

Recycling of Waste PET-Bottles Using Dimethyl Sulfoxide and Hydrotalcite Catalyst

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ABSTRACT: The degradation of PET bottles has been successfully achieved using hydrotalcite as catalyst and dimethyl sulfoxide (DMSO) as solvent. The reaction was carried out at boiling point of DMSO (190°C) and degradation was complete in 10 min. The oligomer (tetramer) obtained was treated with NaOH at room temperature in methanol to get dimethyl terephthalate (DMT) and ethylene glycol (EG). Thus, it is a safe and cleaner process. Oligomer was characterized by MS, ¹³C-NMR, X-ray diffractometric, and thermogravimetric analysis. DMT and EG were characterized by GC-MS. DMT was also characterized by FT-IR. GC-MS analysis shows that the purity of DMT was 99%. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 1513–1519, 2013

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INTRODUCTION

Polyethylene terephthalate (PET) is one of the extensively used polymeric material. The main motivation for the widespread recycling of PET is its extensive use in plastic packaging applications, especially in the beverage industry.¹ The amount of PET production has risen recently, leading to a continuous increase in the generation of plastic waste. India will probably see a rise in waste generation from less than 40,000 metric tons per year to over 125,000 metric tons by the year 2030.² The disposal of this waste plastic has posed serious environmental and economic problems.³ Today, PET bottles have become one of the most valuable and successfully recyclable materials.⁴ Several processes for PET degradation have been put forward, such as the methanolysis process with methanol,⁵ glycolysis processes with ethylene glycol (EG) or other glycols,^{6,7} and hydrolysis under the promotion of acidic or basic conditions.^{8,9} PET could be effectively degraded into monomers or oligomers by these methods; however, there exist disadvantages in these processes. Methanolysis is usually carried out at relatively high pressure and temperature; moreover, it involves the volatilization of methanol. The main drawback of the glycolysis process is that the reaction products are not discrete chemicals but the bis (hydroxyethyl) terephthalate (BHET) monomer along with higher oligomers are formed which are difficult to purify with conventional methods.⁶ Many researchers have reported PET degradation by strong acids or bases as effective catalysts for the hydrolysis of PET to gives terephthalic acid,^{10–13} but the corro-

sion of the equipment and the separation of EG from the waste acid were critical problems in these processes. Various authors^{14–18} have studied the degradation of PET in supercritical methanol using a high-pressure reactor. These methods are unattractive from an economical view point due to their high energy consumption or because they require equipment's that withstand high pressures. Wang et al.¹⁹ have reported the degradation of PET using ionic liquids but this method required high temperature, pressure, and longer reaction time (10 h), so it is economically not feasible.

The literature study reveals that presently known methods are not suitable for degradation of waste PET to pure oligomer at commercial scale which can be transferred to an economically useful product. Hydrotalcite have been reported to be an eco-friendly, inexpensive readily available, and widely used catalyst for organic synthesis.²⁰ This study using hydrotalcite shows that PET bottle chips are degraded in dimethyl sulfoxide (DMSO) within 10 min while other catalyst (like sodium hydroxide, zinc chloride, lithium chloride, magnesium chloride, and ferric chloride)^{19,21,22} required high temperature, pressure, and longer reaction time (8–10 h). Hydrotalcite enhances rate of the reaction due to large surface area, weak Lewis acidity, high adsorption capacity while other commonly used catalyst like (sodium hydroxide, metal acetate (lead, zinc, cobalt, and manganese)²² shows low surface area. Hydrotalcite can be easily recycled and reused and easily separated from the product while various other catalysts, such as titanium phosphate,⁶ metal acetate (lead,

zinc, cobalt, and manganese)²² and solid superacids²³ are difficult to separate from the products.²⁴ Thus hydrotalcite has the advantage of high reactivity, recyclability, nontoxicity, and ease of separation. The oligomer formed can be easily converted to dimethyl terephthalate (DMT) at room temperature resulting in zero effluent reaction.

EXPERIMENTAL

Materials

PET flakes were obtained from postconsumer clear bottles and the bottles were cut into small pieces. The solvents used in the experiments including DMSO and methanol were of chromatographic grade from Merck India and Thermofisher Scientific. Other Chemicals viz, Mg(OH)₂, Al₂O₃, NaHCO₃, NaOH used were purchased from Rankem and Merck India and were of A.R grade.

