Aminolytic Depolymerisation of Polyethylene Terephthalate Wastes using Sn doped ZnO Nanoparticles

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Abstract

Poly(ethylene terephthalate) (PET) is one of the most consumed polymers because of its excellent thermal and mechanical properties. By increasing in PET production and since the disposal of PET waste has growing to be a major global environmental issue each year. Chemical recycling is a most successful method to achieve circular economy in the PET utilizing industries. Current research work aims to complete depolymerization of waste PET from soft drink bottles by the aminolysis method to produce bis (2-hydroxy ethylene) terephthalamide (BHETA) in the presence of Sn doped ZnO. To evaluate catalytic activity, pure and Sn$^{2+}$ doped ZnO nanoparticles prepared using different Sn$^{2+}$ molar ratios at 0.5, 1.0 and 2.0 mol% and calcined at 500 °C for 1h. The synthesized catalysts characterised using FT-IR, XRD, and UV-vis spectroscopy. The surface morphology and percentage doping obtained from SEM and SEM-EDS, respectively. We have observed a reduction in optical band gap and crystallite size of ZnO due to tin doping. Aminolytic depolymerization of PET waste using ethanolamine promoted by Sn doped ZnO effectively under conventional thermal method. Increase in the yield of the BHETA observed with respect to increasing doping percentage of Sn and 1-2 mol% Sn doped ZnO nanoparticles afforded over 90% of BHETA. Structure and purity of BHETA, depolymerised product characterized by FT-IR, $^1$HNMR, $^{13}$C NMR, and MS.

1. Introduction

Zinc oxide (ZnO) is a unique material when compared to other metal oxides because of its cost-effectiveness and tunable catalytic properties. The catalytic efficiency of ZnO inherited from the tailor made electronic properties and nanostructure. Advancements in synthetic procedure as developed widen ZnO in various applications [1–4]. The crystal structure of ZnO comprises zinc blende and wurtzite, a hexagonal structure which can doped with metals and non-metals [1]. Zinc oxide is a binary semiconducting material having pyroelectric and piezoelectric properties (60 meV), ZnO has a high redox potential, superior physical and chemical stability, and non-toxicity [2]. The major advantage of ZnO nanoparticles over others is their large surface area combined with reduced size, which makes it applicable in many areas like biological study including (antimicrobial activity), the photocatalytic and semiconducting properties which make it admit the use of ZnO nanoparticles as a potential candidate for many catalytic transformations [4, 5]. The catalytic activity of ZnO nanoparticles can be tuned by doping process and it is seems to be one of the economical solutions [6]. Doping is mainly of two types: one is cationic and the other is of anionic doping. Introducing cationic impurities into the ZnO structure known as cationic doping, most prominently transition metals used as cationic dopants, eg: Sn, Al, Ga, In, Cd, Cu, Mn, Ni. The doping of an anion into ZnO called anionic doping, eg; As, N, and S are anionic dopants [1, 3].

In the current investigation, we aim to depolymerise post-consumer PET wastes completely into pure terephthalamide monomer using aminolysis. Forasmuch PET is one of the most important engineering polymers and considered being an excellent material for many applications, including clothing applications. It has excellent tensile and impact strength, chemical resistance, clarity, processability, colorability, and reasonable thermal stability [7]. PET is an aromatic polyester mainly utilised for packaging and textile industries and the post-consumer waste recycling of PET using chemical methods rather than physical and land filling method is a most economical method to achieve circular economy in polyester industries because of its widespread commercial applications [8, 9]. The total consumption of plastics in India is about 4 million tons and the waste generated is about 2 million tons. Plastics contributing to about 20% of solid municipal waste in India. The overall world consumption of PET currently amounts to about 13 million tons, of which 9.5 million tons processed by the textiles industry, 2 million tons used in the manufacture of audio and videotapes, and 1.5 million tons used in the manufacture of various types of packaging mainly bottles and jars [10]. PET is a noxious material because of its high resistance to atmospheric and biological agents. Ecological and
economic considerations advocate the introduction of wide-scale PET recycling, similar to the recycling of traditional materials such as glass, paper, or metals [11].

