Glycolysis of Postconsumer Polyethylene Terephthalate Waste

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ABSTRACT: Glycolytic depolymerization of polyethylene terephthalate (PET) bottle waste was attempted using ethylene glycol (EG) in the presence of chlorides of zinc, lithium, didymium, magnesium, and iron as catalysts. Virtual monomer bis (2-hydroxyethyl terephthalate) (BHET) was obtained in all cases with nearly 74% yield, the highest yield being achieved with zinc chloride catalyst 0.5% w/w, PET : EG ratio 1 : 14 and 8 h under reflux conditions. The results were comparable to other catalysts like common alkalis, acids, and salts of some earth metals and zeolites used earlier although parameters of glycolysis were observed to vary depending on the catalyst. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 249–254, 2010

Key words: recycling; polyester; waste

INTRODUCTION

In the contemporary environment, it is becoming increasingly important to recycle plastics, which are abundantly used by virtue of their higher durability and inertness to environmental adversities. Polyethylene terephthalate (PET), in particular, is consumed in large volumes in production of fibers, bottles, tapes, films, food packaging, etc.[1–3] The overall world production of PET in 1997 was about 13 million tons of which 9.5 million tons were processed by the textile industry, 2 million tons were used in the manufacture of audio and video tapes, and 1.5 million tons were used in the manufacture of various types of packaging materials, mainly bottles and jars.[4] The reason behind such a growth is the excellent thermal and mechanical properties, crystal clear transparency, and nontoxic nature of PET.[5] The substantial contribution of PET in solid waste generation and its high resistance to degradative assimilation into the environment labels it as a noxious material.[6] Solid waste management comprises incineration, landfill disposal, or recycling.[7] Of the 1.5 million tons of PET bottles in 1997, about 0.7 million tons were alone collected for recycling in United States which grew to 1.17 million tons in 2007 with a gross recycling rate of 24.6%.[8–10]

The recyclable polyester is gathered from two main sources, manufacturing waste and postconsumer waste.[11] The recycling of postconsumer PET waste may be achieved through physical reprocessing (grinding, melting, and reforming) or it may be chemically treated to recover basic components followed by their reprocessing in manufacture. The EPA has adopted a new nomenclature that refers to physical reprocessing as secondary recycling (2°) and chemical processing as tertiary recycling (3°). The primary recycling (1°) refers to use of preconsumer industrial scrap and salvage to form new packaging, a common occurrence in industry. The EPA considers "recycling" to be the processing of waste to make new articles. Although the EPA does not consider reuse to be a recycling process, using the 1°, 2°, and 3° conventions mentioned above, could be considered "zero order" recycling.[12]

Chemical recycling of PET is achieved through depolymerization via solvolytic action of glycols, water, alcohol, amines, etc. Depending on the reagents used to carry out cleavage of the functional ester groups of PET, various products can be obtained. Glycolysis results in the formation of oligomers or oligoester diols/polyols with hydroxyl terminal groups. This process is used widely even on a commercial scale using ethylene glycol (EG), diethylene glycol, propylene glycol, and dipropylene glycol. Kinetics of glycolysis reaction has also been studied by researchers.[12–14] The depolymerization product thus obtained finds its use in various

applications such as synthesis of plasticizers,[15] unsaturated polyester resins,[2] methacrylated oligoesters,[16] urethane oil varnishes,[17] textile dyes, and softeners.[18,19]

We have earlier reported the results on the kinetics of glycolysis and the use of some ecofriendly catalysts such as common alkalis, acids, and salts of some earth metals in comparison with conventional heavy metal catalysts to produce the virtual monomer bis(2-hydroxyethyl terephthalate) (BHET).[20,21] The use of zeolites has also been shown to catalyze the PET glycolysis and the BHET yields were similar to those obtained by various other catalysts.[22] In all the cases, the BHET yield was found to be comparable. In this study, various chloride catalysts, such as zinc chloride, didymium chloride, lithium chloride, magnesium chloride, and ferric chloride were used. Of these, didymium chloride, which is a mixture of rare earths determined as oxides, is a widely used ecofriendly catalyst in various organic reactions.[23,24] Metal halide catalysts, particularly zinc chloride is an inexpensive, readily available catalyst and associated Lewis acidity is known to enhance the rate of organic reaction to give excellent yield of the product with high selectivity. It has been explored as a powerful catalyst in various organic transformations. Zinc chloride finds many applications in textile processing, metallurgical fluxes, and chemical synthesis.[25] Along with zinc chloride, other metal chlorides, namely didymium chloride, lithium chloride, magnesium chloride, and ferric chloride have also been explored for their efficiency of depolymerizing PET.