Synthesis of Hydrotalcite Catalyst

For hydrotalcite synthesis Mg(OH)₂ (2.33 g) and Al₂O₃ (0.52 g) were suspended in distilled water (100 mL) and mixed in a R.B. flask. Sodium bicarbonate (NaHCO₃) solution (0.1 N) was then added dropwise with stirring until the solution pH reached 9–10; then the contents were refluxed at 80°C for 3 h. The resulting white product was filtered and repeatedly washed with distilled water. It was dried in oven at 100°C for 9–10 h.²⁵

Conversion of PET into Oligomer

PET waste bottle chips (5 g) were added in round-bottomed flask having 20 mL DMSO to this hydrotalcite (Al:Mg:CO₃) (0.5 g) was added. The resultant mixture was heated and maintained at reflux temperature (around 190°C) for 10 min. When polymer chips disappeared, that is, degraded, the contents were decanted to remove hydrotalcite and oligomer was separated out on cooling. Oligomer was filtered and washed with water and dried. Hydrotalcite and DMSO separated can be reused for next batch.

Conversion of Oligomer into Dimethyl Terephthalate

Sodium hydroxide (0.6 g) was stirred in a 100-mL round-bottomed flask containing methanol (20 mL) as solvent. The oligomer (5 g) was added with stirring. The stirring was continued at room temperature (35°C) for 1 h which resulted in the formation of white precipitates of DMT. The precipitates were filtered, washed with water, and dried. From the methanolic filtrate EG and sodium methoxide were separated using simple distillation. Methanol recovered can be recycled.

Product Analysis

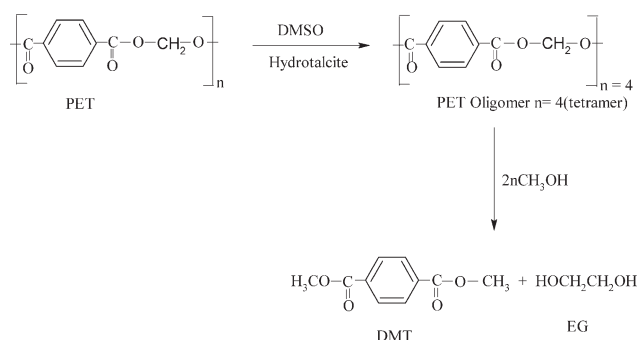
Oligomer was identified using an Agilent 6310 series chromatograph equipped with a mass spectrometer (MS). The mass spectra were recorded in the range of 50–1000 MHz. ¹³C NMR-spectra of the oligomer was recorded with an NMR Spectrometer (DSX-300, Bruker) in the solid state at 75 MHz. The XRD investigation was carried out using an Rigaku's D-300 X-ray diffractometer with a nickel filtered Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) for crystalline phase detection between 4 and 90° (2 θ), scan speed: 2° per min, step size = 0.02 and generator rating 40 kV, 100 mA was used. A thermogravimetric analyzer (TGA-2050) was used to study the thermal stability of oligomer in an atmosphere of nitrogen with a flow rate of 25 mL min⁻¹ over a

temperature range from room temperature to 500°C at heating rate of 10°C min⁻¹. The GC-MS spectra of DMT dissolved in methanol and EG were recorded using Shimadzu GCMS QP 2010 plus (Japan). Column used was Rtx-5 sill injector temp: 270°C, injection mode: split, split ratio: 20, injection volume: 0.5 μ , column flow: 1.0 mL/min (carrier gas: helium) mass range: 50–1000, ion source temp: 200°C, interface temp: 240°C. The FT-IR spectrum of the DMT was recorded by Shimadzu Prestize 21 FT-IR spectrometer. The FTIR spectra were recorded in the range 4000–450 cm⁻¹ in KBr.

RESULTS AND DISCUSSION

Degradation Reaction

The degradation of PET-bottle was achieved in 10 min using hydrotalcite (Al:Mg:CO₃) as catalyst in solvent DMSO. The oligomer on treatment with sodium hydroxide in methanol at room temperature resulted in the precipitation of DMT and EG in methanol, according to the following chemical reaction:



Structural Identification of the Oligomer

Figure 1 shows the ¹³C NMR data for oligomer. This data indicate the presence of carbonilic carbon at δ 60.6, 64.8, and 69.1, aromatic carbon at δ 129.1, and 132.7 and carbonilic carbons at δ 165.8 (Table I) δ values of carbonilic carbons of oligomer were compared with δ values of diethylene glycol (DEG).²⁶ The esterification of an alcohol has an unprotection effect on the C α and a protection effect on the C β .²⁷ In case of oligomer there were also esterification's from the alcohol function. Considering the α and β esterification effects on the δ of DEG and the structure symmetry, δ 64.8 can be attributed to the C α (C-1') and 69.1 to the C β (C-2') of unit 1. Carbon at δ 132.7 and at 165.8 indicating that these carbons were quaternary, or in other words, aromatic carbons.

