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PET Chemical Recycling

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Teijin Fibers Limited started the highly advanced chemical recycling plant, which can recover every kind of waste polyester products to dimethyl terephthalate (DMT) and ethylene glycol (EG), in 2002. Recently, Teijin Fibers has developed the industrial hydrolysis technology to convert the recovered DMT to highly pure terephthalic acid (TPA). This innovative technology enables us to produce the polyester resin for PET bottles from waste polyester. A new plant is planned to start up in Tokuyama, Japan in 2003.

Key words: Chemical recycling, Polyester, Hydrolysis, Terephthalic acid, PET bottles

1. INTRODUCTION

With the arrival of the new century, ever-greater attention is concentrated on the global environment. It is said the cumulative impact of the social and economic activities on the environment during the past millennia has exceeded our planet's capacity to maintain its ecological cycle. However, the present social structure still depends on mass production, mass consumption and mass disposal. The reform of this structure is desired.

Teijin Limited formulated Teijin Global Environmental Charter and Teijin Global environmental Activity Goals in 1992. The actions to conserve the environment have been done with two strategies. One is the "defensive" strategy, which is the basis for manufacturing. It means the reduction of waste, greenhouse gas emission etc. The other is the "offensive" strategy, which is aimed at the expansion of environmental- related business. It involves developing and marketing new technologies and new products that can more positively contribute to the environment.[1] The new technology of chemical recycling consists of DMT recovery and conversion to PTA, which makes possible to reproduce PET bottle grade resin from waste polyester products. The elemental technologies are described.

2. CHEMICAL RECYCLING TECHNOLOGY

Fig.1 shows the scheme of polyethylene terephthalate (PET) synthesis and depolymerization process. There are several ways to recycle PET. The route 1 is ion-exchange of sodium terephthalate derived by alkali hydrolysis of PET. It has not been commercially investigated because of the difficulties in purification of produced terephthalic acid (TPA). The route 2 is direct methanolysis. It is not necessarily suited because of the difficulties in decontamination dealing with every type of waste polyesters. The route 5 is hydrolysis of bishydroxyethyl terephthalate(BHET). But, it is not easy to purify BHET.

Teijin developed highly advanced chemical recycling technology of polyethylene terephthalate products through the route 3 and 4, which allows recovery of dimethyl terephthalate (DMT) and ethylene glycol (EG) from most types of polyester products. It was based on Teijin's long experience of chemical recycling for postindustrial polyester waste. The recovered material has high purity equal to that of the virgins. In 2002, Teijin started up this plant in Tokuyama, Japan. The plant is designed with various kinds of separation and removal technologies and it is applied for most types of contaminants in post consumer polyester wastes, such as PET bottles, fibers and textiles, and films even containing additives of pigments, dyestuffs, processing substances and other polymers.

Recently, Teijin has developed the industrial hydrolysis technology to convert the recovered DMT to highly pure terephthalic acid (TPA) by way of the route 6. This technology is intended to produce the polyester resin for PET bottles, which requires more strict quality because it is used to drinking water and beverages, and PET bottles are more sensitive to contamination in processing.

The principal problem was how to achieve recovery of DMT from waste PET bottles and how to convert DMT to highly pure TPA. The key technology in DMT recovery process is removal of contamination. That in conversion is to achieve almost 100% conversion and fine control of product particle size. In this respect, the process to recover DMT and convert to TPA was studied.

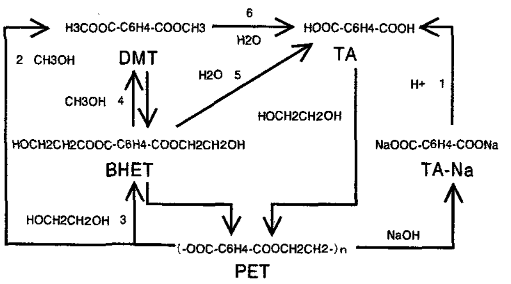

Fig. 1 Scheme of PET synthesis and depolymerization

3. EXPERIMENTS

3.1 Depolymerization of waste PET products [2)]

A bale of post consumer PET bottles weighing 20kg was crushed with hammer mill till the particle size of PET is less than 13mm. 200g of PET particles was washed with water about 5 minutes in 2000ml tank with a propeller agitator. Then it was dried till water content reached 0.2%. 200g of PET particles and 700ml of EG was charged into 3000ml autoclave with a distillation column and depolymerization was conducted at 150℃ under normal pressure for 120minutes. After excess EG was removed from the distillation column, BHET was taken out from the autoclave.

100g of BHET was reacted with 80ml of methanol in 3000ml autoclave with agitating at 80℃ under normal pressure for 60minutes. Then excess methanol was distilled out from crude DMT. Crude DMT was distilled twice with packing column. Pure DMT was taken out from the top of column. Purity of DMT was measured by gas chromatography with a glass capillary column.

3.2 Hydrolysis of DMT

Eight hundred grams of pure DMT obtained as described in 3-1 and 960 g of water was charged into 5 l autoclave with a cooling column. Hydrolysis reaction was conducted at 250 ℃ under 3.9～ 4.1 MPaG for 2.5 hours. During the reaction, methanol was removed from the cooling column with accompanied water. Water was continuously added into the autoclave to keep the molar ratio of water/charged DMT constant. After reaction, the pressure in the autoclave was reduced and TPA was separated from water by filtration. Purity of produced TPA was measured by liquid chromatography.