EXPERIMENTAL

Materials

Postconsumer PET bottles waste with a number-average molecular weight ranging from 18,000 and 20,000 were procured from local market. The bottles after removing caps and labels were cut into approximately 1 cm² chips and subsequently cleaned by boiling in weak detergent solution followed by washing and drying.

Chemicals

All the chemicals including the catalysts zinc chloride, lithium chloride, didymium chloride, magnesium chloride, and ferric chloride were of analytical reagent grade.

Glycolysis of polyester waste

The PET waste was treated with EG under reflux (197°C) in the presence of different catalysts for time periods up to 9 h. The catalysts, namely zinc chloride, lithium chloride, didymium chloride, magnesium chloride, and ferric chloride were varied in concentration ranging between 0.3 and 1% (w/w). At the end of the reaction, distilled water was added in excess to the reaction mixture with vigorous agitation. The glycolyzed product was obtained as a residue after filtration. The filtrate contained unreacted EG, BHET, and little quantities of a few water soluble oligomers. White crystals of BHET were obtained by first concentrating the filtrate by boiling and then chilling it. The glycolyzed residue was then boiled with water to extract any BHET left. White crystalline powder of BHET was purified by repeated crystallization from water, dried in an oven at 80°C, and weighed for estimating the yield. It was subjected to different characterization techniques.

Characterization of BHET

Melting point of the purified BHET was determined in an open capillary. Elemental analysis was carried out by using Heraus Combustion Apparatus. For ^{1}H NMR, the glycolyzed residue was dissolved in solvent CDCl$_3$. Tetramethyl silane was used as an internal standard and the spectrograph was recorded on JEOL, FT-NMR (60 MHz). FTIR spectrum was recorded using KBr disc technique on Shimadzu IR Spectrophotometer (Model 8400S). The melting characteristic was determined by differential scanning calorimeter (DSC) (Shimadzu 60) at the heating rate of 10°C/ min from 20° to 200°C in nitrogen atmosphere.

RESULTS AND DISCUSSION

Nonbiodegradability of PET is a major concern to the environmentalists from the point of view of polymer waste management. During the production of PET, the direct esterification or the transesterification reaction leads to BHET, which is then polymerized to obtain PET.

Earlier, we have shown that simple chemicals such as sodium carbonate, sodium bicarbonate, glacial acetic acid, lithium hydroxide, sodium sulfate, and potassium sulfate can act as catalyst in a way almost similar to the conventionally used zinc acetate and lead acetate, for depolymerization of PET waste into BHET.[20,21] In the present communication, the use of various metal chloride catalysts such as zinc chloride, lithium chloride, didymium chloride, magnesium chloride, and ferric chloride has been reported.

Data in Table I indicate that for all the catalysts, the BHET yield increases up to 0.5% concentration on weight of PET, which decreased thereafter. Glycolysis is always carried out in excess of EG.

TABLE I
Effect of Concentration of Different Catalysts on the BHET Yield

Catalyst conc., % (w/w)	BHET yield (%) in presence of chlorides of				
	Zinc	Lithium	Didymium	Magnesium	Ferric
0.3	56.08	52.30	63.11	62.75	57.40
0.5	60.47	62.90	66.36	66.08	57.58
0.7	50.79	60.54	58.13	55.94	52.83
1.0	48.45	57.44	52.15	52.71	49.93

PET: EG: 1 : 6.
Time: 8 h.

However, the PET : EG ratio required for obtaining maximum BHET yield was found to be different for each catalyst (Table II). Thus, for zinc and didymium chloride catalysts, the optimum PET : EG molar ratio was taken as 1 : 10 since no significant increase in BHET yield was observed by increasing the PET : EG ratio further. For lithium, magnesium, and ferric chloride catalysts, this ratio was found to be 1 : 6. Similarly, the optimum time of glycolysis, as observed from Table III, was 7 h for zinc, magnesium, and ferric chloride catalysts and 8 h for didymium and lithium chloride catalysts. Thus, under optimized parameters of 1 : 10 PET : EG ratio and 7 h reflux, 0.5% (w/w) zinc chloride gave maximum BHET yield of 73.24%, which was highest among all the catalysts studied. This was followed by didymium chloride (0.5% w/w concentration, 1 : 10 PET : EG ratio and 8 h reflux) giving 71.56% yield of BHET. In comparison, our earlier results showed that using 0.5% (w/w) of the conventional heavy metal catalyst (zinc acetate) with PET : EG ratio 1 : 6 and 8 h reflux, the maximum BHET yield was 62.51%[20].

