J Polym Res (2007) 14:475–481
DOI 10.1007/s10965-007-9131-9

Spectroscopic investigation of end products obtained by ammonolysis of poly (ethylene terephthalate) waste in the presence of zinc acetate as a catalyst

Anuj Jain · R. K. Soni

Received: 22 February 2007 / Accepted: 21 June 2007 / Published online: 17 October 2007

Abstract The effect of catalyst on the degradation of poly (ethylene terephthalate) (PET) waste by ammonolysis was investigated at ambient temperature and atmospheric pressure. The products obtained by ammonolysis in the presence and absence of catalyst were separated and characterized by spectroscopic techniques namely FTIR and Mass Spectrometry (MS) together with Scanning Electron Microscopy (SEM) and Differential Thermal Analysis (DTA). The end products were characterized as 1, 4-benzene dicarboxamide in both the cases and were found to be same throughout the course of reaction. The absence of peak for PET and appearance of peak for 1, 4-benzene dicarboxamide in the FTIR spectra of end product along with MS, SEM and thermal analysis confirms the completion of the reaction. The results show that the catalyst cut shorts the time of completion of reaction from 45 to 15 days only.

Keywords Poly (ethylene terephthalate) · Recycling · Ammonolysis · Infrared spectroscopy · SEM

Introduction

Poly (ethylene terephthalate) (PET) has excellent mechanical properties in comparison with other commodity polymers, especially when it is used as a film or fiber. Extensive studies on the thermal [1, 2], chemical and catalytic degradation [3] of PET waste have developed many processes of commercial importance for saving the environment.

Technology is being developed to use mechanical and chemical processes [4] to recycle PET [5, 6]. PET is known to be attacked by different alkalies [7, 8], glycols [9], alcohols [10] and amines [11] by making use of processes namely hydrolysis [12–14], glycolysis [15], alcoholysis [16, 17] and aminolysis [18] respectively where degradation of main chain of PET is supposed to take place through chain scission. However, the disadvantage associated with these processes is the requirement of critical conditions of higher temperature and pressure and consumption of lot of energy.

Very few efforts have been made in carrying out the degradation of PET waste at ambient temperature and pressure conditions. Soni and Singh [19] have reported the ammonolysis and aminolysis of PET waste at normal conditions of temperature and pressure.

An investigation as to reduce the degradation period of PET waste through ammonolysis at ambient temperature and pressure is the subject of the current research by making use of a catalyst avoiding tedious conditions of temperature and pressure. In the present work an attempt has been made to cut short the time of degradation of PET waste by using zinc acetate as a catalyst.

The degradation products obtained by the ammonolysis of PET waste were characterised as 1, 4-benzene dicarboxamide commonly known as terephthalamide with the help of spectroscopic techniques (FTIR and Mass Spectroscopy), SEM, and Differential Thermal Analysis. The aromatic amides can be used as hardeners in epoxies and as intermediate for other applications.

A. Jain (✉) · R. K. Soni
Department of Chemistry, Ch. Charan Singh University,
Meerut 250004, India
e-mail: anuj.ccsu@gmail.com

Experimental

The starting material was obtained from post-consumer PET bottles and chopped into small flakes and cleaned thoroughly by washing with soapy water and then with distilled water. The cleaned PET waste flakes were dried at 80°C for 5 h and then subjected to degradation.

Liquor ammonia solution (Sp. gravity 0.91), Qualigens make, laboratory grade, was used for ammonolysis of PET waste. Zinc acetate (dihydrate), Qualigens make, AR grade was used as catalyst.

The ammonolysis of PET waste flakes was carried out with liquor ammonia separately in the absence and presence of catalyst. In the absence of catalyst, PET waste flakes (10 gm) were reacted only with excess of liquor ammonia (100 ml) whereas in other case, zinc acetate (1% by total weight of reaction mixture) was added along with PET flakes (10 gm) and liquor ammonia (100 ml). The reactions were carried out in a properly sealed reaction vessel with continuous constant stirring at ambient temperature and pressure.

