A Novel Route of Synthesis, Characterization of Terephthalic Dihydrazide from Polyethylene Terephthalate Waste and it's Application in PVC Compounding as Plasticizer

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ABSTRACT: The degradation of polyethylene terephthalate (PET) waste by making use of hydrazine monohydrate was investigated at ambient temperature and pressure. The aminolysed end products obtained were characterized with chemical tests and spectroscopic techniques namely IR, UV-visible spectroscopy and NMR, and the differential scanning calorimeter (DSC). The end product was characterized as terephthalic dihydrazide (TPD) and further used in PVC compounding as secondary plasticizer. The hardness, tensile strength, elongation at break, thermal stability, and compatibility of the PVC sheet were studied and concluded that the aminolysed product may find potential application as secondary plasticizer in PVC formulations. J Appl Polym Sci 113: 1090–1096, 2009

Key words: polyester; recycling; degradation; infrared; NMR

INTRODUCTION

In last few years, different technologies of mechanical and chemical recycling have been developed and commercialized throughout the world. The mechanical recycling includes conversion of PET waste into PET chips which are used in the manufacturing of fibers.[1] The chemical recycling focus on the conversion of PET waste into its monomer such as terephthalic acid, ethylene glycol and plasticizer, polyol unsaturated plasticizer, amides etc.[2]

In a kind of chemical recycling process, which involves hydrolytic degradation of polyester waste in excess MEG at high temperature for extended period in the presence of a catalyst such as acetates of Zn, Mn, Co, Na, or Ca, the process converts the waste into monomers such as bishydroxy ethylene terephthalate (BHET) and oligomers (trimer, tetramer). The glycolysed product, either 100% or blend with virgin monomer, is then fed to polycondensation reactor for polyesterification to PET. PET glycolyzates finds application in the manufacture of unsaturated polyester resins, Polyurethane foams and polyisocynourate foams.[3] The waste is treated with methanol under pressure to recover Dimethyl terephthalate (DMT) and ethylene glycol (EG) at 185°C. The reaction is catalyzed by transesterification catalyst such as zinc acetate, cobalt acetate, lead oxide etc. process involves treating PET with water, acids or caustic soda to give terephthalic acid (TPA) and ethylene glycol (EG), which may be repolymerized after purification.[4,5]

PET waste can be hydrolyzed with water at 150 to 250°C under pressure. The amount of water used is about 2 to 4 times the weight of waste. The hydrolysis is catalyzed by transesterification catalyst such as sodium acetate.[6] Very few efforts have been made in carrying out the degradation of PET waste at ambient temperature and pressure condition.[7] In the present attempt the aminolysis of PET waste with different amine like hydrazine monohydrate has been studied. PET solvolysis end product may be used in epoxy resin, polyurethane resin etc.[8–18]

EXPERIMENTAL

Synthesis of aminolysed product with hydrazine hydrate

The starting material was obtained from postconsumer 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 with hydrazine monohydrate (99–100%), Qualigens.

The aminolysis of PET waste flakes was performed with hydrazine monohydrate. PET waste flakes (10 g)

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TABLE I
Formulations of PVC Sheets with TPD

S. No.	PVC (phr)	DOP (phr)	TPD (phr)	Calcium carbonate (phr)	DBLP (phr)	Stearic acid (phr)	Designation
1	100	25	25	15	8	1	TPD 1
2	100	30	20	15	8	1	TPD 2
3	100	35	15	15	8	1	TPD 3
4	100	40	10	15	8	1	TPD 4
5	100	45	5	15	8	1	TPD 5

were reacted with hydrazine hydrate (20 mL). The reactions were performed in a properly sealed reaction vessel with continuous constant stirring at ambient temperature and pressure.

The light yellow precipitates start appearing in the reaction vessel, within few minutes from the start of the reaction. The aminolysed products from degradation experiment were separated after every 1 h and washed with distilled water severely and the product so obtained was dried under vacuum.

