

# Aminolytic Depolymerization of Poly (ethylene terephthalate) Bottle Waste by Conventional and Microwave Irradiation Heating

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**ABSTRACT:** Poly (ethylene terephthalate) (PET) is the most popular thermoplastic polymer. The ever-growing production and utilization of PET has led to postconsumer waste disposal problems because of its nonbiodegradability. The chemical depolymerization of PET waste is a possible remedy, as it results in some recyclable products. The aminolytic depolymerization of PET bottle waste with hydrazine monohydrate by conventional and nonconventional (with microwave irradiation) heating was carried out with simple chemicals as catalysts, such as sodium acetate and sodium sulfate. The yield of the product was

optimized through variations in the time of aminolysis, the catalyst concentration, and the PET:hydrazine monohydrate ratio. The pure product obtained in good yield (86%) was analyzed by Fourier transform infrared spectroscopy, NMR, and differential scanning calorimetry and was identified as terephthalic dihydrazide. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 1103–1107, 2012

**Key words:** PET bottle waste; aminolytic depolymerization; recycling; microwave; terephthalic dihydrazide

## INTRODUCTION

Poly (ethylene terephthalate) (PET) is the most popular thermoplastic polymer being used in the manufacturing of a variety of products differing widely in their physical characteristics. It is largely used in making of fibers, soft drink bottles, photographic films, packaging, coatings, and so on. The ever-growing production and use of the nonbiodegradable PET has led to waste disposal problems after its use. The recycling of waste polymers, including PET, can be carried out in many ways.<sup>1</sup> Physical recycling is one such solution, although the recycled polymer possesses inferior quality. The only method acceptable according to the principles of sustainable development is the so-called tertiary or chemical recycling; this results in the yield of corresponding virtual monomers. The chemical recycling of PET can be performed via glycolysis,<sup>2,3</sup> methanolysis,<sup>4,5</sup> hydrolysis,<sup>6,7</sup> aminolysis,<sup>8,9</sup> or ammonolysis.<sup>10</sup> All of

these methods have been reviewed by a number of workers.<sup>11–13</sup>

The aminolysis of PET has been explored little compared to other depolymerization techniques. Soni and Singh<sup>14</sup> treated PET waste flakes with aqueous methylamine and ammonia at room temperature in the presence of cetyl ammonium bromide for up to 45 days to obtain *N,N*-dimethyl terephthalamide and terephthalamide, respectively, as fine precipitates. Goje et al.<sup>15</sup> carried out PET aminolysis under reflux with hydrazine monohydrate in the presence of lead acetate as a catalyst and obtained terephthalic dihydrazide, a product used for the preparation of a polyhydrazide comonomer. In our earlier publication,<sup>16,17</sup> the aminolyzed product, terephthalic dihydrazide, shows the potential for further chemical reactions; this has been explored at our laboratory, and some novel heterocyclic derivatives having antibacterial activity and some novel disazo disperse dyes have been synthesized. Spychaj and coworkers<sup>18,19</sup> conducted the aminolysis of PET with polyamines and triethanol amine and tested the products as epoxy resin hardeners and polyol components for rigid polyurethane foam synthesis.

The use of microwave irradiation as a source of heating in chemical reactions has received much attention.<sup>20–22</sup> Microwave-assisted organic synthesis is a comparatively new technique that has revolutionized chemical research.<sup>23,24</sup> Many organic reactions have been accelerated by microwave heating,

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which offers advantages of reducing the reaction time and offering greater convenience.<sup>25,26</sup>

Nikje and Nazari<sup>27</sup> used microwave irradiation for the glycolytic depolymerization of PET with alcohols. Hydrolytic depolymerization of PET under microwave irradiation in a closed system at 2 MPa of pressure for 90–120 min led to the formation terephthalic acid, ethylene glycol, and diethylene glycol as degradation products.<sup>27</sup> Similar studies were carried out by Zhang et al.<sup>28</sup> with pure water at 220–230°C at 2.0–2.5 MPa for 60–120 min. In our previous work on the microwave-assisted aminolysis of PET waste with ethanol amine as an aminolytic reagent, to get bis(2-hydroxyethyl), terephthalamide was obtained in a 90% yield under atmospheric pressure in 7 min.<sup>29</sup>

In this article, the results of the use of conventional heating and microwave irradiation heating for PET aminolysis in hydrazine monohydrate under reflux conditions are reported. The depolymerization catalysts used were simple chemicals, including sodium acetate and sodium sulfate.<sup>30,31</sup> The reaction conditions were optimized. The purified product was characterized by Fourier transform infrared (FTIR) spectroscopy, NMR, and differential scanning calorimetry (DSC) techniques.