Initially, the reaction mixture is biphasic, one solid phase (PET) and a liquid phase (EG). The solubilization of polyester progresses with increase in reaction temperature and is maximum at 197°C. The loss in

TABLE II
Effect of PET: EG Ratio on the BHET Yield in Presence of Different Catalysts

PET: EG	BHET yield (%) in presence of chlorides of				
	Zinc	Lithium	Didymium	Magnesium	Ferric
1 : 4	54.41	59.15	52.91	60.18	44.97
1 : 6	61.63	62.43	65.29	65.93	61.05
1 : 8	64.31	60.25	67.76	66.78	61.27
1 : 10	73.23	59.46	71.01	55.67	56.28
1 : 12	73.86	–	71.75	–	–
1 : 14	74.73	–	67.05	–	–

Catalyst conc.: 0.5% (w/w).
Time: 8 h.

TABLE III
Effect of Glycolysis Time on the BHET Yield in Presence of Different Catalysts

Time (h)	BHET yield (%) in presence of chlorides of				
	Zinc	Lithium	Didymium	Magnesium	Ferric
4	71.77	–	68.82	34.94	–
6	71.93	59.50	70.65	60.21	58.35
7	73.27	60.52	70.58	65.56	62.75
8	73.12	63.08	71.56	65.55	61.12
9	72.66	60.87	72.46	60.53	56.67

PET: EG: 1 : 10 (for zinc and didymium chloride): 1 : 6 (for lithium, magnesium, and ferric chloride).
Catalyst conc.: 0.5% (w/w).

weight of PET is higher at higher temperatures. Glycolysis occurs predominantly in single liquid phase. With increase in the PET : EG ratio at constant catalyst concentration and time, the dissolution of PET was found to be at an earlier stage (within 90 min) there by providing the single liquid phase necessary for glycolysis.[22]

The metal salts are ionized forming a complex with the carbonyl group of ester in PET. This complex facilitates the attack of EG on PET, which in turn leads to the formation of BHET as shown in Figure 1.[21]
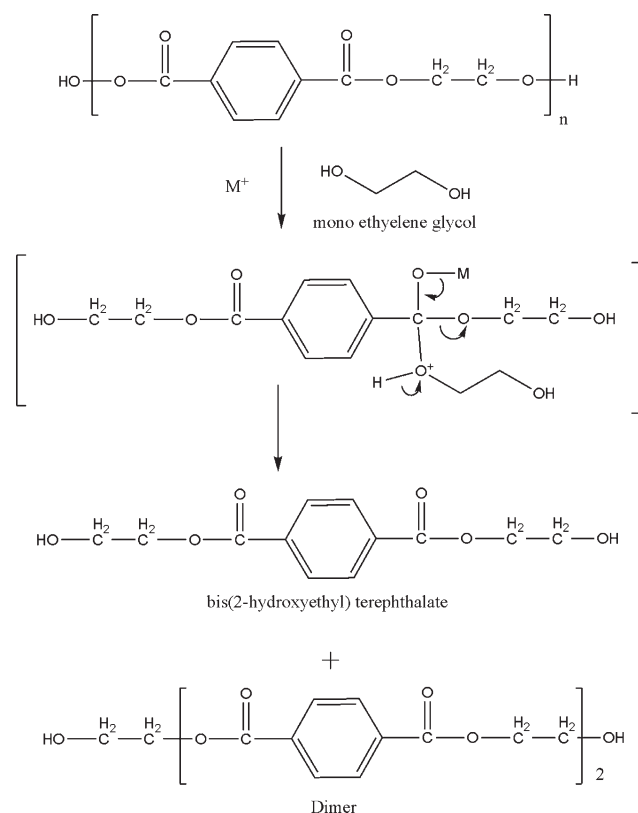

Figure 1 Mechanism of glycolytic depolymerization of PET.

