

Studies on Synthesis and Characterization of *N*-Alkyl Terephthalamides Using Different Amines from Polyethylene Terephthalate Waste

R. K. Soni, Swati Singh, Krishna Dutt

Department of Chemistry, Ch. Charan Singh University, Meerut 250004, Uttar Pradesh, India

Received 17 June 2008; accepted 11 June 2009

DOI 10.1002/app.30986

Published online 2 November 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: This study deals with the degradation of polyethylene terephthalate (PET) waste through aminolysis with various amines. All of these degradation experiments were carried out at ambient temperature and at normal pressure. Although PET is known to be recycled in many ways, but still there is a need of development of other environment friendly recycling techniques. The amines used to study the degradation of PET waste were namely methylamine, ethylamine, and *n*-butyl amine, respectively where the degradation of PET waste completes in 45 days.

The aminolyzed products so obtained were characterized by using various conventional techniques such as spectroscopic techniques namely IR, NMR, and simultaneous differential scanning calorimeter (DSC). In the present research work, a useful method of PET recycling by using various amines was successfully established. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 3074–3080, 2010

Key words: Polyesters; degradation; recycling; IR; NMR; DTA

INTRODUCTION

Polyethylene terephthalate (PET) is the most common thermoplastic polyester, which have a wide range of applications. It is well known that PET has valuable characteristics including strength, toughness, solvent resistance, and heat resistance.¹ However, during the past few decades, the growth in the commercial use of PET has brought with it an increasing opportunity for its reuse. The recycling of polyesters such as this have been the subjects of interest for a large area of polymer science and technology during several decades because of their growing use in wide range of applications.

Growing use of PET creates environmental hazards due to problem of its disposal. PET is being recycled by various ways such as mechanical recycling methods^{2,3} namely gravimetric separation process, solution process etc. and chemical recycling methods namely hydrolysis,^{4,5} methanolysis,^{6–8} glycolysis⁹ etc. But the disadvantage associated with mechanical recycling discussed processes is that PET flakes are subjected to higher temperature and higher pressure, which would change their morphological and chemical structure. Various researchers have made efforts to recycle PET waste by other

processes^{10–15} and such as biodegradation, solvolysis, aminolysis,¹⁶ enzyme degradation, thermal degradation, pyrolysis etc.

The chemical recycling processes such as hydrolysis, methanolysis, and glycolysis have been used to study the degradation of the main chain of PET by chain scission. But not much emphasis had been made on two other recycling methods namely ammonolysis and aminolysis.

Soni and Singh¹⁷ have previously reported the synthesis of terephthalamide through ammonolytic degradation of PET waste at normal conditions of temperature and pressure. Blackmon et al.¹⁸ have also suggested the process for converting PET scrap to diamide¹⁹ monomers. Collins et al.²⁰ have analyzed the molecular weight distributions of aminolyzed PET using gel-permeation chromatography. Ellison et al.²¹ have reported the physical properties of PET fibers degraded by aminolysis, whereas Farrow et al.²² have studied the degradation of PET by methylamine through infrared and X-ray methods. Popoola²³ suggested the aminolytic degradation of PET and mechanism of the reaction.

Spychaj et al.²⁴ describe the chemical degradation of waste PET with polyamines or triethanolamine. They also reported that the solvolysis of polymer ester bonds was caused by diethylenetriamine, triethylenetetramine, their mixtures, as well as mixtures of triethylenetetramine and *p*-phenylenediamine or triethanolamine. Awodi et al.²⁵ have reported the aminolysis of PET.

Correspondence to: R. K. Soni (rksoni_rks@yahoo.com).

TABLE I
Amount of PET Waste Flakes and Aqueous Methylamine (40% weight/weight) Taken for Aminolysis

S.No.	PET waste (g)	Aqueous methylamine (mL)	Water (mL)	Ratio (weight/volume)	Designation
1	10	5	–	2.1	MA21
2	10	10	–	1.1	MA11
3	10	20	–	1.2	MA12
4	10	30	–	1.3	MA13
5	10	40	–	1.4	MA14
6	10	50	–	1.5	MA15
7	10	100	–	1.10	MA110
8	10	5	5	1 : 0.5 : 0.5	MA1.5.5
9	10	10	10	1 : 1 : 1	MA111

The research work is an attempt to maximize the effectiveness of PET recycling as a means of conserving resources and reducing waste. The scope of the present work is in providing an ecological and economical methodology, which works at room temperature, developed for recycling of PET waste.