The white precipitates start appearing in both the reaction vessels, within few hours from the start of the reaction. The ammonolysed products from both degradation experiments were separated after different durations of time such as 3, 7, 15, 21, 25, 30 and 45 days. These precipitates were recrystallized with ethanol, washed with distilled water and dried under vacuum at 60°C for 2 h.

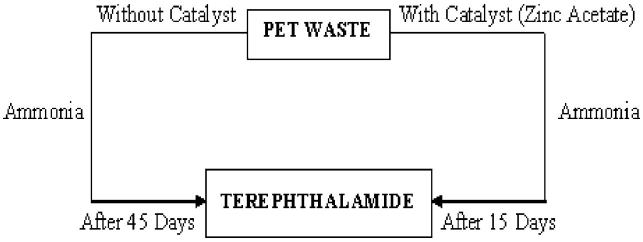
The end products so obtained were characterized with the help of FTIR and Mass Spectroscopy, Differential Thermal Analysis and Scanning Electron Microscopy.

IR spectra were recorded on a Nicolet 5DX IR spectrophotometer (Madison,WI) with KBr discs. MS spectra were recorded on a JEOL JMS-DX 303 mass spectrometer. SEM studies were carried out on JEOL JSM-6300 and DTA thermograms were recorded on Rigaku thermoflex (Tokyo, Japan).

Results and discussion

Ammonolysis of PET waste flakes was investigated avoiding tedious condition of high temperature and pressure in the absence and presence of catalyst (zinc acetate). The PET waste flakes were found to degrade faster in the presence of catalyst as expected.

The white precipitates of amide namely 1, 4-benzene dicarboxamide start appearing within few hours from the start of the reaction in both the degradation experiments (Scheme 1). The concentration of white precipitates increased with the passage of time. These white precipitates were separated from the reaction vessel after different periods of time such as after 3, 7, 15, 21, 25, 30 and 45 days. After 45 days, no PET flakes remain unreacted in the absence of catalyst and after 15 days in the presence of catalyst.



Scheme 1 Ammonolysis under two different conditions

The ammonolysed product so obtained under two different conditions was characterized with the help of spectroscopic techniques namely IR and mass spectroscopy, differential thermal analysis, scanning electron microscopy. The results obtained were also compared with the reference sample of terephthalamide.

FTIR spectral analysis

Figure 1c shows the IR spectrum of the end products obtained by the ammonolysis of PET waste in the absence and presence of catalyst. The IR spectrum of white precipitate shows a pair of absorption bands at 3,353 and 3,162 cm^{-1} that are attributed to N–H str. and are characteristic of primary amides. C=O str. and N–H def., being coupled vibrations give rise to a pair of bands at 1,620 and 1,654 cm^{-1}. The band at higher frequency is attributed to C=O str. and at lower frequency due to N–H def. The C=O absorption band is observed at longer wavelength because of mesomeric effect. The peak at 1,454 cm^{-1} is due to aromatic ring mode and at 1,374 cm^{-1} due to C–N str.

The I.R. spectrum of the ammonolysed products obtained after 3 days (Fig. 1a) and 7 days (Fig. 1b) in the presence of catalyst, shows the peaks at 1,750–1,730 cm^{-1} and 1,100–1,000 cm^{-1}, which are due to aromatic ester C=O str. and aromatic ester C–C–O str. in unreacted PET, but these peaks disappear in the IR spectra of the white precipitate obtained after 15 days (Fig. 1c), which indicates the conversion of PET flakes into terephthalamide within 15 days.

The bands in the finger print region (990–1,400 cm^{-1}) in the I.R. spectra of ammonolysed products in the absence and presence of catalyst (Fig. 1c) are also the same as in the reference sample of terephthalamide (Fig. 1d).

Table 1 represents the infrared spectral data of the reaction mixture separated after different intervals of time and their corresponding functional groups.