## EXPERIMENTAL

### Materials

Discarded PET soft drink bottles were obtained from a local market, cut into small pieces approximately 5 × 5 mm<sup>2</sup> in size after they were separated from the non-PET components such as labels and caps. They were cleaned by boiling with a solution containing 2 g/L detergent for 1 h followed by thorough washing with water and drying in air.

### Chemicals

All of the chemicals, including hydrazine monohydrate, sodium acetate, and sodium sulfate, were analytical-reagent grade (obtained from SD Fine Chemicals, Mumbai, India) and were used without any further purification.

### Aminolysis of PET waste

#### Conventional heating method

Hydrazine hydrate was used for the aminolysis of PET waste under reflux in the presence of sodium acetate and sodium sulfate as depolymerization catalysts for time periods varying up to 6 h. At the end of the reaction, distilled water was added in excess to the reaction mixture with vigorous agitation to precipitate out the product, terephthalic dihydrazide,

which was redissolved by boiling followed by hot filtration. We obtained a yellow crystalline powder by first concentrating the filtrate by boiling and then chilling it. It was purified by repeated crystallization from water, dried in an oven at 70°C, and weighed to estimate the yield.

#### Microwave irradiation method

A 700-W Electrolux (17L) domestic microwave oven (Mumbai, India) was used for the aminolysis. It was modified to allow fitting of a condenser, as described in a previous article.<sup>32</sup> The PET waste was treated with hydrazine hydrate under reflux with a microwave oven at its maximum power in the presence of sodium acetate/sodium sulfate as a catalyst for a time period up to 20 min. The catalyst concentration was varied between 0.5 and 2% (w/w). The rest of the procedure for obtaining the product, terephthalic dihydrazide, was the same as given previously.

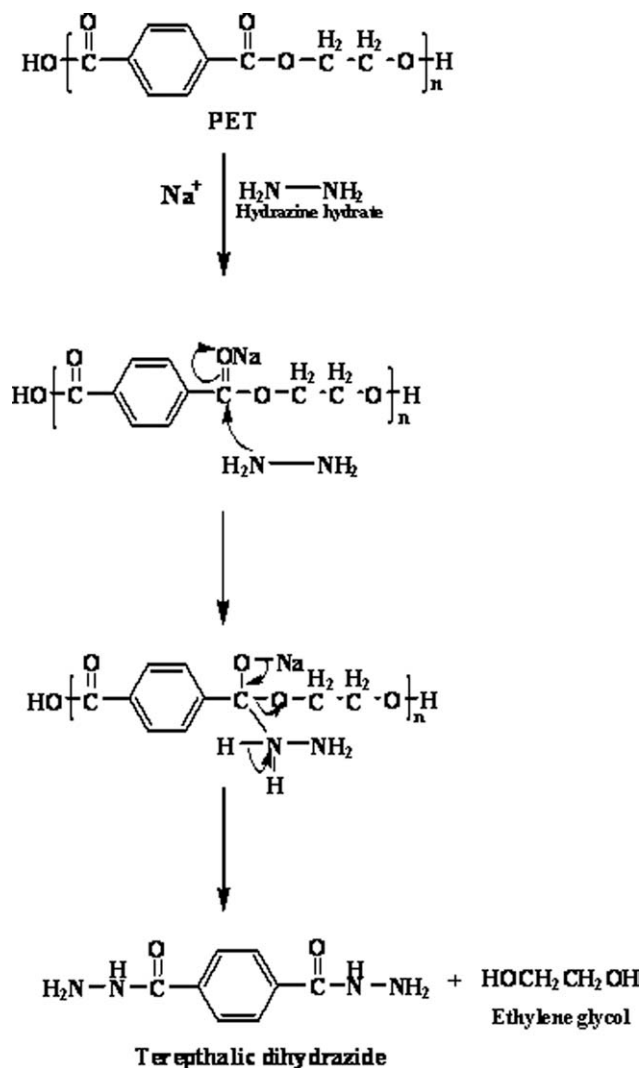
#### Characterization of terephthalic dihydrazide

The product obtained, terephthalic dihydrazide, was characterized with the help of ultraviolet–visible (UV–vis) spectroscopy, FTIR spectroscopy, DSC, and NMR.