EXPERIMENTAL

Material and characterization

PET waste was of consumable soft drinks bottle grade. PET waste was made to react with different amines at normal conditions of temperature and pressure. Degradation studies were carried out on postconsumer PET waste. The postconsumer PET waste used in this study was washed with soap solution prior to use to remove dirt and other contaminants and then washed, dried, and chopped. The PET flakes free from impurities so obtained were subjected to degradation reactions. Thus, three samples were prepared by treating PET waste flakes with methylamine, ethylamine, and *n*-butyl amine as under:

Preparation of Sample I

The PET waste flakes were treated with aqueous methylamine in a properly sealed reaction vessel. The reaction proceeds at room temperature with continuous stirring. The white precipitate starts appearing within few hours from the start of the reaction in the vessel and after 45 days no PET flakes left unreacted. The ratio of PET to aqueous methylamine solution was investigated. Different reactions containing different ratios as 2 : 1, 1 : 1, 1 : 2, 1 : 3, 1 : 4, 1 : 5, 1 : 6, 1 : 7, 1 : 8, 1 : 9, 1 : 10 (g/mL) etc. were carried out to determine the best ratio of aminolysis of PET waste with aqueous methylamine (40% weight/weight). Table I summarizes the amount of PET waste flakes, aqueous methylamine, and water taken for aminolysis of PET waste.

Preparation of Sample II

Aminolysis of PET waste with ethylamine was also carried out in a properly sealed reaction vessel with continuous constant stirring at normal conditions of temperature and pressure. The white precipitate starts appearing within few hours from the start of the reaction. The reaction was studied for different weight/volume ratio of PET with ethylamine. The reaction was also observed for different periods of time to study the advancement of the reaction. The degradation period of PET waste through aminolysis with ethylamine was also found to be 45 days. Table II summarizes different weight/volume ratios of PET waste flakes to aqueous ethylamine (70% weight/weight) taken to study the aminolysis of PET waste with aqueous ethylamine.

Preparation of Sample III

Aminolysis of PET waste with an aqueous solution of *n*-butylamine (98% weight/weight) (Table III) proceeds in a similar manner as in case of aminolysis with methylamine and ethylamine and the white precipitate starts appearing within few hours from the start of the reaction.

The aminolyzed products so obtained from different degradation experiments were characterized with the help of various conventional techniques

TABLE II
Amount of PET Waste Flakes and Aqueous Ethyl Amine (70% weight/weight) Taken for Aminolysis

S.No.	PET Waste (g)	Ethylamine (mL)	Ratio (weight/volume)	Designation
1	10	10	1.1	EA11
2	10	20	1.2	EA12
3	10	30	1.3	EA13
4	10	40	1.4	EA14
5	10	50	1.5	EA15
6	10	100	1.10	EA110

TABLE III
Amount of PET Waste Flakes and Aqueous *n*-Butyl Amine (98%weight/weight) Taken for Aminolysis

S.No.	PET Waste (g)	<i>n</i> -Butyl amine (mL)	Ratio (weight/volume)	Designation
1	10	10	1.1	nBA11
2	10	20	1.2	nBA12
3	10	30	1.3	nBA13
4	10	40	1.4	nBA14
5	10	50	1.5	nBA15
6	10	100	1.10	nBA110

such as spectroscopic techniques namely IR, NMR, and differential scanning calorimeter (DSC).