Thus, the appearance of peaks for terephthalamide and disappearance of peaks for PET indicates the complete

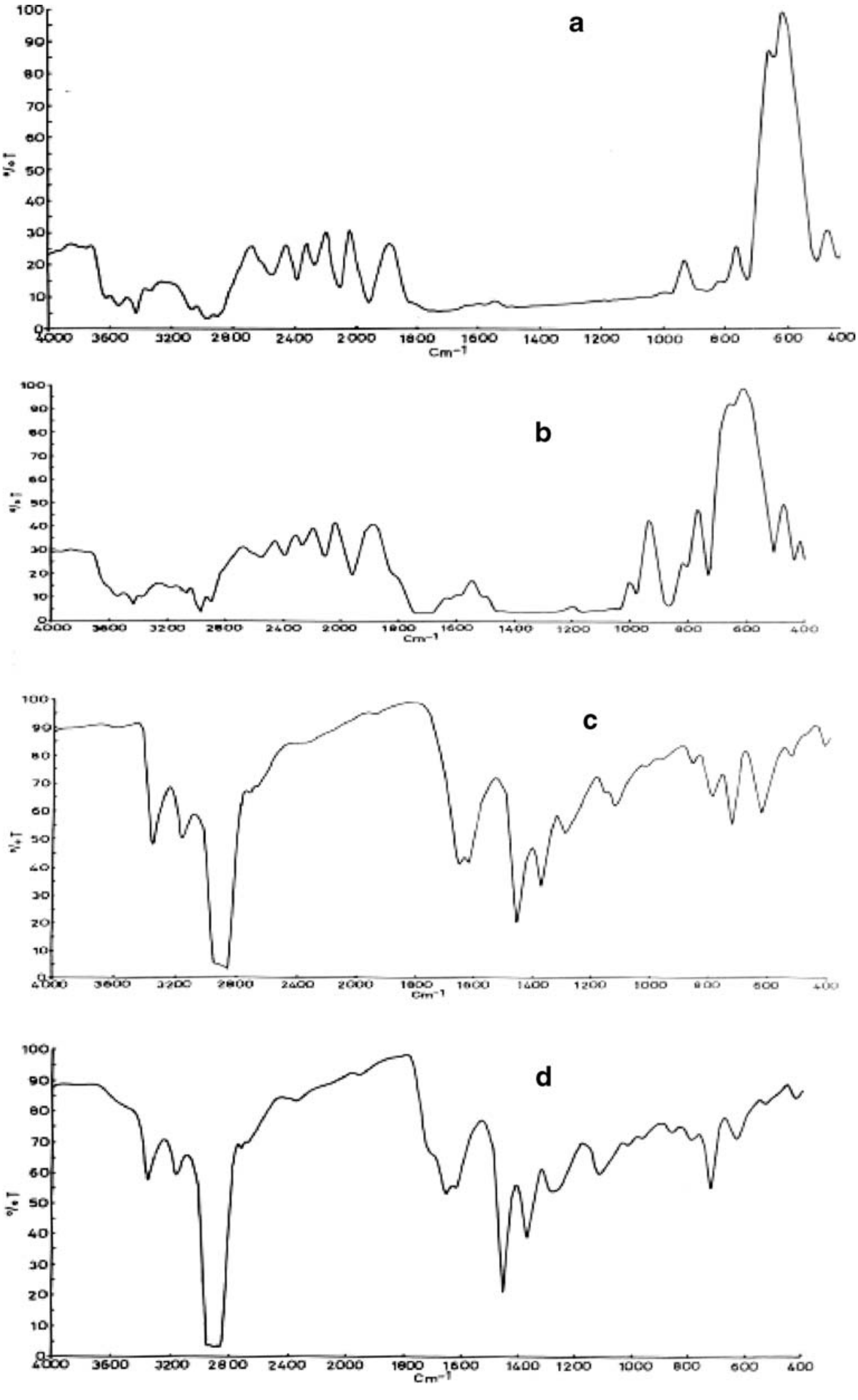


Fig. 1 IR Spectra of **a** ammonolysed end product after 3 days **b** after 7 days **c** after 15 days in presence of catalyst **d** reference sample

degradation of PET waste flake into terephthalamide within 15 days. The I.R. spectra of white precipitates obtained after 21, 25, 30 and 45 days show the same characteristic peaks as shown in the sample after 15 days and also as reference sample of terephthalamide so only one IR spectra (Fig. 1d) is given for each condition. This shows that the