TABLE IV
Characterization of BHET Obtained

Formula:	$C_{12}H_{14}O_6$
Molecular weight	254
Melting point:	109–112°C
Elemental analysis (%)	
C	55.9
H	5.4
O	38.7

In the presence of excess glycol, the oligomers produced at high conversion of methyl ester end groups are mostly dimers and the BHET concentration reaches a steady state.[26] A similar observation was made by Baliga and Wong,[8] who found that after a long time of reaction (up to and above 8 h), equilibrium is attained between the dimer and BHET. It is possible to recover the excess of unreacted glycol using different techniques such as salting out,[14] distillation,[27–29] and pervaporation separation,[30–32] making the process economical.

The purified product was characterized by elemental analysis and melting point. These results, given in Table IV, confirm that the purified product after depolymerization of PET is BHET. Single spot was obtained through thin-layer chromatographic analysis using the eluent chloroform : ethanol (9 : 1) as shown in Figure 2, indicating the purity of the glycolyzed product, BHET.

The FTIR spectrographs of PET and the purified monomer are shown in Figures 3 and 4, respectively. Figure 4 clearly indicates the —OH band at 3450 cm^{-1} that is absent in the spectrograph of PET. The other common bands for PET and the purified monomer are observed at 1135 cm^{-1}, C=O stretch-
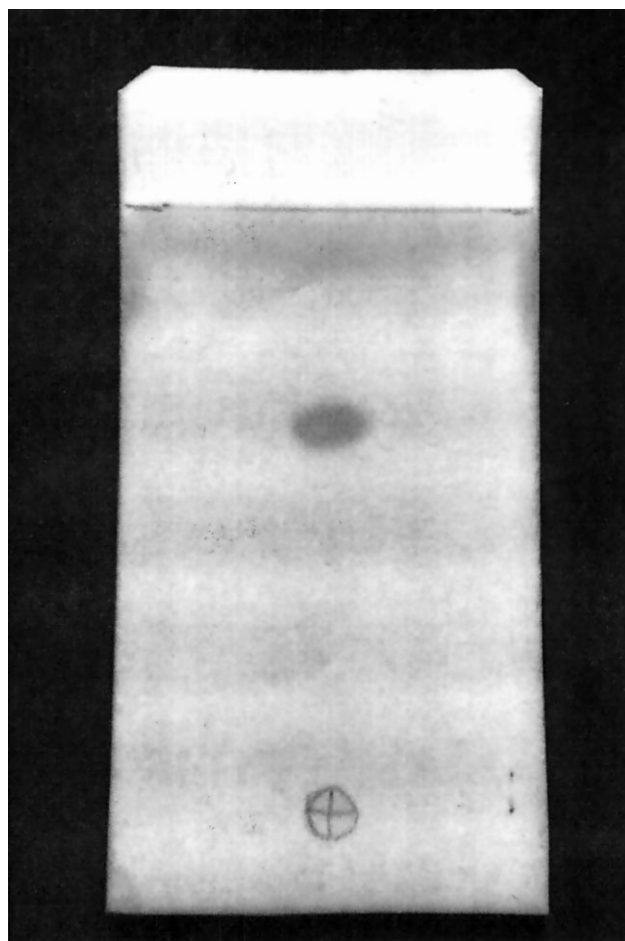

Figure 2 TLC of BHET.

