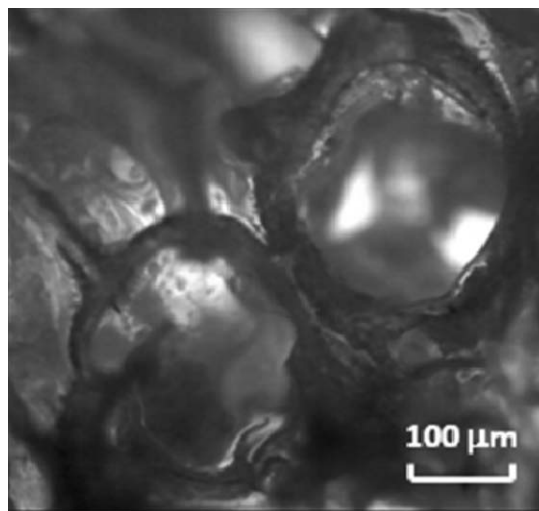

Figure 2. Morphology of PU foams observed parallel to the blowing direction by using a optical microscope ($\times$100 magnifications).
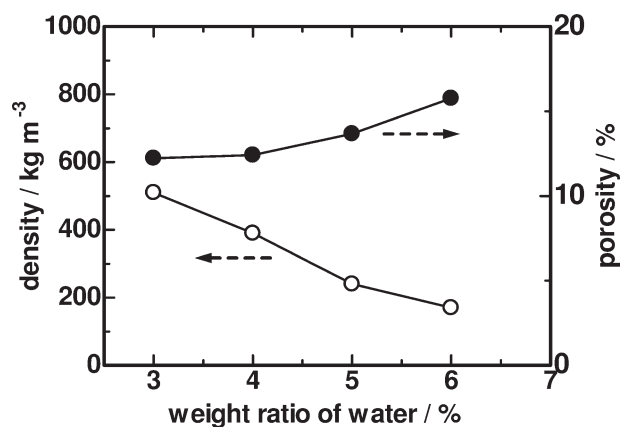
Figure 3. Variation of PU foam density (hollow circles) and porosity (solid circles) with the weight ratio of distilled water.

Figure 5. Dependence of compressive strength (hollow circles) and compressive displacement (solid circles) on the weight ratio of DMMP.

Excess amount of CO_2 leads to the foam collapse, while little amount of CO_2 is not enough to blow the foam up. Therefore, appropriate amount of blowing agent is important. In this study, the distilled water was used as a blowing agent. The dependence of the foam density and porosity on the weight ratio of water was studied with the constant weight ratio of catalyst (5.5) and weight ratio of distilled water from 3.0 to 6.5. The variations were showed in Figure 3. When the amount of water increased in this range, the density decreased from 510 to 150 kg m^{-3}, while the porosity increased from 12.23% to 16.89%.

The influence of the foam density on the added flame retardant had been reported.[21] In this study, the variation of foam density with the weight ratio of DMMP was also investigated. The density of DMMP-PUFs was lower than that of PUFs, although the density of DMMP (1.079×10^3 kg m^{-3}) was much higher than that of PUFs. Moreover, the increasing of DMMP ratio in PUFs resulted in the decrease of foam density and increase of porosity (Figure 4), because of the formation of big cells and the rupture of the cell walls (Figure 2).

Compressive Strength
As PUFs were applied as the thermal insulation wall materials or packing materials, its CS property was important. The effects
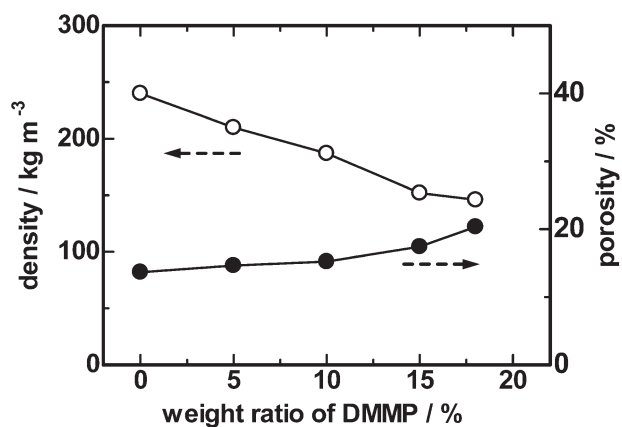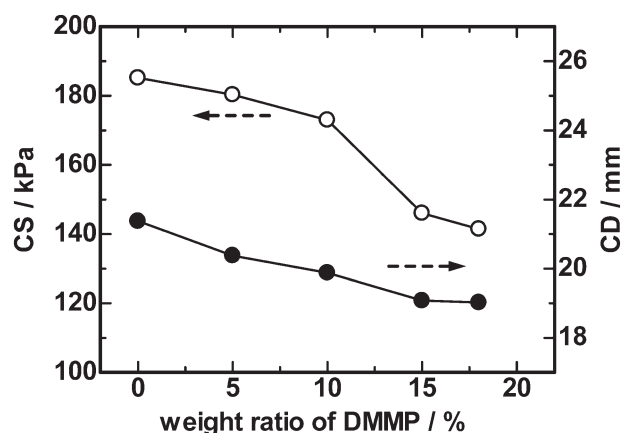
of DMMP on the CS properties of PUFs were studied. The CS decreased with the increasing of DMMP ratio while the CD decreased indistinctively from 21.375 to 19.022 mm (Figure 5). The decreasing of CS should be due to the doping of DMMP, which is a typical additive flame retardant. The doped DMMP dispersed in the cell walls of the PUFs physically. Contrast with the reactive flame retardant adhere to the PUFs by binding force, the adhesion of doped DMMP with the PUFs was heterogeneous, which reduced the CS of the PUFs.