The solubility of the crystalline product was determined in different solvents, and it was found to be soluble in dimethylformamide and dimethyl sulfoxide (DMSO). The UV–vis spectrum was recorded with a double-beam UV–vis spectrophotometer (model 8500, TECHCOMP, Hong Kong) by dissolution of 0.1 mg of sample in 10 mL of DMSO. FTIR spectra were recorded on a Shimadzu (model 8400S, Japan), FTIR spectrophotometer with the attenuated total reflection technique. The product was also characterized with the help of DSC (Shimadzu 60) at a heating rate of 10°C/min from 40 to 400°C under a nitrogen atmosphere. <sup>1</sup>H-NMR spectra were recorded on a Bruker DRX-400 spectrometer at 400 MHz in DMSO solution. The chemical shifts were reported in parts per million (ppm) and with Tetramethyl silane (TMS) as an internal standard.

## RESULTS AND DISCUSSION

Although the depolymerization of PET to produce virtual monomers that could be reused for the synthesis of new products holds potential for sustainable recycling, the attempts reported have generally made use of heavy-metal catalysts, such as zinc or lead acetate, which cause further concern about environmental protection. We reported earlier that simple and cheap chemicals, such as sodium carbonate, sodium bicarbonate, glacial acetic acid, sodium sulfate, sodium acetate, and potassium sulfate can



**Scheme 1** Mechanism of the aminolytic depolymerization of PET with hydrazine monohydrate.

very well substitute for the heavy-metal catalysts for PET glycolysis and aminolysis.<sup>28-31</sup>

Microwave-irradiated reactions have been reported to be helpful in reducing the time of reaction

**TABLE I**  
Effect of the Time on the Yield of Terephthalic Dihydrazide

Time (h)	Terephthalic dihydrazide (% yield) with catalyst	
	Na acetate	Na sulfate
1	40	41
2	57	57
3	74	75
4	86	85
5	86	85
6	86	86

Conditions: conventional heating, catalyst concentration = 1% w/w, and PET:hydrazine hydrate = 1 : 6.

**TABLE II**  
Effect of the Catalyst Concentration on the Yield of Terephthalic Dihydrazide

Catalyst concentration (% w/w)	Terephthalic dihydrazide (% yield) with catalyst	
	Sodium acetate	Sodium sulfate
0.5	77	76
1.0	86	85
1.5	85	86
2.0	85	85

Conditions: conventional heating, time = 4 h, and PET:hydrazine hydrate = 1 : 6.

and simultaneously affording greater convenience. Thus, to make the PET depolymerization process more ecofriendly, in this work, we report the results of the aminolytic depolymerization of PET waste with hydrazine monohydrate under reflux by conventional heating and in a microwave-heated setup. The catalysts used were simple chemicals, namely, sodium acetate and sodium sulfate. In this reaction, one of the amine groups of hydrazine hydrate attacked the ester linkage of PET. The catalyst formed a complex with the carbonyl group<sup>33,34</sup> and increased its polarity. The terephthalic dihydrazide was then obtained, as shown in Scheme 1.

The results of the optimization of the reaction parameters, namely, the time of reaction (Table I), catalyst concentration (Table II), and PET:hydrazine monohydrate ratio (Table III) by conventional heating indicated that the maximum yield of terephthalic dihydrazide was obtained with a PET:hydrazine hydrate molar ratio of 1 : 6 with a 1% w/w concentration of either of the two catalysts for a 4-h time. The yield of the purified product was as high as 86%.

