Asian Journal of Chemistry; Vol. 36, No. 12 (2024), 2772-2782

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2024.32662

Closing the Loop on Polyester: A Green Approach to Chemical Recycling with Zn[L-Proline]$_2$ Supported Kaolin Catalyst

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Received: 4 September 2024; *Accepted*: 15 October 2024; *Published online*: 30 November 2024; AJC-21817

In present work, the depolymerization process utilizes kaolin-supported Zn[L-proline]$_2$ (ZnP@K) as a recyclable Lewis acid catalyst, paving the way for the cost-effective production of recycled materials. The supported catalyst is characterized using FTIR, X-ray diffraction, SEM and BET analysis. The depolymerization of polyester textile waste, especially coloured threads, promoted by ZnP@K to yield more than 90% of monomers in pure form. In addition, irrespective of the colour of polyester threads, the process exhibited 100% conversion of polyester threads and obtained pure colourless monomers, *bis*(2-hydroxyethyl)terephthalate (BHET) and *bis*(2-hydroxyethyl)-terephthalamide (BHETA). The monomers are assessed for their structure and purity using FTIR, mass and NMR spectral techniques. While comparing with ZnO nanoparticles, ZnP@K depolymerized the polyester wastes in terms of yield and purity and it proved efficient and sustainable for recycling textile polyester waste.

Keywords: Aminolysis, Chemical recycling, Circular economy, Glycolysis, Kaolin, Polyester.

INTRODUCTION

Unfortunately almost 80% of the world's 334.83 million metric tons of plastic is deposited in landfills, where it accumulates and poses significant threats to ecosystems and marine life cycles in sanitary landfills and oceans. Plastic wastes, mainly encompassing polyethylene (PE), polyethylene terephthalate (PET), polystyrene (PS), polycarbonate (PC) and polyphenylene oxide (PPO), may have a significant effect on the ecosystem globally [1,2]. Approximately 60 million tonnes of scented shapable materials are generated yearly, of which 50 million are dumped into the biosphere. It is particularly disheartening to discover that merely 7% of PET can be recycled into bottles [3-6]. While different plastics degrade at varying rates, a single-use plastic bottle has an average lifespan of at least 450 years, however, some bottles could take a thousand years to degrade [7].

Techniques for recovering monomers from PET waste are frequently investigated for closing the loop, which include the breakdown of ester linkages in the polymer chain and its subsequent conversion to monomers through glycolysis and aminolysis of polyester textile fibers. Owing to problems with catalyst solubility, dyes and pigments, the recovery of monomers is challenging to achieve, closing the loop process or being integrated into another product that replaces virgin material and serves a new purpose [8,9]. Chemical recycling is becoming more popular than other methods since the quality of the products produced using it is comparable to that of original materials. It could, therefore, be the greenest way to recycle plastic [7,10].

Among the clay materials frequently utilized in various applications is kaolin. These applications include cracking catalysts, cement, paint extenders, rubber fillers, plastic fillers, paper coating, *etc*. [11,12]. Kaolin clay is prospective support because of its fascinating properties, including high thermal stability, Lewis and Brønsted acid site density, cost-effectiveness, intrinsic acidity, higher thermal stability up to 500 ºC and easily adjustable structural morphology. Structures with large specific surface areas are commonly used as best catalyst carriers [13-17].

Polyethylene terephthalate (PET) trash can be chemically transformed to quickly and thoroughly depolymerize into two different compounds: aminolysis, which yields the monomer *bis*(2-hydroxyethyl) terephthalamide (BHETA) while through glycolysis, *bis*(2-hydroxyethyl) terephthalate (BHET) was obtained. Clay catalysts offer robust support due to their natural acidity, exceptional thermal stability and appealing structural features, including easily controlled morphology. The catalysts, namely, bentonite [15,18], niobia [19] and calcined kaolin [20], *etc*.

The primary obstacles arise from the intrinsic characteristics, activity, selectivity and stability of the high-surface-area, thermally stable supported catalysts. For preparations with high surface areas, the narrowest size distributions may achieved by producing ultra-small metal particles with an additional filtration step [21-24]. Combining two oxides enhances the catalytic sites by altering the electronic structure of active metals, thereby improving the substrate catalyst interaction and increasing the reaction rate. Examples include Mg-Al LDH, Zn-Al hydrotalcite [25], (Mg-Zn)-Al [26], sulfated cobalt oxide (SC), zinc-modified sulfated cobalt oxide (SCZ) and spinel-type catalysts, *etc*. Despite its importance in earth's abundance of heterogeneous catalysts, zeolites have been investigated less extensively in PET chemolysis. Due to their uniform pore size, shape selectivity and large surface area, zeolites as acid catalysts suitable for esterification, such as ZnO@ZSM-5, *etc*. [27,28]. Catalysts developed at the nanoscale exhibit excellent catalytic performance owing to their high surface area and increased number of active sites. The particle size of these nanocatalysts significantly influences monomer yield due to their large surface area and specific pore volume [29].

The present work attempted the depolymerization of red, blue and green polyester (PES) fabrics through aminolysis and glycolysis, employing Zn[L-proline]$_2$-impregnated kaolin as a catalyst and following activated charcoal treatment produced colourless monomers BHET and BHETA, which were then confirmed with ^{1}H NMR, ^{13}C NMR, mass and FT-IR spectroscopies, while the supported catalyst was characterized by SEM-EDX, FT-IR and XRD analyses.

EXPERIMENTAL

L-Proline, zinc nitrate hexahydrate, ethanolamine, ethylene glycol, kaolin and all other chemicals are acquired from Loba and SRL Pvt. Ltd., India and were utilized without additional purification. The trash PES was collected and broken into fine tiny particles. It was made up of red, green and blue coloured threads that were 100% pure polyester (Brand: Vardhaman, India).

Synthesis of Zn[L-proline]$_2$: L-Proline (20 mmol) and KOH (20 mmol) were dissolved in 50 mL absolute ethanol under constant stirring. To attain a 1:2 metal-to-ligand ratio, 10 mmol of $Zn(NO_3)_2 \cdot 6H_2O$ was dissolved in 10 mL of double distilled water. The resultant mixture was then added dropwise to the alkaline L-proline solution and then vigorously mixed for 6 h at room temperature. Zn[L-proline]$_2$ complex obtained as white solid was filtered and dried at 70 ºC for 6 h (Fig. 1) [30].

Impregnation of Zn[L-proline]$_2$ with kaolin catalyst: In a 250 mL beaker, 100 mL of ethanol, ~5 g of kaolin and 0.5 g of Zn[L-proline]$_2$ were mixed and then stirred for 6 h at room temperature and the resulted solid was dried in a hot air oven at 70 ºC. By evaporating ethanol, obtained 10 wt.% ZnP-impregnated kaolin was dried and then stored in a desiccator. (yield: 10.30 g) (Fig. 1). Similarly, another sample consisting 5 wt.% ZnP@K was also prepared.

Depolymerization of polyester (PES) textile waste using microwave irradiation

Aminolysis of PES: *Bis*(2-hydroxyethyl)terephthalamide (BHETA), a monomer obtained from the aminolysis of polyester textile waste utilizing ethanolamine as depolymerizing medium in the presence of ZnP@K at molar ratios of 10 mol%. Post-consumer PES textile waste of red, blue and green were used in the investigation in order to evaluate the efficiency of process to achieve pure colourless monomers. After cleaning and drying, the PES was divided into fibers.