The IR spectra of aminolyzed products were recorded on Nicolett 5DX-USA IR spectrophotometer using KBr disc and were interpreted for various bonds. The ¹H-NMR spectra were recorded on JEOL-JNM-FS-100 FT-NMR at 100 or 300 MHz for the ultimate degraded products obtained as the result of aminolysis of PET waste. The compound was taken in deuterated dimethylsulfoxide (DMSO) and was exposed to a powerful magnetic field using trimethylsilane (TMS) or DMSO as a standard. In the present work, DSC thermograms of the white precipitates from the degradation of PET waste flakes with different amines (aminolysis) were recorded on Mettler star SW 9.01 under the nitrogen atmosphere. All of these instruments were available at University Scientific Instrumentation Centre, University of Delhi, Delhi.

RESULTS AND DISCUSSION

The degradation of PET waste flakes was studied with methylamine, ethylamine, and *n*-butylamine. The white precipitates were obtained, which were separated by simple filtration and dried under vacuum. The white precipitates obtained from degradation reactions of PET waste as mentioned above were characterized by spectroscopic techniques (IR, ¹H-NMR) and DSC, which have been discussed below:

Characterization of Sample I

The most significant ratio for aminolysis of PET waste with aqueous methylamine¹⁵ was found to be 1 : 10 (g/mL). Thus, (10 g) of PET waste flakes were treated with (100 mL) of aqueous methylamine and the degradation products so obtained were separated and characterized as under:

Figure 1 shows the IR spectrum of the white precipitates obtained during aminolysis. The absorption bands at 3310 cm⁻¹ and at 1670 cm⁻¹ have been attributed to N-H stretching and C=O stretching, respectively and further these bands are characteristic of a secondary amide. C=O absorption of amides occur at longer wavelength than the normal carbonyl absorption due to mesomerism. Absorption bands, characteristic of a benzenoid compound are also observed in the region 1660–2000 cm⁻¹. Further, the finger print region (990–1400 cm⁻¹) and the large number of unassigned vibrations in this region were found to be same in all IR spectra. This proof of

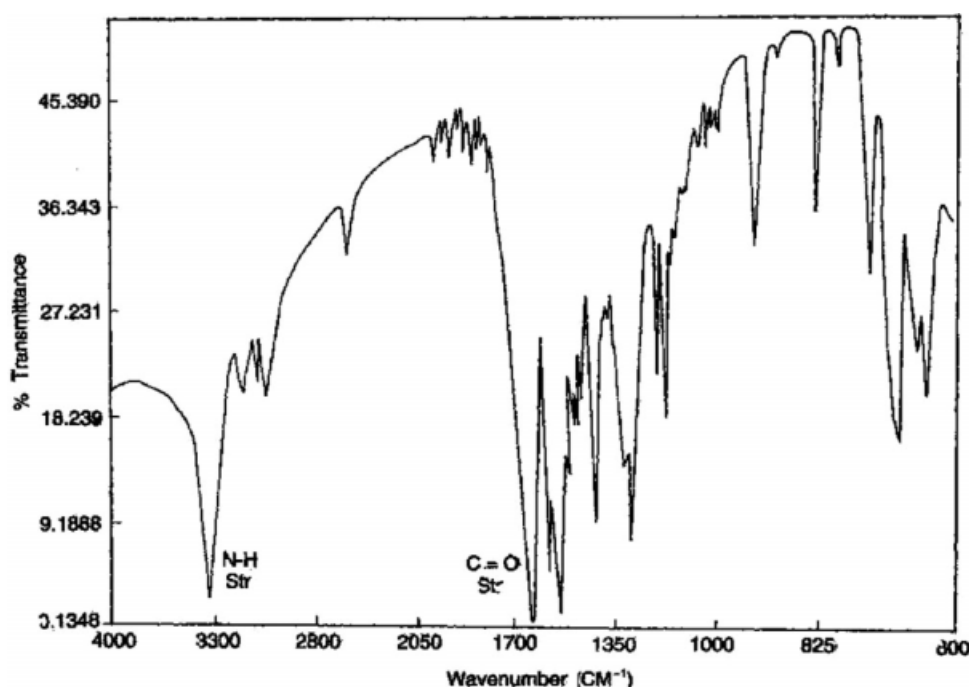


Figure 1 IR spectrum of *N,N'*-dimethyl terephthalamide synthesized by aminolysis of PET waste with methylamine.

