

Preparing Terephthalic Acid from Hydrolysis of Polyethylene Terephthalate Waste

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Abstract: PET (polyethylene terephthalate) plastic wastes have been accumulating increasingly in the environment, which made it a huge problem all over the world and because they cannot be recycled. So its depolymerization to getting terephthalic acid is considered to be the best way for dealing with its wastes. PET depolymerization was carried out by sodium hydroxide at different concentrations, temperatures and particle sizes in the presence of many phase transfer catalysts. Then terephthalic acid was purified and its UV and FTIR spectra were measured. The best conditions for the alkaline hydrolysis are 120°C temperature, cetyl ammonium chloride as a catalyst, 10% sodium hydroxide concentration and less than 1 mm particle size.

Key words: PET • Plastic Wastes • Depolymerization • Terephthalic Acid

INTRODUCTION

Polymeric materials were synthesized from phenol and formaldehyde in 1907 by Leo Baekeland where they were called Bakelite [1]. This material has spread widely in our daily life and its annual production exceeded 200 million tons in 2017 [2] and it is still increasing due to the many characteristics that distinguished it.

Among these characteristics are the low cost of chemical production, the ease of manufacturing, low melting point compared to minerals and low density, the diversity of their uses, their inability to rust and their tolerance to conditions such as temperature changes, but they have caused harmful environmental effects of their inability for vital disintegration, as it remains as a waste for a long time, until it reached the poles and caused many damages and death to animals, birds, marine mammals and fish [3], studies and pressures calling for reducing the negligence of factories that cause environmental pollution with these materials increased it.

Therefore, the United Nations Environment Program has described the massive pollution observed in the land and sea environment with plastic materials as a "toxic time bomb" [4] and this has called researchers to conduct many researches on the methods necessary to reduce their harm to the environment and these methods include educating citizens to reduce its use and seeking to use biodegradable alternatives and considering that the application of these two methods requires the concerted efforts of many researchers and many experiences and a

long time, the fastest environmental solutions began to recycle, which is the recycling of the polymeric types that can be done and adding the used polymer powder to materials or common industrial mixtures such as cement and other products and then studying the effect of additives on the properties of these materials [5]. Thus, some of the leading factories in the automotive industry began using polyethylene terephthalate (PET) wastes in the manufacture of their car body [6], is used in packaging of drinking water and soft drinks.

PET is characterized by its toughness and durability towards various solvents, in addition to its high flexibility and transparency and therefore it represents one fifth of the global production of polymeric materials [3].

Its production increases annually in many countries greatly [1], but it suffers from a big problem that it cannot be recycled and from here we see that research on other methods to take advantage of polymeric wastes in general and polyethylene terephthalate in particular is very important [4] and several studies have been conducted in this area such as the thermal dissolution of polymers by heating them To relatively high temperatures with careful control of the heating speed to prepare materials that have a variety of industrial uses [7] alkaline hydrolysis (saponification) in different reaction conditions to prepare terephthalic acid and to produce ethylene glycol [3] and alkaline hydrolysis using ethylene glycol as a more effective and safe solvent [8] and the solubility of PET wastes with different amines [9].

Paszun and Spychaj [10] hydrolyzed PET waste by using glycols as solvents such as (ethylene glycol and propylene glycol) with high boiling points, allowing the reaction to be carried out at a higher temperature and giving higher yields. But it can only be separated from water by distillation under low pressure, which greatly raises the economic cost. Vakili and Haghshenas have got 92% conversion of PET hydrolysis by sodium hydroxide at 180°C temperature and 1.5 bar pressure [11]. While Al-tamimi and Khalaf [12] studied the acidic hydrolysis of PET using sulphuric acid and heating and his method is characterized by a low expense of the chemicals needed for the reaction, but he was unable to reach a good return. The best yield of hydrolysis using various surface-active derivatives of quaternary ammonium and phosphonium salts was by 4BuPH (Tetrabutylphosphonium hydroxide) at 80°C [13].

Polyethylene terephthalate is characterized by its widespread use in the manufacture of special bottles to fill water and other liquids because it is safer and more durable than other common polymers, but its problem is that it cannot be recycled, so the importance of research lies in studying methods of disposing of polyethylene terephthalate waste through its alkaline hydrolysis to obtain the base raw material terephthalic acid.