PES red-coloured fabric (1 g) was added to 20 mL of ethanolamine (1:20 ratio), which was irradiated to 180 W with constant agitation. The polyester yarns were dissolved in ethanolamine after the reaction mixture had been heated to the appropriate temperature and stirred for 10-15 min followed by the addition

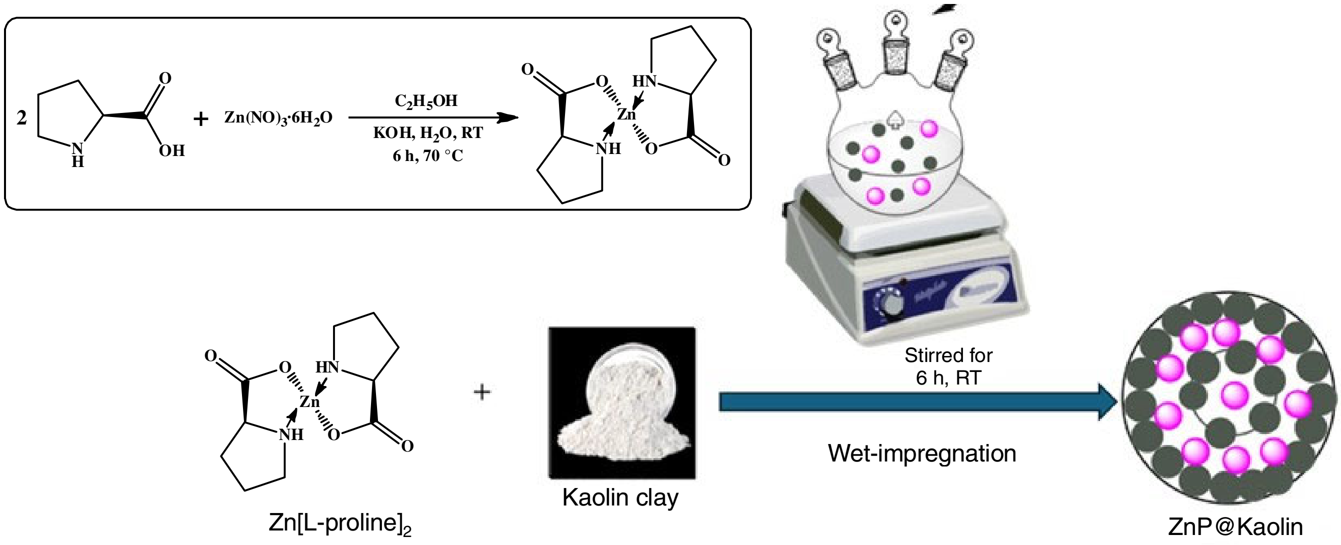


Fig. 1. Laboratory synthesis of ZnP and ZnP@kaolin

of ZnP@K catalyst (100 mg). After the reaction completion, the reaction liquid was vigorously agitated and 50 mL of double distilled water was added, before filtering out the catalyst. The final product of red PES thread, an amide derivative of *bis*(2-hydroxyethyl)terephthalamide (BHETA), was obtained as an orange coloured needle-shaped crystal. Similarly, the treatment of blue and green coloured PES with ethanolamine gives pink and white coloured crystals, respectively. The FT-IR, mass, ^{1}H NMR and ^{13}C NMR techniques were utilized to establish the purity and structure of BHETA. The conversion of PES and resulting yield of BHETA was calculated to be 97% and 95%, respectively.

Glycolysis of PES: At 300 W of microwave power, about 1 g of red-coloured PES thread wastes were dissolved in 20 mL of ethylene glycol (1:20 ratio). ZnP@K catalyst (100 mg) was added after PES had completely dissolved. Precoated aluminium TLC plates (E-Merck, silica gel G 60 F_{254} indicator and the spots were observed using a 356 nm UV detector) were used to monitor the reaction. A spot of the reaction mixture was compared to BHET reference using *n*-hexane and ethyl acetate solvent mixtures at 70:30 by volume to determine the progress of the reaction. After reaction, 50 mL double distilled water was added and aggressively agitated, and the catalyst was filtered off.

The glycolyzed products were recovered and separated by filtration following the removal of catalyst. The product was collected using a rotary evaporator (Equitron Evator, 230 VAC, 50 Hz) and concentrated. *Bis*(2-hydroxyethyl)terephthalate (BHET), the end product was obtained as an orange coloured needle shaped crystal. From the weight of unreacted PES and BHET, the conversion of PES and yield of the monomers were determined. The same procedure was repeated for blue and green coloured thread wastes giving pink and yellow coloured needle shaped crystals of BHET product. The conversion of PES and the yield of BHET were found to be 97% and 93%, respectively.

Purification of BHETA and BHET monomers: Due to the presence of pigments and the other impurities, the obtained BHETA and BHET monomers were coloured. After dissolving the resulting monomer in 50 mL of hot demineralized water, 500 mg of activated carbon was added to remove the colourants. Following crystallization, colourless monomers of BHETA and BHET were obtained by removing the activated carbon using a Whatmann filter paper.

The percentage of PES degradation was calculated using the following equation:

$$\text{PES}_{\text{conversion}}\ (\%) = \frac{W^0_{\text{PES}} - W^t_{\text{PES}}}{W^0_{\text{PES}}} \times 100$$

where W^0_{PES} (g) is the initial weight of PES flakes and W^t_{PES} (g) is the PES weight at a specific reaction time, respectively.

The yield of glycolysis (BHET) was calculated by using eqn. 2:

$$\text{BHET}_{\text{yield}}\ (\%) = \frac{W^t_{\text{BHET}} / \text{MW}_{\text{BHET}}}{W^0_{\text{PES}} / \text{MW}_{\text{PES}}} \times 100$$

where W^t_{BHET} (g) and W^0_{PES} (g) refer to the weight of BHET at a specific reaction time and the initial weight of PES, respectively; MW_{BHET} and MW_{PES} are the molecular weights of BHET and PES monomers, respectively. Similarly, the yield of aminolysis (BHETA) was calculated using eqn. 3:

$$\text{BHETA}_{\text{yield}}\ (\%) = \frac{W^t_{\text{BHETA}} / \text{MW}_{\text{BHETA}}}{W^0_{\text{PES}} / \text{MW}_{\text{PES}}} \times 100$$

Characterization: The crystal structure of the supported catalyst was analyzed by X-ray diffraction (XRD) using powder diffractometer (PAN Analytical Empyrean, Netherlands X2 pert PRO Model X-ray diffractometer) utilizing monochromatic Cu*K*α radiation (α = 1.5406 Å). The XRD analysis was conducted with a scan rate of 2θ and a range of 20-80º. The FT-IR spectrum was obtained using a Bruker FT-IR spectrophotometer (IRTRACER 100, Shimadzu, Japan) at room temperature using KBr pellet method. ^{1}H and ^{13}C NMR spectrum of BHET and BHETA products was analyzed using NMR spectrometer (Avance III, Bruker, Switzerland) operating at 500 MHz in $CDCl_3$ solvent. The mass spectrum of BHET and BHETA was acquired by a mass spectrometer (LCMS-2020, Shimadzu, Japan) using the electrospray ionization technique.

RESULTS AND DISCUSSION

Spectral characterization of catalyst

XRD studies: The synthesized Zn[L-proline]$_2$ complex exhibited the X-ray patterns across the range of 2θ diffraction angles, from 5 to 90º (Fig. 2). The diffraction peaks with certain d-values demonstrated the orthorhombic crystal structure of ZnP. Even though the catalyst was recently recovered from an aqueous solution, there was no change in its shape or stability observed [30]. The XRD analysis verified that ZnP was finely dispersed on the kaolin support. The XRD patterns of ZnP/kaolin composites, ZnPK01 and ZnPK02 loaded at 5 and 10 wt.% respectively, are also displayed in Fig. 2. The diffraction pattern provide that the metal in the catalyst was molecularly and finely distributed on the kaolin support. Further, this study demonstrated the retention of crystalline structure of the ZnP@kaolin composites.

