

## Using ionic liquid catalyst for conversion of waste polyethylene terephthalate and soybean oil to polyester polyol

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**ABSTRACT:** An imidazolium ionic liquid was synthesized, characterized and used as a catalyst for conversion of polyethylene terephthalate (PET) and soybean oil to polyester polyol (PE polyol). The degradation of PET waste was carried out using glycerol and low cost soybean oil that resulted in the formation of PE polyols. Formed PE polyols were characterized using Fourier transform infrared (FT-IR) and mass spectra method, thermo gravimetric and differential thermal analysis and gel permeation chromatography. The first step in the overall process is proposed to be the transesterification of soybean oil with glycerol to form monoglyceride or/and diglyceride of soybean oil fatty acids. In the second step, the obtained glycerides can react with PET to form PE polyol. Both steps could be combined in one process and acidic catalyzed by an ionic liquid. Ionic liquid can be used as active catalyst and show a high reusability. The influence of some factors such as amount of glycerol used in transesterification of soybean oil with glycerol, PET degradation time, and temperature on PET conversion were investigated to find the suitable conditions for the process. Under suggested optimum parameters (mass ratio of soybean oil to glycerol of 2:1, a time of 8 h and a temperature of 180 °C for PET degradation), a PET conversion of 87.3% was reached. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43920.

**KEYWORDS:** catalysts; degradation; ionic liquids; polyesters; recycling

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### INTRODUCTION

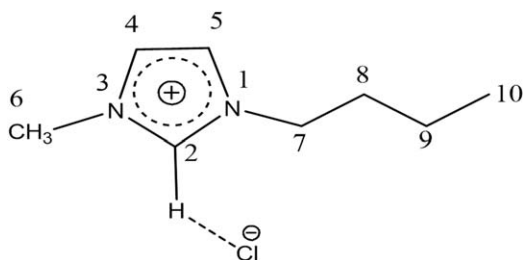
Polyethylene terephthalate (PET) is widely used as a packaging material in the food and beverage industries.<sup>1</sup> From 2000 to 2010, world demand for PET increased from 27.6 to 56.0 million tons. According to statistics on the production and processing of polyester, PET now accounts for 8% by weight and 12% by volume of the world's solid waste.<sup>2</sup> The inferior biodegradability of PET waste is a serious and growing environmental pollution hazard.

During the past several decades, extensive research to address the PET waste problem has been initiated in industrial and academic research laboratories. PET chemical recycling methods such as hydrolysis,<sup>3</sup> glycolysis,<sup>4–8</sup> methanolysis,<sup>9,10</sup> and aminolysis<sup>11–13</sup> have been investigated. These processes have produced a large variety of valuable products, such as monomers (for production of PET), polyols, polyesters, or oligoesters, which can be successfully utilized to generate new polymers such as saturated and unsaturated polyesters,<sup>14</sup> alkyd resins,<sup>15</sup> polyurethanes,<sup>16–18</sup> and polyisocyanurate foams.<sup>19</sup>

Ionic liquids show promise as environmentally friendly and less hazardous solvents or catalysts in chemical industries. Ionic

liquids have been widely used in extraction,<sup>20</sup> catalysis,<sup>21</sup> electrochemistry,<sup>22</sup> and organic synthesis.<sup>23,24</sup> In 2002, Deng *et al.* first reported that ionic liquids can be used as catalysts in the depolymerization of polycarbonate.<sup>25</sup> Chloroaluminate (III) ionic liquids have been reported to be used in the catalytic cracking of polyethylene to light alkanes.<sup>26</sup> Kamimura *et al.*<sup>27</sup> have employed quaternary ammonium ionic liquids to depolymerize polyamide plastics, and the caprolactam monomer was obtained. Ionic liquids not only display catalytic effectiveness in the degradation process, but they can also be used as solvents. Some imidazolium ionic liquids were used as a catalyst for the glycolysis of PET to bis (hydroxyethylterephthalate) and minor amounts of dimer and oligomers.<sup>28,29</sup>

