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# Chemical recycling of waste poly(ethylene terephthalate) fibers into azo disperse dyestuffs

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In this study, waste poly(ethylene terephthalate) (PET) fibers were chemically recycled into azo disperse dyestuffs. First, waste PET fibers were glycolytically degraded by excess ethylene glycol utilizing zinc acetate dehydrate as a catalyst. The glycolysis product, bis(2-hydroxyethyl) terephthalate (BHET), was purified through recrystallization and hydrolyzed into terephthalic acid (TPA). Thereafter, BHET and TPA were nitrated, reduced and azotized to obtain diazonium salts. Finally, the obtained diazonium salts were coupled with *N,N*-dimethylaniline to obtain azo disperse dyestuffs (dye A and dye B, respectively). The depolymerized products (BHET and TPA) and azo disperse dyestuffs (dyes A and B) were characterized by FTIR and <sup>1</sup>H NMR spectroscopy. Nylon and polyester filaments were dyed with the synthesized azo dyestuffs with the dye bath pH ranging from 3.6 to 5.8. The performances of the dyestuffs were described by maximum absorption wavelength, *K/S*, *L\**, *a\** and *b\** values.

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## Introduction

Poly(ethylene terephthalate) (PET) is one of the most useful synthetic polymer in our daily life. It is made into blow molded bottles, packaging films, electrical insulating materials, textiles, *etc.* Because of the convenient production process and low production cost, most PET products are disposable products or FMCG (fast moving consumer goods). The used PET products will be discarded as waste and disposed of by landfill or incineration. Although PET is non-toxic, its degradation in natural environments is limited and it generates noxious gases while burning.<sup>1</sup> The global production of PET in 2010 was 55 million ton and increases year by year, and most PET will become solid waste in the next few years. A method for dealing with the increasing PET waste has become an important issue in recent years.<sup>2–6</sup>

Researchers degrade PET into oligomers or monomers by hydrolysis, glycolysis, aminolysis, methanolysis, *etc.*<sup>7–13</sup> The major degradation products of PET are dimethyl terephthalate (DMT), bis(2-hydroxyethyl) terephthalate (BHET) and terephthalic acid (TPA). They have been transformed into value added products<sup>14,15</sup> such as curable resins,<sup>16</sup> epoxy resins,<sup>17</sup> activated carbon,<sup>18</sup> polyurethane products,<sup>19,20</sup> textile auxiliaries,<sup>21,22</sup> polymeric plasticizer,<sup>23</sup> *etc.*

In fact, more than half of the PET products are textiles used in clothing and decorative cloth made of PET fibers. Here, we

discuss a method for recycling PET fibers into azo disperse dyestuffs, which can be used for dyeing nylon, polyester and other textiles. In addition, PET bottles or films can also be recycled by this method because of the higher purity of PET in these produced compared to PET fibers.

## Experimental

### Materials

Ethylene glycol (EG), zinc acetate dihydrate, conc. nitric acid, conc. sulfuric acid, conc. hydrochloric acid, tin chloride dehydrate, *N,N*-dimethylaniline, sodium hydrate, sodium nitrite, sodium carbonate and carbamide, all of CP grade, were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Phosphate buffer solution was prepared by mixing potassium dihydrogen phosphate solution and dipotassium hydrogen phosphate solution in ratio. Waste PET short fibers, polyester and nylon filaments were washed with water and dried at 80 °C for 8 h to a constant weight.

### Depolymerization of PET

The glycolysis of PET fibers was carried out by the method that we introduced in our previous report.<sup>20</sup> PET fibers were depolymerized at 198 °C under a nitrogen atmosphere for 4 h with EG as the depolymerizing agent and zinc acetate dehydrate as the catalyst. The reaction process is shown in Scheme 1(a). The glycolysis product was purified through repeated crystallization according to the following procedure. The product was filtered and the residue was completely dissolved in distilled water in a tube at 90 °C; then the tube was placed in an ice water mixture for 6 h for crystallization; and the generated white crystal