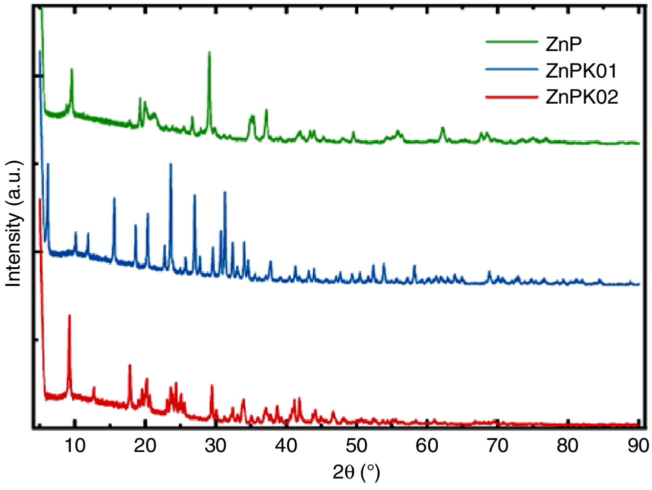


Fig. 2. XRD pattern of pure kaolin & ZnP impregnated kaolin catalysts

TABLE-1
SURFACE AREA, PORE VOLUME AND BJH AVERAGE DIAMETER FOR PURE KAOLIN AND ZnP LOADED KAOLIN CATALYSTS

Catalyst	BET surface area (m^2/g)	Pore volume (cm^3/g)	BJH average diameter (Å)
Kaolin (VSK01)	67.975	0.136	19.451
5 wt.% ZnP@kaolin (ZnPK01)	58.059	0.101	15.517
10 wt.% ZnP@kaolin (ZnPK02)	123.539	0.221	23.627

The crystalline structure of ZnP catalyst comprising kaolin clay was demonstrated with a significant peak at 2θ value of 29.10º. This peak is responsible for the reflections of the (001) plane of 5 wt.% (ZnPK01) and 10 wt.% (ZnPK02) ZnP loaded kaolin. Every sample displayed a diffraction peak at 29.10º and 9.85º confirming the presence of kaolin and quartz catalysts, respectively [19].

BET studies: The typical pore volume and pore diameter of supported clay and zeolite materials were also calculated using the BJH model. The BET and BJH models were constructed using the nitrogen adsorption-desorption isotherm, which is used to compute the porosity and surface area (Fig. 3).

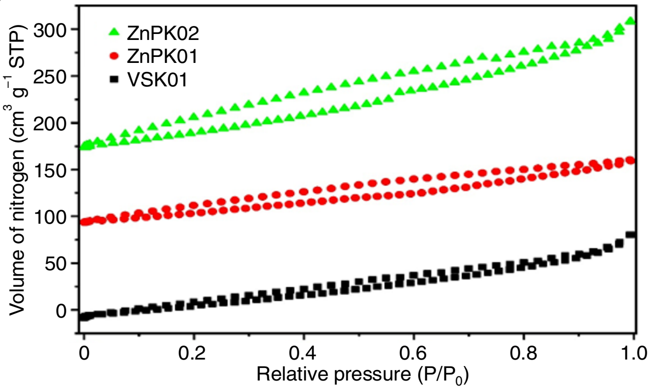


Fig. 3. BET isotherm of pure kaolin & ZnP impregnated kaolin catalysts

In Table-1, the BET surface area, average pore diameter and pore volume computed with the BJH model are compiled. In 10 wt.% ZnP@K, the porosity of kaolin support was unaffected by the metal impregnation. Studies on nitrogen adsorption and desorption revealed that 10 wt.% ZnP@K had a surface area of 123.53 m^2/g, a pore volume of 0.221 cm^3/g and an average diameter of 19.45 Å. With an average diameter of 23.62 Å and a pore volume of 0.13 cm^3/g, pure kaolin clay had a surface area of 67.97 m^2/g. On the other hand, 5 wt.% ZnP@K showed relatively lower surface area, pore volume and average pore diameter. The 10 wt.% ZnP@K showed a significant increase in the pore volume and surface area in comparison to pure kaolin.

FT-IR studies: FT-IR spectra of Zn[L-proline]$_2$ and pure kaolin and ZnP@K at 5 wt.% (ZnPK01) and 10 wt.% (ZnPK02) were recorded in the 4000-400 cm^{-1} range (Fig. 4). Since kaolin is an aluminosilicate framework, Si-O-Al vibrations observed at 831.31 cm^{-1}, whereas peripheral Al-OH bending vibration is appeared at 935.54 cm^{-1}. The peak at 1022.27 cm^{-1} is associated with Si-O-Si in-plane vibration, whereas the peak at 1130.28 cm^{-1} is asymmetric Si-O-Si stretching vibration. The -OH stretching vibration of Si-OH and Al-OH in the aluminosilicate framework appearing at 3668.60 cm^{-1}, is linked to a hydroxyl group. The results revealed the distinct band and wavenumbers, which may imply significant interaction between ZnP and kaolin. These results also matched with the literature regarding the successful impregnation of kaolin clay in ZnP complex [25,26].

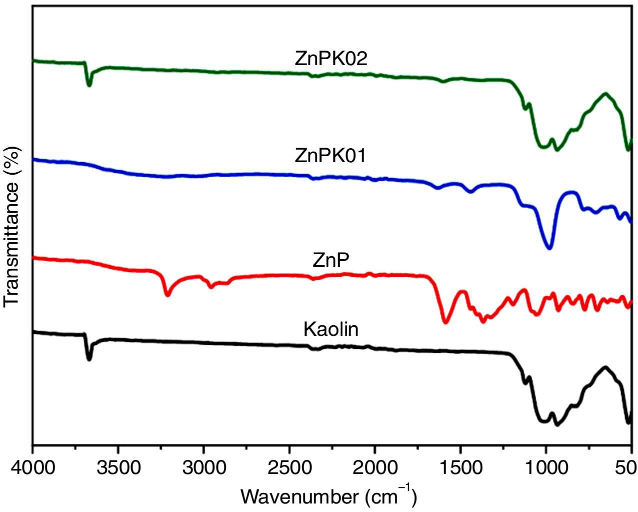


Fig. 4. FT-IR spectrum of ZnP-doped kaolin catalyst

SEM-EDS studies: According to SEM examination, the 10 wt.% ZnP@K catalyst have different sizes, crystal shapes and morphologies (Fig. 5). The altered morphological characteristics of kaolin were visible in SEM images taken both before and after wet impregnation treatment with ZnP. The macroscale particles that seemed to have been generated by the aggregation of flaky layered shreds were visible in the SEM micrograph of kaolin. The wet impregnation method in alcoholic medium resulted in the total disaggregation of the clay structures and size reduction. The SEM images of treated kaolin (Fig. 5c-f) showed both the presence of clusters of well-bonded agglomerated particles and the disintegration of smaller particles. The range of 500 nm, 30 µm and 1 µM shows that the morphology remained unaffected by encapsulation.

Table-2 summarises the elemental composition values, while Figs. 6 and 7 displays the elemental mapping and EDS

TABLE-2
WEIGHT AND ATOMIC PERCENTAGE OF ELEMENTS IN ZnP LOADED KAOLIN

Element	Pure kaolin		ZnP doped kaolin	
	Weight (%)	Atom (%)	Weight (%)	Atom (%)
C	–	–	2.02	3.57
N	–	–	0.76	1.15
O	54.47	65.39	35.77	47.51
Al	17.16	12.22	45.41	35.77
Si	22.55	15.42	15.73	11.91
Zn	–	–	0.31	1.10