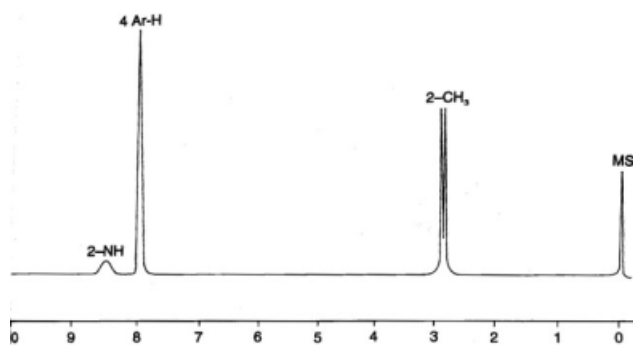


Figure 2 $^1\text{H-NMR}$ Spectrum of *N,N'*-dimethyl terephthalamide synthesized by aminolysis of PET waste with methylamine.

identity of the white precipitates is far more characteristic than the comparison of any other physical property.

The infrared spectrum of the white precipitate obtained after aminolysis of PET waste and the infrared spectra of all the white precipitates obtained during the course of degradation through aminolysis of bottle grade PET waste for various lengths of time were also found to be same and therefore only one spectrum is presented.

Figure 2 shows the $^1\text{H-NMR}$ spectrum of the products obtained as a result of aminolysis of PET waste flakes. The spectrum shows three absorption peaks. The peak at 8.4δ as a broad low hump is attributed to CO-NH protons. A doublet at 2.9δ accounts for N-CH₃ protons, and a sharp singlet at 7.9δ are associated with four Ar-H protons. When the $^1\text{H-NMR}$ spectra of the products separated by aminolysis of PET waste flakes were recorded after 3, 7, 15, 21, 25, 30, and 45 days of the reaction, the peak positions were found exactly same as mentioned above.

Figure 3 shows the DSC thermogram recorded for the precipitates obtained as the result of aminolysis of bottle grade PET waste and for reference sample prepared separately in the laboratory, from 40 to 450°C at the heating rate of 10°C per minute. The thermogram shows an endothermic peak at 340°C indicative of their melting point and degradation peak at 350°C formation of a single compound.

Characterization of Sample II

The reaction of PET waste with ethylamine was found to be significant in case of EA10 i.e., 1 : 10 (g/mL) ratio of PET to ethylamine. The reason for this is probably the same as that for aminolysis with methylamine. PET waste (10 g) was treated with ethylamine (100 mL) in a sealed reaction vessel with continuous stirring at room temperature. Fine white precipitates start appearing within few hours from the start of the reaction. Complete degradation of PET waste in ethylamine environment occurred in

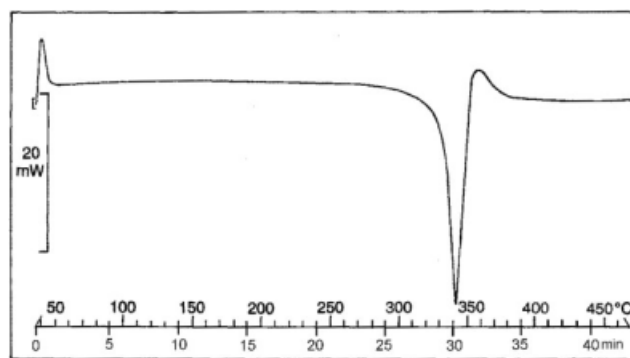


Figure 3 DSC thermogram of *N,N'*-dimethyl terephthalamide synthesized by aminolysis of PET waste with methylamine.

45 days. After 45 days, these white precipitates were filtered, washed and dried in oven and then characterized as above.

Figure 4 shows the IR spectrum of the compound, which shows one absorption band in the region $3300\text{--}3500\text{ cm}^{-1}$ (at 3300 cm^{-1}) can be assigned to a secondary —NH— group. The presence of carbonyl group at about 1670 cm^{-1} in addition to —NH— stretching supports the presence of an amide. The band at 2877 cm^{-1} account for C—H stretching in alkyl chain is present in the compound. The peaks at 1538 cm^{-1} and 1287 cm^{-1} are for N—H bend for aromatic secondary amide and C—N stretching for aromatic secondary amide, respectively. Finally, the peaks at lower region in the spectrum at 856 cm^{-1} suggest that the benzene ring is para-disubstituted.