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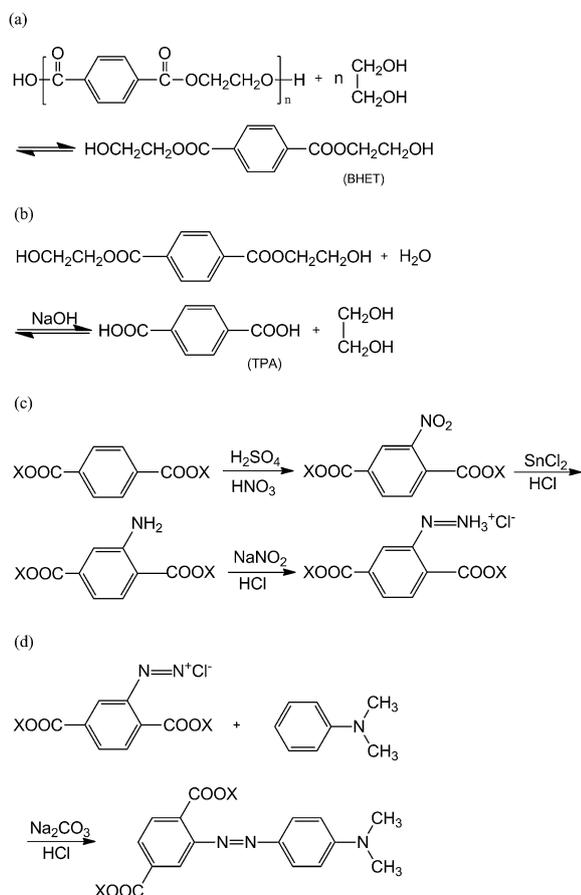
(BHET) was purified through filtration. The above mentioned procedure was carried out three times to obtain a greater than 82% yield of BHET.

Twenty grams of BHET and 6 g sodium hydroxide were mixed with 100 ml distilled water and poured into a three-necked round-bottom glass flask, which was equipped with a thermometer, a reflux condenser and a magnetic stirrer. BHET was hydrolyzed at 80 °C for 40 min and then filtered. Hydrochloric acid (15%) was added to the abovementioned filtrate slowly with adequate stirring.

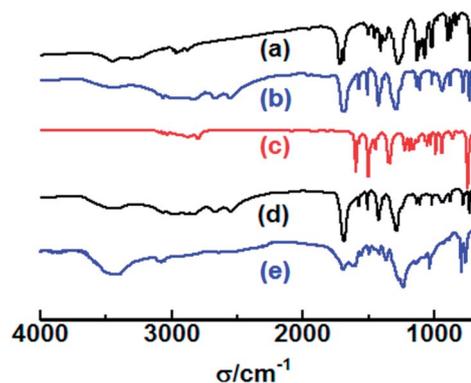
Thereafter, the mixture was filtered. The filtrate was crystallized and dried at 60 °C for 3 h to obtain crystals of TPA (80.5% yield), as shown in Scheme 1(b).

### Synthesis of diazonium salts *via* BHET and TPA

BHET and TPA were nitrated, reduced and synthesized into diazonium salts following the processes shown in Scheme 1(c). A three-necked round-bottom glass flask equipped with a magnetic stirrer, thermometer and reflux condenser was charged with 20 g BHET (or TPA) and 55 ml conc. sulfuric acid (1.840 g ml<sup>-1</sup>). Then, 12 ml conc. nitric acid (1.395 g ml<sup>-1</sup>) was added to the glass flask slowly with stirring. The reaction