The structural characterization of high mass molecules can be often achieved by mass spectrometry,^{28,29} which is complementary to NMR analysis as a powerful structural tool. The mass spectrum of oligomer is shown in Figure 2. This spectrum shows a peak at m/e 934. The intense peaks at m/e 401, 505, 549, 593, 637, 741, 785 can be assigned to the tetramer ($n = 4$), mol. wt. 934 g/mole and mol. formula HOOC[C₆H₄COO(CH₂)OOC]₄C₆H₄COOH (Lit.³⁰ Tetramer ($n = 4$) can be assigned to the oligomer. (Table II) The characteristic fragments of the oligomer in mass spectrum are given in Table III.

Figure 3 shows the XRD profile of the oligomer which indicate that the oligomer exhibits a high degree of crystallinity. The

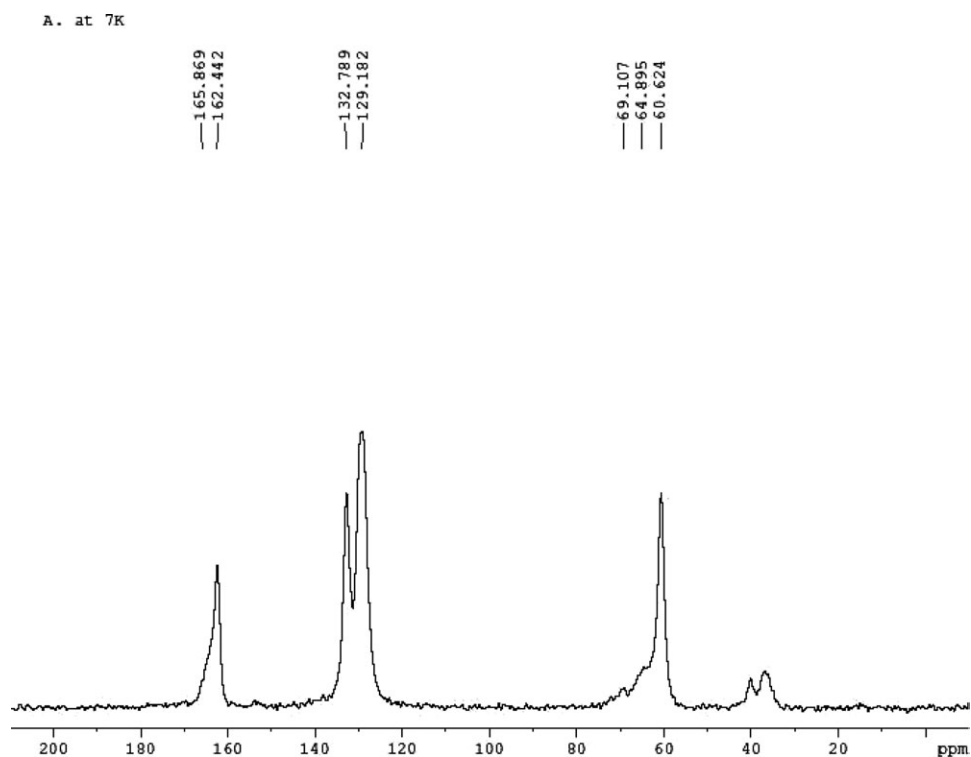


Figure 1. ¹³C-NMR of oligomer (tetramer).

typical diffraction peak of the oligomer are at $2\theta = 16.4, 17.7, 25.9, 26.1, 29.3^\circ$. The comparison of XRD profile of oligomer with PET has shown in literature¹⁹ support a crystalline structure. The peaks of PET are broader while that of oligomer are sharp.

TGA curves of the oligomer is illustrated in Figure 4. The TGA curve exhibits three main regions over the temperature range 240–350°C, 350–450°C, and 450–700°C which involves a total weight loss of 81.54% at 350–450°C for decomposition. This shows that oligomer degrades thermally at higher temperature but in presence of hydrotalcite and DMSO leads to oligomer formation at 190°C.