The IR spectrum suggests the compounds to be *N,N'*-diethylterephthalamide which is supported by the $^1\text{H NMR}$ spectrum of the compound discussed below:

The NMR spectrum of the end products obtained by the aminolysis of PET waste with ethylamine shows peaks at 7.89 (s), 8.58 (s), 3.25 (m), 1.1 (t), and at 2.5 (s).

The four types of signals in the spectrum suggest that there are four different types of protons in the compound as shown in Figure 5. The sharp singlet

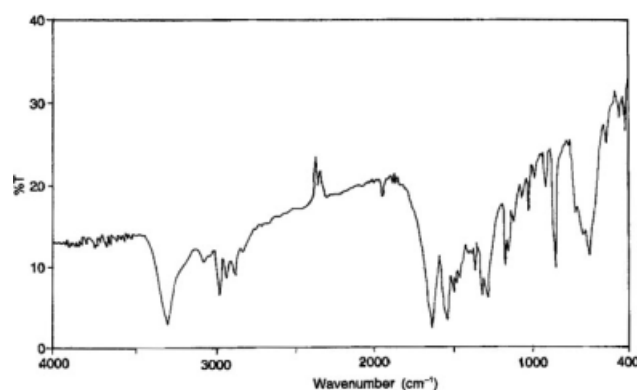


Figure 4 IR spectrum of *N,N'*-diethyl terephthalamide synthesized by aminolysis of PET waste with ethylamine.

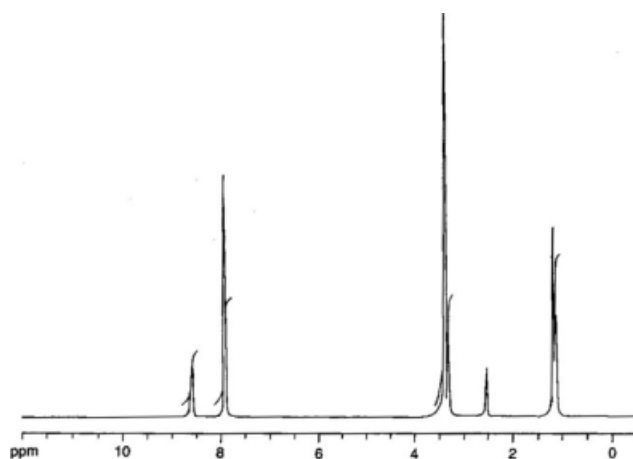


Figure 5 $^1\text{H-NMR}$ of N,N' -diethyl terephthalamide synthesized by aminolysis of PET waste with ethylamine.

at δ -value 7.89 is associated with four aromatic protons. A sharp singlet at 8.58 is attributed to $-\text{NH}-$ proton. A multiplet at 3.25 accounts for methylene protons. The $-\text{CH}_3$ protons occur at δ -value 1.1 as a triplet. The signal at δ -value 2.5 is due to the solvent (DMSO-d_6).

The DSC thermogram was recorded for the white solids obtained by aminolysis of PET waste with ethylamine from 40 to 450°C at the heating rate of 10°C per minute. The thermogram shows peaks at 267°C as shown in Figure 6. The endothermic peak at 267°C indicative of their melting point and formation of a single compound.

Characterization of Sample III

Aminolysis of PET waste with n -butylamine was also investigated in the same ratio and in similar fashion as in aminolysis with ethylamine. The white precipitates start appearing within few hours from the start of the reaction and the complete degradation of PET waste take place in 45 days. The white precipitates so obtained were also analyzed with the help of chemical tests and infrared spectroscopy and DSC.