Characterization of end products obtained by aminolysis of PET waste with hydrazine hydrate

The amine content of end product was determined by boiling 2 g of end products in 300 mL of standard NaOH solution. The unreacted NaOH was titrated with standard oxalic acid solution.

The amine value of end products were determined with the following formula:

$$\text{Amine value} = \frac{M.\ Wt.\ \text{of}\ \mathrm{NH_3} \times N \times (V_1 - V_2) \times 100}{1000 \times W}$$

where N, normality of NaOH; V_1, volume of NaOH taken; V_2, volume of NaOH consumed; W, weight of end product.

The solubility of end products was determined in different solvents and was found soluble in ethanol, dimethyl formamide and dimethyl sulfoxide.

The end products so obtained were characterized with the help of UV, FTIR, proton-NMR and differential scanning calorimeter. The amine value of the end product was also determined. The 1H-NMR spectra of the end product was recorded by Bruker. The UV-Visible spectra was recorded by dissolving the sample in DMSO at Double beam UV-Visible spectrophotometer, Systronic 2201 at the scan rate 2 nm/s. FTIR spectra were recorded on a Shimazdu IR spectrophotometer with KBr discs at scan rate 4 cm^{-1}/s.The sample was also analyzed with the help of DSC, Mettler Star SW 9.01 at heating rate of 20°C/min from 40 to 400°C.

Preparation of PVC compounded sheets

The compounding of PVC was made by adding various additives such as plasticizer, stabilizer, filler, processing aids to PVC resin. The PVC compounding was made by mixing different ingredients in an internal batch mixer. All the ingredients except plasticizer were mixed thoroughly at 60°C with increasing rpm from 400 to 500 for 5 min.

The requisite amount of plasticizer was added to this mixture and further mixed for 20 min with constant rpm of 500.

The PVC sheets were prepared on two-roll mill and compression molding press.

The pre mixed PVC compound was prepared on two roll mill at constant temp (148°C). The sheets were then prepared in compression molding machine at 150°C with hold time 1.5 min and cooling time 1 min at under pressure 70 kg/cm^2. The sheets obtained were light yellow in color.

The PVC sheets of different formulations were prepared. The different formulations have been presented in Table I. The amount of DOP and terephthalic dihydrazide (TPD) varies from 25–55 phr and 5–25 phr. Different sheets prepared by compression molding press were designated as TPD 1, TPD 2, TPD 3, TPD 4, TPD 5, and D1, D2, D3, D4, and D5 as listed in Tables I and II.

TABLE II
Formulations of PVC Sheets with DOP

S. No.	PVC (phr)	DOP (phr)	Calcium carbonate (phr)	DBLP (phr)	Stearic acid (phr)	Designation
1	100	25	15	8	1	D1
2	100	30	15	8	1	D2
3	100	35	15	8	1	D3
4	100	40	15	8	1	D4
5	100	45	15	8	1	D5

