Post consumer poly(ethylene terephthalate) depolymerization by waste of battery acid hydrolysis

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Abstract

The reaction of post-consumer poly(ethylene terephthalate) (PET) with waste of battery acid (sulfuric acid solution as 7.8M determine by chemical titration) was investigated in terms of temperature, and time at particle size about 2mm. The reaction extent reached 80% in four days at 100°C and 90% in 5 hours at 132°C (boiling point of waste of battery acid solution). Terephthalic acid (TPA) obtained was purified and considered in the same level of quality of the commercial. It was concluded that the hydrolysis occurred preferentially at the chain ends and superficially, having as controller mechanism the acid diffusion into the polymer structure.

Keywords: Chemical recycling, Hydrolysis, PET, waste of battery acid, TPA

1-Introduction

Poly(ethylene terephthalate) (PET) is one of the versatile engineering plastics and shows excellent thermal and mechanical properties. It is semi-crystalline, thermoplastic polyester with high strength, transparency and safety. Although its main application was, by far, in the textile industry, tremendous quantities of this material are consumed in the manufacture of video and audio tapes, X-ray films, food packaging and especially of soft-drink bottles. The overall world consumption of PET amounts to about 26 million tons a year [1], compared to about 13 million tons, reported in 1997 [2]. The global growth in consumption of PET during the years 2001–2004 was estimated to be 2.3 million tons [3]. Consumption in Western Europe alone was reported to be 3.8 million tons (2003) representing 10% of the total thermoplastic consumption [4]. PET is produced by the polycondensation reaction of a diacid and a dialcohol. The industrial practice was to use dimethyl terephthalate (DMT) and ethylene glycol (EG) as the two monomers for the production of PET by transesterification and polycondensation reactions. However, nowadays the use of the polyesterification reaction between terephthalic acid (TPA) and EG is gaining space.

PET recycling represents one of the most successful and widespread examples of polymer recycling. PET bottle collection in Europe is growing steadily. In 2001 344,000 tons were collected, a 20% increase in comparison with 2000. By 2006, Petcore announced that European postconsumer PET collection rates reached 796,000 tons in 2005, a 15.1% increase over the previous year (Petcore report, July 2006) [5]. The main driving force responsible for this extremely increased recycling of post-consumer PET is its widespread use, particularly in the beverage industry. A very important feature of PET, decisive in the choice of its wide application in the manufacture of packaging for the food industry is that it does not have any side effects on the human organism. It should be pointed out, that PET does not create a direct hazard to the environment but, due to its substantial fraction by volume in the waste stream and its high resistance to the atmospheric and biological agents, it is seen as a harmful material [6]. Therefore, the recycling of PET does not only serve as a partial solution to the solid-waste problem but also contributes to the conservation of raw petrochemical products and energy. Products made from recycled plastics can result in 50–60% energy saving as compared to making the same product from virgin resin.

The recycling of waste polymers including PET can be carried out in many ways. Four main approaches have been proposed [6–8] glycolysis, methanolysis, hydrolysis, and other processes such as ammonolysis and aminolysis. Neutral hydrolysis of PET, performed only with water, presents high depolymerization rates when the reaction occurs in temperatures close to that of the polymer melting point (which is about 250°C) and by using pressurized systems [9–12]. The nitric acid and sulfuric acid are the most common acids used to catalyze PET hydrolysis. The sulfuric acid is highly utilized because it allows reactions to occur at high temperatures demanding lower time and lower activation energies [12–20].

The purpose of this study concerned with the use waste of battery acid to the post consumer PET depolymerization process through hydrolysis reactions by waste acid at 1 atmosphere where the use of this waste acid do not studied at yet. The influences of temperature and time over the reaction productivity were analyzed. The optimized reaction in terms of time, and temperature was used to define procedures to extract and purify the TPA produced. The purified TPA was later characterized and compared to the commercial TPA. This study has, therefore, produced results that allow the chemical recycling process through acid hydrolysis to be better understood, beginning with the reaction itself all the way to obtaining and purifying the TPA. The study investigated lacks in literature such as: reaction of postconsumer and industrial waste from mechanical recycling PET, use of maximum temperature that allows atmospheric pressure, method proposal for the recovery of purified TPA and comparison of properties between the obtained and commercial terephthalic acid.

2. Experimental part

2.1. Materials and Equipment

The PET utilized was obtained from soft drink bottles, which were crush to particle size approximately 2mm and battery acid solution as a waste. Ammonium hydroxide, hydrochloric, and sulphuric acid supplied from Aldrich company. IR spectra were recorded on Shimadzu FTIR-8400S.