ing at 1715 cm^{-1}, alkyl C—H at 2879 and 2964 cm^{-1} and aromatic C—H at 1456–1504 cm^{-1}. Figure 5, giving the ^{1}H NMR spectrum, also confirms that the
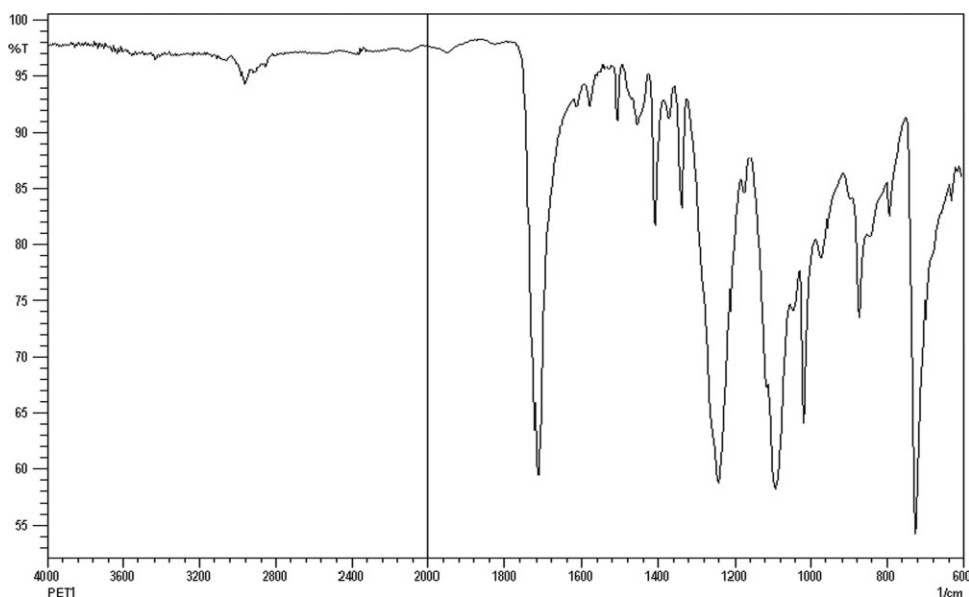

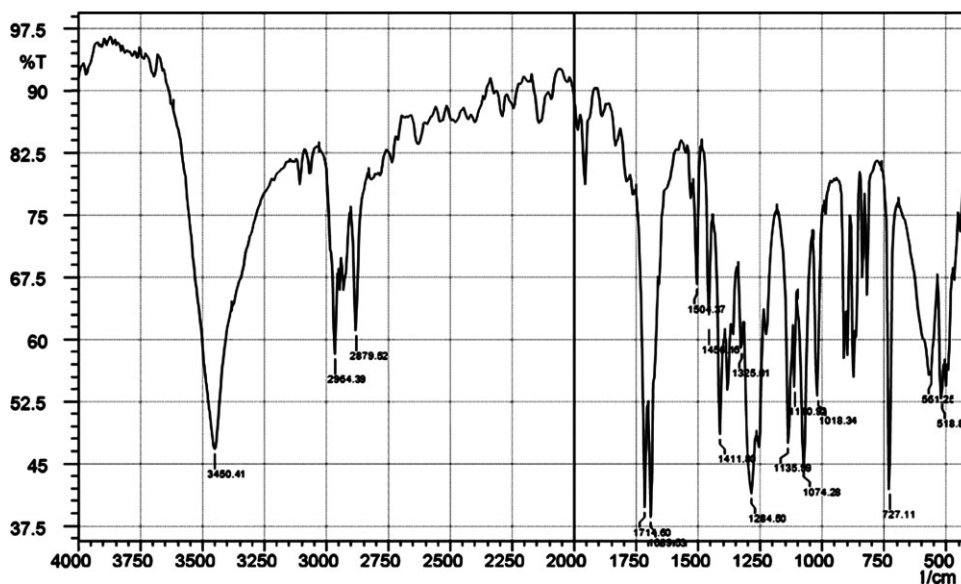**Figure 3** FTIR spectra of PET.

Figure 4 FTIR spectra of BHET.

compound is pure BHET as in earlier communication.[16] Thus, the signal at δ 8.1 ppm indicates the presence of the four aromatic ring protons. The peak at δ 1.9 corresponds to —OH groups, δ 3.95 corresponds to aliphatic (—CH$_2$) proton and δ 4.51 to aliphatic (—CH$_2$) proton. The DTG scan of the purified fraction (Fig. 6) shows reasonably sharp single endothermic peak at 111°C, which agrees well with the known melting point of BHET reported in the literature.[33] The BHET is thermally stable till 198°C thereafter the weight loss increases and after 450°C, 78%

weight loss was observed. From all these observations, it was concluded that the structure of the purified monomer is that of BHET.

