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Recycling Technology of Poly(ethylene Terephthalate) Materials

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Abstract: Poly(ethylene terephthalate) (PET) has become one of major post consumer plastics wastes, in addition to polyethylene (PE), polypropylene (PP), polystyrene (PS) and poly(vinyl chloride) (PVC). The challenge to large-volume plastics companies is to learn how to collect, separate, reprocess and market their low-cost products and make a profit, too. The effort of PET recycling, however, is the most successful story in the plastic recycling technology, including both reclaim and upgrade of PET waste. Beverage bottles made of PET are recycled more than 20 % of the total production. The technology of today can reclaim the post-consumer PET bottles to produce high-quality granulated PET with better than 99 % purity. A practical reclaim process for recycling PET bottles (including bottle, HDPE base cup, aluminum cap, liner, label and adhesive) is available by the Center for Plastics Recycling Research in USA. PET recycling process, like for other plastics, can be divided into three categories: incineration, physical recycling, and chemical recycling. To make the plastic recycling business pay requires more than simple recovery and marketing. Greatest profit potential is in upgraded and value-added reclaim products. Upgrading involves compounding with additives to make material more processable, adding reinforcement, or producing extrusions or finished parts from reclaim resins. For instance, a modified injection-moldable resin made from PET bottle scrap is claimed to provide high impact and processability at less cost than competitive materials. It is foreseen that chemical recycling of waste PET bottle becomes feasible if the price of raw material goes up. Three economical processes are involved in this technology: pyrolysis, hydrocracking, and hydrolysis. The hydrolysis process is presently employed to recover the raw material for unsaturated polyester resin manufacture or polyols for the production of polyurethane resin. It is reported in this presentation that polymer concrete could be a huge potential market for chemical reclaim of PET materials, especially for green or mixed-color PET, which are priced lower than colorless PET reclaim materials.

INTRODUCTION

A serious challenge confronts the industrial countries worldwide: the huge disposal of waste that pours annually into municipal solid waste streams to be burned or less often, recycled (Ref. 1). Plastics waste can be combusted to produce energy, recycled to preserve energy and petroleum feed stocks or pyrolyzed to produce feed

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stock equivalents. Depending on the type of plastics, the heat of combustion ranges from 8 000 to 21 000 BTU/lb. However, the total energy input to manufacture plastics ranges from 25 000 to 90 000 BTU/lb. Therefore, a successful recycling process would have a substantial economic and energy incentive compared to combustion or pyrolysis. Although the management of waste plastics is reaching a crisis, PET waste has become one of the valuable recyclable materials today. The overall world consumption of PET in 1990 was about 15 million tons. Among them, 10 million tons were processed by textile industry, 3 million tons were used for audio- and video-tapes, and 2 million tons were consumed for different-type packagings, mainly as bottles and jars. The U.S. consumption of blow-molding resins in 1990 was about 2.3 and 1.1 billion lbs for HDPE and PET, respectively, versus about 500 million lbs for all other resins. The technology of today can reclaim the post-consumer PET bottles to produce high-quality granulated PET with better than 99% of purity. This sells at 35 to 60 % of virgin PET costs depending on its color. Colorless PET is more salable and priced higher than green or mixed-color. Therefore, the color reclaim PET can be obtained at cheaper price on the market. A very important feature of PET, decisive in wide use in the packaging manufacture for foodstuff, is the absence of an adverse effect on the human organism. An increasing interest in PET recycling is associated with the common utilization of packagings made of this polymer, mainly as bottles. Like other plastics items, the PET bottle has been a target of a recent restrictive laws. As a result, the challenge to PET companies is to learn how to collect, separate, reprocess and market their low-cost products and make a profit, too. It is, however, also the area of the industry's most effective response and it has already become an outstanding plastics recycling success today. Converters were provided with recycled PET produced from the bottles to produce such products as carpet, industrial strapping, tennis-ball containers and sheet. The Coca-Cola Co. has introduced PET bottles made with a blend of 25% recycled resin and 75% virgin resin (Ref. 2). Hoechst Celanese's Fibers and Film Group uses a chemical system to separate the complex plastics into its basic components and then regenerates it into a resin identical to pure-source PET.

Recycled PET is also chemically converted back into original raw materials for PET.

