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Alkaline Hydrolysis of Polyethylene Terephthalate at Lower Reaction Temperature

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Alkaline hydrolysis of polyethylene terephthalate (PET) resin in water-ethanol mixed solvent was examined and found to produce good results for the product, terephthalic acid, after protonation. The reaction proceeded smoothly at lower temperatures than previous methods. The highest yield (89%) was obtained when PET was heated at 110°C for 0.5 hr in 10% NaOH solution of water-ethanol mixed solvent (ratio 20:80 by weight). However, even this reaction condition is still unsatisfactory for the saving of petroleum resources by recycling and is short of affirming the significance of recycling itself.

Key words: Hydrolysis, Alkali, Polyethylene terephthalate, PET bottle, Chemical recycle

1. Introduction

Polyethylene terephthalate (PET) is a plastic widely used to manufacture bottles for soft drinks, fibers, and films. PET production is growing rapidly, and the world's annual consumption amounts to 13 million tons.[1)] On the other hand, the widespread application and non-biodegradability of PET create a huge amount of waste to dispose of, causing a serious problem. Therefore, from the awareness and concern for environmental pollution, recycling and reprocessing of waste PET have developed. Thus, the effective use of PET waste is an important problem for environment-protection researchers.

Various recycling methods for PET waste have been proposed. Among them, chemical recycling has attracted attention, by which PET bottles are chemically degraded and purified into raw materials to remanufacture PET resin.

PET is a polyester with functional ester groups and the ester group can be cleaved by various reagents, including water, alcohols and so on. The cleavage of an ester linkage by water is called hydrolysis and there is growing interest in hydrolysis because it is the only method which produces the monomers from which PET is produced.

Many types of hydrolysis of PET have been reported, but these reactions need a high reaction temperature, implying much usage of energy; for example, a supercritical methanol method[2,3)] and a supercritical water method[4)] require high reaction temperatures over 700°C. Glycolysis by ethylene glycol also gave good results but required high reaction temperatures over 200°C.[5,6)] As for alkaline hydrolysis, many reports have been published, but heating to about 200°C was still necessary in the reaction of aqueous ammonia solution.[7)]

In order to develop a more convenient hydrolytic method for PET at lower reaction temperatures, we

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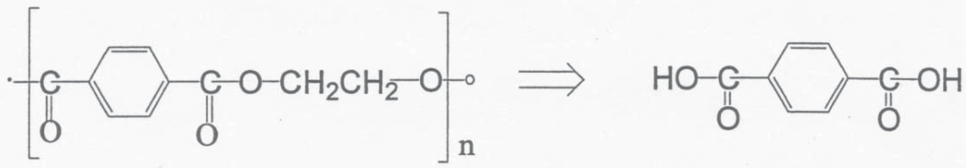


Scheme 1

examined the reaction in several solvents and found that ethanol is a good co-solvent with water. Here, we report a simple terephthalic acid (TPA) recovery reaction using ethanol as a solvent. (Scheme 1)

2. Experimental

2.1. *General*

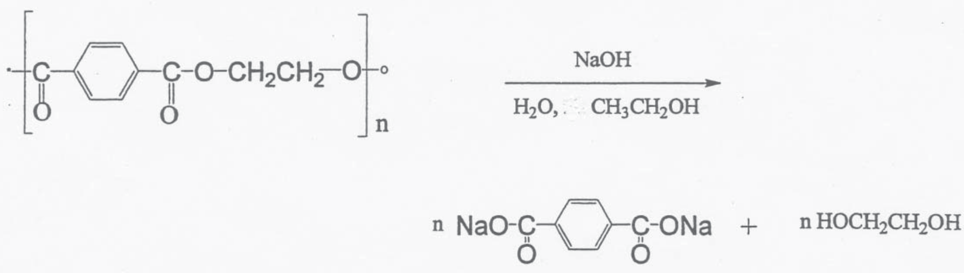
The solvents and reagents were all commercial products and used without further purification. Commercially available PET bottles were used as PET resin after cutting into 3-4 mm square pieces, washed with water and dried. Infrared(IR) spectra were measured on a Horiba FT-700 spectrometer.

2.2. *Hydrolysis of PET resin in NaOH solution*

The typical reaction procedure was as follows. To a 10% NaOH solution in 100 ml mixed solvent of ethanol and water (20:80) in a 300 ml flask, 2g PET resin was added and the flask was heated to 110°C for 0.5 hr. Unreacted residue was filtered and the filtrate was acidified by 20% hydrochloric acid to give a solution with white solids. White solids separated by filtration were washed with water, dried, and identified by IR and melting point measurements as terephthalic acid (TPA). The yield of TPA was 89%.

3. Results and Discussion

PET resin was decomposed to disodium terephthalate (**1**) (Scheme 2) by the reaction with NaOH, which was then protonated to terephthalic acid (TPA) (**2**) (Scheme 3) by hydrochloric acid. As the protonation of



(1)

Scheme 2

(2)

Scheme 3

disodium terephthalate (**1**) to TPA (**2**) is easily achieved by acidification of the solution, we investigated the favorable reaction conditions for the formation of the disodium salt (**1**).

3.1. *Alkaline hydrolysis of PET resin using ethanol as a solvent.*

First, several reactions were conducted using ethanol to elucidate its efficiency as a solvent.