The same optimized reaction parameters, namely, the PET:hydrazine hydrate ratio and catalyst concentration, were employed in the depolymerization of PET bottle waste under microwave irradiation with the time of reaction varied from 5 to 20 min.

**TABLE III**  
Effect of PET:Hydrazine Hydrate Ratio on the Yield of Terephthalic Dihydrazide

PET:hydrazine hydrate (molar ratio)	Terephthalic dihydrazide (% yield) with catalyst	
	Sodium acetate	Sodium sulfate
1 : 2	60	59
1 : 4	73	72
1 : 6	86	85
1 : 8	85	85
1 : 10	86	86

Conditions: conventional heating, catalyst concentration = 1% w/w, and time = 4 h.

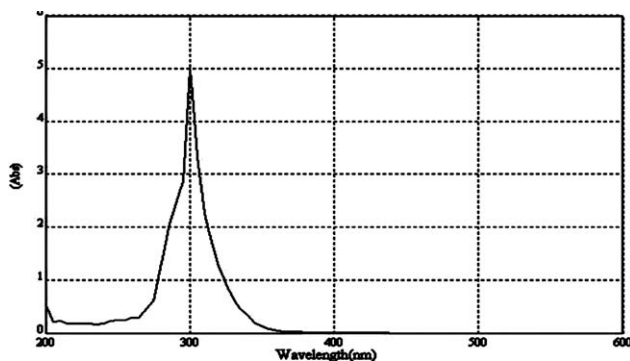
**TABLE IV**  
Effect of the Time on the Yield of Terephthalic Dihydrazide

Time (min)	Terephthalic dihydrazide (% yield) with catalyst	
	Sodium acetate	Sodium sulfate
5	75	74
10	85	86
15	85	86
20	86	86

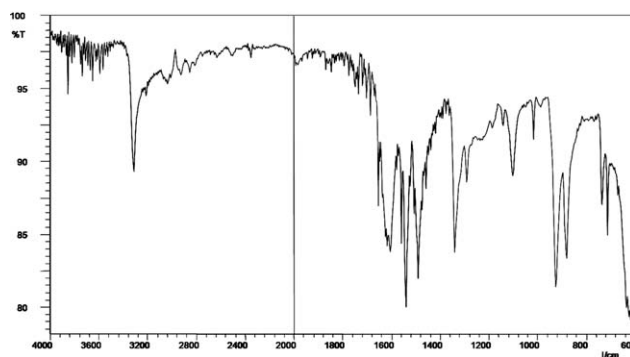
Conditions: microwave irradiation heating, catalyst concentration = 1% w/w, and PET:hydrazine hydrate = 1 : 6.

It was observed (Table IV) that only 10 min was required to obtain the maximum yield (85–86%) of terephthalic dihydrazide comparable to that obtained by conventional heating. Thus, a significant decrease in the time of the aminolytic depolymerization reaction from 4 h to 10 min was achieved with microwave irradiation as a heating source for refluxing the reaction mixture. This may be attributed to the fact that microwaves do not affect the activation energy of the reaction but provide the momentum to the reactant molecules to overcome the barrier to reach the higher state. This helps in the completion of the reaction at a faster rate than by conventional electric heating, which employs conduction and convection of heat energy, first to the surface of reactants and then penetrating the reaction mass slowly.

Microwaves are known to couple directly with the molecules present in a reaction mixture and lead to a rapid but controllable rise in the temperature. The transfer of energy from microwaves to the substance being heated takes place through dipole rotation and ionic conduction. Dipole rotation is an interaction between the polar molecules that try to align themselves with the rapidly changing electric field of the microwaves; this results in a transfer of energy. Ionic conduction results if there are free ions or ionic species present in the substance, which try to orient themselves to the rapidly changing electric field and generate ionic motion.<sup>35</sup>