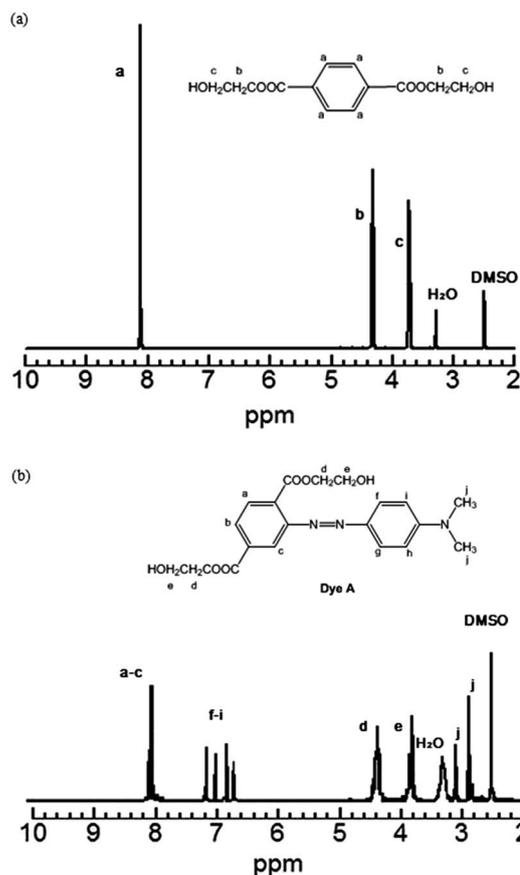


**Scheme 1** Synthesis of azo dyestuffs from PET fibers: (a) glycolysis of PET fibers; (b) hydrolysis of BHET; (c) synthesis of diazonium salts from BHET and TPA; (d) coupling reactions of diazonium salts, where -X is -H of TPA or -CH<sub>2</sub>CH<sub>2</sub>OH of BHET.



**Fig. 1** FTIR spectra of BHET (a), TPA (b), *N,N*-dimethylaniline (c), dye A (d) and dye B (e).

temperature was increased to 60 °C gradually over 1 h, then increased to 80 °C gradually over 1 h and held at this temperature for 10 h. Thereafter, the mixture was cooled using ice water to room temperature and filtered. The filtrate was recrystallized to obtain nitro-bis(2-hydroxyethyl)terephthalate (NBHET) or nitro-terephthalic acid (NTPA), successively. The formed crystals were dried in the oven at 60 °C to a constant weight.



**Fig. 2** <sup>1</sup>H NMR of BHET (a) and dye A (b).

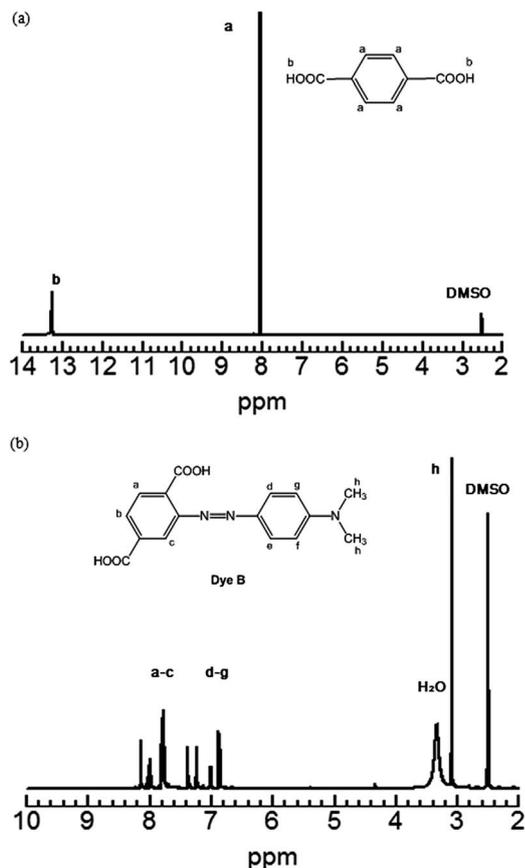


Fig. 3  $^1\text{H}$  NMR of TPA (a) and dye B (b).

Table 1 Variation of the maximum absorption wavelength ( $\lambda_{\text{max}}$ ) and relative color values ( $K/S$ ,  $L^*$ ,  $a^*$ ,  $b^*$ ) of samples dyed with dye A with varying bath pH

pH	$\lambda_{\text{max}}/\text{nm}$	Nylon				Polyester			
		$K/S$	$L^*$	$a^*$	$b^*$	$K/S$	$L^*$	$a^*$	$b^*$
3.6	521	2.28	57.10	18.93	17.37	1.36	68.54	27.94	17.80
4.0	519	1.64	64.44	22.66	16.16	1.50	67.54	27.74	19.65
4.5	515	1.39	63.15	14.25	13.79	1.24	68.20	23.14	16.45
5.0	451	0.94	66.94	6.99	11.80	1.08	69.65	13.66	19.74
5.5	451	0.67	71.16	3.92	11.07	0.70	77.64	10.65	21.93
5.8	443	0.43	75.17	0.73	7.76	0.53	82.30	4.13	22.09