2.1.1. Hydrolysis Reaction and TPA Production

The hydrolysis reaction by waste of battery acid solution as the medium reaction is shown in Figure 1. The concentration of the solution used, 7.8 M, was based on the study of Yoshioka et al., who pointed out that only with concentrations higher than 7.0M it is possible to depolymerize more than 90% of PET in a reaction that carried through for 5 h at a temperature of 150°C [14], and was based on the study of Mancini et al. [21] who pointed out that only with concentrations 7.5M it is possible to depolymerize 90% of PET in a reaction that carries through for 5 h at a temperature of 135 °C and 80% PET in a reaction that carries through for four days at a temperature of 100°C, where we gained similar results compare with Mancini et al [21].

An aqueous solution of battery acid (25 ml) was added to 2.94 g of PET flakes within the same granulometric range and magnetic stirrer were placed into a glass reactor of 250ml capacity with a reflux condenser (P = 1 atm)[21]. The system was then placed in a heated oil bath. As soon as the desired temperatures of 100°C and 132°C were reached, the counting of the reaction time began, with a maximum period set at 144 h (6 days). The highest temperature reached by the solution of waste of battery was 132°C, therefore chosen since higher temperatures used by other researchers could only be reached by applying a pressurized system [14–16]. Afterwards the reactor was placed in a water bath at room temperature. Then the solution was filtered separating the solid part, containing PET not completely reacted and TPA, from the liquid part, containing water and ethylene glycol (EG). The solid phase was dried at room temperature for 12 h and then at 74°C for 5h. The extent of the reaction was measured considering the percentage of TPA formed through out the reaction. A known mass sample of the dry solid fraction was placed in a test tube to which added 15 ml of a 5M solution of ammonium hydroxide. After 10 min of reaction with magnetic stirring, the solid fraction was separated from the liquid fraction by means of filtration, dried and weighed. The TPA (%) was determined by the mass difference, before and after the reaction with ammonium hydroxide, divided by the initial mass. With the purpose of obtaining pure TPA, sulfuric acid was added to the liquid fraction obtained from various gravimetric determinations containing the salt (diammonium terephthalate), which caused the TPA to precipitate in a purer form than that obtained through hydrolysis. This TPA was then filtered, separating it from the new liquid phase and then washed dried (12 h at room temperature and for 5 h at 74°C). The obtained product was then considered to be purified TPA.

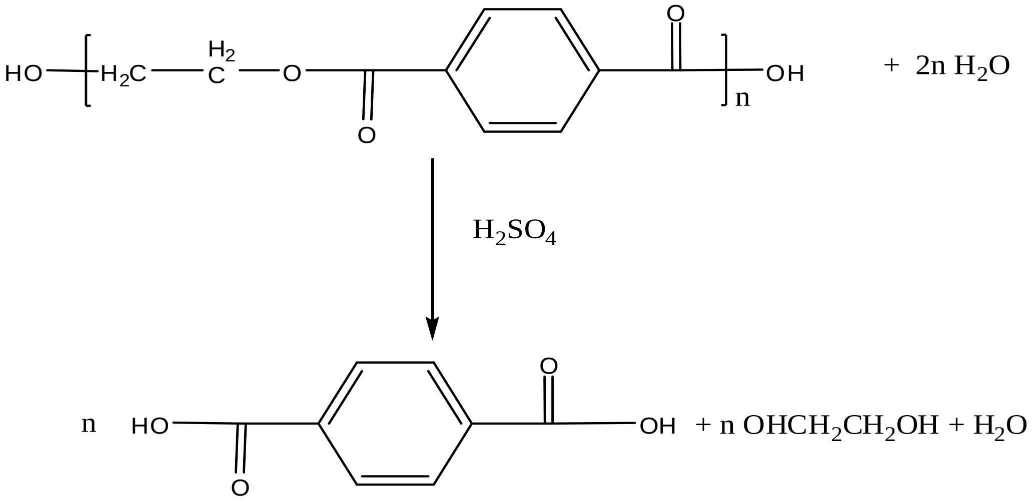

Figure 1: the scheme for the terephthalic acid production by acid hydrolysis for PET bottles

2.1.2. Characterization of Commercial and Purified TPA

The purified TPA obtained from small flakes and the commercial TPA supplied from Aldrich company were both submitted to comparative tests of FTIR spectra , melting point , and acid number.

3. Results and discussion

3.1. Hydrolysis

Figures 2 and 3 shows the results of gravimetric tests for PET particle 2 mm submitted to hydrolysis in 7.8M sulfuric acid solutions at 100°C and 132°C, respectively.

The gravimetric and titrimetric curves both presented the same sigmoidal characteristics (that is why only the former is shown), with a single inflection point at half conversion. Figures 2 and 3 show a clear effect of the temperature on the polymer acid hydrolysis. The conversion at 100°C (Figure 1) ceased at about 80% of TPA after 96 h. After using a temperature of 132°C (Figure 2) 90% conversion of TPA was achieved in 5 h.