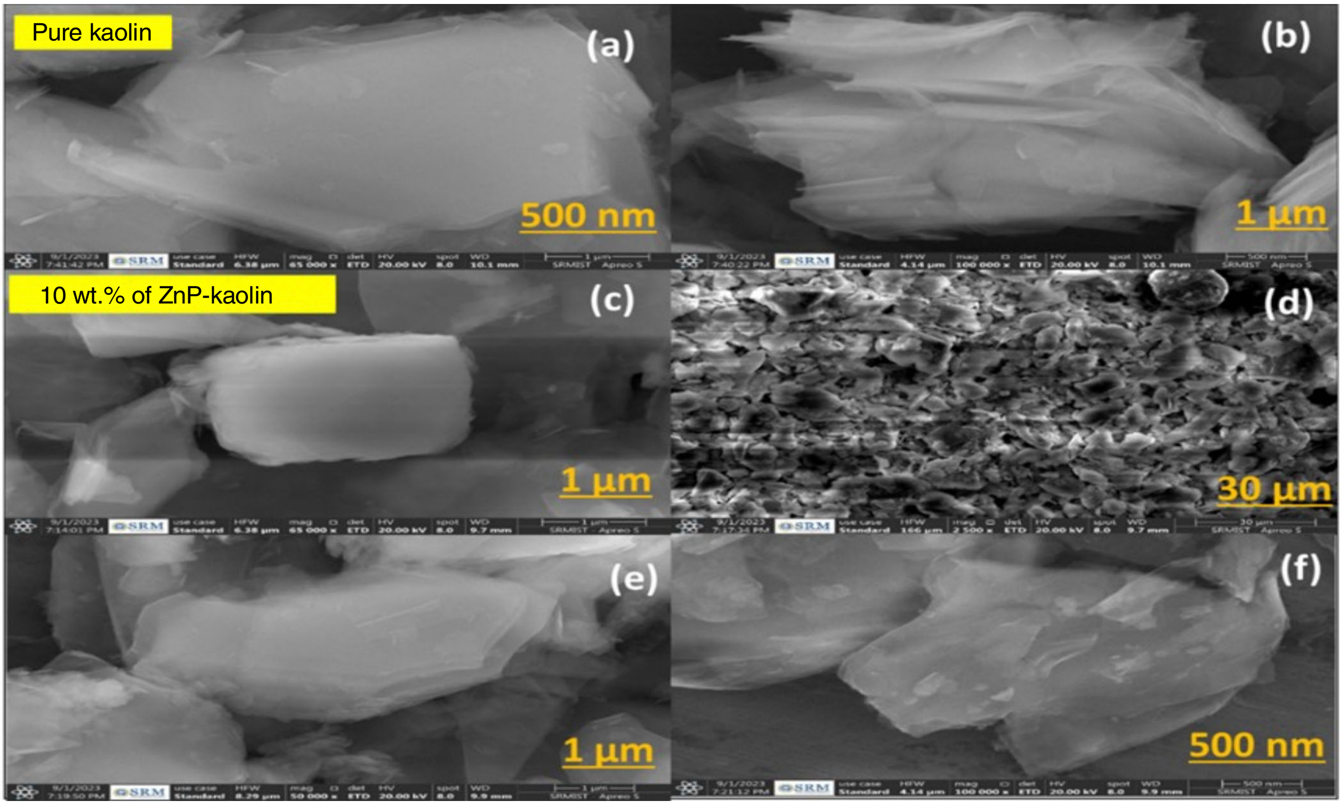
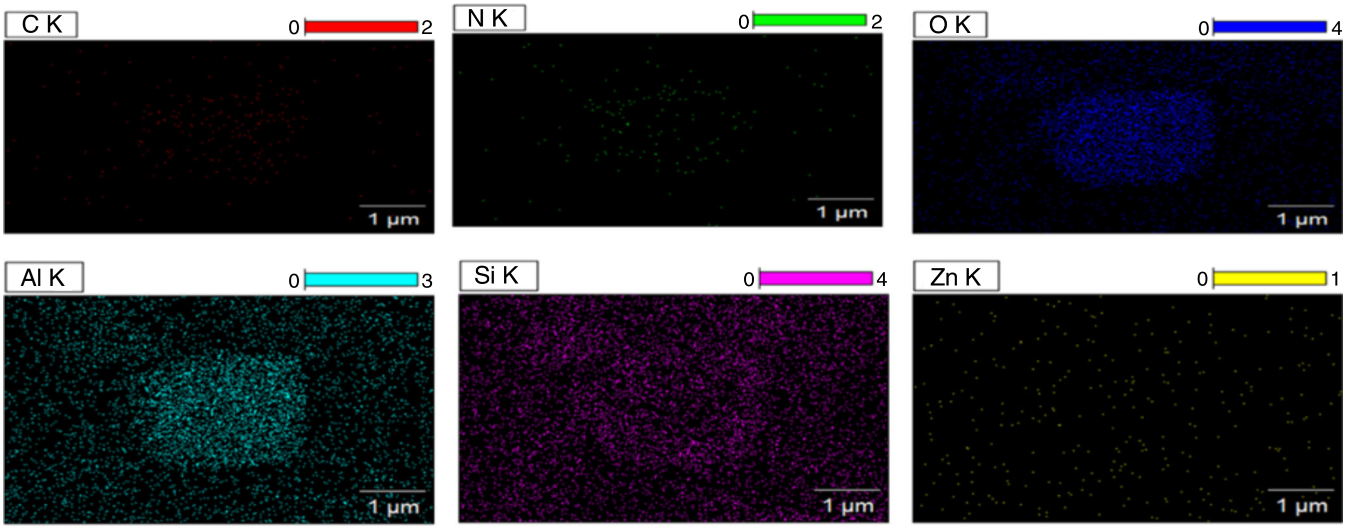
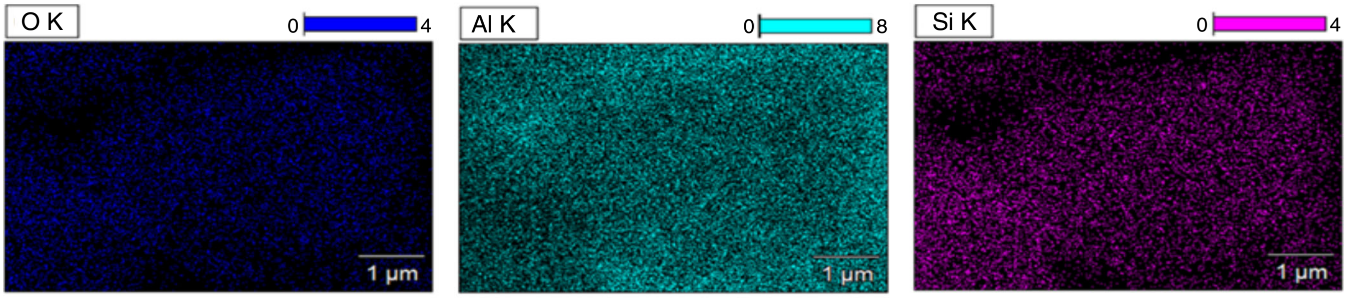


Fig. 5. SEM images of (a) pure kaolin (500 nm), (b) pure kaolin (1 µm), (c) 10 wt.% of ZnP-kaolin 1 µm, (d) 10 wt.% of ZnP-kaolin (30 µm), (e) 10 wt.% of ZnP-kaolin (1 µm) and (f) 10 wt.% of ZnP-kaolin (500 nm)



10 wt.% Kaolin doped ZnP



Pure kaolin catalyst (VSK01)

Fig. 6. Elemental mapping images of 10 wt% ZnP loaded kaolin and pure kaolin

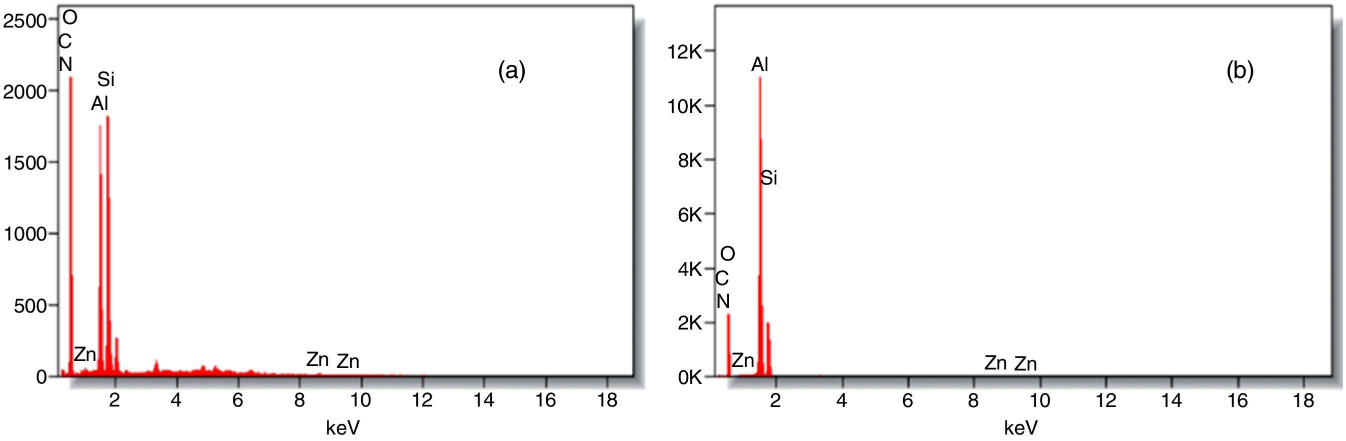


Fig. 7. EDS spectra of (a) 10 wt% ZnP loaded kaolin and (b) 5 wt% ZnP loaded kaolin

spectrum of the composites, respectively. Through their separate EDS mapping, all of the composites revealed the newly prepared 10 wt.% ZnP@K shows the presence of dopants in addition to C, N, Zn, Si, Al and O elements with uniform distribution [11,27].