Eighty milliliters of conc. hydrochloric acid ( $1.179 \text{ g ml}^{-1}$ ) was added to a three-necked round-bottomed glass flask fitted with a stirrer, a reflux condenser and a thermometer. Tin chloride dehydrate (25 g) was added gradually to the glass flask with stirring until it dissolved completely. Thereafter, 10 g NBHET or NTPA was added to the glass flask and reacted with the solution at  $80^\circ\text{C}$  for 3 h. After the reaction, the mixture was filtered with distilled water and the precipitate was dried in an oven at  $60^\circ\text{C}$  for 2 h to form amino-bis(2-hydroxyethyl)terephthalate (ABHET) or amino-terephthalic acid (ATPA), successively.

Table 2 Variation of the maximum absorption wavelength ( $\lambda_{\text{max}}$ ) and relative color values ( $K/S$ ,  $L^*$ ,  $a^*$ ,  $b^*$ ) of samples dyed with dye B with varying bath pH

pH	$\lambda_{\text{max}}/\text{nm}$	Nylon				Polyester			
		$K/S$	$L^*$	$a^*$	$b^*$	$K/S$	$L^*$	$A^*$	$b^*$
3.6	515	18.78	44.50	50.20	37.99	12.23	51.94	49.89	35.41
4.0	510	17.66	44.35	50.31	36.11	11.04	52.78	48.31	34.74
4.5	502	17.47	44.36	52.25	35.84	10.65	53.12	48.93	36.10
5.0	500	17.00	44.73	51.41	33.54	4.17	60.85	37.96	33.03
5.5	500	16.32	45.91	52.31	31.02	2.61	64.39	31.33	31.88
5.8	420	14.10	51.99	52.48	30.67	1.02	73.83	15.36	24.03

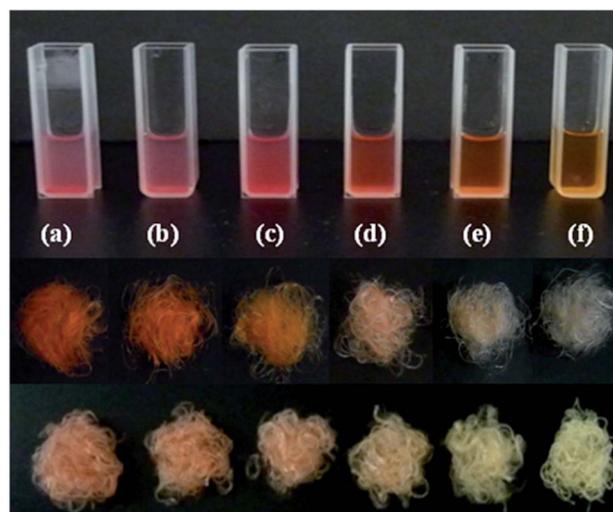


Fig. 4 Photographs of dye baths prepared from dye A, dyed nylon filaments and dyed polyester filaments from top to bottom, respectively. The pH of the dye bath was: (a) 3.6, (b) 4.0, (c) 4.5, (d) 5.0, (e) 5.5, and (f) 5.8, respectively.

Ten grams ABHET or ATPA was mixed with 40 ml 15% hydrochloric acid ( $1.073 \text{ g ml}^{-1}$ ) at  $8^\circ\text{C}$  with magnetic stirring. Then 28.5 g 20% sodium nitrite aqueous solution was added gradually to the mixture and reacted at  $5^\circ\text{C}$  for 3 h to obtain diazonium salt solutions. The excess sodium nitrite was removed by carbamide.

#### Coupling reactions with *N,N*-dimethylaniline

*N,N*-dimethylaniline (3.5 g) was mixed with 6.2 ml 10% hydrochloric acid ( $1.047 \text{ g ml}^{-1}$ ) and cooled to  $10^\circ\text{C}$ . The resultant 5 grams diazonium salt solutions were mixed with the above mixture immediately, and the pH was adjusted to 5.0 utilizing 15% sodium carbonate solution. The reaction, which is shown in Scheme 1(d), was carried out at  $5^\circ\text{C}$  for 2 h, and the resulting dyestuffs (dye A and dye B) were filtered, washed with distilled water and dried at  $60^\circ\text{C}$  for 2 h.