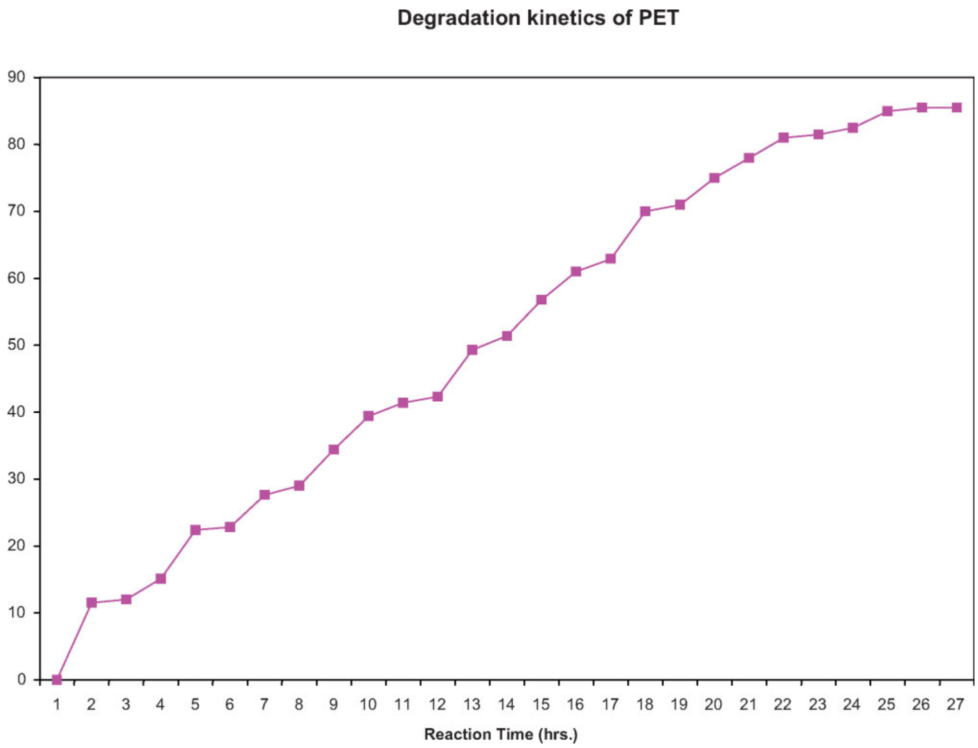

Figure 1 Degradation kinetics of PET with hydrazine monohydrate. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Mechanical properties

Tensile of PVC sheets

The tensile properties of the sheets were determined with the help of UNIVERSAL TENSILE TESTING MACHINE. These are tensile strength, tensile modulus and % elongation.

Tensile Strength = Value of Load/Thickness * width % elongation at break = (Final elongation-Initial elongation) / Initial distance

Hardness shore A (ASTM D 2240)

It was determined with the help of Durometer, a hardness tester.

Compatibility (ASTM D 3291)

The loop compatibility of polymeric plasticizer (TPD) was determined. The specimen (1/2 in. * 1 in.) was used to determine the compatibility.

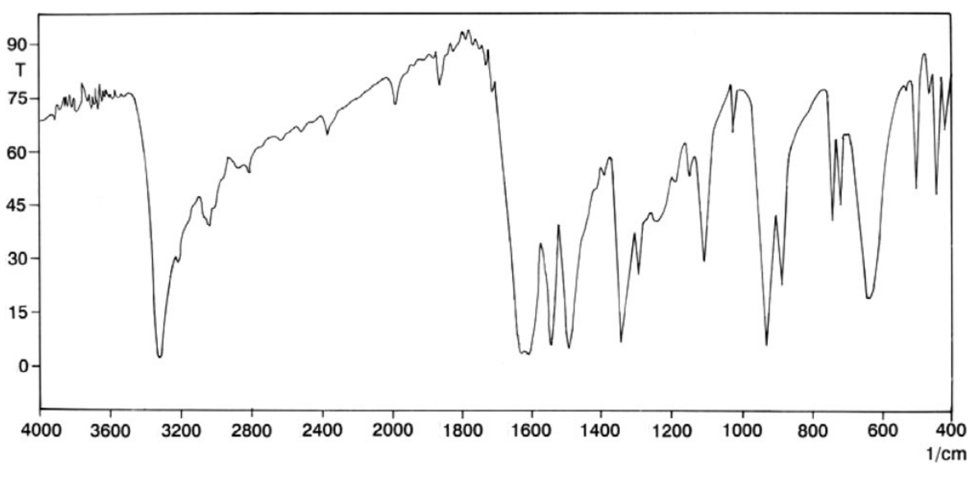

Figure 2 FTIR Spectra of aminolysed end product with Hydrazine monohydrate.