Depolymerization of polyester textile fibres: By using aminolysis and glycolysis, the polyester (PES) textile fibers are depolymerized into *bis*(2-hydroxyethyl)terephthalamide (BHETA) and *bis*(2-hydroxyethyl)terephthalate (BHET) under microwave irradiation. The PES textile fibers were made of 100% polyethylene terephthalate. The reaction parameters, such as the effect of ZnP loading, effect of MW irradiation time, MW input, PET to solvent ratio and recycling studies were also optimized to achieve the maximum yield of BHETA and BHET.

Effect of ZnP loading: The transesterification of PES threads promoted by Lewis acid catalyst, Zn-Proline. The depolymerization of PES textile fibers was carried out using kaolin impregnated with 10% wt.% ZnP (Fig. 8a). About 1 g of PES threads and 100 mg of catalyst were utilized at a catalyst-to-PES ratio of 1:10 to continue the depolymerization under 180 W and 300 W microwave irradiation for aminolysis and glycolysis, respectively. Compared to other proportions, the higher yield of the aminolytic monomer, BHETA obtained than the glycolytic depolymerized product, BHET. The aminolysis process rather faster and occurred at lower MW input than glycolysis. In addition, the ethanolamine medium facilitate solubility of PES rather than ethylene glycol.

Effect of microwave (MW) irradiation: The effect of MW power was investigated for the depolymerization of PES threads under various microwave input (Fig. 8b). Dissolution of PES in the reaction medium is crucial for the complete depolymerization of PES. The optimum temperature 140-160 ºC and 190-210 ºC were required for the aminolysis and glycolysis, respectively. The range of 100-300 W of MW input have been used and the MW power for aminolysis and glycolysis was optimized to be 180 and 300 W, respectively. The total yield of the reaction mixture was measured following 30 min of MW radiation exposure. At the lowest power of 100 W, yield transition and PES breakdown was slower (60-80 ºC). In the aminolytic depolymerization of PES, utilizing a 1:20 ratio of PES to ethanolamine, the reaction mixture was subjected to 180 W (140-160 ºC) of MW radiation for 30 min to yield > 90% of BHETA. After comparing the ethanolamine and ethylene glycol media, it was found that the former broke down PES completely in 20 min at a faster rate. The similar procedure was used to accomplish glycolytic PES depolymerization. The irradiation power for microwaves varied *viz.* 100, 150, 200, 250 and 300 W. With the lowest power of 100 W for PES breakdown, 58% yield was achieved. At 300 W, PES dissolves entirely and the maximal yield of BHET was obtained. For the glycolytic depolymerization, an optimal microwave irradiation of 300 W, achieved at 180-200 ºC.

Effect of PES and solvent ratio: Fig. 8c depicts the polyester fabric, whereas ethylene glycol and ethanolamine are the reactants used in the relevant processes. The PES concentration was maintained at 1 g during the entire study. The volume of reagent 5, 10, 15, 20 and 25 mL were used for solvent proportions were weight by volume ratio maintained to be 1:5, 1:10, 1:15, 1:20 and 1:25. While the BHET yield increases from 45, 59, 70, 89 and 92% at 300 W to maximize the microwave irradiation length, the BHETA yield increased progressively from 50, 65, 75, 93 and 95% at 180 W. The ratio of 1:20 represents the recommended possible products based on the reaction data. Dissolving polyester could become problematic if the reaction conditions and ratio are lowered.

Effect of irradiation time: PES waste depolymerization by aminolysis and glycolysis reaction carried out under various reaction time duration (Fig. 8d). The microwave irradiation time varied from 5, 10, 15, 20 and 25 min has been reported for the aminolysis process utilizing 1 g of PES and 100 mg of catalysts in 20 mL of ethanolamine irradiated at 180 W. The PES fully dissolved and afforded 65 to 90% in 10 to 15 min. In 15 min, the PES waste had entirely dissolved (100%) and a 95% yield had been achieved with BHETA.

Similarly, the glycolytic depolymerization performed using a mixture containing 1 g of PES and 100 mg of catalyst in 20 mL ethylene glycol and 300 W PES breakdown time range for irradiation timing is 5, 10, 15, 30 and 60 min. In 1 h, the glycolysis PES is 100% fully depolymerized with an elevated product of BHET, which demonstrated that important determinants were identified for the completed depolymerization time of aminolysis and glycolysis.

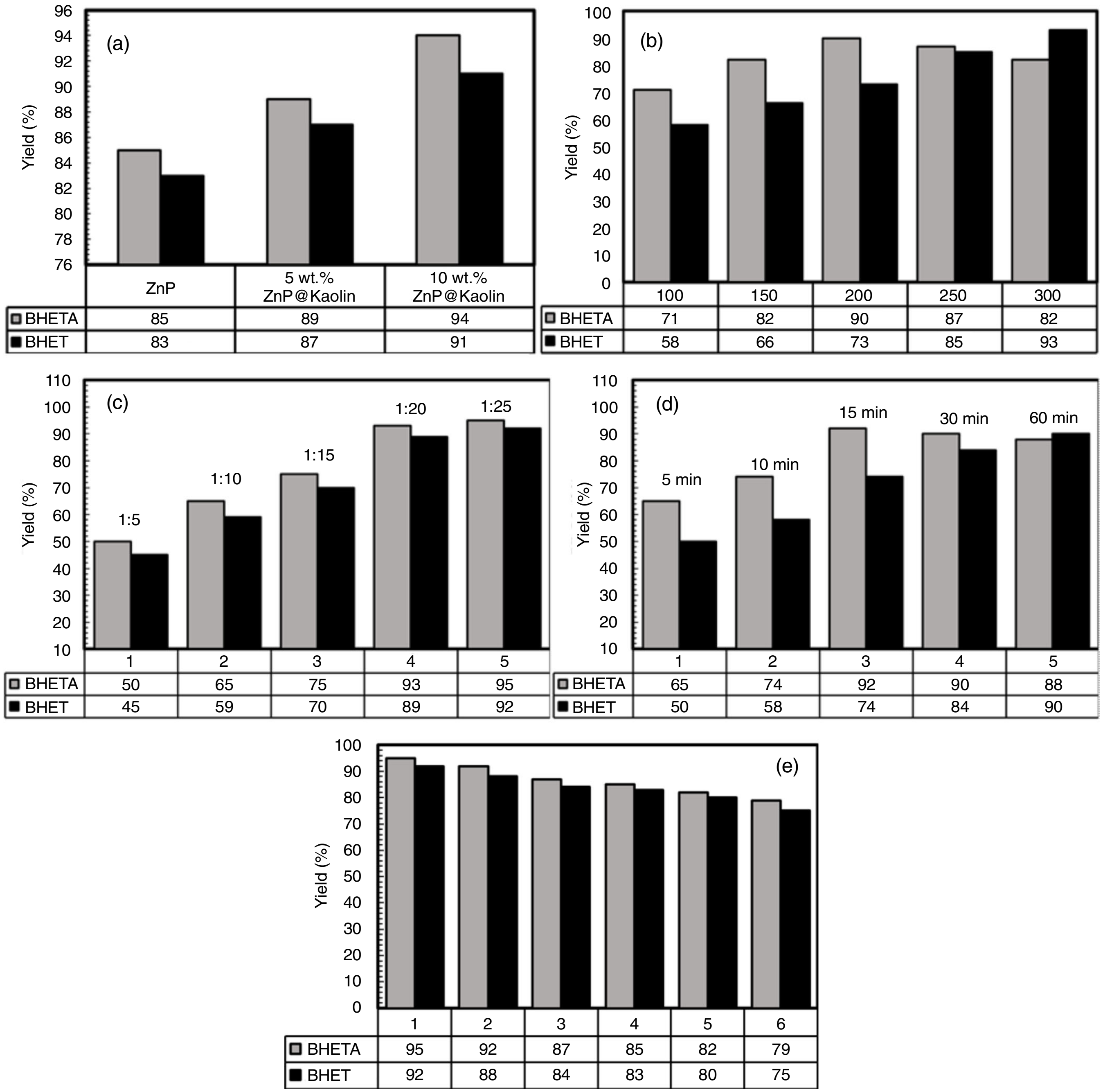


Fig. 8. Depolymerization reaction parameters (a) effect of loading, (b) effect of MW input, (c) PES:solvent ratio, (d) effect of MW irradiation time and (e) effect of catalyst recycling