CONCLUSIONS

The chlorides of different metal catalysts can be used for glycolyzing PET bottle waste with EG into the pure monomer BHET with good yield. The structure of BHET was confirmed by FTIR and NMR spectroscopy indicating characteristic groups in the
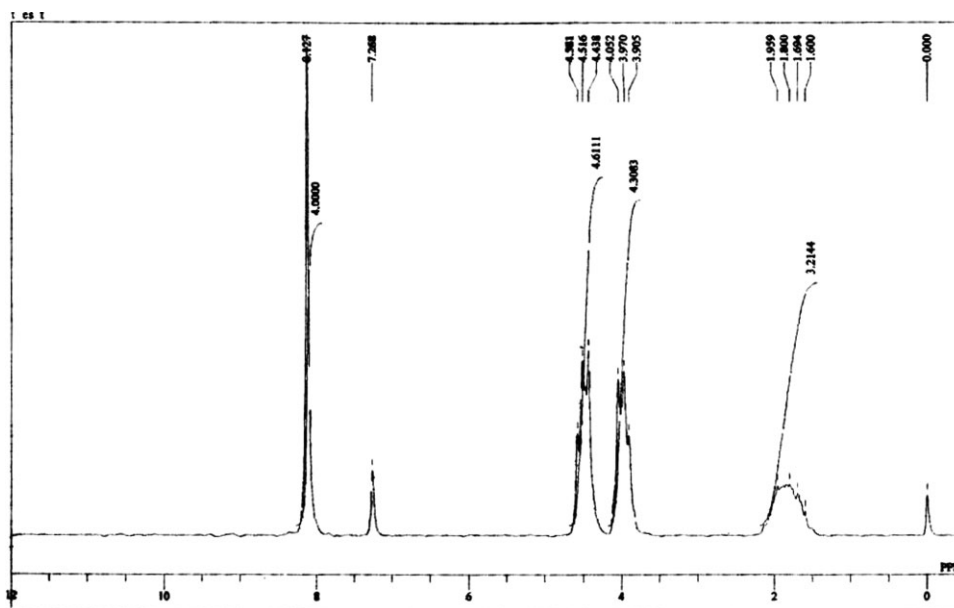

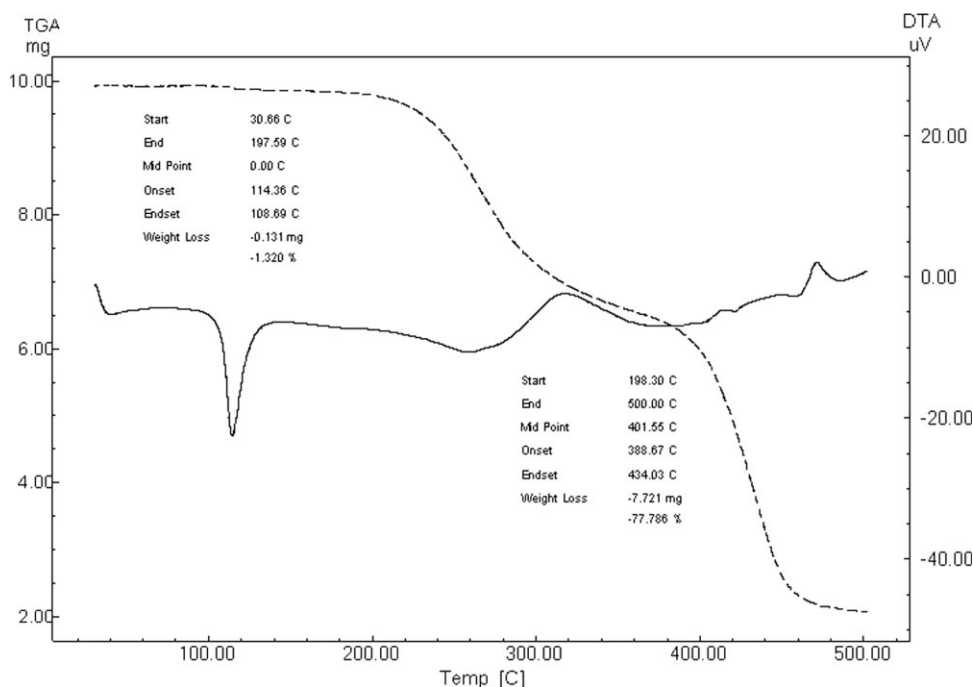**Figure 5** NMR spectra of BHET.

Figure 6 DTG of BHET.

structure. DSC analysis further confirms the melting point of BHET as reported in the literature.

Considerably high yield coupled with purity of BHET indicates the potential of BHET being recycled into certain products useful in the field of textile application, such as dyes, softener, dye retardant, dye fixing agents, etc., which is being explored.

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