3.1.2 Purified TPA Obtaining

After separating the solid phase from the solution used to determine the percentage of TPA, sulfuric acid was added in order to decrease the pH from 11.0 to approximately 3.0. This procedure allows for all the TPA to precipitate, which was recovered after filtration. This material was then dried and ground, and a powder obtained was considered purified TPA. Studies preformed with liquid portions from reactions to the extent of 60%, allows us to determine that 97% of the TPA produced (stoichiometrically calculated from the PET consumption) can be recovered when using this procedure (the initial PET particle size and the hydrolysis temperature were not taken under consideration).

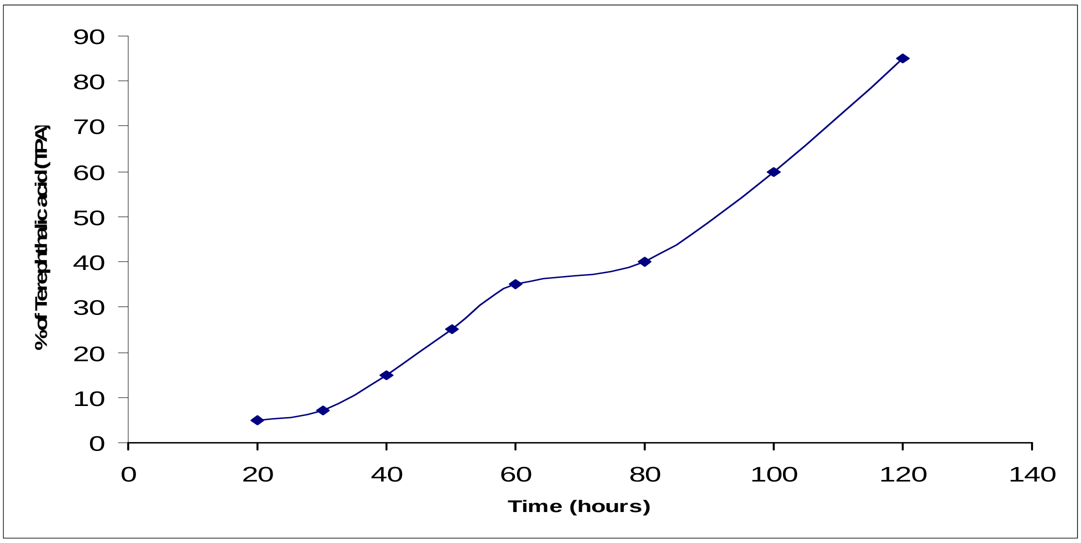

Figure 2: Effect of time on percentage yield of TPA at 132^{O}C

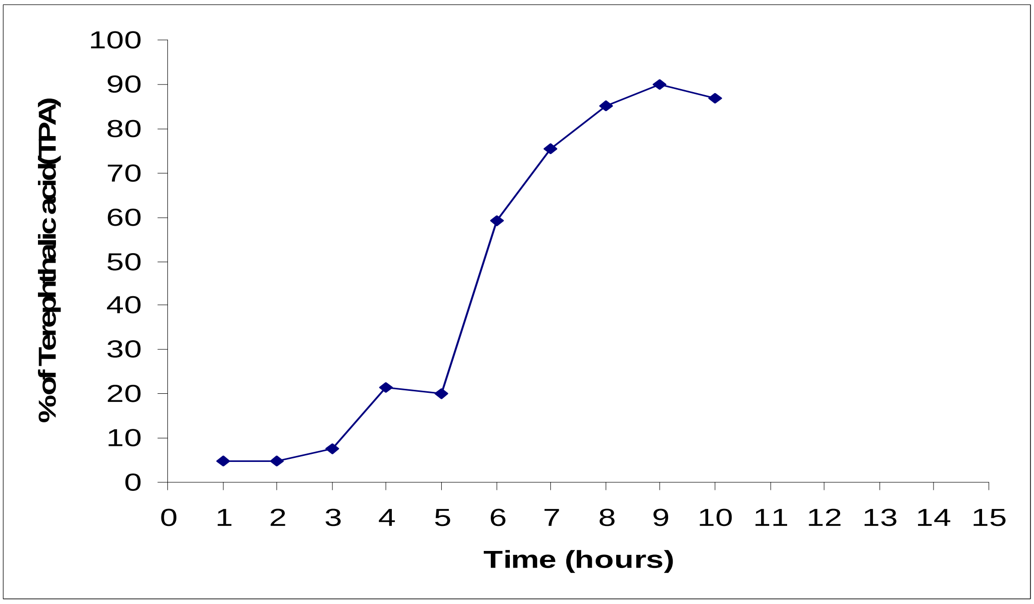

Figure 3: Effect of time on percentage yield of TPA at 100^{O}C

3.1.3 Purified TPA Characterization

The FTIR in figure 4 shows that the product obtained from acid hydrolysis of waste PET bottles has the same characteristic peaks as commercial and analytical TPAs. These characteristic peaks correspond to aromatic rings are at wave numbers of 700-800 cm^{-1} and 1680 cm^{-1} , while the characteristic peaks correspond to carboxylic groups are at wave numbers of 1300, 1440, and 2500-3100 cm^{-1} (broad). This suggests that the obtained product is TPA because its spectra are similar to those of commercial and analytical TPAs.