**Figure 1** UV-vis spectrum of terephthalic dihydrazide.



**Figure 2** FTIR spectrum of terephthalic dihydrazide.

### Analysis

#### UV-vis spectrum

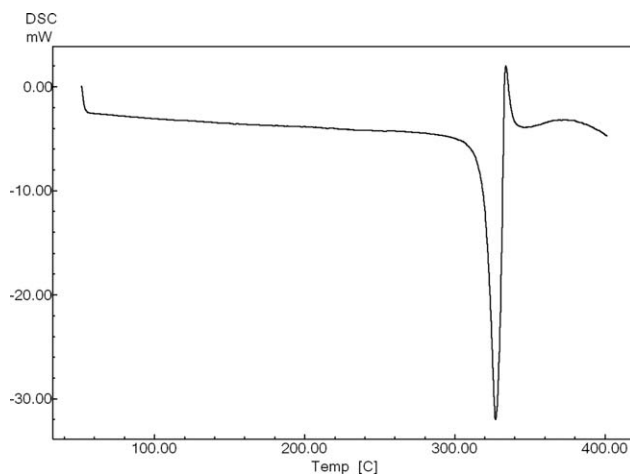
Figure 1 shows the UV-vis spectrum of the terephthalic dihydrazide obtained by the aminolysis of PET waste with hydrazine monohydrate. The figure shows a strong absorption peak at about 300 nm, which suggests the presence of a carbonyl group and aromatic ring.

#### FTIR spectral analysis

Figure 2 shows the FTIR spectrum of the product, indicating a pair of absorption bands at  $3312\text{ cm}^{-1}$ , attributed to N-H stretching and characteristic of primary amides. The C=O stretching appeared at  $1628\text{ cm}^{-1}$ . The peak at  $1490\text{ cm}^{-1}$  was due to the aromatic ring, and the peak at  $1339\text{ cm}^{-1}$  was due to C-N stretching. A peak was observed at  $3030\text{ cm}^{-1}$  due to aromatic C-H stretching and at  $1288\text{ cm}^{-1}$  due to N-N stretching.

#### Thermal analysis

The DSC thermogram recorded in Figure 3 indicated a large endothermic peak at  $327^\circ\text{C}$  attributed to the



**Figure 3** DSC scan of terephthalic dihydrazide.

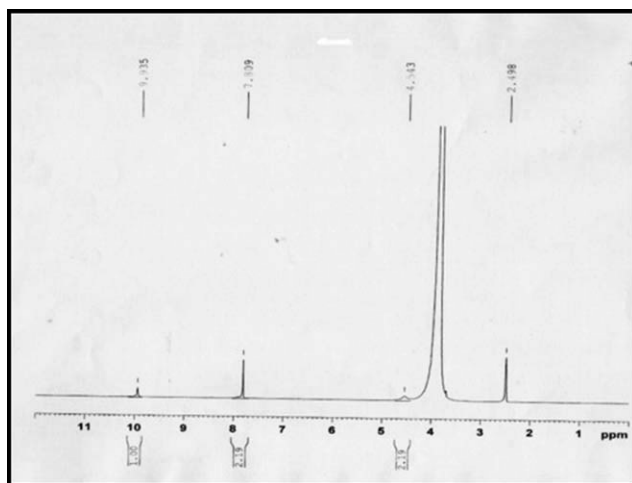


Figure 4 NMR of terephthalic dihydrazide.

melting point of the aminolyzed product. However, the exothermic peak at 339°C, followed by the melting of the product showed complete thermal decomposition at 339°C.

#### <sup>1</sup>H-NMR

Figure 4 shows the <sup>1</sup>H-NMR spectra of the aminolyzed product. Three NMR peaks were observed at 4.543 ppm (s, 4H, NH<sub>2</sub> of —CONHNH<sub>2</sub>), 7.809 ppm (s, 4H, Aromatic —H), and 9.935 ppm (s, 2H, NH of —CONHNH<sub>2</sub>).

Thus, the product after purification was characterized and identified to be terephthalic dihydrazide. These observations were in good agreement with the reported literature.<sup>36</sup>

### CONCLUSIONS

Microwave irradiation was found to be an efficient energy source in completion of the PET waste depolymerization reaction, as indicated by the very short reaction time, which led to a substantial conservation of energy. It offers an economical and convenient technology for producing terephthalic dihydrazide as a product compared to conventional heating without affecting the yield.

The product of the depolymerization of terephthalic dihydrazide has the potential for recycling it into useful products through various chemical reactions. This is being explored.

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