FT-IR spectra of DMT have been shown in Figure 5. It can be seen that IR shows peaks at 3421 cm^{-1} which relates to carboxylic group. The peak at 1408 cm^{-1} is related to aromatic ring and at 1720 cm^{-1} relates to carbonyl group. These values matches to that reported in literature for DMT.³¹ From the GC-MS tech-

nique, the purity of synthesized DMT was found to be 99%. The mass spectra of DMT is shown in Figure 6. This spectrum shows molecular ion peak at 194 supporting formation of DMT.³¹

Role of Solvent

The effect of solvents (20 mL) was studied using EG, acetone, tetrahydrofuran (THF), water and DMSO. It was observed that out of these solvents only DMSO could degrade PET bottle chips in the presence of hydrotalcite catalyst (Al:Mg:CO₃). The other solvents (EG, THF, acetone) in the presence of hydrotalcite (Al: Mg:CO₃) could not degrade PET bottle chips up to 7–8 h. Solvent studies indicated that the conversion depends on the polarity of the solvents (Table IV). This is because higher polarity solvent such as DMSO swell the polymer and to cause crystallization in the swollen state.³² The effect of solvent volume on the yield of oligomer was studied and is given in Figure 7. It shows that the yield of the product increases with increasing volume of DMSO and reaches a constant value at 20 mL. The results suggest that optimum DMSO volume is 20 mL for 5 g plastic bottle (PB/DMSO = 1/4).

Influence of Reaction Temperature and Time

The effect of degradation temperature on the degradation of PET with hydrotalcite catalyst in temperature range (120–190°C) at different time periods is shown in Figure 8. The results show that the catalytic activity increased with an increase in reaction temperature and the rate of degradation is also enhanced as the reaction temperature rises and maximum conversion of 98% was observed at 190°C in 10 min. The remaining 2% oligomer stay dissolved in DMSO which got separated on recovery of DMSO by distillation. Hence, this temperature was selected for further studies. It was observed that

Table I. ¹³C-Data for Oligomer (Tetramer)

Unit	C	¹³ C
II,III	1',2'	60.6
I	1',2'	69.1
I	1',2'	64.8
III	3,4,6,7	129.1
I/II	4,6/3,7	129.1
I/II	3,7/4,6	132.7
I,II,III	2,5	162.4
I,II,III	1,8	165.8

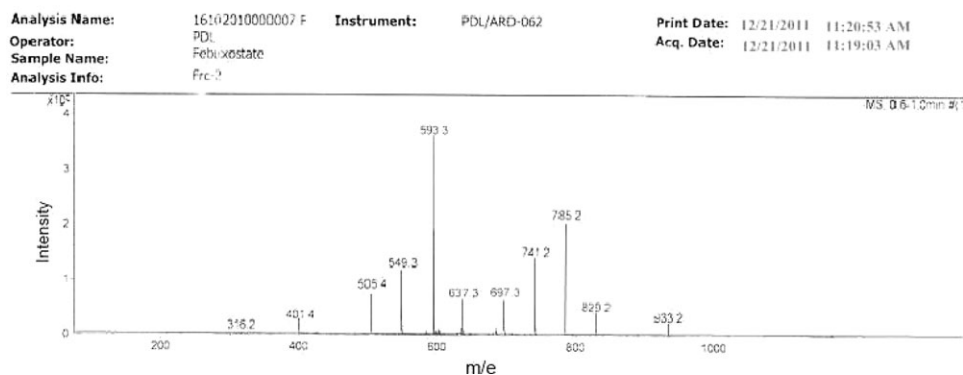
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Figure 2. Mass spectra of oligomer (tetramer).

degradation was slow at 180°C and degradation was completed in 180 min and further decreases in temperature from 180 to 160°C and 160 to 120°C increased degradation time from 180 to 360 min and 360 to 540 min, respectively. We used different concentration of catalyst but PET was completely depolymerized at 0.5 g hydrotalcite in 10 min. At lower concentration of catalyst (0.05), PET was not completely depolymerized and conversion time was too high.