**Aminolytic depolymerization of PET waste**

PET recycling is one of the most successful and best examples of polymer recycling. There are many processes by which post-consumer PET waste recycled, but the sustainable method is the chemical recycling process because it leads to the formation of monomers from which the polymer made [8, 12]. In contrary, the conventional disposal methods such as landfilling become severe threat terrestrial and aquatic lives due to microplastics pollution [13, 14]. Chemical recycling process of PET divided: (i) glycolysis, (ii) methanolysis, (iii) hydrolysis, (iv) aminolysis, and (v) ammonolysis. Among the chemical recycling techniques, glycolysis and aminolysis depolymerization of the PET wastes produced bis (2-hydroxy ethyl) terephthalate (BHET) and bis (2-hydroxymethyl) terephthalamide catalysed by Lewis acidic heterogeneous catalysts [15, 16]. Aminolysis is any chemical reaction in which post-consumer PET waste completely depolymerized into monomers by reacting with a molecule of an amine. Aminolysis is a method for PET chemolysis which has been relatively lesser explored when compared to other processes. There are only a few literature references regarding the chemolysis of the waste PET using different amines such as ethanolamine, tri-ethanol amine, allylamine, and polyamines [17–19]. The catalytic systems reported for glycolysis and aminolysis recycling of PET wastes summarised in Table 1.
In the current study, the chemical recycling of post-consumer PET polymer wastes, especially wastewater bottles, using the aminolysis process. The aminolysis of the PET wastes using the Sn(II) substituted ZnO nanoparticles as catalyst. Sn/ZnO catalysts showed enhancement in photocatalytic, electron transport behaviour and sensitive to organic molecule containing carbonyl group such as formaldehyde [30–33]. The doping of Sn on ZnO reduced the band gap and promote catalytic behaviour. Sn(II) substituted ZnO nanoparticles prepared by the sol-gel method at different Sn$^{2+}$ to Zn$^{2+}$ molar ratio and characterised using FTIR, XRD, UV-Vis and SEM-EDS analysis. Depolymerization of PET wastes using aminolysis under various parameters such as temperature, PET-to-catalyst ratio, and PET-to-aminolytic reagents. The final product of the aminolysis process characterised using $^1$H, $^{13}$C NMR and MS.

### 2. Materials And Methods
Common chemicals such as zinc nitrate hexahydrate, tin(II) chloride dihydrate, diethylamine, sodium hydroxide, ethanolamine, acetone, ethyl acetate, and n-hexane, all chemicals purchased from SRL and Loba Pvt, Ltd India and used without further purification. Post-consumer PET waste obtained from wastewater bottles collected, cleaned PET bottles dried at 80°C for 6 hours and cut into smaller pieces. All glassware and Quickfits we employed in the experimental work made up of coming/borosil glass. These glasswares washed thoroughly and dried in a hot air oven before use.

2.1 Synthesis of catalyst

Tin-doped ZnO nanoparticles were synthesized by the sol-gel method. Zinc nitrate hexahydrate and tin(II) chloride dihydrate dissolved in 50 ml of distilled water. NaOH used as the base and diethylamine was used as a stabilizer to get the desired pH value of 11. The mixture kept under constant magnetic stirring for 5 h. After stirring the solution with reflux at 70-75°C for 4 hours and filtered by vacuum. During the filtration, the solution washed with distilled water many times to avoid impurities. After filtration, the filtered sample heated to 80°C in the oven for 24 hours. The heated sample was ground and calcined at 500°C for 1 hour. ZnO nanoparticles substituted with Sn²⁺ in different Sn²⁺ molar ratios of 0.0, 0.05, 0.1 and 0.2 prepared by a sol-gel process [32].

2.2 Catalytic activity

The catalytic activity of Sn²⁺-substituted ZnO nanoparticles studied toward aminolysis of poly (ethylene terephthalate) waste using ethanolamine as aminolyzing agent. Sn²⁺-substituted ZnO in different Sn²⁺ molar ratios 0.5%, 1.0% and 2.0% were prepared by the same procedure [20].

Aminolysis of PET wastes using ethanolamine

The aminolysis of PET wastes collected from post-consumer beverage bottles was depolymerized using ethanolamine as an aminolyzing agent afforded bis(2-hydroxyethyl) terephthalamide (BHETA) as a depolymerized product (Scheme 1) [32].