Flame Retardation
PU foams are thermolabile and flammable because of the combustible hydrocarbon chains in their molecular structure.

Table II. Dependence of LOI on the Weight Ratio of Distilled Water, Catalysis, and DMMP

Distilled water (parts by weight)[a]	Catalyst (parts by weight)[a]	DMMP (parts by weight)[a]	LOI (%)
3.0	5.5	0.0	24.87
4.0	5.5	0.0	24.73
5.0	5.5	0.0	24.25
6.0	5.5	0.0	24.13
6.5	5.5	0.0	24.06
5.0	2.5	0.0	25.38
5.0	3.5	0.0	25.23
5.0	4.5	0.0	24.95
5.0	5.5	0.0	24.25
5.0	6.5	0.0	23.27
5.0	5.5	0.0	24.25
5.0	5.5	5.0	26.04
5.0	5.5	10.0	26.82
5.0	5.5	15.0	27.50
5.0	5.5	18.0	27.69

[a] Parts per hundred of BHET by weight.

Figure 4. Variation of PU foam density (hollow circles) and porosity (solid circles) with the weight ratio of DMMP.

According to the LOI of 16–18%, PUFs belong to the flammable materials. Because of the low density, porous structure, and large specific surface area, PUFs have a high flame rate and amounts of mass loss while burning. Furthermore, the released toxic gas while burning endangers personal safety. Therefore, kinds of flame retardant are doped to increase the flame retardation of the PUFs.[24–27] As the result showed in Table II, the LOI of PUFs prepared from BHET without any flame retardance was 23.27–25.38%. It was much higher than the LOI of common PUFs. According to the structure analysis, the aromatic substituent of BHET gave the stiff-rodlike structures to the formed PUFs. This structure increased the thermostability and decomposition temperature,[28] and then improved the flame retardance of PUFs.

The influence of distilled water on the LOI was studied with the constant weight ratio (5.5) of tin(II) bis(2-ethylhexanoate) as catalyst. When the weight ratio of distilled water increased, LOI of the PUFs showed indistinctive variation around 24.00% (Table II). The influence of catalyst on the LOI was also studied with the constant weight (5.0) of distilled water. When the weight ratio of catalyst increased, the LOI decreased from 25.38% to 23.27% (Table II). The increased catalyst facilitated the generation of carbon dioxide and increased the porosity of PUFs. These improved the breathability of gas, thus made the PUFs more flammable. Therefore keeping the balance of foaming rate and the flame retardation was very important.

The variation of LOI with the weight ratio of DMMP was showed in Table II. The weight ratio of distilled water and catalyst were 5.0 and 5.5. When the weight ratio of DMMP increased from 0% to 18%, the LOI increased from 24.25% to 27.69%. The LOI increased slowly when the ratio was larger than 15%. After flame time of the PUFs without DMMP was longer than 60 s. With the effect of DMMP, the after flame time of DMMP-PUFs were decreased from 32 to 14 s when the ratio of DMMP increased from 5% to 18%.

CONCLUSIONS

Waste PET textiles were glycolytically degraded by ethylene glycol and chemical recycling into flame-retardant rigid PUFs. The cellular structures of the PUFs were approximately homogeneous spherical. DMMP was doped to improve the flame retardance of PUFs. The foam density decreased with the increasing of the blowing agent, distilled water, while the porosity increased. The doped DMMP decreased the foam density because of the partial rupture of the cell walls. The compression properties decreased while the weight ratio of DMMP increased. The LOI of PUFs without doped DMMP, 23.27–25.38% while changing the weight ratio of distilled water or catalyst, indicated the flame retardance of PUFs, which produced from recycle PET textile waste. The increasing ratio of doped DMMP into the PUFs increased the LOI to 27.69% and decreased after flame time from 32 to 14 s.

ACKNOWLEDGMENTS

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