Effect of catalyst recycling: The yield of BHETA and BHET were compared after seven catalytic cycles of 10 wt.% ZnP@K (Fig. 8e). It was observed that the yield of BHETA and BHET was reduced about 5% in every subsequent reaction cycle because of the leaching of ZnP@K favoured in ethylene glycol and ethanol amine medium. However, the recycling studies showed that ZnP supported kaolin can reusable upto three reaction cycles.

Spectral characterization of BHET and BHETA

FT-IR studies: The FT-IR spectra of depolymerized monomer, *bis*(2-hydroxyethyl)terephthalamide (BHETA) from PES textile waste of red (ZKRA01), blue (ZKBA02) and green (ZKGA03) threads were recorded as KBr pellets using a double beam spectrophotometer in the wavelength range of 4000- 400 cm^{-1} (Fig. 9). The amide (N-H) stretching is indicated by sharp peaks at 3309 cm^{-1}, which conformed the formation of the terephthalamide group, whereas the primary hydroxyl (-OH) groups are detected at 3387 cm^{-1}. Extended aromatic C-H vibrations are correlated with the band range at 2930-2899 cm^{-1} and the aliphatic C-H bending vibrations showed at 1004.91 cm^{-1}. The strong signal at 1624.06 cm^{-1} appeared for BHETA obtained from all PES indicate the presence of an amide bond (CO-NH). The aromatic C=C stretching is shown by the weak band at

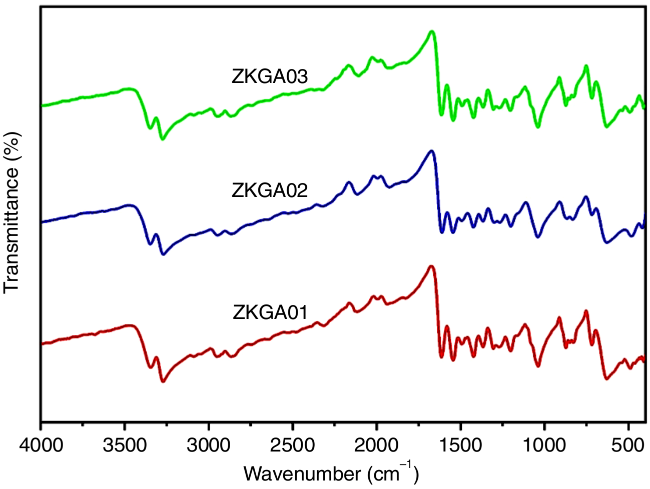


Fig. 9. FTIR spectra of aminolysis of PES threads using ZnP doped kaolin catalyst

1560.41 cm^{-1}, whereas the bands at 2985.80 cm^{-1} indicate the stretching vibrations of the aliphatic C-H domain. The -OH bending vibration showed at 1192 cm^{-1} for all three PES threads.

The FT-IR spectrum of glycolytic depolymerized monomer, *bis*(2-hydroxyethyl)terephthalate (BHET) from PES textile waste of red (ZKRG01) thread was recorded as KBr pellets in the 4000-400 cm^{-1} range (Fig. 10). The stretching of the primary alcoholic -OH group in the depolymerized products of red coloured thread revealed a prominent absorption band at 3352 cm^{-1}. Intermolecular hydrogen bonds were formed as a consequence of this stretching. The aromatic C-H stretching frequencies have maximum values at 2966 cm^{-1}, whereas the aliphatic C-H stretching frequencies observed at 2864 cm^{-1}. The presence of depolymerized products is confirmed from the presence of the ester carbonyl group at 1687 cm^{-1}, which implies that hydrogen bonds are being formed by the ester group when it is isolated. The IR absorption peak at 1400 cm^{-1} corresponds to the aromatic -C=C- stretching and 1274 cm^{-1} assigned to the asymmetric vibration of the C-O ester bond, respectively. Around 1051 cm^{-1}, a symmetric vibration of the C-O ester bond is also observed. Bending frequencies at 439.77 cm^{-1} and 732.95 cm^{-1} further support the existence of aromatic compounds in the glycolytic products.

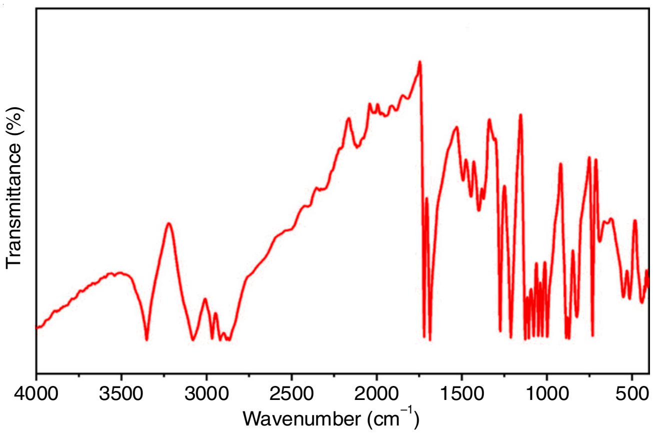


Fig. 10. FTIR spectrum of glycolysis of PES threads using ZnP doped kaolin catalyst

^{1}H NMR studies: The ^{1}H NMR spectrum of the monomer BHETA produced from the depolymerizing process of green PES (ZKGA03) is shown in Fig. 11. The symmetrical appearance of four aromatic hydrogens (C1, C2, C4 and C5) as a singlet at 7.92 ppm in the BHETA molecule suggests that PES underwent complete depolymerization to form BHETA by aminolysis. Between the chemical shift ppm ranges of 8.54 and 8.56, a triplet of amide N-H protons linked to the methylene group (C9, C10) and the carbonyl (C=O) atoms C7 and C8 were observed. The two hydrogens in BHETA bind to methylene carbon to amide N-H showed as multiplet at 3.33-3.37 ppm. A triplet of methylene hydrogens attached to carbon next to -OH are found at 3.52-3.54 ppm. A terephthalaoyl group was attached to 2-aminoethanol to form BHETA, as shown by the ^{1}H NMR confirmed the presence of -NH and -OH protons [28].