The research aims to determine the optimum conditions for the polyethylene terephthalate hydrolysis and then apply it to prepare, isolate and purify a sufficient amount of terephthalic acid and to ensure its purity measure its infrared and ultraviolet spectra.

MATERIALS AND METHODS

From MERCK: Methanol 99% purity. From: Surechem Sulfuric Acid 98%, Sodium Hydroxide 99.5%. From: BDH Calcium Chloride 95% Anhydrous from Himedia: Cetyl Ammonium Chloride 95%.

Industrial and commercial sources include: Sodium Dodecyl Benzene Sulfonate, Betaine, Nonyl Phenol Ethoxylate.

- Melting point model B-540 from BÜCHI

The polymer was ground and sorted according to its particle size, then alkaline hydrolysis experiments were carried out by fixing the reaction conditions of the polymer amount 10 g, heating (Velp heater with magnetic mixer, model V-18) at 95°C, the concentration of the alkali 10% sodium water and the reaction time 5 hours, using different catalysts, with a control experiment without A

catalyst to determine the best catalyst, then add 5% sulphuric acid, filter the formed precipitate, wash it with water, then place it in a Petri dish in a glass desiccator with vacuum in the presence of anhydrous calcium chloride for a period of one day and then measure the infrared spectrum using potassium bromide disk (Alpha infrared spectroscopy from Bruker) and ultraviolet spectroscopy (UV-530 from Jasco) after dissolving in methanol, to verify the resulting terephthalic acid.

After determining the best catalyst, alkaline hydrolysis was carried out by fixing the previous reaction conditions from the polymer weight 10 g, temperature 95°C and reaction time 5 hours, use the best catalyst and change the alkali concentration to determine the best concentration.

Finally, alkaline hydrolysis was conducted by fixing the previous reaction conditions from the polymer weight 10g, using the best catalyst, the best alkali concentration, the best reaction time and temperature 95°C, to determine the effect of the polymer particle size.

RESULTS AND DISCUSSION

Table (1) shows the results of the reaction yield change by changing the catalyst used with fixing the other reaction conditions on the concentration of sodium hydroxide 10% and the temperature of 95°C and the reaction time of five hours and it is noted that the reaction without catalyst gave the least yield while a cetyl ammonium chloride catalyst gave the highest yield.

Table (2) shows the results of the change in the reaction yield by changing the concentration of alkali to determine the best concentration with fixing the other reaction conditions from the polymer weight 10g and the temperature 95°C and the reaction time 5 hours and using the best catalyst and the high yield is noticed by increasing the concentration of sodium hydroxide to 10%, then the yield was decreased.

Table (3) shows the results of the reaction yield change by changing the temperature with fixing the other reaction conditions on the following values: the concentration of the sodium hydroxide 10% and the temperature of 95°C and the use of the best catalyst the cetyl ammonium chloride and it is noted that the reaction at a temperature of 120°C was carried out in the autoclave (Autoclave) gave the highest payoff.

Table (4) shows the results of the change in the reaction yield by changing the reaction time with fixing the other reaction conditions, the concentration of 10%

Table 1: Study the effect of the type of catalyst on the reaction yield

Catalyst	Without	Sodium Dodecyl Benzene Sulfonate	Cetyl ammonium chloride	Betaine	Nonyl Phenol Ethoxylate
Yield %	12.5	40.7	86.2	33.2	70

Table 2: Study the effect of concentration of alkali on the reaction yield

Alkali concentration w.w %	5	7	10	15	20
Yield%	20	43.9	86.8	64	37

Table 3: Study the effect of temperature on the reaction yield

Temperature	25	50	95	120
Yield%	3	43.9	86.8	100

Table 4: Study the effect of reaction time on the reaction yield

Reaction time (hrs.)	1	3	5
Yield%	52	60	86.8

Table 5: Study the effect of particle size on the reaction yield

Particle size mm.	<1	1-2	2-2.5	< 2.5
Yield%	100	87	66.4	52

Table 6: Functional groups bands of terephthalic acid

Wave number cm^{-1}	3450	1686	1570	781
Bond	Carboxylic OH	Aromatic carboxylic C = O	Conjugated C = C	Aromatic C-H