Mechanism of the Process

For PET degradation a mechanism as shown in Scheme 1 is proposed. During the degradation process, DMSO first penetrated into the PET chips, causing swelling of the chips. The metallic group of the hydrotalcite interacts with the carbonyl oxygen O=C in the ester. Meanwhile the OH⁻ attacks the carbon atom of the ester group leading to the formation of a tetrahedral intermediate. These two interactions result in the breakage of the C=O bond as well as the decrease of the mol. wt. of PET.¹⁹ The degradation increases with increase in temperature and time (Figure 8). Similar behavior has been observed by Bendak et al.³³ The solubility of oligomer only in DMSO help in higher activity. This may be due to improved desorption of product from the catalyst surface.³⁴ This supports the observation that high polarity of DMSO and solubility of oligomer in DMSO play an important role.

Table II. Mass Spectral Fragments of Oligomer (Tetramer)

m/e	Fragments
934	HOOC [C ₆ H ₄ COO (CH ₂) ₂ OOC] ₄ C ₆ H ₄ COOH
889	HOOC [C ₆ H ₄ COO (CH ₂) ₂ OOC] ₄ C ₆ H ₄
830	(CH ₂) ₂ OOC [C ₆ H ₄ COO (CH ₂) ₂ OOC] ₃ C ₆ H ₄ COO (CH ₂) ₂ OH
742	HOOC [C ₆ H ₄ COO (CH ₂) ₂ OOC] ₃ C ₆ H ₄ COOH
697	HOOC [C ₆ H ₄ COO (CH ₂) ₂ OOC] ₃ C ₆ H ₄
638	HO (CH ₂) ₂ OOC [C ₆ H ₄ COO (CH ₂) ₂ OOC] ₂ C ₆ H ₄ COO (CH ₂) ₂ OH
594	HOOC [C ₆ H ₄ COO (CH ₂) ₂ OOC] ₂ C ₆ H ₄ COO (CH ₂) ₂ OH
550	HOOC [C ₆ H ₄ COO (CH ₂) ₂ OOC] ₂ C ₆ H ₄ COOH
505	HOOC [C ₆ H ₄ COO (CH ₂) ₂ OOC] ₂ C ₆ H ₄
401	HO (CH ₂) ₂ OOC C ₆ H ₄ COO (CH ₂) ₂ OOC C ₆ H ₄ COO

Analysis

The presence of hydroxyl-carbonyl ended oligomers where $n = 2$ or 3, $n = 1$ are water soluble while carboxyl-carboxyl ended $n = 4$ oligomer (It is supported by the high acid value (AV) and relatively low hydroxyl value (HV) of the product) has poor solubility.³⁰ To determine the purity of the oligomer formed, its dissolution in various solvents was tried. The insolubility of the oligomer formed has restricted gel permeation

Table III. Characterization of Oligomer (Tetramer) Obtained from Plastic Waste

S. No.	Oligomer obtained from plastic bottle	Standard oligomer
Formula	HOOC C ₆ H ₄ CO (OCH ₂ OOC C ₆ H ₄ CO) _n OH	HOOC C ₆ H ₄ CO (OCH ₂ OOC C ₆ H ₄ CO) _n OH
Molecular weight	934	934
Melting point (C)	254	252-254
n-value	4	4

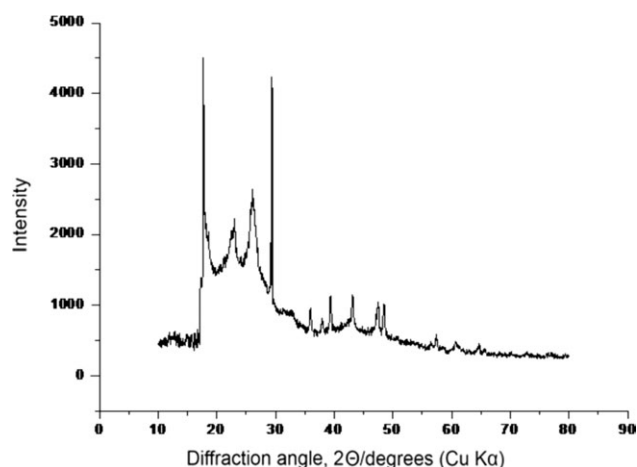


Figure 3. XRD data of oligomer (tetramer).