Table 1 Infrared spectral data of ammonolysed product separated after different intervals of time

Peak position (cm^{-1})			Reference sample	Functional group
After 3 days	After 7 days	After 15 days		
1,750–1,730	1,750–1,730	Absent	Absent	Aromatic ester (C=O Str.)
1,100–1,000	1,100–1,000	Absent	Absent	Aromatic ester (C_C_O Str.)
–	–	3,355	3,355	$-NH_2$ Str.
–	–	3,164	3,164	$-NH_2$ Str.
–	–	3,000	3,000	Ar–H Str.
–	–	1,654	1,654	C=O Str.
–	–	1,621	1,621	$-NH_2$ Bending
–	–	1,454	1,454	Aromatic ring C–C
–	–	1,374	1,374	C–N Str.

product formed from the ammonolysis of PET waste was single and same during the course of the reaction.

Mass spectral analysis

The mass spectra of end product obtained from ammonolysis of PET waste in the absence and presence of catalyst are identical as shown in Fig. 2a. The white precipitate on an electron impact is found to yield a molecular ion peak at *m*/*z* 148 (100%). Subsequent fragmented peaks at *m*/*z* 120, 104, 76 which could result only from terephthalamide also appear in the mass spectra of white precipitates. Figure 2b shows the mass spectra of the reference sample of terephthalamide, which shows the molecular ion peaks and subsequent fragment peaks with the same *m*/*z* values as observed for white solids obtained from ammonolysis of PET waste in the absence and presence of catalyst (Fig. 2a). This also provides a supportive evidence for the formation of terephthalamide within 15 days from the commencement of reaction.

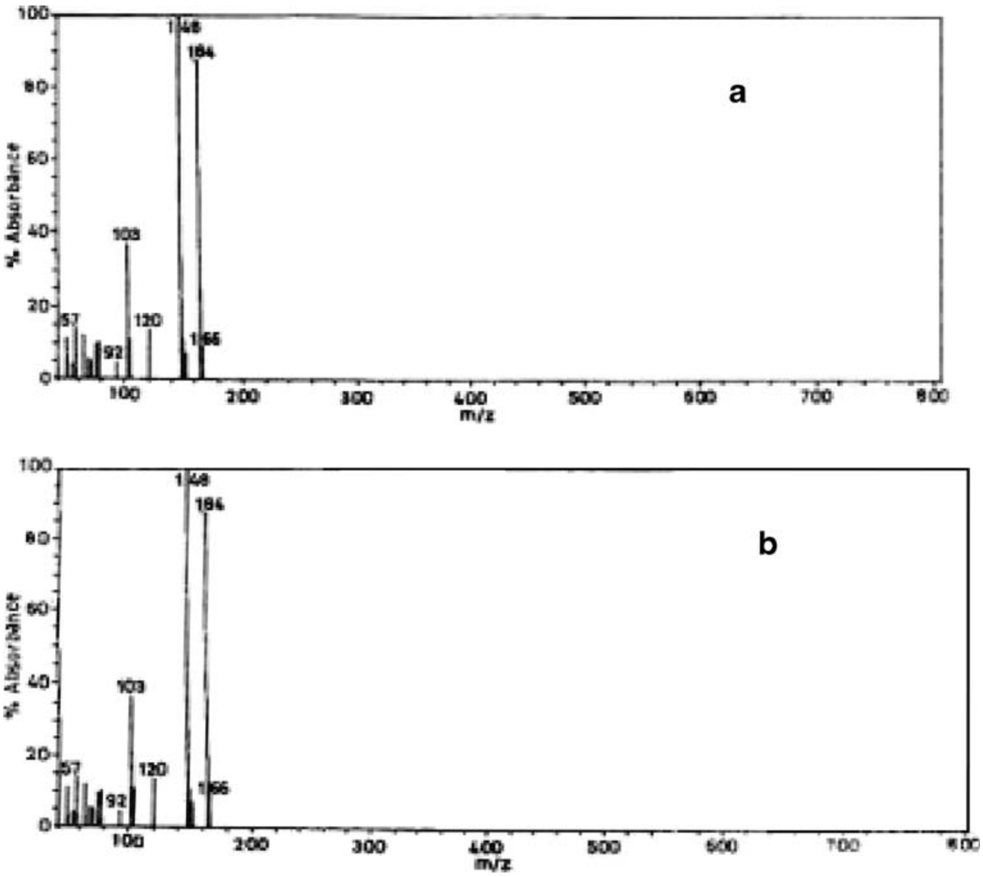
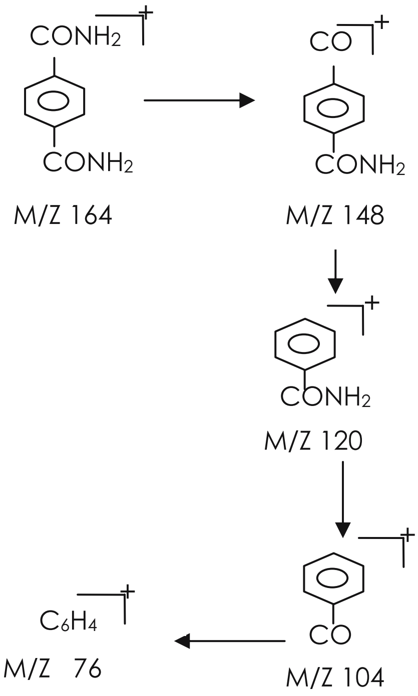