For depolymerization, the aminolysis of Post-consumer PET bottles was collected. After removing the cap and labels they were cleaned thoroughly with soap water followed by distilled water. 100 ml round-bottom glass equipped with a condenser, thermometer and magnetic stirrer. PET flakes (500 mg) were treated with 20 ml of ethanolamine and heated to 150-160°C using magnetic stirring. After reaching the desired temperature, the reaction mixture stirred for 1 hour. The PET was dissolved in ethanolamine. And then 50 mg of Sn²⁺-substituted ZnO nanoparticles catalyst was added. The temperature of the reaction was maintained using a temperature controller. After 1 h, 1 ml of the reaction mixture was diluted with acetone and the progress of the reaction was monitored using precoated aluminium TLC plates (E-Merck, UK, Silicagel G60 F254 indicator) and the spots identified using 356 nm UV detector. The reaction progress was monitored by the TLC method using 70:30 v/v mixtures of n-hexane and ethyl acetate solvents and spot of BHETA compared with reference BHETA compound. The reaction mixture was stirred for 3 h. At the end of the reaction, 50 ml of distilled water was added in excess to the reaction mixture with vigorous agitation and followed by filtration to remove the catalyst. After removal of catalysts, the filtrate heated to 70°C for 15 min and kept in 15-20°C for 12-16 hrs. BHETA obtained as white needle crystals, which filtered and dried at 70°C for 2 h at vaccum. Finally, the yield of the reaction is calculated from the weight of the final product. Further, the final product subjected to FT-IR, ¹H, ¹³C NMR and MS to confirm the structure and purity of BHETA. Likewise, the same procedure used for Sn²⁺-substituted ZnO nanoparticles having 0.5%, 1.0% and 2.0% molar ratio of Sn(II) dopant.

2.3 Characterization techniques used for catalysts
2.3.1 X-ray diffraction (XRD): XRD is a very important experimental technique used to determine the crystal structure of solids, including lattice constant and geometry, identification of unknown materials, atomic spacing, the orientation of the single crystal, preferred orientation of polycrystal, defects, stresses, etc. XRD was performed using a wide-angle X-ray diffractometer with a graphite monochromator and Cu Ka sources. The X-ray generator was operated at 40 kV and 30 mA. XRD analysis was performed on a PANalytical Empyrean powder diffractometer at a 2θ angle between 20 and 80°.

2.3.2 FT IR spectroscopy: FTIR analysis is an analytical technique used to identify functional groups of synthesised SZO catalysts and depolymerised products. The IR absorption of the SZO nanoparticles shows an absorption band for hydroxyl, carbonyl and alkyl groups. IR spectra of the SZO and BHETA recorded on FT-IR SHIMADZU, IRTRACER 100 on solid sample as KBr pellet.

2.3.3 UV–Vis spectroscopy: UV–vis spectroscopy used to characterize the optical absorption properties of Sn(II) doped ZnO. The effect of doping on the optical band gap and crystalline quality investigated using ultraviolet-visible (UV-vis). Light absorption properties were measured by UV Vis 3600 PLUS - SHIMADZU in the wavelength range of 200–800 nm.

2.3.4 SEM-EDS: The morphological changes, elemental mapping and elemental composition of pure and Sn(II) doped ZnO nanoparticles were observed and determined using FE-SEM (Thermoscientific Apreo S) connected with energy dispersive X-ray spectroscopy (EDS).

2.3.5 NMR and MS: $^1$H and $^{13}$C NMR spectrum of BHETA was analysed using Bruker Avance III operating at 500 MHz in CDCl$_3$ solvent. The mass spectrum of BHETA was obtained using Shimadzu LCMS-2020.