TABLE III
Amine Value and Elemental Analysis of TPD

S. No.	Solvent used	End product	Abbreviation	Theoretical amine value	Experimental amine value
1.	Hydrazine monohydrate (99–100%)	Terephthalic dihydrazide	TPD	35.05	33.40
		% of constituents	C%	49.34	49.28
			H%	5.14	5.15
			N%	28.80	28.42

Thermal stability

It was determined with the help of thermal stability tester by Cango Red Method. The thermal stability of the PVC sheets was determined at 200°C in terms of time required to change the color of pH paper to red.

RESULTS AND DISCUSSION

Synthesis of TPD

It was seen that PET flakes have been completely depolymerized and only a few small pieces left unreacted in this case. The reaction was completed in 24 h. A fresh reaction was started by mixing PET waste (10 g) with hydrazine monohydrate (20 mL). The reaction was stopped after 1 h by pouring reaction mixture in the water. The product was filtered and dissolved in DMSO, refiltered to separate the unreacted PET waste. The product was recovered then dried. The yellow precipitate was separated and dried at 70°C under vacuum for 4 h till constant weight is obtained.

Figure 1 shows the conversion of PET waste into TDP after each interval of an hour time and in this case reaction was completed in 24 h. Although it has been mentioned in our research article the reaction[1,5] of PET waste with other amine such as methyl amine, ethyl amine and *n*-butyl amine completed in 40, 60, and 30 days. The higher rate of reaction is a boon to study of aminolysis at ambient pressure and temperature.

Differences in the reactivity with different amines were observed. In case of ethyl amine, complete degradation of PET flakes takes 60 days and use of methyl amine reduces this time to 40 days.[5] This degradation time further gets shortened to 30 days with *n*-butyl amine and hydrazine monohydrate takes only 24 h for the complete degradation of PET waste.

Thus, the time required for complete degradation of PET waste was shortened by the use of hydrazine hydrate. The reason for the time reduction in the process of degradation is due to the increase in the nucleophilicity of the amine group affecting the ester bonds in polyethylene terephthalate. Because the reaction proceeds according to nucleophilic mechanism, amines act as nucleophile on the carbonyl group, thus the difference in the reactivity of various amines towards carbonyl group can be explained on the basis of their nucleophilicity and the concentration of the amino group.

It can be observed from the Figure 2 that kinetics of PET degradation is exponential whether in days or hours. This shows that the mechanism of PET degradation is same in ammonia and other amines. The mechanism of the degradation of PET waste with hydrazine mono hydrate is appeared to be same as reported as earlier research publications and clear.

Characterization of terephthalic dihydrazide

The amine value and elemental analysis of TPD was determined and is presented in Table III.

The experimental amine values are slightly less than the theoretical amine values. Lesser amine value may be attributed to higher homologues. The results of elemental analysis of end product show a close equivalent with theoretical value. These end products were found sparingly soluble in methanol, ethanol and completely soluble in DMSO and DMF.

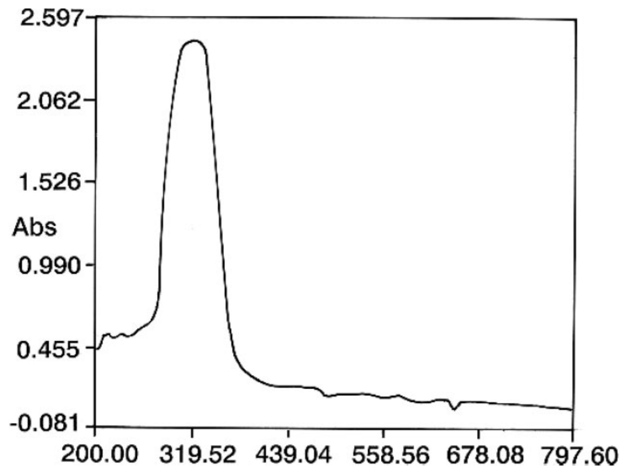

Figure 3 UV-Visible Spectra of aminolysed end product with Hydrazine monohydrate.