Fig. 2 MS spectra of **a** ammonolysed end product with and without catalyst **b** reference sample

The proposed scheme for fragmentation of terephthalamide is shown in Scheme 2 as follows:



Scheme 2 Proposed scheme for fragmentation of terephthalmide

SEM analysis

Figure 3a shows SEM micrograph of PET flakes, recorded at a magnification of 2,000× before subjecting to degradation. It presents a smooth and continuous flake structure.

Figure 3b and 3c shows the SEM micrographs of products obtained as a result of degradation of PET waste with liquor ammonia in the absence of catalyst after 15 days and after 45 days respectively. It is apparent from the Fig. 3b that degradation of PET flakes is increasing and whole mass degrades uniformly where as after 45 days the SEM micrograph shows the complete degradation of PET waste into the end products (Fig. 3c; Scheme 3).

The SEM micrograph of PET waste degraded through ammonolysis in the presence of zinc acetate as a catalyst after 15 days shows the complete degradation of PET waste into the degradation products as represented in Fig. 3d.

On comparison of all these micrographs, it is evident that after 15 days the SEM micrograph of ammonolysed products of PET waste in the presence of catalyst reflects the complete degradation of PET waste into the end products. However, no such results are shown by the SEM micrograph of ammonolysed products after the same length of time in the absence of catalyst. Figure 3d resembles with Fig. 3c but not with Fig. 3b.