3. Results And Discussions

3.1 Synthesis of Sn(II) substituted ZnO nanoparticles using the sol-gel method: The commercially available zinc nitrate hexahydrate, tin(II) chloride dihydrate, diethylamine, sodium hydroxide, and ethanolamine were purchased from Loba Chem Pvt Ltd, India. Sn(II) substituted ZnO nanoparticles were synthesized from a sol-gel method [30, 31]. Initially, Zn(NO$_3$)$_2$.6H$_2$O and SnCl$_2$.2H$_2$O (1 mol% with respect to Zn$^{2+}$) were dissolved in 50 ml of distilled water, the mixture was kept under constant magnetic stirring for 15 minutes at room temperature. Then, diethylamine (30 ml) was added dropwise using a burette. Mean the time (NH$_4$HCO$_3$) (2M) was also added dropwise for mainiting pH at 11. After that, the solution was kept under constant magnetic stirring for 5 hours at room temperature. A milky white precipitate was observed. Then, the obtained residue (SZO) was filtered and cleaned many times with deionized water. The final product was kept in an oven at 80°C for 24 hours to dry the product and remove moisture. Finally, the product of ZnO substituted ZnO was heated in a static air furnace at 500°C for 1 h. Sn(II) substituted ZnO in different Sn(II) molar ratios of 0.5%, 1.0% and 2.0% were prepared using the same procedure and the yield of Sn(II) doped ZnO NPs summarised in Figure 1.

3.2 XRD pattern of tin-doped zinc oxide nanoparticle catalysts: The XRD pattern of Sn(II) doped ZnO nanoparticles synthesized by the sol-gel method. The powder XRD patterns have been recorded from 20 to 80° two theta angles. Figure 2 shows the XRD patterns of the tin-doped ZnO nanoparticles with molar ratios of 0.5, 1.0 and 2.0% of Sn(II).

The change in the crystalline pattern of the Sn(II) substituted ZnO compared with pure zinc oxide nanoparticles. The obtained diffraction patterns of the nanopowders suggest that ZnO showed sharp peaks confirm the good crystalline
with a hexagonal wurtzite structure. The peak observed at 2θ = 31.50, 33.76, 35.90, 47.23, 56.18, 62.20 and 67.60 corresponds to the lattice plane (100), (002), (101), (102), (110), (103) and (112), respectively, indicative of the hexagonal structure of wurtzite of ZnO [30, 31].

The reflections (100), (002) and (101) are of high intensity, and other reflections (102), (110), (103) and (112) are of lower intensity. Since the (101) reflection is the highest in all samples, we can conclude that that the particles are oriented mostly in the [101] direction. It means that Sn$^{2+}$ has been successfully doped. The substitution of different Sn$^{2+}$ catalysts did not change the hexagonal crystal structure of the wurtzite phase.

| Material      | Lattice parameters | Volume (nm$^3$) | Crystallite size (nm) |
|---------------|--------------------|-----------------|----------------------|
|               | a (Å)              | c (Å)           | (Scherrer equation)  |
| ZnO           | 1.69 5.19 3.05     | 12.98           | 37.65                |
| 0.5mol% Sn-ZnO| 1.69 5.17 3.05     | 12.89           | 19.3                 |
| 1.0mol% Sn-ZnO| 1.93 5.19 2.67     | 16.92           | 21.75                |
| 2.0mol% Sn-ZnO| 2.05 5.2 2.53      | 19.02           | 15.2                 |
|               |                    |                 | Crystallite size (nm) |
|               |                    |                 | (W-H equation)       |
| ZnO           |                    |                 | 80.4                 |
| 0.5mol% Sn-ZnO|                    |                 | 38.1                 |
| 1.0mol% Sn-ZnO|                    |                 | 49.9                 |
| 2.0mol% Sn-ZnO|                    |                 | 15.7                 |
|               |                    |                 | Lattice strain ε X 10$^{-3}$ |
| ZnO           |                    |                 | 1.4                  |
| 0.5mol% Sn-ZnO|                    |                 | 2.25                 |
| 1.0mol% Sn-ZnO|                    |                 | 2.275                |
| 2.0mol% Sn-ZnO|                    |                 | 2.5                  |

The crystallite size was calculated by the Scherrer equation and the Williamson-Hall equation. The crystallite size determined from the three peaks (100), (002) and (101) and the average size is calculated. The crystallite size obtained from Scherrer equation is smaller than the size obtained from the Williamson-Hall equation is observed from Table 1. The crystallite size is decreased on increasing the doping amount of tin % [31]. The crystallite size calculated using Scherrer and W-H method coincide that doping of Sn(II) reduced the crystallite size with respect to the dopant concentration. Similar trend have reported by Siva et al (2020 [31]. In contrary, the lattice strain increased from 1.4 to 2.5 while increasing the dopant concentration due to incorporation of higher ionic radius of Sn(II) in ZnO framework.