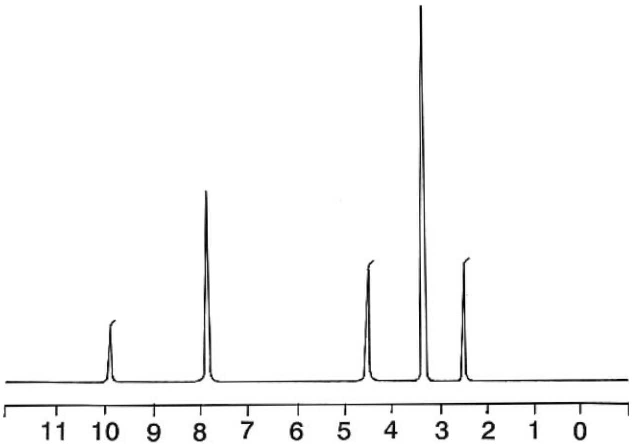

Figure 4 Proton-NMR spectra of aminolysed end product with Hydrazine monohydrate.

FTIR spectral analysis

Figure 2 shows the FTIR spectrum of the end products obtained by the aminolysis of PET waste with hydrazine monohydrate. The FTIR spectrum of yellow precipitate shows a pair of absorption bands at 3315 cm^{-1} that is attributed to *N*—H str. and is characteristic of primary amides. The peak at 1490 cm^{-1} is due to aromatic ring and at 1340 cm^{-1} is due to C—N str., C=O str. appears at 1628 cm^{-1}, a peak was observed at 3034 cm^{-1} due to Ar—H str and *N*—N str appears at 1290 cm^{-1}. The FTIR spectrum of Terephthalic dihydrazide was also downloaded from website "Spectral database for organic compound" as follows. It shows following peaks: 3327 3213, 3071, 3061, 3050, 3036, 1629, 1616, 1608, 1544, 1492, 1343, 1292, 1246, 1240, 1187, 1143, 1106, 1017, 930, 889, 882, 738, 714, 641, 631, 503, and 497.

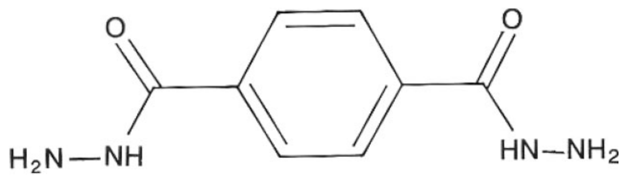

Figure 6 Terephthalic dihydrazide.

The comparison of the FTIR spectra of our product was found to be matching exactly with downloaded reported spectra. It confirms the formation of Terephthalic dihydrazide as evidenced by elemental analysis also.

UV-visible spectra

Figure 3 shows the uv-visible spectra of the product obtained by the reaction of aminolysis of PET waste with hydrazine monohydrate. The UV spectra suggest the presence of carbonyl group and aromatic ring which was further confirmed by NMR spectra. The figure shows strong absorption about 200–400 nm.

Proton-NMR

Figure 4 shows the proton-NMR spectra of aminolysed end product of hydrazine monohydrate. The three NMR peaks were observed at 4.537 (s, 4H, $NHNH_2$), 7.864 (s, 4H, ArH), and 9.880 (s, 2H, $NHNH_2$).