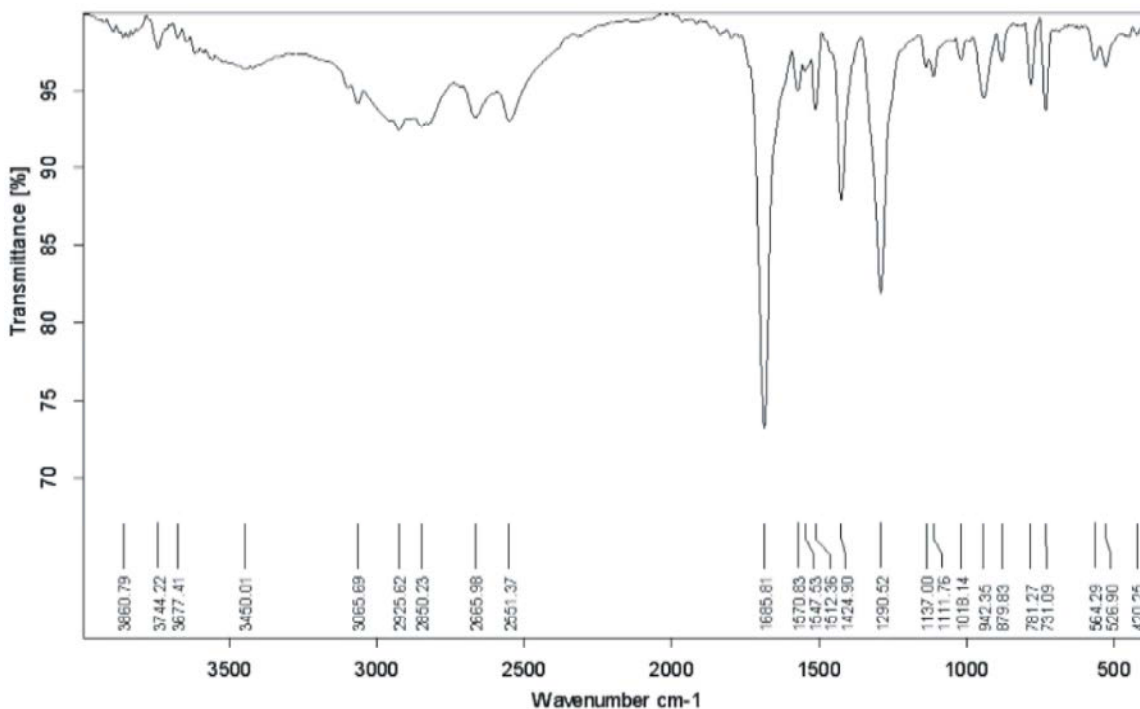


Fig. 1: The spectrum of FTIR for terephthalic acid prepared in the laboratory

sodium hydroxide, the use of the best catalyst, cetyl ammonium chloride and the temperature of 95°C. It is noted that the reaction time that gave the best yield is 5 hours.

Table (5) shows the results of the change of reaction yield by changing the particle size with fixing the other reaction conditions, the concentration of the sodium hydroxide 10%, the temperature is 95°C,