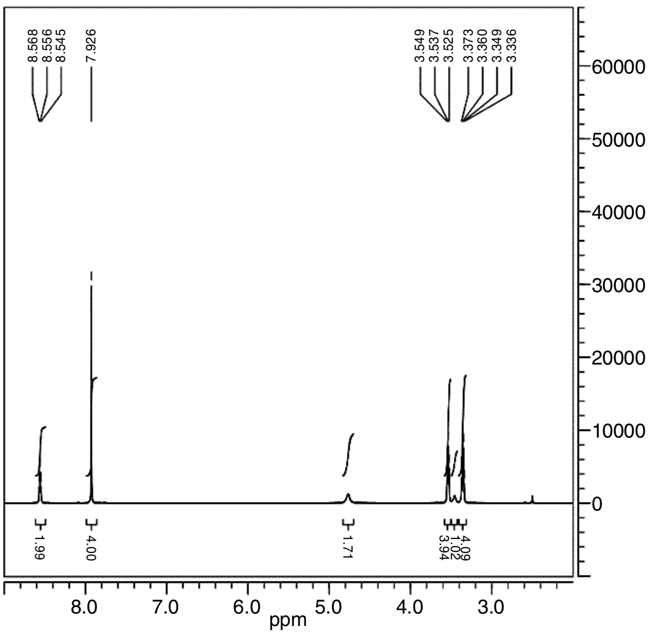


Fig. 11. ^{1}H NMR spectrum of depolymerized green PES (ZKGA03) using ethanol amine (BHETA)

The ^{1}H NMR spectra of BHET monomer obtained from green (ZKGG03) and red (ZKRG01) PES wastes in ethylene glycol as solvent are shown in Fig. 12a-b. The presence of four aromatic protons (C1, C2, C4 and C5) appeared as singlet at 8.12 ppm (ZKGG03) and 8.11 ppm (ZKRG01) indicated that the BHET molecule is symmetrical and exclusively formed as a monomer from glycolysis process. In the range of 3.70-3.73 ppm (ZKGG03) and 3.35-3.73 ppm (ZKRG01), the protons of the methylene group (-CH$_2$-) (C9 and C10) that are attached to the hydroxyl group -OH were appeared. The protons of the methylene group (C8 and C7) connected to the ester (-COO-) group are represented by a triplet at 4.30-4.32 ppm (ZKGG03 and ZKRG01). The appearance of the singlet peak owing to aromatic protons confirms the formation of BHET. The residual water molecules present in DMSO-d_6 appeared as a singlet at 3.33 ppm [29].

^{13}C NMR studies: The ^{13}C NMR spectrum of the aminolytic depolymerization product, BHETA is shown in Fig. 13a. The amide carbonyl carbon of BHETA is detected at 165.77

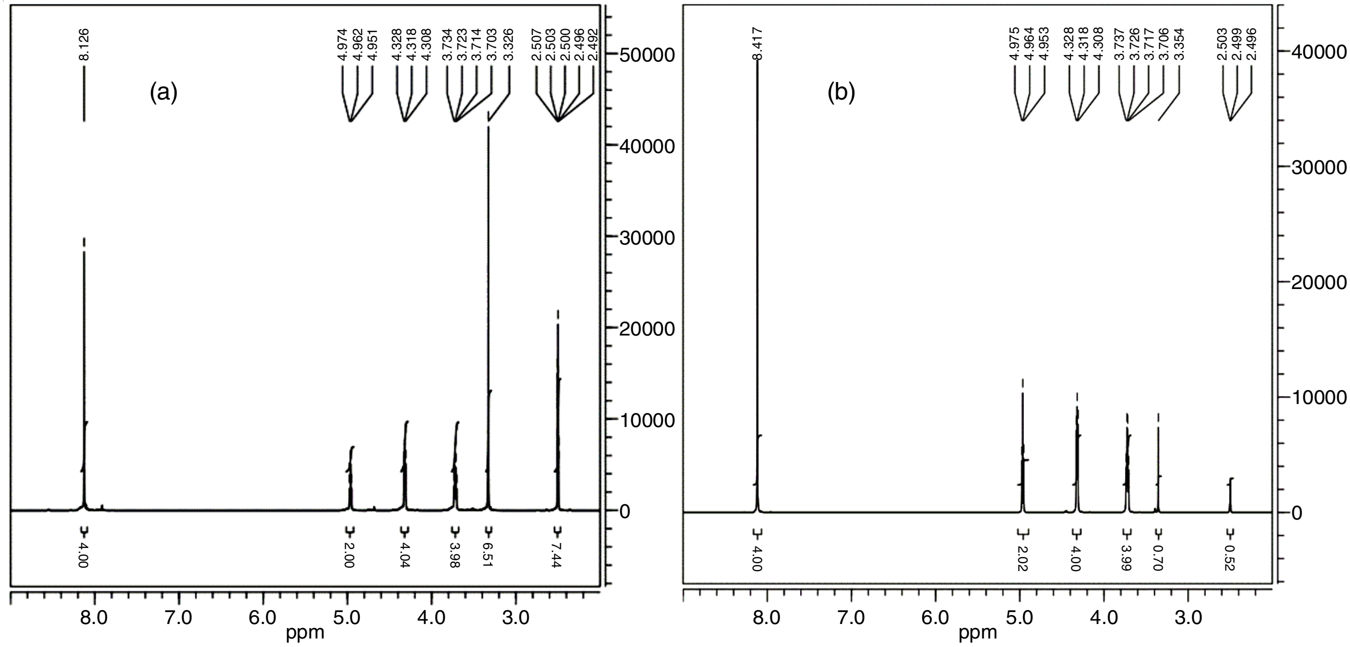


Fig. 12. ^{1}H NMR spectra of BHET obtained from (a) green PES (ZKGG03) and (b) red PES (ZKRG01) using ethylene glycol (BHET)

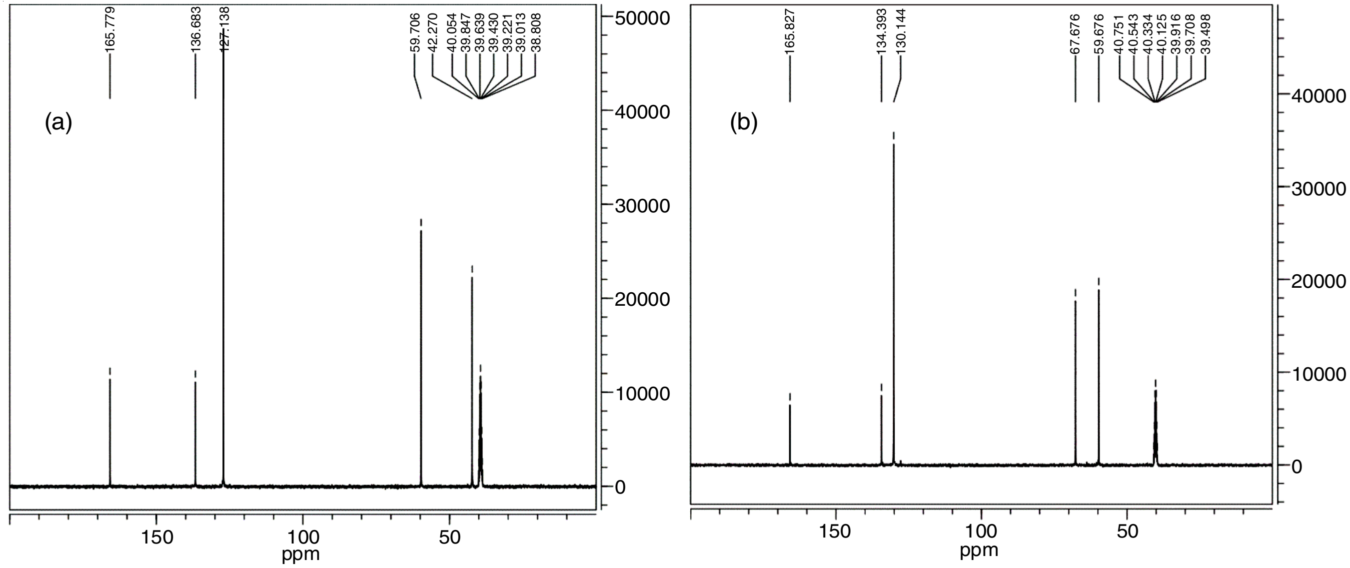


Fig. 13. ^{13}C NMR spectra of depolymerized product from green PES (ZKGA03) (a) BHETA using ethanol amine and (b) BHET using ethylene glycol (BHET)

ppm (ZKGA03), which validates the symmetrical structure of the BHETA product. Being a symmetrical molecule, BHETA was found to have two aromatic carbons at 136.68 ppm and 127.13 ppm, whereas C2, C3, C5 and C6 coupled to hydrogen are appeared at 127.13 ppm, while C1 and C4 coupled to the amide carbonyl are appeared at 136.68 ppm. BHETA found the aliphatic chain carbons C9 and C10 at 42.27 ppm, linked to the amide -NH. The methylene carbons C11 and C12 connected the hydroxyl and methylene groups at 59.70 ppm [28].