3.2 FT-IR spectra of pure and Sn-doped ZnO nanoparticles

FT-IR transmittance spectra of pure and Sn(II) doped zinc oxide nanoparticles of different molar ratios shown in Figure 3, respectively. The spectrum was recorded from 500 to 3500 cm$^{-1}$. In the pure and different molar ratio of 0.5%, 1.0%, and 2.0% Sn$^{2+}$, no significant change in vibrational stretching of ZnO observed in the SZO samples compared to the pure synthesized ZnO. For all the samples, major and broad peaks were found between 500 cm$^{-1}$ and 800 cm$^{-1}$ assigned to the stretching vibration of Zn-O. These vibrational frequencies change to 800 cm$^{-1}$ with an increase in Sn doping. The signals were found in the region 1400 cm$^{-1}$ - 1700 cm$^{-1}$ and may be due to C=C and C=O vibrations. Other signals near between 2000 cm$^{-1}$ and 2400 cm$^{-1}$ were also observed. Finally, significant peaks were found between 3200 cm$^{-1}$ and 3500 cm$^{-1}$. These peaks were attributed to the H$_2$O stretching vibration in the ZnO lattice [34].

3.4 UV-vis absorbance spectra of pure and Sn-doped ZnO nanoparticles:
UV absorption spectra are analyzed for all samples from 200 nm to 800 nm. The optical properties of prepared Sn-doped ZnO nanoparticles were examined by UV Vis spectroscopy (UV Vis 3600 PLUS - SHIMADZU). The UV-visible spectra of the sample Sn (II) doped ZnO nanoparticles showed in Figure 4. Different molar ratios of 0.5%, 1.0%, and 2.0% of the Sn$^{2+}$ doped ZnO samples exhibit a well-defined absorption peak that corresponds to the hexagonal wurtzite phase [30, 31].

The peaks of the the excitonic absorption was between 380 and 400 nm, which are typical characteristic ZnO NPs peaks, thus, confirm their presence. The bandgap of Sn doped ZnO (molar ratio 1%) is decrease compared to the other molar ratios are 0.5 and 2%. The shifting in absorption peak to the higher wavelength results in decreasing the band gap for Sn- ZnO nanoparticles from 3.23 to 3.12 eV. The incorporation of Sn(II) enhanced photocatalytic activity. The optical direct band gap calculated from the formula $E_g = hc/\lambda$ is 3.24 eV [31].

**3.5 HR SEM-EDS:**

SEM-EDS study was carried out to examine the morphological changes, particle size, elemental composition of the pure and Sn doped ZnO NPs. SEM images, elemental mapping and EDS signals and their percentage composition of pristine and 1 mol% Sn doped ZnO NPs are shown in Figure 5a-5f. For un-doped ZnO NPs, sharp signals were found for zinc and oxygen, which confirms the formation of ZnO NPs. For 1 mol% Sn-doped sample along with Zn(II), O and Sn(II) signals observed in EDS.

Figures 5a and 5b showed HR-SEM images of pure ZnO and 1mol% Sn doped ZnO magnified at 1µm and 800 nm. SEM images showed that nanoparticles are well dispersed. The ZnO nanoparticles formed are found to be 30 – 40 nm in size. The ZnO NPs formed in clusters with well-distinguished nanoparticles. The crystallite size calculated using the Scherrer equation and the William – Hall method obtained from the XRD data also confirmed the formation of 30- 40 nm ZnO nanoparticles. Further, Figure 5b presented 1 mol% Sn doped ZnO nanoparticles magnified at 1 µm, the size of Sn/ZnO nanoparticles found to be in the range of 30 – 40 nm. The XRD pattern also supported the crystallite size observed to be in the range of 30 to 40 nm, as shown in in Table 1. Elemental mapping and the EDS spectrum of pure ZnO and 1 mol% Sn doped ZnO are shown in Figures 5c – 5f (percentage composition of pure ZnO and 1mol% Sn doped ZnO given in supplementary information, Table S1 and Table S2). The ZnO doped with 1 mol % Sn appeared to be well defined nanoparticles cluster at 1 µm magnification. Elemental mapping of 1 mol % Sn/ZnO showed the presence of both Zn as well as Sn atoms (Figure 6c and 6d) [31]. In addition, the EDS spectrum for 1 mole Sn doped ZnO showed the presence of Zn as well as Sn and elemental composition showed as shown in Figure 5e and 5f determined Zn$^{2+}$ at 80.13% and Sn$^{2+}$ and at 0.74%, which is very close to 1 mol% Sn(II) doping on ZnO [35, 36].