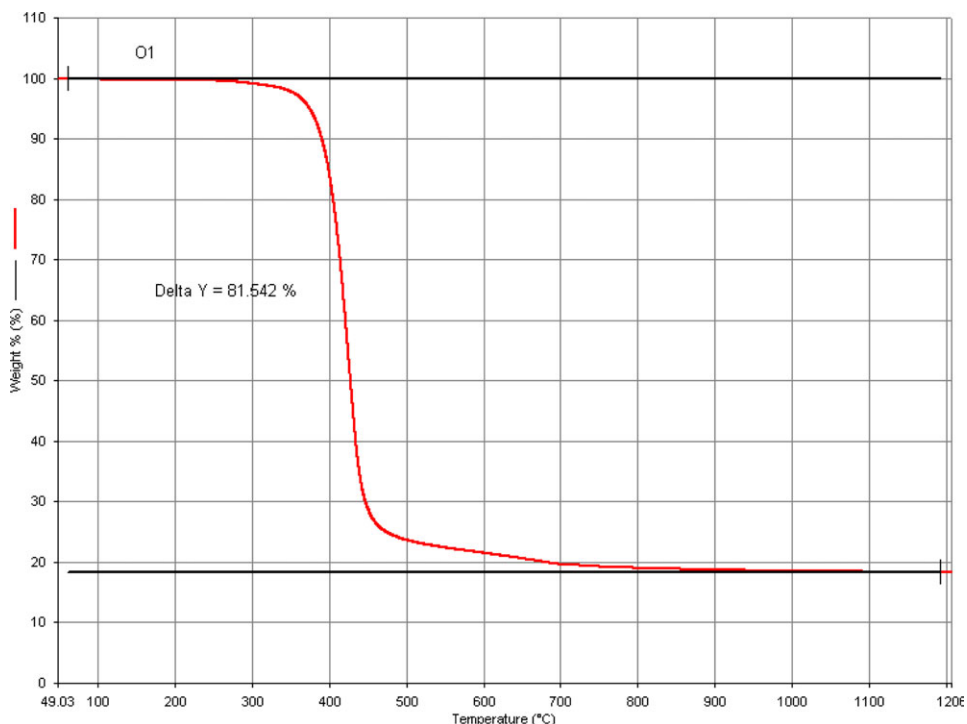


Figure 4. TGA curves of the oligomer (tetramer). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

chromatography. The oligomer was extracted with water in order to separate oligomer where $n = 1$. The water was cooled but absence of precipitate shows the absence of oligomer ($n = 1$). Now the oligomer was refluxed with chloroform (CHCl_3) to extract oligomer ($n = 2$). It was observed that there was no oligomer in the chloroform fraction. This shows that the oligomer ($n = 4$) obtained is pure.

Recycling of the Solvent and Catalyst

From the viewpoint of environmental conservation and economics of the process, recycling of used solvent and catalyst after the degradation of plastic bottles is shown in Scheme 2. Hydrotalcite catalyst (Al: Mg: CO_3) can be decanted from the reaction mixture and can be reused further. Experimental results have shown that the recycled hydrotalcite (Al: Mg: CO_3) worked efficiently when it was

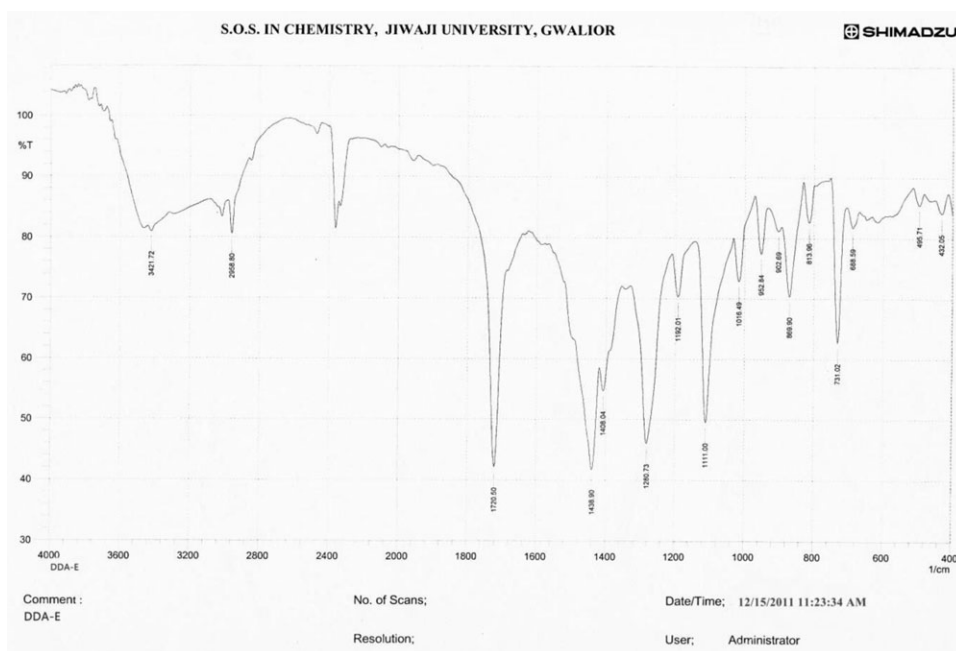


Figure 5. FT-IR spectra of DMT.

