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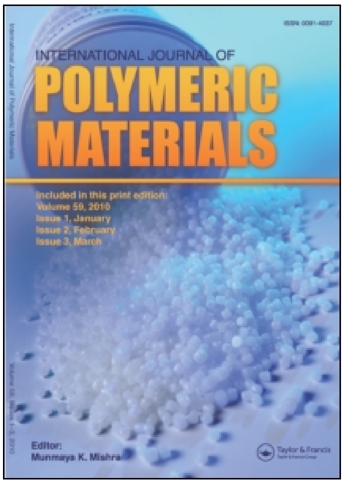

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Chemical Degradation of Poly(Ethylene Terephthalate)

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Chemical Degradation of Poly(Ethylene Terephthalate)

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The possibility of converting polyethylene terephthalate (PET) waste into terephthalic acid as a primary material by using different techniques through trans-esterification, with an alcohol and through hydrolysis in basic medium, has been investigated. In addition, utilization of activating agents such as inorganic salts and phase transfer catalysts has been investigated.
Mineral water and beverage bottles were collected, cleaned and crushed into flakes suitable for the intended experiments. Also, the main products of chemical conversion of such wastes were isolated and confirmed by authentication with standard terephthalic acid through Thin Layer Chromatography (TLC) technique. The reaction yield % was determined to optimize the corresponding experimental conditions and the obtained results have been presented and discussed.

Keywords: chemical degradation, depolymerization, phase transfer catalysis, poly (ethylene terephthalate), terephthalic acid

INTRODUCTION

Strategies for recycling of plastic wastes can be categorized under one of the following main directions: A) Reutilization of plastic wastes in some applications that require lower standards, especially those which are not in direct contact with edible materials. Polyethylene and polystyrene are examples for thermoplastics [1–3] while melamine-formaldehyde polymers and unsaturated polyester products are examples

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for the thermosetting materials [4–6]. B) Chemical conversion of the plastic waste into different products with different characteristics such as the conversion of PET waste into unsaturated polyesters. Such modified materials can be used as adhesives and in the production of new materials as well. For instance, synthetic marble and particleboard are produced using such materials [7–9], C) Depolymerization of the plastic waste into their primary components such as terephthalic acid and ethylene glycol in case of PET [10–12], in addition to minor amounts of other dicarboxylic acids such as maleic, succinic, tartaric and isophthalic acids and propylene glycol [13–14].

The last strategy can be considered beneficial as it avoids most hazards produced from the use of these materials before disposing of them, such as the probability of their microbial and/or viral contamination. Production of materials with low-level specifications and short lifetime can be avoided as well.

From the above, one can conclude that the depolymerization of plastic wastes into their primary constituents is a more gainful alternative although it may not be the easiest. There are several problems leading to low efficiency of the depolymerization process such as the penetration of chemical reagents into the polymer matrix as a result of its resistance to such reagents. In addition, the difficult solubilization of the plastic wastes makes it more complicated.

In the present study, the depolymerization reactions of PET wastes into their primary materials have been considered under several conditions. Depolymerization of PET waste was achieved through trans-esterification with methanol and ethanol and through alkaline hydrolysis in the presence of different types of catalysts. Factors that may affect the depolymerization yield, indicated by the produced terephthalic acid as a main component of the depolymerization products, will be considered.

EXPERIMENTAL

Preparation of PET Waste

Different types of bottles used for bottled drinking water were collected. Their caps and labels were removed. The empty bottles were crushed into small flakes of about 0.4 cm^2 area. The crushed material was washed thoroughly with distilled water and methanol and finally dried in a vacuum oven at 40°C for 24 h.

Trans-esterification of PET with Ethanol

An amount of 2 g (10 mmole based on the repeating unit) of PET waste flakes was mixed with 100 ml ethanol in the presence of a few

TABLE 1 Reaction Yield % and the Weight in mg of the Product of the Chemical Degradation Reactions of 2 g PET

		Time, h				
No.	Yield % (Wt., g)	12	24	48	96	120
a)	$C_2H_5OH + H_2SO_4$	0.86 (20)	6.49 (150)	13.84 (320)	19.03 (440)	20.33 (470)
b)	NaOH	2.31 (40)	4.63 (80)	11.57 (200)	16.19 (280)	16.87 (290)
c)	$NaOH + ZnSO_4$	4.63 (80)	9.25 (160)	20.81 (360)	27.76 (480)	28.34 (490)
d)	$NaOH + Ca(ACO)_2$	3.47 (60)	8.10 (140)	19.01 (330)	25.45 (440)	26.03 (450)
e)	NaOH + TEAC	5.78 (100)	15.04 (260)	32.97 (570)	45.11 (780)	45.67 (790)

drops of concentrated sulfuric acid. The reaction mixture was boiled for different time intervals (12, 24, 48 and 96 h) while stirring. The residual solids in the reaction mixture were then filtered off, washed with distilled water and finally dried in an oven. The filtrate was poured into 50 ml of distilled water and the excess of ethanol was removed by distillation. After the complete removal of ethanol, 50 ml of benzene was added and the mixture was shaken vigorously. The organic layer was separated off and dried with anhydrous sodium sulfate. The trans-esterification product, identified as diethylterephthalate, was obtained after evaporation of the organic layer (benzene) under reduced pressure. The viscous liquid crude product was solidified by time and cooling. The reaction yield % was determined gravimetrically and the data are summarized in Table l.