#### Characterization

The FTIR spectra of BHET, TPA and synthesized dyestuffs were obtained on a Nicolet Nexus-470 IR spectrometer (USA) with KBr

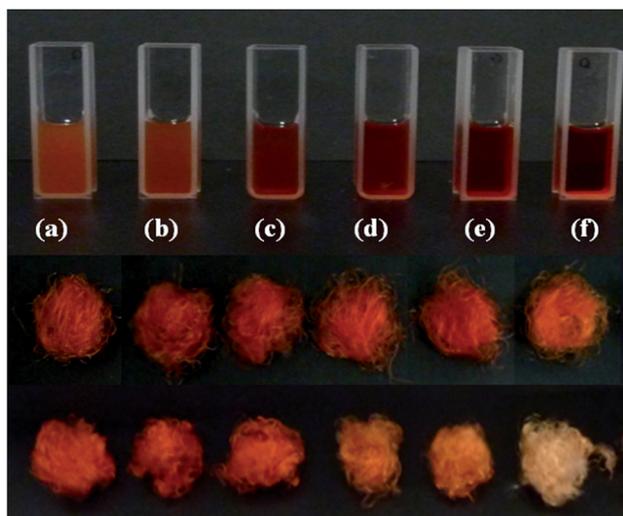


Fig. 5 Photographs of dye baths prepared from dye B, dyed nylon filaments and dyed polyester filaments from top to bottom, respectively. The pH of the dye bath was: (a) 3.6, (b) 4.0, (c) 4.5, (d) 5.0, (e) 5.5, and (f) 5.8, respectively.

as a reference material. The scanning range was 650–4000  $\text{cm}^{-1}$  and the resolution was 1  $\text{cm}^{-1}$ .

Proton nuclear magnetic resonance ( $^1\text{H}$  NMR) spectra of BHET, TPA and synthesized dyestuffs were recorded on a Bruker DRX-400 spectrometer (Germany) at 400 MHz in deuterated dimethylsulphoxide ( $\text{DMSO}-d_6$ ), and the chemical shifts  $\delta$  were measured using tetramethyl silane as an internal reference.

The performances of synthesized azo dyestuffs were evaluated by the maximum absorption wavelength and the relative color values ( $K/S$ ,  $L^*$ ,  $a^*$ ,  $b^*$ ) of the dyed polyester and nylon filaments, respectively.

Both the dyestuffs were prepared as a dye bath by dispersion in distilled water at 3% (o. w. f.) with a dispersing agent. The pH of the dye baths were varied from 3.6 to 5.8 by utilizing phosphate buffer solution. Dyeing of polyester filaments was carried out in closed stainless steel beakers in a high-temperature dyeing machine at 120  $^\circ\text{C}$  for 60 min at a liquor ratio of 80. The dyed polyester filaments were washed with distilled water and dried in an oven at 70  $^\circ\text{C}$ . Nylon filaments were immersed in the dye bath at the liquor ratio of 80 at 95  $^\circ\text{C}$  for 40 min, washed by distilled water and dried in an oven at 70  $^\circ\text{C}$ , successively.

Relative color values ( $K/S$ ,  $L^*$ ,  $a^*$ ,  $b^*$ ) and the maximum absorption wavelength ( $\lambda_{\text{max}}$ ) of each dyed sample was measured by a COLOR-Eye-7000A spectrophotometer (GretagMacbeth, USA).

## Results and discussion

### FTIR spectroscopy

Fig. 1 showed the Fourier-transform infrared (FTIR) spectra of BHET, TPA, *N,N*-dimethylaniline, dye A and dye B. The peaks at 1417, 1426, 1426, and 1417  $\text{cm}^{-1}$  in Fig. 1(a), (b), (d) and (e) were due to the stretching vibration of  $-\text{COO}-$  of BHET, TPA, dye A and dye B, respectively. The absorption bands due to  $-\text{OH}$  group

shown at 3650–3250  $\text{cm}^{-1}$  in Fig. 1(a) and (d) and at 3685–3370  $\text{cm}^{-1}$  in Fig. 1(b) and (e) indicated the completely depolymerization of PET. The absorption peaks around 1600, 1515 and 1428  $\text{cm}^{-1}$  for all compounds in Fig. 1 were due to the benzene ring groups. The absorption bands at 1350–1250  $\text{cm}^{-1}$  in Fig. 1(c)–(e) were due to the stretching vibration of C–N.