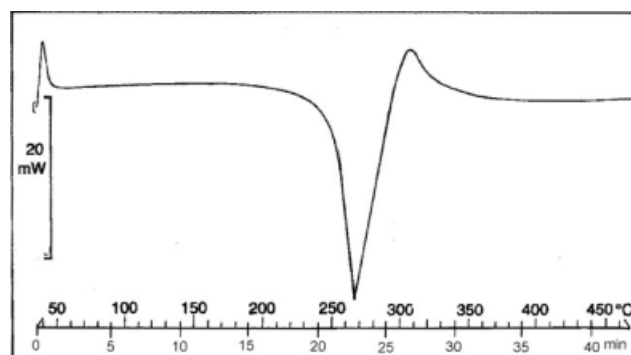


Figure 6 DSC thermogram of N,N' -diethyl terephthalamide synthesized by aminolysis of PET waste with ethylamine.

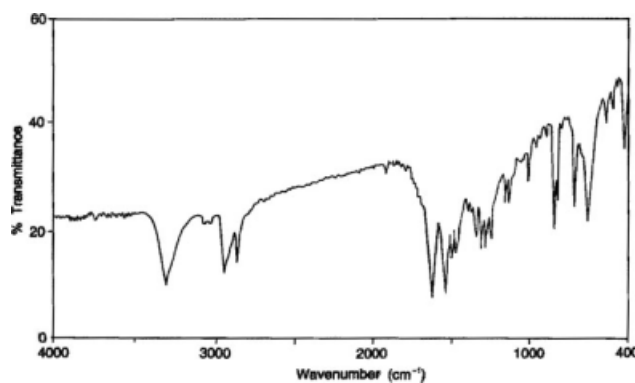


Figure 7 IR spectrum of N,N' -dibutyl terephthalamide synthesized by aminolysis of PET waste with n -butylamine.

The white precipitate obtained through aminolysis of PET waste with n -butylamine was also characterized on the basis of infrared spectroscopy.

Figure 7 shows the IR spectrum of the aminolyzed product of PET waste with n -butylamine shows a single peak in the region 3300–3500 (at 3318 cm^{-1}), suggesting a secondary $-\text{NH}-$ group. The absorption bands at 2870 and 2857 cm^{-1} are due to the C–H stretching in alkyl chain. The peak at 1660 cm^{-1} is assigned to a carbonyl group of amide. The N–H band appears at 1540 cm^{-1} in the IR spectrum. The absorption bands at 1540 and 1472 cm^{-1} are due to the C–H band in alkyl group. The rocking vibration at 861 cm^{-1} confirms the benzene molecule to be para-disubstituted.

The NMR spectrum of the end products obtained by the aminolysis of PET waste with ethylamine shows peaks at 7.882 (t), 8.566 (d), 3.239(m), 2.505 (d) 1.553 (q), 0.893 (t), and at 3.362 (s).

The seven types of signals in the NMR spectrum suggest that there are seven different types of protons in the compound as shown in Figure 8. The sharp triplet at δ -value 7.89 is associated with four aromatic protons. A sharp doublet at 8.566 is attributed to $-\text{NH}-$ proton. A multiplet at 3.25 accounts for NHCH_2 methylene protons, a doublet at 2.510 attributed to $\text{NH}-\text{CH}_2-\text{CH}_2$ of second CH_2 protons,

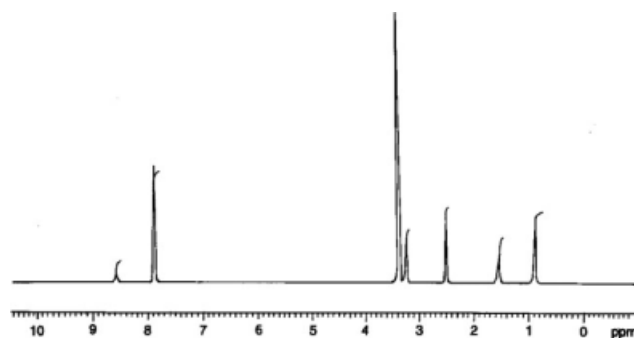


Figure 8 $^1\text{H-NMR}$ of N,N' -dibutyl terephthalamide synthesized by aminolysis of PET waste with n -butylamine.