Alkaline Hydrolysis of PET

An amount of 2 g (10 mmole based on the repeating unit) of PET waste flakes was mixed with 100 ml of 5 wt% aqueous solution of NaOH. The reaction mixture was boiled for different time intervals (12, 24, 48 and 96 h) while stirring. The reaction mixture was then left to cool and the residual solids were filtered off. The alkaline filtrate containing the hydrolysis products was then neutralized with dilute hydrochloric acid. The precipitated product was filtered off under suction, dried in a vacuum oven at 40°C for 24 h in presence of P_2Cl_5 as desiccant and subjected to characterizing analysis. The reaction yield % was calculated and the data are summarized in Table 1.

Catalyzed Alkaline Hydrolysis of PET

Using Zinc Sulfate as Catalyst

An amount of 2 g (10 mmole based on the repeating unit) of PET waste flakes was mixed with 100 ml of 5 wt% aqueous solution of NaOH.

A small amount of about 0.1 g of zinc sulfate was also added to the reaction mixture which was then boiled for different time intervals (12, 24, 48 and 96 h) while stirring. The reaction mixture was then left to cool and the residual solids filtered off. The alkaline filtrate containing the hydrolysis products was then neutralized with dilute hydrochloric acid. The precipitated product was filtered off under suction, dried in a vacuum oven at 40°C for 24 h in the presence of P_2Cl_5 as desiccant and subjected to characterizing analysis. The reaction yield % was calculated and the data are summarized in Table l.

Using Calcium Acetate as Catalyst

An amount of 2 g (10 mmole based on the repeating unit) of PET waste flakes was mixed with 100 ml of 5 wt% aqueous solution of NaOH. A small amount of about 0.1 g of calcium acetate was also added to the reaction mixture which was then boiled for different time intervals (12, 24, 48 and 96 h) while stirring. The reaction mixture was then left to cool and the residual solids filtered off. The alkaline filtrate containing the hydrolysis products was then neutralized with dilute hydrochloric acid. The precipitated product was filtered off under suction, dried in a vacuum oven at 40°C for 24 h in the presence of P_2Cl_5 as desiccant and subjected to characterizing analysis. The reaction yield % was calculated and the data are summarized in Table 1.

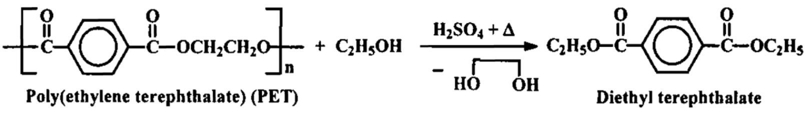
Using Tetraethylammonium Chloride (TEAC) as Catalyst

An amount of 2 g (10 mmole based on the repeating unit) of PET waste flakes was mixed with 100 ml of 5 wt% aqueous solution of NaOH. A small amount of about 0.1 g of tetraethylammonium chloride (TEAC) as phase transfer catalyst was then added to the reaction mixture which was then boiled for different time intervals (12, 24, 48 and 96 h) while stirring. The reaction mixture was then left to cool and the residual solids filtered off. The alkaline filtrate containing the hydrolysis products was then neutralized with dilute hydrochloric acid. The precipitated product was filtered off under suction, dried in a vacuum oven at 40°C for 24 h in the presence of P_2Cl_5 as desiccant and subjected to characterizing analysis. The reaction yield % was calculated and the data are summarized in Table 1.

RESULTS AND DISCUSSION

Trans-esterification of PET with Ethanol

The trans-esterification reaction of PET with ethanol led to the formation of diethyl terephthalate as a major product (m.p. 41°C) in addition to minor amounts of the diethyl ester of dicarboxylic acids. Also, the presence of ethylene glycol in the reaction products has been confirmed by the borate test for glycols. The trans-esterification reaction of PET with ethanol is represented by Eq. (1).

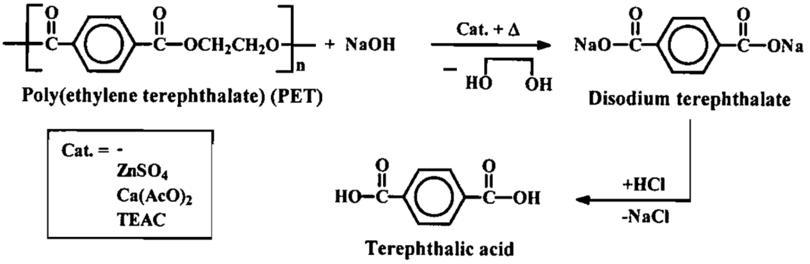


Alkaline Hydrolysis of PET

PET has been hydrolyzed in an aqueous solution of NaOH. After work-up of the reaction, the obtained product has been weighed and characterized with the aid of elemental and spectroscopic analyses. Scheme 1 represents the alkaline hydrolysis of PET. Thin layer chromatographic test matches from an authentic sample of commercially available terephthalic acid, in addition to some faint clouds corresponding to phthalic acid, can be neglected at this concern. The reaction yield % at the investigated time intervals is summarized in Table 1 and its time dependence is represented in Figure 1.