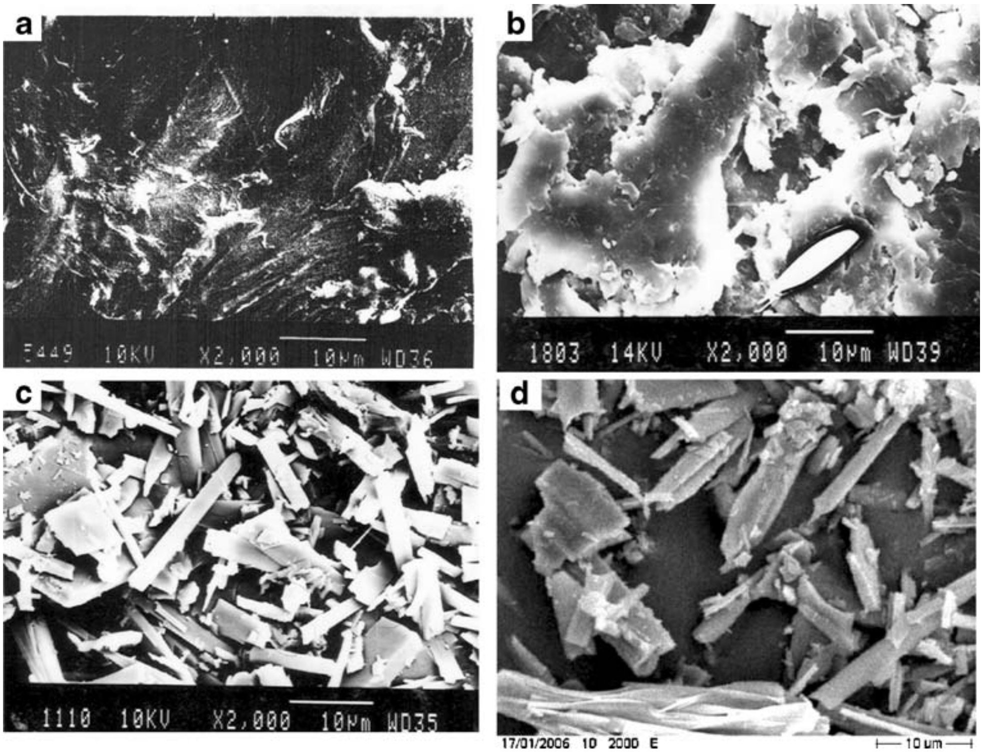


Fig. 3 SEM micrograph of PET flakes **a** before degradation **b** after 15 days without catalyst **c** after 45 days without catalyst **d** after 15 days with catalyst

Thermal analysis

The thermograms were recorded from room temperature to 400°C at a heating rate of 10°C per minute under air atmosphere.

DTA thermogram of PET flakes recorded before subjecting them to degradation is shown in Fig. 4a. Figure 4b shows DTA thermograms for the white precipitates obtained by the ammonolysis of PET waste in the absence and presence of catalyst. It shows a single endothermic peak at 333.7°C indicative of the melting point of the compound and the formation of a single and identical compound under two different reaction conditions. The results are also in good agreement with reference sample of terephthalamide (Fig. 4c).

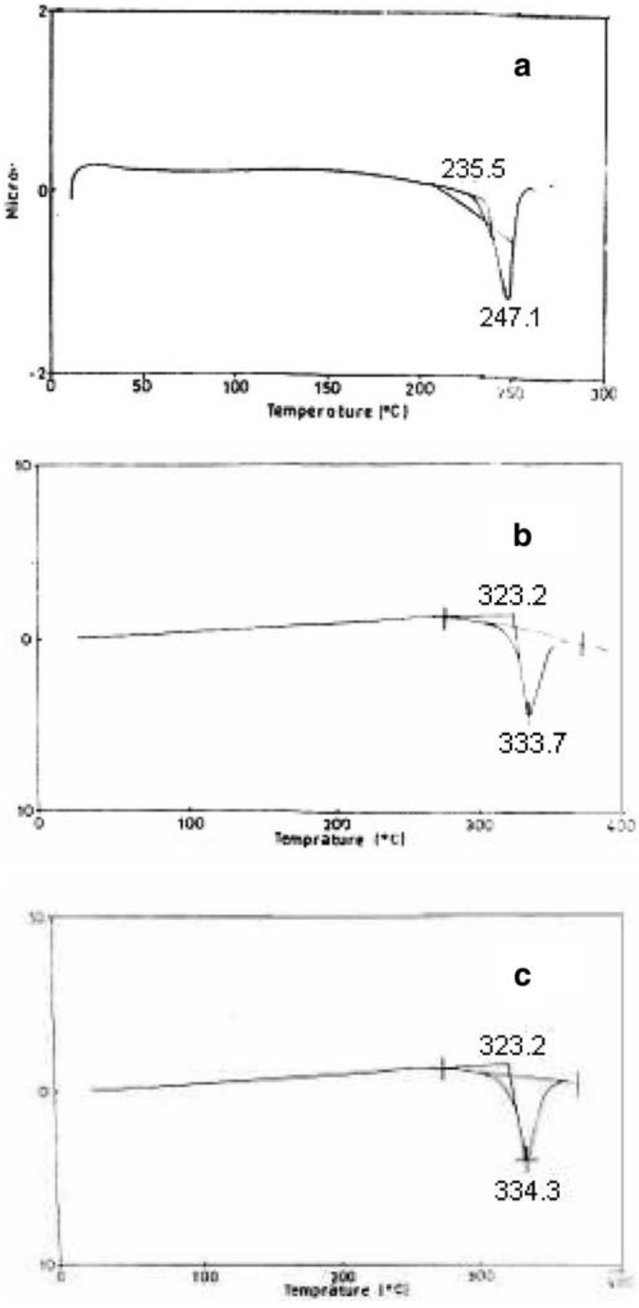
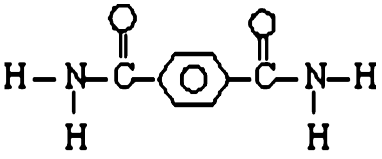