3.1a. *Effect of heating temperature*

To examine the most effective heating temperature appropriate for the reaction in Scheme 2, we conducted several reactions using water/ethanol solvent (ratio 15:85) and 10% NaOH for 0.5 hr. The results are shown in Table 1.

Table 1 demonstrates that the amount of insoluble matter that remained unreacted decreases as the temperature rises. All PET pieces were decomposed when heated at 110°C, leaving no residual matter, and the yield of TPA (**2**) reached 87%.

3.1b. *Examination of water/ethanol ratio*

To determine the water/ethanol ratio appropriate for hydrolysis in this study, we conducted an experiment under the following conditions (heating temperature: 110°C, reaction time: 0.5 hr, and 10% NaOH solution). The results are shown in Table 2.

Table 2 demonstrates that the water/ethanol ratio by weight is a critical parameter for this hydrolysis. The TPA yield increased markedly from 4.9 to 89.0% with changes in the ratio of water/ethanol from 100:0 to 20:80, while the insoluble matter decreased markedly from 94.3 to 0%. The TPA yield was highest (89.0%) at a water/ethanol ratio of 20:80. Thus, in these reactions, it was found that 20:80 was the optimal water/ethanol ratio by weight.

3.1c. *Examination of reaction time*

To determine the appropriate reaction time for this hydrolysis we conducted an experiment under the following conditions: water/ethanol ratio: 20:80, heating temperature: 110°C, and 10% NaOH solution. The results are shown in Table 3.

Table 1. Effect of Temperature.

Entry	temperature(℃)	TPA yield (%)	insoluble matter content (%)
1	90	80.8	7.9
2	100	79.6	5.4
3	110	87.6	0.0

Table 2. Effect of Water/Ethanol ratio.

Entry	Water : Ethanol	TPA yield (%)	insoluble matter content (%)
4	100 : 0	4.9	94.3
5	80 : 20	28.7	71.1
6	60 : 40	77.9	14.8
7	50 : 50	85.7	1.3
8	40 : 60	86.6	0.9
9	20 : 80	89.0	0.0
10	15 : 85	87.6	0.0
11	10 : 90	87.3	0.0
12	5 : 95	82.6	7.5
13	0 : 100	81.6	9.8

Table 3. Effect of Reaction Time.

Entry	reaction time (h)	TPA yield (%)	insoluble matter content (%)
14	0.5	89.0	0.0
15	1.0	88.3	0.0
16	3.5	87.7	0.0

Table 3 demonstrates that the degradation reaction of the resin proceeds in 0.5 hr. It seems that degradation reaches its highest state at 0.5 hr and a prolonged reaction causes undesirable side reactions which reduce the yield of TPA. Actually, the yield gradually decreased. Thus, this study demonstrated that the appropriate reaction time was 0.5 hr.

3.1d. *Concentration of NaOH in a solution*

To determine the NaOH solution concentration appropriate for this hydrolysis, we conducted an experiment under the following reaction conditions: water/ethanol ratio: 20:80, heating temperature: 110°C, and reaction time: 0.5 hr. The results are shown in Table 4.

Table 4. Effect of NaOH Concentration.

Entry	Conc. of NaOH (wt%)	TPA yield (%)	insoluble matter content (%)
17	5	42.0	50.2
18	6	76.2	17.7
19	8	86.1	6.7
20	9	87.6	1.3
21	10	89.0	0.0
22	15	89.2	0.0

Table 4 demonstrates that the yield was greatly influenced by the NaOH concentration in the solution. From these results, the NaOH concentration was found to be a critical parameter in this hydrolysis. Entry 17-20 demonstrates that reactions with low concentration NaOH afforded undissolved PET residues, however, with over 10% NaOH concentration, all PET pieces degraded (Entry 21 and 22). As the TPA yields were correlated with that of the remains of insoluble matter, 10% concentration of NaOH (Entry 21) was found to be sufficient and optimal.

3.2. *Hydrolysis of PET using methanol*

Methanol is usually a better solvent than ethanol because it dissolves many inorganic salts; therefore, we attempted this reaction using methanol as the solvent instead of ethanol. As shown in Table 5, an almost comparable yield of the product (TPA) was obtained. Although methanol is less expensive than ethanol, it is considered to be more poisonous in the case of ingestion, inhalation or percutaneous absorption. Ethanol is therefore recommended for this hydrolysis from health and environmental aspects.

3.3. *Hydrolysis of PET using m-cresol*

As a representative of an aromatic hydroxyl compound, *m*-cresol was investigated as a solvent in this hydrolysis reaction. In this reaction, the optimum yield of 93.6% TPA was obtained when PET was heated in 100ml water/*m*-cresol (20:80) with 8% NaOH at 100°C for 1 hr; however, judging from its high boiling point and human toxicity, *m*-cresol is not recommended as the solvent for this purpose.

4. Conclusion

Increased PET bottle waste is becoming a social problem and several recycling methods have been found

Table 5. Hydrolysis in Water/Methanol solution.

Entry	Water:Methanol	Temp(℃)	Time(h)	Yield(%)
23	20:80	110	0.5	86.2

that NaOH hydrolysis of PET in water-ethanol co-solvent was the preferable method to recover terephthalic acid, however, this method still required heating up to about 100°C. In order to increase recycling for the global environment, more effective methods should be developed.

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