3.3 Polymerization using recovered TPA

Thirteen kilograms of EG and 18kg of TPA produced in hydrolysis of DMT were esterificated at 250℃ under 0.1MPaG in nitrogen atmosphere with agitating for 3.5hours in esterification reactor.

The liquid phase polymerization of the esterification product was conducted at 275℃ under reduced pressure for 3hours with addition of 200g of 1wt%-EG solution of germanium oxide, and 7g of 25wt%-EG solution of phosphoric acid. The polymer was extruded from the polymerization reactor through a chilled water bath into a strand cutter to yield 16kg of polymer pellets so-called "pre-chips". The pre-chips had an inherent viscosity of 0.510 dL/g and contained 1.92wt% of diethylene glycol.

The pre-chips were crystallized at 160℃ for 4hours in nitrogen atmosphere and then placed in the tumbler typed solid phase polymerization reactor to perform solid phase polymerization at 215℃under 0.13kPa in nitrogen atmosphere for 27hours. The resulting PET chips had an inherent viscosity of 0.78dL/g.

The PET chips were dried with a dehumidifying drier and molded with a injection molding machine FN2000(Nissei Plastic Industrial Co., Ltd) with the cylinder temperature of 275℃ and the molding cycle of 30 seconds to produce a colorless transparent preforms having a weight of 56g.

The preform was blow-molded to a 1.5liter self-supporting bottle with RHB-L blow molding machine (Cincinnati Milacron Co., Ltd).

4. RESULTS AND DISCUSSION

As shown in Table 1 and 2, quality of recovered DMT and converted TPA from polyester post consumer wastes by the new chemical recycling and hydrolysis technology is the same quality as that in the market. Table 3 and 4 show the bottle was transparent and had good appearance. This proves that polyester resin for bottle use can be obtained by using the recovered TPA. Through this process, no problem in quality of both resin and bottles produced was found.

Table I Quality of recovered DMT

		Recyled	From Crude Oil
Capacity	t/year	30,000 60,000(from 2003)	230,000
Quality			
Appearance		white flakes	white flakes
Freezing Point	℃	140.6	140.6
Acid Value	KOHmg/g	0.01	0.045
Ash	ppm	10	10
Iron	ppm	0.5	1
Purity	%	99.99	99.98
Energy Comsunption	%	70	100

Table II Quality of synthesized TPA

Item	Unit	Recycled	Commercial
Appearance		white powder	white powder
Acid Value	KOHmg/g	675±2	675±2
Ash	ppm	5	5
Iron	ppm	0.1	0.1
Total Metal	ppm	1	1
4-CBA	ppm	20	20

There are two key technologies in hydrolysis of DMT to TPA. One is that this reaction is an equilibrium reaction and sufficient removal of produced methanol is very important to achieve full conversion of DMT for highly pure TPA. The other is to control particle size of TPA by optimizing reaction conditions to stabilize the following polyester polymerization process.

Table III Quality of prepared PET

Item	Unit	Using Recycled TPA	Using Commercial TPA
Appearance before SSP	-	transparent	transparent
Appearance after SSP	-	white	white
IV before SSP	dL/g	0.510	0.516
IV after SSP	dL/g	0.784	0.782

Table IV Quality of molded products

Item	Unit	Using Recycled TPA	Using Commercial TPA
Appearance of preform	-	transparent	transparent
IV of preform	dL/g	0.671	0.681
Appearance of bottle	-	transparent	transparent
Haze of bottle	dL/g	0.5	0.4

Worldwide polyester production is about 28 million tons per year and will be expanded to about 60 millions in 2009. The consumption of PET bottles in Japan is about 360 thousands tons and the collection is about 130 thousands tons in 2000.[3] The estimation of the consumption and collection in 2004 is about 450 thousands tons and about 230 thousands tons, respectively. The collected bottles have mainly been processed to fiber and sheets by mechanical recycling. However, mechanical recycling involves quality problems such as yarn breakage and decolorization caused by impurities in PET bottle flakes. These problems are getting more serious as the capacity of collection and mechanical recycling is increased. Though many researches are seen, further investigation is required to completely solve these quality problems. On the contrary, the recycling technology Teijin has developed can recover DMT, which is one of the raw materials for some kinds of PET resin, from waste polyester products. The conversion technology can make almost complete hydrolysis from DMT to TPA, which is another raw material for PET resin without any contamination. By the development of these technologies, most types of waste polyester products can be converted to virgin polyester resins for any use. Especially, the technology to convert DMT to TPA can realize the bottle-to-bottle recycling first in the world.

5. CONCLUSION

Teijin developed new chemical recycling technologies to recover DMT and TPA from waste products made mainly from polyester. Teijin aims at the realization of the recycling-based society based on the chemical recycling technology of used polyester products and manufacturing environmentally-friendly products by using the chemically recycled raw materials.

Table 5 is the history of PET recycling in Teijin. Hereafter, Teijin continues to make every effort to develop and market new technologies and new products that can positively contribute to the environment.

Table V History of PET recycling in Teijin

1958	Production of PET
1962	PET Chemical Recycling (post-industrial waste) 1962-71 Liquid Phase Methanolysis 1971- Glycolysis & MeOH Ester Interchange 1971- 4,000t/year 1982- 12,000t/year
1996	PET Bottle Recycling Fiber by "Mechanical Recycling " Technology
1999	"ECOCIRCLE ", System for Collecting and Recycling Textile Goods from Consumers
2000	"Highly Advanced Chemical Recycling " (30,000t/year)
2003	"Bottle to Bottle "Recycling (60,000t/year)

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