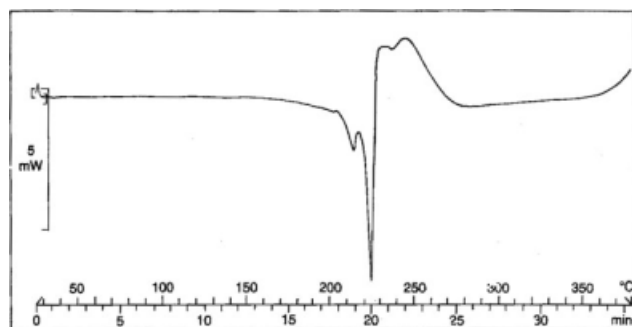


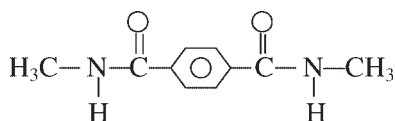
Figure 9 DSC thermogram of *N,N'*-dibutyl terephthalamide synthesized by aminolysis of PET waste with *n*-butylamine.

a quadrate at 1.553 accounts four $\text{CH}_3\text{—CH}_2$ methylene proton and the —CH_3 protons occur at δ -value 0.893 as a triplet. The signal at δ -value 3.362 is due to the solvent ($\text{DMSO-}d_6$).

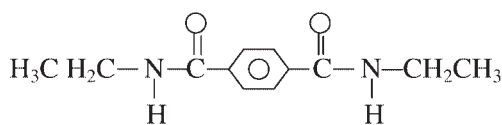
The DSC thermogram was recorded for the white solids obtained by aminolysis of PET waste with *n*-butylamine from 40°C to 400°C at the heating rate of 10°C per minute. The thermogram shows melting endothermic peak at 225°C and degradation exothermic peak at 243°C as shown in Figure 9.

CHEMISTRY OF AMINOLYSIS WITH DIFFERENT AMINES

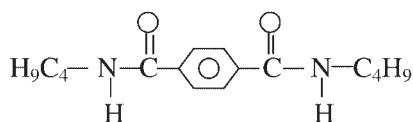
On the basis of above characterization and spectral analysis of the white precipitates obtained from different reactions of aminolysis of PET waste flakes with methylamine, ethylamine, and *n*-butylamine were proposed to be *N, N'*-dimethylterephthalamide, *N, N'*-diethylterephthalamide, and *N, N'*-dibutylterephthalamide, respectively with the following structures:



***N, N'*-Dimethylterephthalamide**

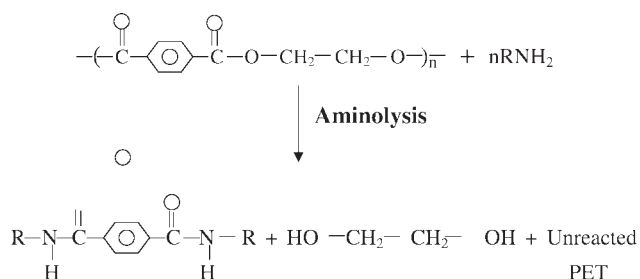


***N, N'*-Diethylterephthalamide**



***N, N'*-Dibutylterephthalamide**

Chemical structures of aminolysed end products



Scheme 1 Chemical reaction of different amines with PET waste.

Aminolysis of PET waste gave *N*-alkyl terephthalamides (Scheme 1) and the proposed picture of PET degradation by different reactions of aminolysis.

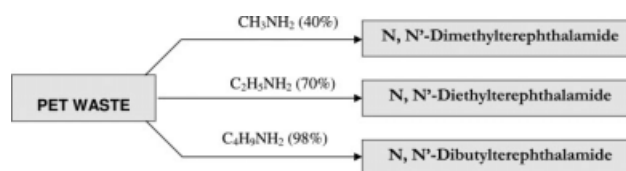
Where R = CH_3 (with methylamine); C_2H_5 (with ethylamine); C_4H_9 (with *n*-butyl amine).

Higher homologues of terephthalamide were obtained through degradation of PET waste with aqueous methylamine, aqueous ethylamine, and *n*-butylamine respectively. Scheme 2 gives a clear summarized picture of the terephthalamides obtained through ammonolysis and different reactions of aminolysis of PET waste.