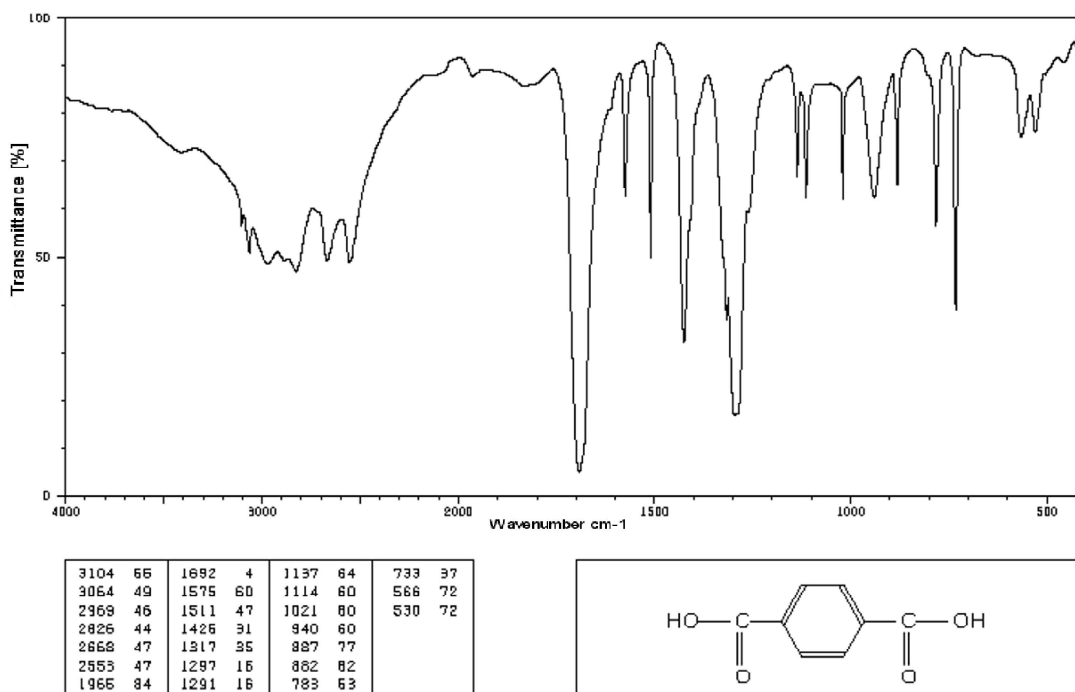


Fig. 2: The infrared spectrum for terephthalic acid reference

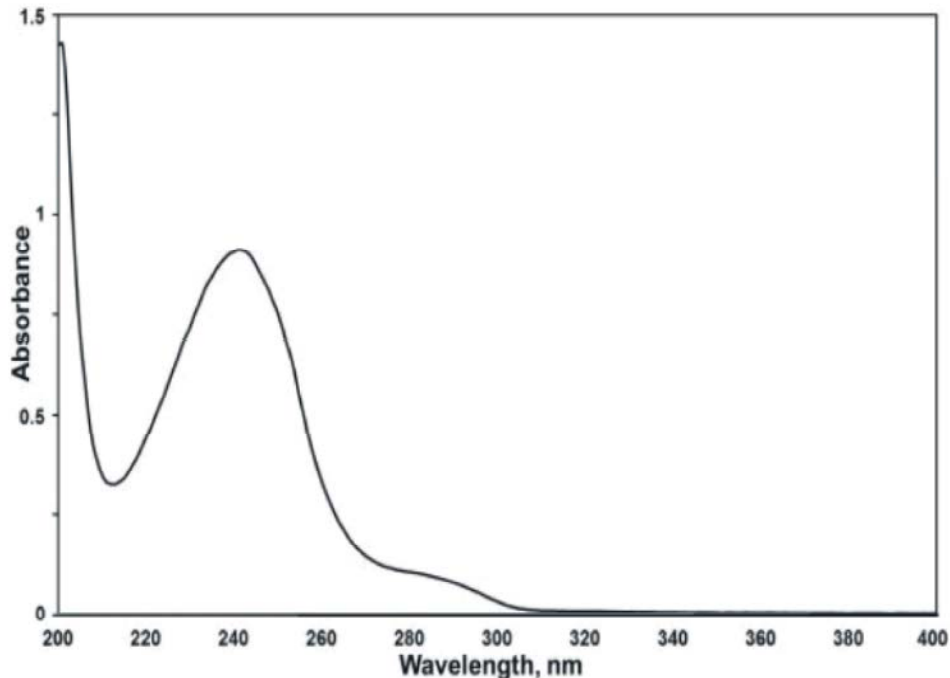


Fig. 3: The UV -Vis spectrum of terephthalic acid

the reaction time is 5 hours and the use of the best catalyst is cetyl Ammonium chloride. It is noted that the granular volume less than 1mm gave the higher yield.

When trying to determine the melting point of the prepared terephthalic acid it was found that it escalates without melting starting from the degree 340°C and this

corresponds to Merck [14] and the infrared spectrum of FTIR was obtained by using a KBr method and Figure (1) shows the spectrum of FTIR for terephthalic acid prepared in the laboratory, while Table (6) shows functional groups bands of terephthalic acid prepared with inference of the existing functional groups [15, 16]. Figure 2 shows the infrared spectrum for terephthalic acid reference [17] SDBS.

Figure 3 shows the UV -Vis spectrum of terephthalic acid at a concentration of 0.5 mg / ml100 in methanol where the peak absorption peak appears $\lambda_{max} = 241$ nm and corresponds to the reference value NIST.

CONCLUSIONS

- Sodium hydroxide concentration of 10% is preferable.
- Cetyl ammonium chloride is the best catalyst.
- The reaction at temperature 120° C (in the autoclave) gave the best yield.
- The reaction time of 5 hours gave the highest return.
- Particle size less than 1 mm gave the best yield.

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