### $^1\text{H}$ NMR spectroscopy

Fig. 2 shows the structures and  $^1\text{H}$  NMR spectra of BHET (a) and dye A (b). In addition, the structures and  $^1\text{H}$  NMR spectra of TPA (a) and dye B (b) are shown in Fig. 3.  $^1\text{H}$  NMR of BHET ( $\text{DMSO}-d_6$ )  $\delta$ : 8.12 (t, 4H, ArH), 4.92 (t, 2H, OH), 4.33 (t, 4H,  $\text{CH}_2$ ), 3.74 (q, 4H,  $\text{CH}_2$ );  $^1\text{H}$  NMR of dye A ( $\text{DMSO}-d_6$ )  $\delta$ : 8.10 (m, 3H, ArH), 7.21, 7.02, 6.81, 6.70 (4H, ArH), 4.33 (t, 4H,  $\text{CH}_2$ ), 3.83 (m, 4H,  $\text{CH}_2$ ), 3.10, 2.88 (6H,  $\text{CH}_3$ );  $^1\text{H}$  NMR of TPA ( $\text{DMSO}-d_6$ )  $\delta$ : 13.26 (s, 2H, OH), 8.06 (s, 4H, ArH);  $^1\text{H}$  NMR of dye B ( $\text{DMSO}-d_6$ )  $\delta$ : 8.14, 7.99, 7.78 (3H, ArH), 7.38, 7.23, 7.00, 6.88 (4H, ArH), 4.33 (s, 6H,  $\text{CH}_3$ ).

### Variation of dyeing performances with pH

CIE 1976  $L^*a^*b^*$  (CIELAB) is the most commonly used color space to characterize colors. The three coordinates of CIELAB represent the lightness of the color ( $L^* = 0$  yields black and  $L^* = 100$  indicates diffuse white), its position between red and green ( $a^*$ , negative values indicate green while positive values indicate red) and its position between yellow and blue ( $b^*$ , negative values indicate blue and positive values indicate yellow).<sup>24</sup> According to the Kubelka–Munk equation, the data of color values ( $K/S$ ) are representative of the color depth of the dyed fabrics.<sup>25</sup>

The relative color values of samples dyed with dye A and dye B are given in Tables 1 and 2, respectively. For both the synthesized azo dyestuffs, the  $K/S$  values of dyed nylon samples were higher than that of the dyed polyester at the same pH. This indicated the higher dyeing capacity of the dye molecules for nylon compared to polyester. For all the samples, the  $K/S$  value increased when the pH of dye bath decreased. It was considered that the hydron facilitated the adsorption and fixation of dyestuff on nylon or polyester fibers through hydrogen bonding. The positive  $a^*$  and  $b^*$  values indicated the red and yellow tones of the dyestuffs, whereas the higher  $L^*$  values confirm the color brilliancy at lower pH. The maximum absorption wavelength ( $\lambda_{\text{max}}$ ) of dyed samples prepared by dye A was 443–521 nm when the pH varied from 5.8–3.6, which corresponded to a color change from a yellow tone to a red tone (Fig. 4). In addition, a similar variation of the  $\lambda_{\text{max}}$  of samples prepared with dye B also occurred with the change in pH, and the color of the samples changed from an orange tone to a red tone (Fig. 5). In brief, the bathochromic shifts occurred in both dye A solution and dye B solution when the solution pH decreased.

## Conclusions

In this work, waste PET fibers were chemically degraded into BHET and TPA. The resulting monomers were converted into azo disperse dyestuffs. The synthesized dyestuff could be applied for dyeing nylon and polyester filaments. Both of the

dyestuffs presented good coloration characteristics especially when the dye bath pH was lower than 5.5. The fibers dyed by dyestuffs synthesized *via* BHET showed a shift from an orange-red tone to a yellow tone when the dye bath pH increased from 3.6 to 5.8, while the fibers dyed by dyestuffs synthesized *via* TPA showed a shift from a red tone to an orange red. These results show the potential to recycle waste PET fibers into value added products.

## Acknowledgements

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