TECHNOLOGY OF RECYCLING

PET Bottle Recycling Processes (Ref. 3)

The technologies of most commercial PET bottle recovery processes have been first developed by DuPont or Goodyear, but no longer operated by them. Complete systems built to customer specification are available from Lummus Development Corp., in the U.S., which built recycling facilities for St. Jude Plastics. A processing system for PET bottles, starting with the entire container - the bottle, HDPE base cup, aluminum cap, liner, label, and adhesive has been in operation at the Center for Plastics Recycling Research (CPRR) of the U.S. since 1985 (Ref. 4). The CPRR process is illustrated in Fig.1.

The processing steps are as follows:

- Shredding of bottles to facilitate a fast proceeding of the feed into a granulator; grinding to 1/4-inch particles.
- Conveyance via a loader tube to an air classification system to separate paper and light contaminants.
- Washing and rinsing, similar in principle to household washers or dishwashers.
- Floatation to separate the lighter HDPE, cap liner and plastic label from the heavier PET and aluminum. Rotating paddle wheels help to overcome surface tension.
- Separate spin drying of lights and heavies.
- Hot air drying of each stream.
- Electrostatic separation of PET and aluminum.
- Packaging and sale of clean, uniform, granulated resins.

PET Bottle

↓ ↗ (paper, light contaminants)

granulator → air classification → washing, rinsing →

↗ (HDPE, cap liner) → (spin drying) → (hot air drying) → **HDPE**

floatation

↘ (PET, Al) → (spin drying) → (hot air drying) →

↗ PET

(magnetic separation)

↘ Al

Figure 1 CPRR process for recycling of PET bottles

The CPRR states that it is willing to share its process. Estimates indicate that a minimum investment of US$ 1.5 to 2.0 million is required for a plant of 10 million pounds per year production capacity. Except for the electrostatic separator, the CPRR process, called a "wet-sorting system", is roughly similar in principle to six other commercial-scale operations: Envipco, Nyconn, Procedyne, Puretech, Wellman and St. Jude in U.S.A. In Taiwan, we have one wet process plant currently in operation to manage the local PET bottle recycling problem.

Upgraded Reclaim Products

Public reaction to the solid waste issue threatens to limit growth in packaging, while recycling programs threaten many blow-molding resins. PET bottle recyclers agree that making the business pay requires more than simple recovery and marketing. Greatest profit potential is in upgrading and value-added reclaim products. Upgrading involves compounding with additives to make material more processable, or adding reinforcements or producing extrusions or finished parts from reclaim resins. Typical are materials being introduced by such compounders as M.A. Industries and MRC Polymers. Malon Compounds within M.A. Industries include an extrusion grade of polyester for sheet, fiber, film or blow-molding applications. Mamox injection-moldable polyester compounds are filled and reinforced materials. Maloy materials, alloys of PET with other resins for special uses, are rounding out its slate of recycled PET compounds. MRC Polymers 'Stanuloy', a modified injection-moldable resin made from PET bottle scrap, is claimed to provide high impact and processability at less cost than competitive (Ref. 5).

Chemical Recycling Methods

If the price production of the raw material goes up, the chemical recycling of waste PET is foreseen to become feasible. For instance, recycled PET is chemically converted back into raw materials for the manufacture of saturated and unsaturated polyester resin or into polyols for the production of polyurethane resins (Ref. 6) or poly(vinyl chloride) plasticizers (Ref. 7). A leading role in this area is played by the Chardonal Division of Freeman Chemical, Pt. Washington, WI, which converts an estimated 25 million lbs of PET annually. The current major application for these polyols is in rigid PU foams. Applications confirm reliability and consistency of reclaimed PET as a raw material. In mid-1989, Goodyear's Polyester Division claims a chemical process that depolymerizes PET bottle flakes into ethylene glycol and terephthalic acid - the original monomers. High temperatures in the process would destroy potential contaminants, and perhaps permit reuse of reclaim in food-contact application. It is reported by the author that a pressure glycolysis of PET waste produces its original monomer - bis(2-hydroxyethyl) terephthalate (BHET) (Ref. 8) with purity of 99 % (melting point 109-110 °C).