**Depolymerization of PET polymer using ethanolamine:**

The depolymerisation of PET wastes using ethanolamine as aminolyting agent which yield BHETA as a single product [37, 38]. The aminolysis reaction activated by Lewis acidic nature of ZnO, in which carbonyl group of terephthalic ester carbonyl group attracted by ZnO [24]. Further, the incorporation of Sn(II) enhances its catalytic activity to give BHETA as a single product. Figure 6a – d showed the aminolysis of PET wastes using ethanolamine (EA) carried out to study the effect of Sn(II) loadings (Fig. 6a), PET-to-EA ratio (Fig. 6b), catalyst-to-PET ratio (Fig. 6c), and efficiency of catalyst with respect to reaction cycle (Fig. 6d).

Figure 6a showed the effect of Sn$^{2+}$ loading on the yield of bis (hydroxy ethyl) terephthalimide. The increasing doping of Sn$^{2+}$ has positive influence on the yield of (BHETA). However, ZnO NPs showed yielded 83% of BHETA. 1 and 2 mol% of doping of Sn$^{2+}$ on the ZnO enhanced BHETA yield upto 95%. The increase in BHETA yield could speculated due to the addition of 2 mol% Sn$^{2+}$ reduced the bandgap from 3.25 to 3.17 eV, which increased the catalytic efficiency
of the ZnO. The optical bandgap calculated from the Tauc plot (Figure 3) indicates the decrease in the band gap when increasing the amount of Sn$^{2+}$ doping reported that increasing the amount of Sn$^{2+}$ doping from 3 to 5% as prepared using the coprecipitation method increased the photocatalytic efficiency of ZnO. According to Fig. 6a, the doping of 1 mol % and 2 mol % Sn loaded ZnO showed BHETA yield more than 95% the single product. The BHETA is hot-water soluble, which have been isolated and crystallised as needle shaped pale yellow-coloured crystals without any further purification. As observed in Fig. 6a, the pristine ZnO showed almost 85% BHETA without Sn doping. The analysis of BHETA showed the formation of single depolymerised product using the eluent 40:60% of EA:Hex. In order to confirm the structure, FT-IR, $^1$H NMR, $^{13}$C NMR and MS analysis have been carried out. Both $^1$H and $^{13}$C NMR spectra showed pure form of BHETA.

Figure 6b showed the effect of PET to EA ratio has been studied at various weight % of PET:EA ratios. In this study, the amount of PET was kept constant at 1g, with respect to the volume of ethanolamine that varied from 1 ml, 5 ml, 10 ml, 15 ml, 20 ml and 25 ml to achieve a ratio of 1:1, 1:5, 1:10,1:15, 1:20 and 1:25 of the PET: EA ratio. The study revealed that the the 1:1, 1:5 and 1:10 ratio provided 60 to 70% of BHETA. Whereas, 1:15-1:25 ratio afforded more than 80% of BHETA in particular, 1:20 ratio of PET:EA delivered 94% yield, while is almost comparable with yield obtained for 1:25 ratio. The dissolution of PET in lower ratio of EA is a major issue for the progress of the reaction (Gopal Jeya et al 2020, APM). Whereas, the 1:20 ratio could be more optimum for the smooth running of the reaction.

Figure 6c summarises the effect of the catalyst-to-PET ratio, which is crucial for the effective aminolysis of PET wastes. In this study, the amount of catalyst (1 mol % Sn doped ZnO) has been fixed at 50 mg throughout the study with respect to catalyst weight, the amount of PET wastes has been varied from 100 mg to 500 mg to achieve 1:2, 1:5, 1:10, 1:15, and 1:20 ratio. The study clearly indicated that the increasing amount of catalyst, that is, the catalyst-to-PET ratio at 1:2, 1:5, 1:20, afforded the yield of BHETA above 90%. However, the ratio at 1:15 almost gives an 85% yield of BHETA. The study revealed that the ratio of catalyst: 1: 5 to 1: 5 to PET could be optimal to achieve more than 85% of the aminolysed product, BHETA in pure and single product.