Fig. 4 DTA Thermogram of **a** PET Flake before degradation **b** ammonolysed end product with and without catalyst **c** reference sample

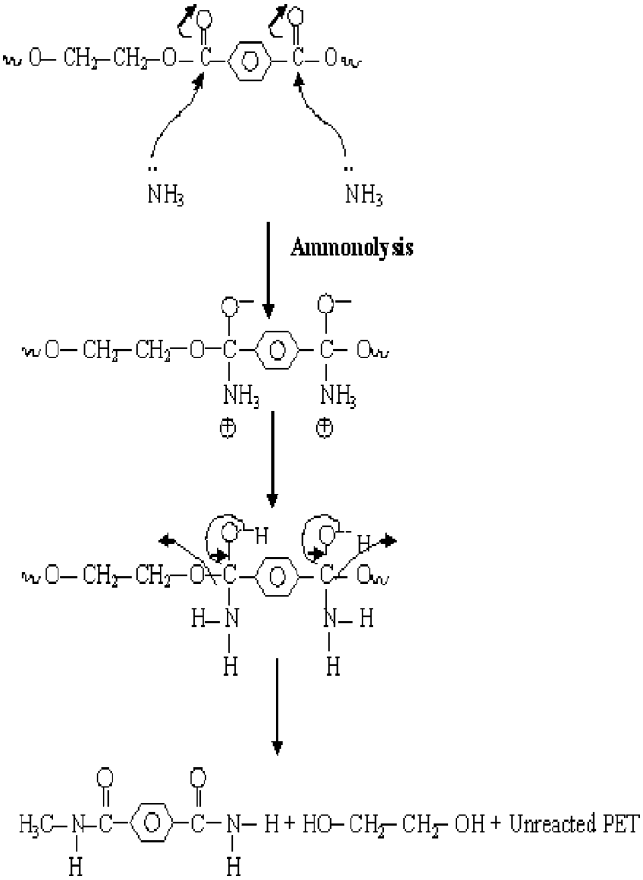
Thus, on the composite analysis of the white precipitates obtained from ammonolysis of PET waste flakes under two different conditions the end product is confirmed to be terephthalamide with the following structure:



Terephthalamide

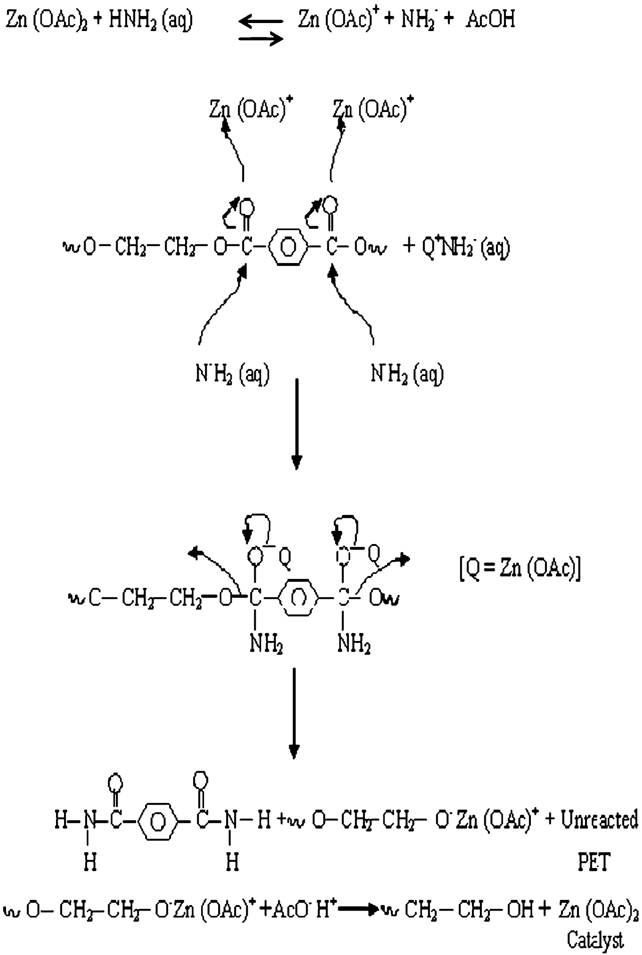
Proposed mechanism of degradation of PET waste through ammonolysis