CONCLUSIONS

In the present work, studies on a series of degradation experiments of postconsumer PET waste had been made to observe the aminolysis by making use of a variety of amines namely, methylamine, ethylamine, and *n*-butylamine. All of these degradation experiments were carried out at normal conditions of temperature and pressure and were also studied in varying weight/volume ratio of PET to amine to study the reactions quantitatively. The complete degradation of PET waste was achieved after 45 days in case 1 : 10 weight/volume ratio of PET to amine. The aminolyzed end products so obtained were characterized by using various conventional techniques such as spectroscopic techniques namely IR, NMR, and simultaneous DSC.

Therefore, a process for recycling of PET waste at ambient temperature was developed, which makes the present recycling system more important and highly beneficial from ecological as well as



Scheme 2 Preparation of different *N*-alkylterephthalamides from PET waste.

economical point of view as it reduces the amount of solid waste and provides technology for value added recycling of PET waste.

References

1. Myriam, B. L.; Gérard, D.; Gilles, T. *J Polym* 2002, 43, 21.
2. La Mantia, F. P. *Prog Rubber Plast Recycl Technol* 2004, 20, 1.
3. Pergugini, F.; Mastellone, M. L.; Arena, U. *Prog Rubber Plast Recycl Technol* 2004, 1, 69.
4. Amboori, C. G. G.; Haith, M. S. *J Appl Polym Sci* 1999, 12, 1968.
5. Launay, A.; Thominette, F. *J Polym Degrad Stab* 1994, 46, 319.
6. Goto, M.; Koyamoto, H.; Kodama, A.; Hirose, T.; Nagaoka, S.; McCoy, B. J. *AIChE* 2004, 48, 136.
7. Goto, M.; Koyamoto, H.; Kodama, A.; Hirose, T.; Nagaoka, S. *J Phys Condens Matter* 2002, 14, 11427.
8. Genta, M.; Iwaya, T.; Sasaki, M.; Goto, M.; Hirose, T. *Ind Eng Chem Res* 2005, 44, 11.
9. Wood, A. *Future* 1993, 283.
10. Kobe, J. P.; Ibo-Gun, J. P. U. S. Pat. 6,730,709 (2004).
11. Malinconico et al.; *Polym Recycl* 1997/98, 3, 4.
12. Lim et al.; *J Korean Fiber Soc* 2000, 37, 1.
13. Yoo et al.; *Macromol Symp* 1997, 118, 739.
14. Polaczek, J.; Pielichowski, J.; Lisicki, Z.; Chrzaszcz, R.; Kowalska, M.; Florsch, Z. *Polish Pat.* 151,346 (1987).
15. William, E. A.; William, P. T. *J Anal Appl Pyrolysis* 1997, 40, 347.
16. Shukla, S. R.; Hard, A. M. *J Polym Degrad Stab* 2006, 91, 1850.
17. Soni, R. K.; Singh, S.; *J Appl Polym Sci* 2005, 96, 5.
18. Blackmon, K. P.; Fox, D. W.; Shafer, S. J. *Eur. Pat.* 365, 842 (1988).
19. Terephthalic Diamide. *Ind Patent* 154,774; CA 104: 51243e (1985).
20. Collins, M. J.; Zeronian, S. H.; Marshall, M. L. *J Macromol Sci Chem* 1991, 28, 775.
21. Ellison, M. S.; Fisher, L. D.; Alger, K. W.; Zeronian, S. H. *J Appl Polym Sci* 1982, 27, 247.
22. Farrow, G.; Ravens, D. A. S.; Ward, I. M. *Polymer* 1962, 3, 17.
23. Popoola, V. A. *J Appl Polym Sci* 1988, 36, 1677.
24. Spychaj, T.; Fabrycy, E.; Spychaj, S.; Kacperski, M. *J Material Cycles Waste Manage* 2001, 3, 24.
25. Awodi, Y. W.; Johnson, R. H.; Popoola, A. V. *J Appl Polym Sci* 1987, 33, 2503.