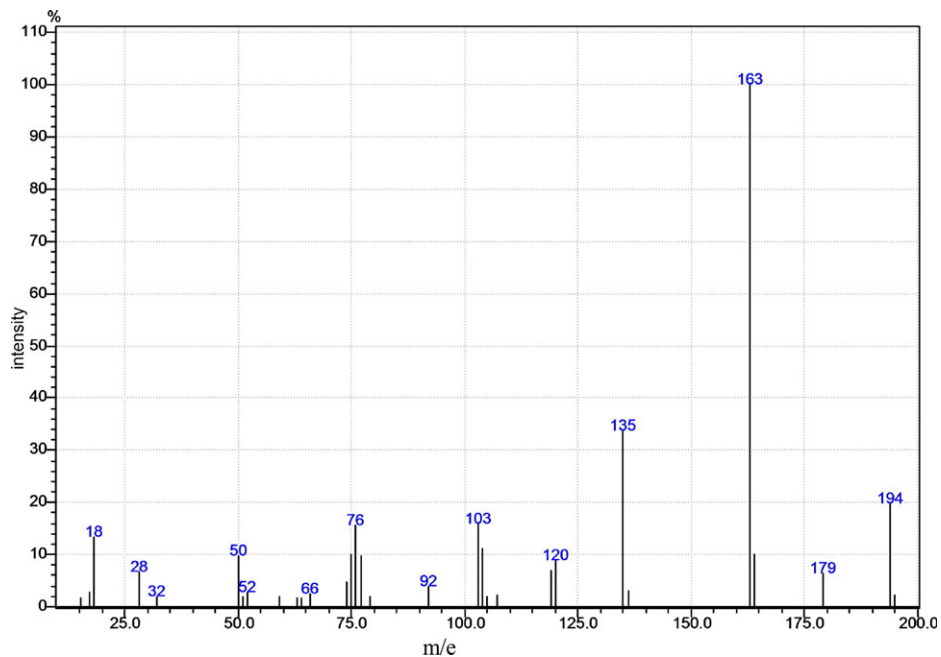


Figure 6. MS data of DMT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table IV. Effect of Solvent Polarity on PET Degradation

S. No.	Solvent used	Dielectric constant
1	DMSO	47.2
2	THF	7.5
3	EG	38.7
4	Acetone	20.9

reused six times. In the remaining mixture, oligomer (tetramer) can be filtered and solvent (DMSO) can be reused.

In the second step, oligomer can be converted into DMT and EG by using methanol as a solvent and sodium hydroxide (NaOH) as catalyst. In this reaction, NaOH act as transesterification catalyst similar to that reported with vegetable oils where triglycerides to monomers.³⁵ After the reaction EG, methanol and sodium methoxide can be recovered and reused. The

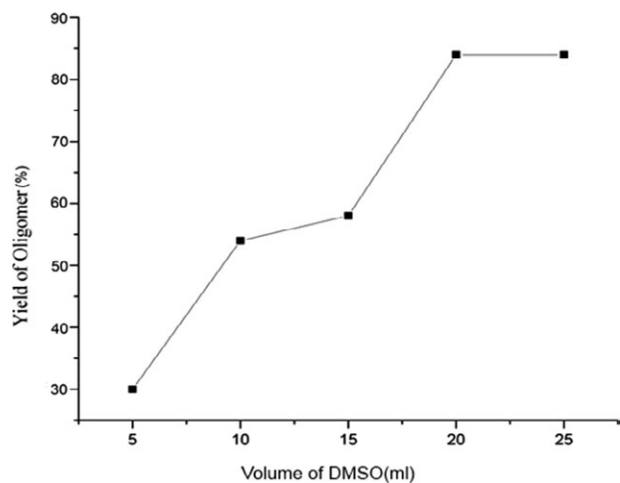


Figure 7. Effect of volume of solvent (DMSO) on the yield of oligomer (tetramer).