The degradation of PET waste through ammonolysis is supposed to take place according to the following reaction:



Scheme 3 Proposed mechanism of PET degradation by ammonolysis (in absence of catalyst)

When zinc acetate [Zn $(OAc)_2$] is added to the mixture, it is expected to exchange its anion with the excess of nucleophile in the aqueous phase. Scheme 4 gives the proposed mechanism for PET degradation by ammonolysis in the presence of catalyst. Zn $(OAc)^+$ and NH_2^- attacks the polymer and displacement occurs with the product formation. Regeneration of catalyst occurs as follows:



Scheme 4 Proposed mechanism of PET degradation by ammonolysis (in presence of catalyst)

Conclusion

The present work involves the formation of 1,4-benzene dicarboxamide, commonly known as terephthalamide from PET waste at ambient temperature and atmospheric pressure through ammonolysis in the absence and presence of catalyst. The degradation period of PET waste in the absence of catalyst was found to be 45 days and 15 days in the presence of zinc acetate. Thus, the degradation period of PET waste under normal conditions of temperature and pressure was significantly reduced to a much greater extent. The ammonolysed products obtained under two different conditions were characterized and compared with the reference sample on the basis of spectroscopic techniques, Scanning electron microscopy and thermal analysis and found to be identical.

Thus, an environment friendly technology for recycling of PET waste under normal conditions of temperature and pressure was developed as it reduces the amount of solid waste, consumes lesser time and saves energy.

Acknowledgement The authors are thankful to University Grants Commission, New Delhi for providing financial assistance.

References

1. Kirby JR, Baldwin AJ, Heigner RH (1965) Anal Chem 37:130
2. Oromiehie A, Mamizadeh A (2004) Polym Int 53(6):728–732
3. Tindall GW, Perry RL, Spaugh AT (1994) US Pat 5(328):982
4. Paszun D, Spychaj T (1997) Ind Eng Chem Res 36(4):1373–1383
5. Ayers J (1994) Mod Plast Int 46
6. Schwartz JA Jr (1995) US Pat 5(395):858
7. Cudmore WJG (1986) US Pat 4(578):502
8. Benzaria J (1993) US Patent 5(254):666
9. Mansour SH (2003) J Elastomers Plast 35(2):133–148
10. Goto M, Koyamoto H, Kodama A, Hirose T, Nagaoka S (2002) J Phys Cond Matter 14:11427–11430
11. Atta AM, Abdel-Rauf ME, Maysour NE, Abdul-Rahiem AM, Abdel-Azim AA (2006) J Polym Res 13:39
12. Doerr ML (1986) US Patent 4(578):510
13. Rosen BI (1992) US Patent 5(095):145
14. Campanelli JR, Kamal MR, Cooper DG (1993) J Appl Polym Sci 48:443
15. Shukla SR, Harad AM (2005) J Appl Polym Sci 97(2):513–517
16. Donahue CJ, Exline JA, Warner C (2003) J Chem Educ 80(1):79
17. Genta M, Iwaya T, Sasaki M, Goto M, Hirose T (2005) Ind Eng Chem Res 44(11):3894–3900
18. Spychaj T, Fabrycy E, Spychaj S, Kacperski M (2001) J Mater Cycl Waste Manag 3(1):24–31
19. Soni RK, Singh S (2005) J Appl Polym Sci 96(5):1515–1528