Figure 6d displayed the recycling ability of 1 mol% Sn-doped ZnO NPs towards aminolysis of PET. About 1g of PET wastes dissolved in 20 ml and stirred at 155-160 $^0$C in the presence of 100 mg of 1 mol% Sn doped ZnO. The study showed the catalyst could be reusable upto 7 cycles without losing its activity.

**Spectral characterisaion of BHETA**

The complete depolymerisation of PET wastes generate BHETA as a single product. However, there could be possibility of forming dimer and oligomeric products due to incomplete depolymerisation. Thus, spectral characterisation such as $^1$H and $^{13}$C NMR, and MS and FT-IR analysis have been carried out. The structural characterisation of depolymerised product, BHETA have been carried out to confirm the purity and structural confirmation. $^1$H and $^{13}$C NMR spectra of BHETA is given Fig. 7a and 7b respectively (Full spectrum given in supplementary information Figure S3 and S4), and chemical structure of Fig. 7e. The ESI-MS and FT-IR spectrum of BHETA given in Fig. 7c and 7d respectively. The $^1$H NMR spectrum of BHETA showed two NH protons attached with amide carbonyl (C7 and C8) (-C=O) and ethylene carbons (C9 and C10) (-CH$_2$) appeared as triplet at 8.35 – 8.55 with J value of 5.5 Hz. The presence of NH protons conrms the depolymerisation and formation of BHETA. The number, position and multiplicity of aromatic protons give valid information on monomer, dimer and oligomeric nature of the depolymerised products. The skeleton of BHETA molecule is symmetrical, which confirmed from signal of aromatic protons attached to C1, C2, C4 and C5 appearing as singlet at 7.92 ppm that shows not only BHETA is the pure and single product but also indicates complete depolymerisation of PET wastes. In addition, two -OH protons attached to methylene carbons (C11 and C12) (-CH$_2$) appeared as triplet at 4.74 – 4.76 ppm with 5.5Hz. The protons of methylene group (C11 and C12) attached to -OH
appeared as a quartet between 3.51 and 3.54 ppm with J value of 6 Hz. Another, methylene protons (C9 and C10) attached to amide -NH group gives quartet at 3.33-3.37 ppm with J value of 6Hz. The presence of eight aliphatic protons attached to two ethylene group (-CH$_2$-CH$_2$-) confirms the attachment of two 2-hydroxy ethyl group to terephthaloylamido group (-NH-CO-C$_6$H$_4$-CO-NH-) of BHETA. Fig. 7b is $^{13}$CNMR spectrum of BHETA. The presence of two amide carbonyl (C7 and C8) (NH-C=O) appeared as single peak at 166.1 ppm indicates that BHETA is formed as a single product in pure form from the complete depolymerization of PET wastes. The two aromatic carbons (C3 and C6) attached to amide carbonyl appeared at 137.1 ppm and all other four carbons (C1, C2, C4 and C5) appeared as a triplet at 127.63 – 127. 53 ppm. The methylene carbon (C11 and C12) attached to the hydroxyl group appeared as a single peak at 60.19 ppm. Whereas methylene carbons (C9 and C10) attached to NH-group at amide appeared at 40.7 ppm. Both $^1$H and $^{13}$C NMR confirmed the formation of BHETA as a single pure product. The product is isolated in pure form without the need for purification.

The mass spectrum of aminolysed product, bis (hydroxy ethyl) terephthalamide is given Fig. 7c (Full spectrum given in supplementary information, Figure S5). The molecular formula of BHETA is C$_{12}$H$_{16}$N$_2$O$_4$ with molecular weight is 252.27 g/mol. The spectrum recorded using the electron spray ionisation method revealed the molecular ion peak at 253.15 (M + H) in the protonated form. Another peak at m/z 275.10 indicates the formation of Na+ form of BHETA due to electron spray ionisation.