The authors have synthesized a polyurethane resin from BHET obtained from reclaim PET as reported in our previous papers (Refs. 9,10). It has been investigated by the authors that unsaturated polyester resin is synthesized from the polyol products by the glycolysis of the reclaim PET with ethylene glycol. It is believed that BHET is a valuable starting chemical for many useful products. This new route of PET bottle chemical recycling is summarized in Figure 2.

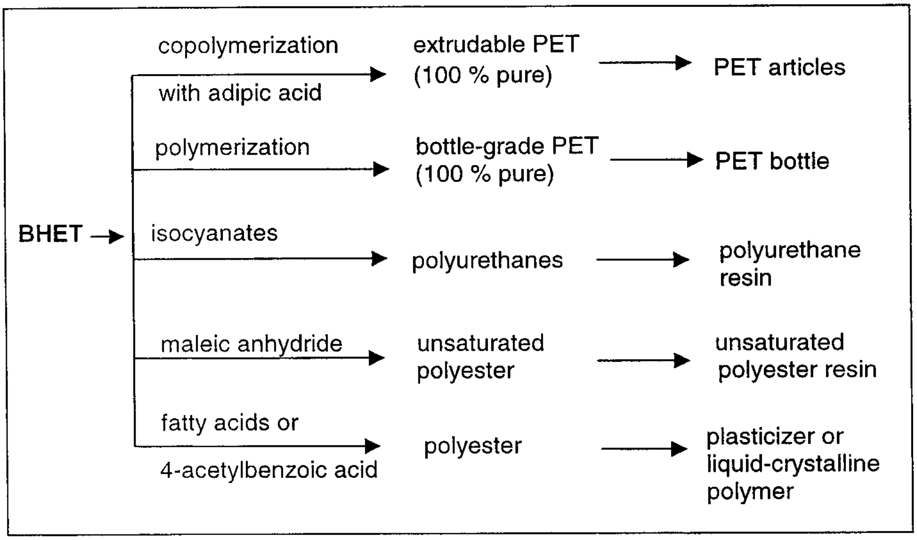

Figure 2 Synthetic products from BHET as starting material

Meanwhile, a continuous depolymerization process was developed (Ref. 11) in which the polyester can be depolymerized to low-molecular-weight oligomers at atmospheric pressure. Recently, glycolysis of poly(ethylene terephthalate) with Bisphenol A at high temperatures was reported (Ref. 12). This glycolyzed product could be utilized as the reactant for the synthesis of heat-resistant polyarylates.

Polymer Concrete

Polymer concrete is a composite material that consists of inorganic aggregates bonded together by a resin binder. The material can be used effectively in a variety of structural applications such as transportation, utility, marine, and building components.

An unsaturated polyester based on the polyester oligomer was prepared by Tong et al. (Ref. 13). Physical properties of reinforced polyester concrete using recycled PET were investigated by Rebeiz et al. (Refs. 14 and 15). The authors have been long engaged in producing an effective polymer concrete from reclaim PET and in its application (Refs. 16 and 17) because the latter is a major component in unsaturated polyester resins. A new type of polyester concrete composite is developed by mixing an unsaturated polyester resin from reclaim PET products with Portland cement, sand and water in proportions similar to those used for cement mortar materials for construction purposes. This polymer concrete exhibits a high strength of up to 83 MPa in compressive strength and 21 MPa in flexural strength. The new product shows a high corrosion resistance, high adhesive strength, imperviousness and fast setting. Applications confirm reliability and consistency of reclaim PET regardless of its color as an economical raw material for polymer concrete. Some typical properties of the polymer concrete obtained from the reclaim PET waste by our formulation are shown in Table 1.

Table 1 Physical properties of the polymer concrete

Compressive strength	1 h	360 kg/cm^2
	1 day	700 kg/cm^2
	28 days	900 kg/cm^2
Flexural strength	28 days	167 kg/cm^2
Tensile strength	28 days	50 kg/cm^2
Modulus of elasticity	28 days	1.1×10^5 kg/cm^2
Abrasion resistance		six times that of controlled concrete
Corrosion resistance		resistant to sea water, most acid and alkaline solutions

CONCLUSION

Ecological concern over the disposal of wastes provided the initial impetus for considering PET as a raw material. Because the economic advantages were apparent, it was logical to use reclaim PET as a potential supply source for unsaturated polyesters, especially for colored or mixed-colored products, at lower costs than competitive, and for polymer concrete which has an unlimited market in civil engineering applications.

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