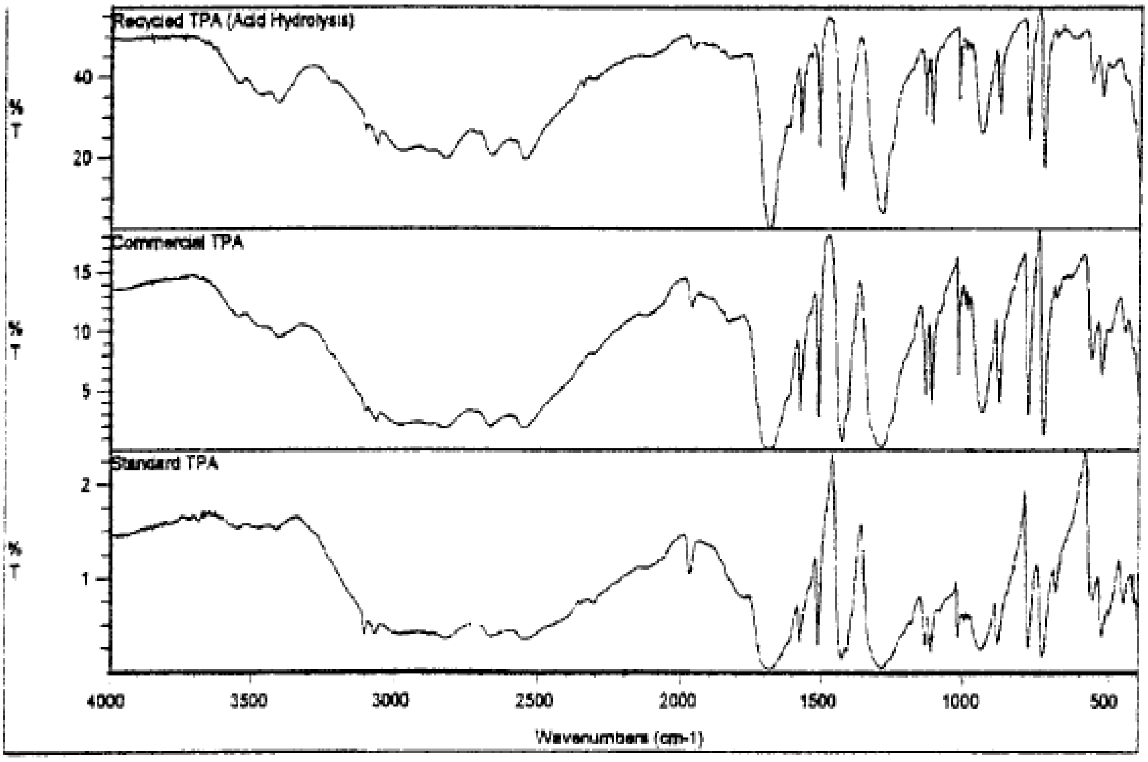

Figure 4: FTIR spectra of the PTA : Recycled, Commercial and Standard

The other characterization of the obtained and commercial TPA was shown in table 1, which represent the melting point and acid number for TPA (commercial and obtained) .

Table 1. Characterization of the commercial and prepared terephthalic acid (TPA)

Samples	Melting point	Acid number (mg KOH/g)
Commercial TPA	300°C in a sealed tube (sublimes at 402°C (675 K) in air)	675
Prepared TPA	Sublimate above 300 °C	673

Conclusion

Generally, the use of waste battery acid is first time for recycling polyethylene terephthalate post consumer soft drink bottle to production high purity terephthalic acid , aqueous solution of waste of battery acid 7.8M at 100C depolymerized 80% of post consumer PET after four days. Depolymerization of 90% was obtained at a temperature of 132C in 9h. This reaction was determined considering PET as weight loss, which allowed purify 97% of the possible terephthalic acid. Both commercial (petrochemical) and purified TPA were compared and to be similar after test of melting point, FTIR, and acid numbers.

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