Catalyzed Alkaline Hydrolysis of PET

PET has also been hydrolyzed in an aqueous solution of NaOH in the presence of different materials in catalytic amounts. Some of them are inorganic salts, namely, zinc sulfate and calcium acetate, in addition to tetraethyl-ammonium chloride as a representative phase transfer catalyst, PTC. After work-up of the reaction, the obtained product has been weighed and characterized—in a similar way to that for the un-catalyzed alkaline hydrolysis investigation—with the aid of elemental and spectroscopic analyses. Scheme 1 represents the catalyzed alkaline hydrolysis of



SCHEME 1 Alkaline chemical degradation of PET.

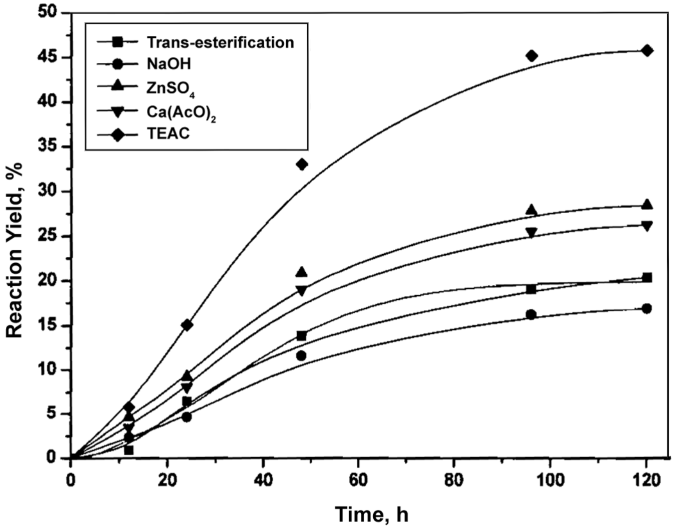


FIGURE 1 Time dependence of reaction yield % of chemical degradation of PET.

PET. Thin layer chromatographic test for the products matches that for an authentic sample of commercially available terephthalic acid in addition to some faint clouds corresponding to phthalic acid that can be neglected in this context. The reaction yield % at the investigated time intervals for the investigated catalysts is summarized in Table 1 and its time dependence is presented in Figure 1.

From Figure 1 one can conclude that under all the investigated conditions, there is a gradual increase in the degradation rate reflecting the ability of PET to be chemically degraded under such mild conditions. From Figure 1, it is also apparent that the un-catalyzed degradation process is the least effective one among the investigated processes. This can be attributed to the difficult penetration of the degrading reagent, NaOH, into the polymeric matrix due to their different wetting nature and hydrophilicity. Therefore, great effort has been paid to overcome such penetration difficulties through the application of vigorous conditions for degradation, such as the application of high pressure and temperature or utilization of chemicals enhancing the reaction efficiency. Such chemicals, in most cases, are expensive, with a negative impact on economic feasibility, and hazardous, necessitating the process be performed under special circumstances.

In this context, many researchers degraded PET through trans-esterification by using ethylene glycol [13], butylene glycol [15] and more recently methanol [16,17]. Formation of some oligomers on using the different glycols can be considered a drawback in this process, reflecting the incomplete conversion of PET. Moreover, toxicity of methanol is an additional drawback apart from the high cost of the hazardous materials.

On the other hand, catalyzed alkaline hydrolysis of PET proved itself to be beneficial over the previous techniques, as can be concluded from Figure 1. Phase transfer catalysis was a better technique than both the inorganic salts used where the chemical degradation reaches its maximum efficiency after about 96 h. This is, of course, due to ease of penetration of PT-catalyst (PTC) through the PET matrix and also is less contaminating to the reaction system than the inorganic salts. Finally, one can conclude that although PTC technique does not overcome the above-mentioned drawbacks, it is still a cheap and easy technique and is economically feasible.

CONCLUSIONS

The following conclusions can be derived from the current investigation:

- The chemical degradation of PET is not easy to approach without considering the physical properties and mechanical history of the PET waste, such as the compact nature attained during processing. This may hinder or even prevent the chemical reagents from diffusing into the polymer matrix.
- Under all the investigated conditions, PET has a measure of ability to be chemically degraded under rather mild conditions.
- The non-catalyzed alkaline degradation process is the least effective of the investigated processes.
- Utilization of catalysts in the alkaline hydrolysis of PET proved itself beneficial over the non-catalyzed techniques.
- Phase transfer catalysis was a more efficient technique than both the inorganic salts used.
- Finally, although PTC technique does not overcome the above mentioned drawbacks, it is still easy technique and it is economically feasible.

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