The ^{13}C NMR spectrum of BHET is depicted in Fig. 13b. The ester carbonyl carbon of BHET, at 165.827 ppm (ZKGG04), indicates the presence of one type of ester carbonyl in the structure, confirming BHET as a single product with no other carbonyl carbons. Due to the symmetry of the BHET molecule, two aromatic carbons were detected at 134.39 ppm and 130.14 ppm (ZKGG04), respectively. The peaks at C1, C2, C4 and C5 correspond to the aromatic hydrogen peak at 130.14 ppm, while the peaks at C3 and C6 correspond to the ester carbonyl peak at 134.39 ppm [29].

Mass spectral studies: The mass spectra of *bis*(2-hydroxyethyl)terephthalamide (BHETA), which prevailed from red, blue and green PES threads, is shown in Fig. 14a-c, respectively. Electron spray ionization spectra of the BHETA obtained from red PES thread (ZKRA01) (Fig. 14a) revealed the presence of a protonated molecular ion peak at *m/z* 253.05 (M + H). In the protonated form, a molecular ion peak was observed at 253.25 (M + H) in the mass spectra of blue PES (ZKBA02) analogue (Fig. 14b). Depolymerization of green-coloured PES was

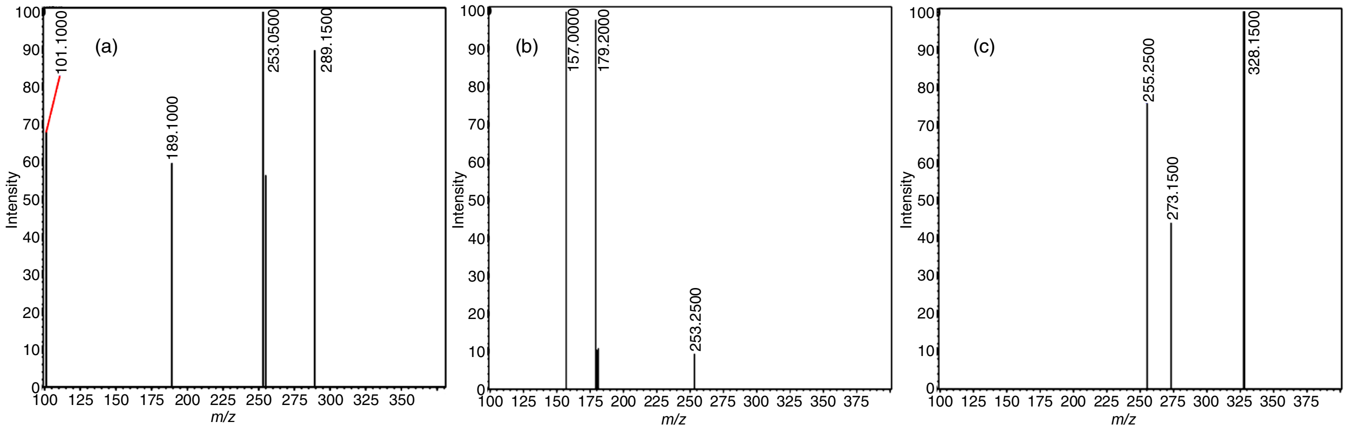


Fig. 14. Mass spectra of BHETA obtained from (a) red PES (ZKRA01), (b) blue PES (ZKBA02) and (c) green PES (ZKGA03) using ethanol amine

produced BHETA (ZKGA03) as the major product is indicated by a peak at 255.25 (M + H) in Fig. 14c [28].

The mass spectra of *bis*(2-hydroxyethyl)terephthalate (BHET) monomer obtained by glycolysis from red and green PES is shown in Fig. 15a-b, respectively. The absence of additional compounds in the mass spectra indicates monomers obtained with excellent purity. The BHET from red PES (ZKRG01) exhibited a molecular ion peak at *m/z* 253.10 (M + H) with 100% intensity in its ESI-MS spectra, which is consistent with BHET ionization (Fig. 15a). An important characteristic of green PES (ZKGG03) is the presence of a primary mass peak at 255.90 (M + H) for BHET molecular ions in the Na^+ form [29].

Conclusion

In this work, two pure colourless monomers *viz*. *bis*(2-hydroxyethyl)terephthalate (BHET) and *bis*(2-hydroxy-ethyl)-terephthalimide (BHETA) monomers were obtained by chemical recycling of polyester (PES) fabrics, to provide a sustainable solution for the polyester textile wastes. Extensive study has demonstrated a significant possibility of ester bond cleavage *via* aminolysis and glycolysis pathways. The optimized strategies may decrease environmental problems associated with recycling by lowering the amount of textile waste dump into the environment. Thus, we have evaluated the Zn[L-proline]$_2$ impregnated kaolin (ZnP@K) performance for PES depolymerization. It was found that the synthesized ZnP@K catalyst have shown better performance in aminolysis than glycolysis. Furthermore, the synthesized catalyst has been found effectively recycled for three times demonstrating its cost-effectiveness.

ACKNOWLEDGEMENTS

One of the authors, V. Sivamurugan, thanks the University Grants Commission (UGC) for providing financial support in the form of a minor research project [File No. F: MRP-6393/16(SERO/UGC)]. The authors are also grateful to the Centralized Sophisticated Instrument Facilities, Interdisciplinary Institute of Indian System of Medicine (IIISM), SRM Institute of Science and Technology and SRM Central Instrumentation Facility, Nanotechnology Research Centre, Katankulathur, India for various characterization.

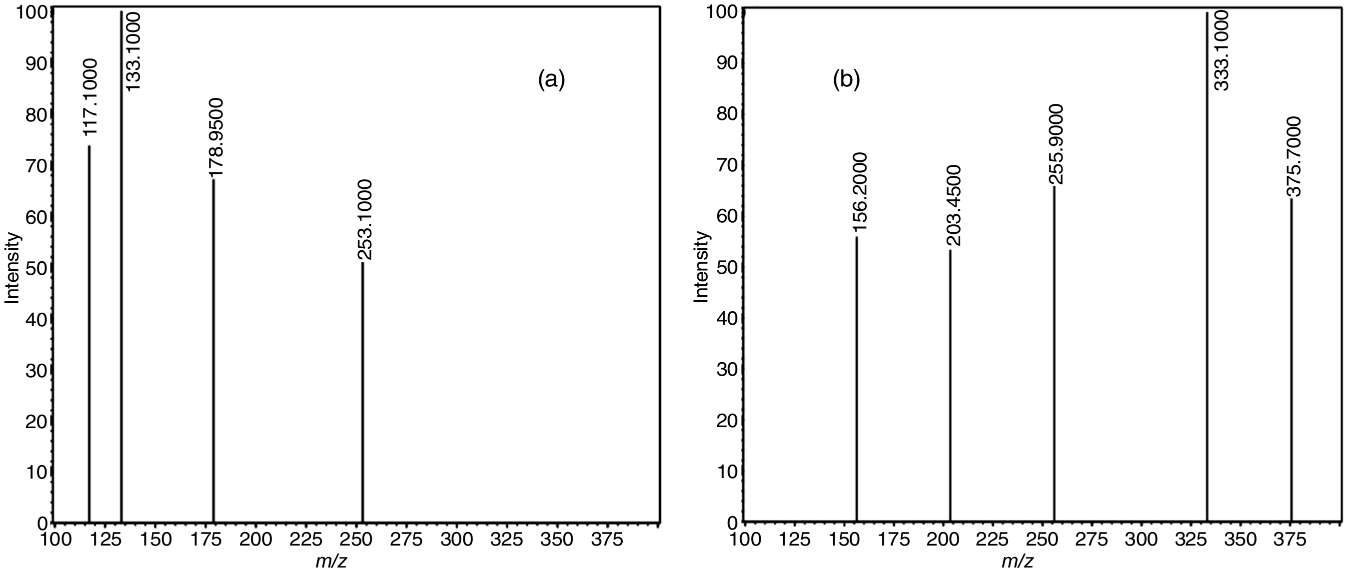


Fig. 15. Mass spectra of BHETA obtained from (a) red PES (ZKRG01) and (b) green PES (ZKGG03) using ethylene glycol

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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