Furthermore, the FT-IR spectrum (Fig. 7d) of BHETA has been carried out as a KBr disc, and vibrational frequencies have been recorded from 400 to 4000 cm$^{-1}$ (Full spectrum given in supplementary information, Figure S6). In 3250 – 3400 cm$^{-1}$ two sharp peaks observed due to the presence of -NH and -OH groups connected methylene carbon C9 and C10, and C11 and C12 in BHETA, respectively. The intermolecular H-bonding ascertained from the broadness of the peaks. The aromatic -CH- stretching vibration observed at 2830 – 2860 cm$^{-1}$ and aliphatic CH$_2$ stretching vibration frequencies observed at 2920 – 2960 cm$^{-1}$. The amide carbonyl (C7 and C8) (-NH-C=O) stretching vibration is observed at 1635cm$^{-1}$. The aromatic (C1-C6) -C=C- stretching vibration observed in 1550cm$^{-1}$. In addition, -OH bending shown at 1180 cm$^{-1}$ and aliphatic -CH skeletal vibration observed at 1090cm$^{-1}$. The presence of an aromatic and aliphatic -OH and -NH stretching vibration as well as amide carbonyl vibration confirmed the formation of BHETA.

**Conclusion**

In conclusion, compared with ZnO, Sn-doped ZnO showed excellent aminolysis yield of BHETA. The Sn-doped ZnO was synthesised by the Sol-gel method and was successfully characterised by XRD, UV-vis, FT-IR, and SEM-EDX techniques. Diffraction patterns of the nanopowders suggest that ZnO has sharp peaks, which confirm the good crystalline structure with a hexagonal wurtzite structure. FT-IR spectroscopy shows the pure and different molar ratio of 0.5%, 0.1%, and 0.2% Sn$^{2+}$ no significant change was observed in these samples as compared to the pure synthesized ZnO. The reduction in bandgap of ZnO is observed upon doping with Sn. In addition, as observed from XRD, doping resulted in an increase in the crystallite size of the nanoparticles. The SEM analysis of Sn doped ZnO NPs showed 30 – 40 nm size of the ZnO NPs comparable with the crystallite size calculated from powder XRD. The aminolysis of PET wastes has been successfully accomplished using Sn-doped ZnO nanoparticles. The depolymerization of PET polymer waste has been successfully achieved using a pure and different molar ratio of 0.5, 0.1 and 0.2 Sn-doped ZnO nanoparticle catalyst aminolysis reaction at 155-160 ° C. 1 mol% Sn-doped ZnO yielded 95% of BHETA at 155- 160 °C. The product is isolated in pure form without requiring further purification. Hence, from out investigation, we proposed Sn doped ZnO nanoparticles could be effective catalyst for aminolytic depolymerisation of PET wastes. We also observed is reusable up to 7 cycles without a a major loss in the BHETA yield. The study provide that the use of Sn doped ZnO could be economical reusable catalyst for aminolysis of PET.
wastes. Currently, we are investigating ZnO doped with Ag, In and Cd towards catalytic depolymerisation various kinds of PET wastes including dyed polyester fabrics.

**Declarations**

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**Conflict of Interest**

The authors have declared that they have no conflict of interest.

**Samples availability**

The sample of catalysts and BHETA available from the corresponding author.

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Scheme

Please see the Supplementary Files for the Scheme 1.
Figure 1

Yield of Sn$^{2+}$ doped ZnO nanoparticles prepared by sol-gel method
Figure 2

XRD patterns of pure and Sn doped ZnO nanoparticles
Figure 3

FT-IR spectra of pure and Sn-doped ZnO nanoparticles
Figure 4

(a) UV-vis absorbance spectra of pure and Sn-doped ZnO nanoparticles, (b) Tauc’s plot for optical band gap
Figure 5

(a) HR SEM of ZnO, (b) HR SEM of 1 mol% Sn doped ZnO, (c) Elemental mapping of ZnO, (d) Elemental mapping of 1mol% Sn doped ZnO, (e) EDS spectra of ZnO and (f) EDS spectra of 1 mol% Sn doped ZnO
Figure 6

The aminolysis of PET using Sn doped ZnO nanoparticles and ethanolamine (EA): (a) Yield of BHETA at different Sn doping, (b) Yield of BHETA at PET and EA ratio, (c) Yield of BHETA at catalyst to PET ratio and (d) Catalyst recycling studies

Figure 7

Structural Characterisation of BHETA (a) $^1$H NMR, (b) $^{13}$C NMR, (c) mass spectrum, (d) FT-IR spectrum and (e) Chemical Structure of BHETA

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