Thermal analysis

The DSC thermograms recorded from room temperature to 400°C at a heating rate of 20°C per minute

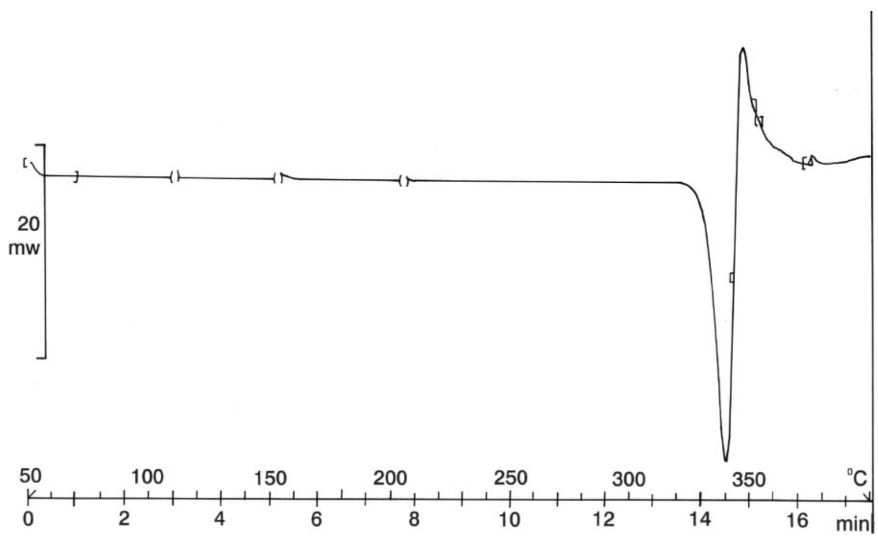

Figure 5 DSC of aminolysed end product of PET waste with Hydrazine monohydrate.

TABLE IV
Mechanical Properties and Thermal Stability of PVC Sheets with TPD

S. No.	Designation	Hardness shor A	Tensile strength Kg/cm^2	Elongation at break %	Thermal stability (min)
1	TPD1	82	135	195	100
2	TPD2	79	140	200	95
3	TPD3	77	138	221	90
4	TPD4	77	136	236	85
5	TPD5	70	134	265	81

TABLE V
Mechanical Properties and Thermal Stability of PVC Sheets with DOP

S. No.	Designation	Hardness shor A	Tensile strength Kg/cm^2	Elongation at break %	Thermal stability (min)
1	D1	95	120	61	95
2	D2	91	125	78	93
3	D3	86	135	104	85
4	D4	80	140	150	76
5	D5	78	138	200	70

under air atmosphere is shown in Figure 5. The large endothermic peak at 340°C indicates the melting point of the aminolysed product which shows good thermal stability. However, exothermic peak at 346°C followed by the melting of the product shows the complete thermal decomposition 346°C.

On the basis of FTIR, NMR and elemental analysis, the structure of the product can be view in Figure 6.

APPLICATION OF TEREPHTHALIC DIHYDRAZIDE

Tensile strength and elongation at break

Tables IV and V show results of the tensile properties of PVC designated as TPD1, TPD2, TPD3, TPD4, and TPD5. It can be revealed from Table IV that the elongation at breaking is in the range of 195–265% for different formulation as presented in Table II. In the presented results the amount of DOP was increase from 25 to 50 phr and additional amount of TPD was added to study as plasticization effect in PVC sheets. The PVC sheets were also prepared by using DOP only as plasticizer so that the comparatively action of TPD with DOP plasticizers can be evaluated. It can be understood by Tables IV and V by comparison of the elongation at the break values for TPD1–TPD5 with corresponding elongation at break values for the TPD shows plasticization effect without making any appreciable change in tensile strength of PVC sheets.

Hardness (ASTM D 2240)

Tables IV and V show variation in hardness with and without the use of TPD. The hardness of PVC sheets decrease with the increase the amount DOP/TPD.

Thermal stability

Table IV shows that the thermal stability of the PVC sheets increases with increasing amount of the TPD. The thermal stability of PVC sheets is improved by 5–15%.

CONCLUSIONS

1. The time required for complete degradation of PET waste was shortened by the use of Hydrazine monohydrate.
2. The aminolysed end product may have potential application as plasticizer in PVC formulation.
3. The mechanical properties and thermal stability of PVC sheets were also improved by the use of TPD.

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