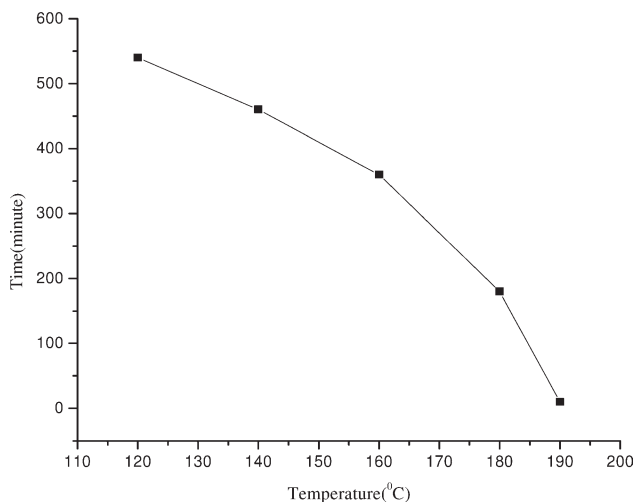
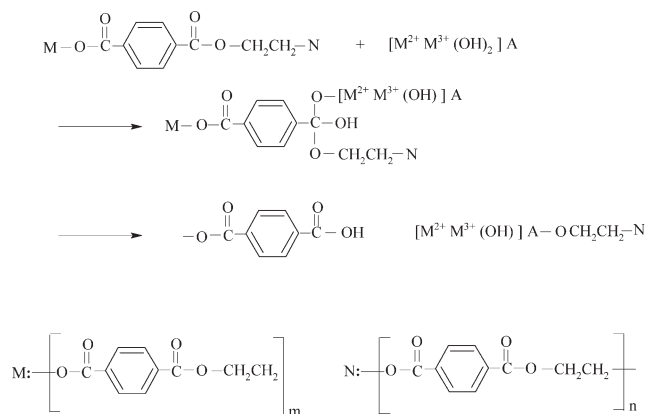
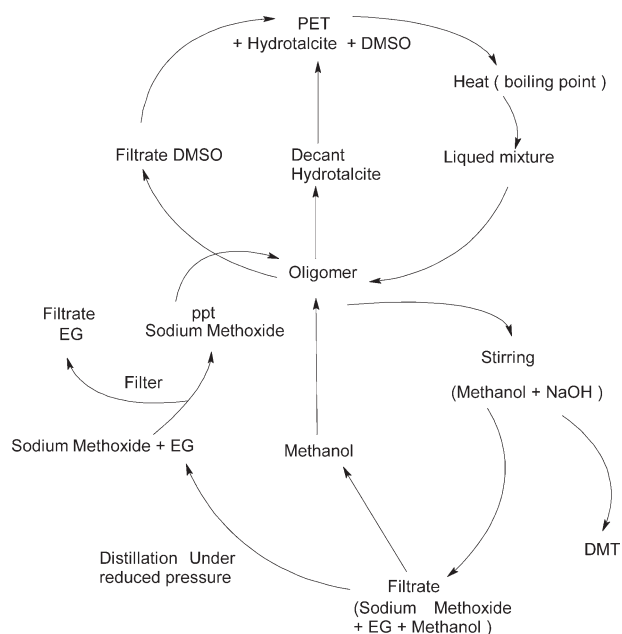


Figure 8. Effect of temperature on the time of reaction.



Scheme 1. Possible mechanism of the degradation of PET using hydrotalcite.



Scheme 2. Cycle showing regeneration and reusability of catalyst and solvent.

recycled EG was also analyzed by mass spectra. The comparison of mass spectra of the recycled EG with reference sample shows that, EG exhibit m/z 31 as a result of cleavage of the C–C bond. Other values too matches to that reported in literature.³⁶ This indicate that solvent and catalyst can be reused.

CONCLUSION

It can be concluded that hydrotalcite in presence of DMSO as solvent can degrade PET within 10 min to afford oligomer (tetramer), mol. wt. 934 and molecular formula $\text{HOOC}[\text{C}_6\text{H}_4\text{COO}(\text{CH}_2)\text{OOC}]_4\text{C}_6\text{H}_4\text{COOH}$ (Lit.³⁰ Tetramer). The oligomer (tetramer) using sodium hydroxide can be transesterified to DMT and EG at room temperature. The hydrotalcite can be recycled again. The oligomer (tetramer) has been found to be pure. The EG recovered is pure as confirmed by GC-MS. Thus, hydrotalcite can be used as recyclable catalyst for the degradation of PET to DMT and EG.

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