Over the past decade, the rapid rise in cost of petroleum-based raw materials has rekindled interest in using renewable raw materials, such as natural oils in PET chemical recycling methods. For example, natural oils and their derivatives bearing active functional hydroxyl groups have been successfully applied as raw materials in polyurethane synthesis.<sup>30–32</sup> However, only little has been published about the use of natural oil-based chemicals for polymer degradation. Patel *et al.* and Hynek Benes



**Figure 1.** Structure of butyl methyl imidazolium chloride ionic liquid.

*et al.* reported on a successful PET degradation process to form polyester polyol (PE polyol) using castor oil, but this expensive oil results in high cost products.<sup>33,34</sup> Furthermore, the catalysts used in their research cannot be recovered and thereby heightens the environmental problem.

In this article, we describe a new method for the conversion of PET waste. It involves the formation of PE polyol by reacting waste PET and glycerides of soybean oil fatty acid using an ionic liquid catalyst. Because of the lack of hydroxyl groups in soybean oil, glycerol was also used during the degradation of PET waste. Our effort was to develop a soft condition process of PET using ionic liquid catalyst and a renewable natural oil-based reagent, such as soybean oil, the cost of producing the PE polyol product is reduced.

The organization of this article is as follows:

In experimental section, we described (i) the synthesis and characterization of the ionic liquid used in this study, (ii) the protocol used for the degradation of PET waste to PE polyol, (iii) the purification and reuse of the ionic liquid after PET degradation, and (iv) the spectroscopic characterization of the polymeric products.

In results and discussion section, we provide a detailed description of the synthesis of the ionic liquid 1-n-butyl-3-methylimidazolium chloride [(BMIM)Cl] and its characterization using FTIR, <sup>1</sup>H-NMR (Nuclear magnetic resonance), <sup>13</sup>C-NMR, and mass spectra. The characterization of the reaction products during PET degradation is undertaken using FTIR, mass spectroscopy (MS), thermogravimetric and differential thermal analysis (TGA and DTA), and gel permeation chromatography (GPC). Based on the

characterization, we propose a reaction scheme for the degradation of PET waste.

In this section, we also discuss key factors that influence the PET conversion. These include the glycerol content used in the transesterification step, the specification of the PET degradation time, and the specification of the degradation temperature. We conclude this section with a discussion on the reusability of the ionic liquid ([BMIM]Cl) and its chemical characterization.

## EXPERIMENTAL

### Materials

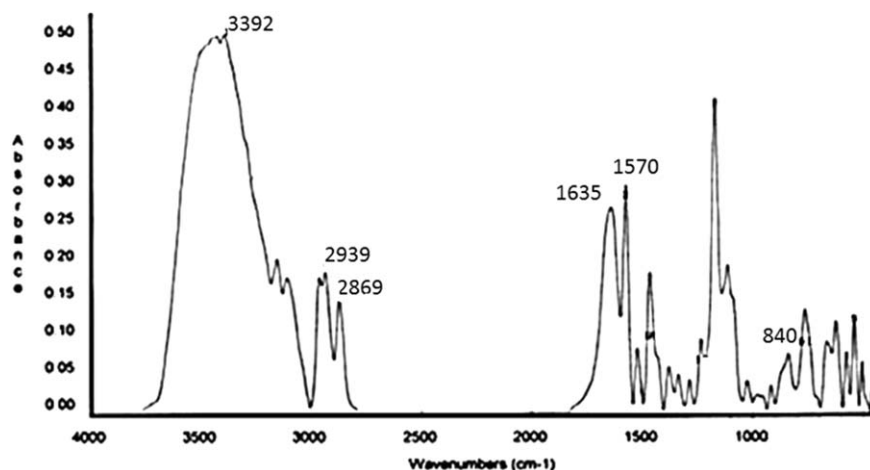
PET waste composed of clear drinking bottles was washed with water, dried, chopped to pieces about 5 mm × 5 mm and washed again with ethanol. Soybean oil was supplied by Cai Lan Oils and Gases Industries Company, Vietnam and was used as received as a reagent for the PET degradation. 1-methylimidazol 99.5% and 1-chlorobutane 99.5% were supplied by Merck Schuchardt OHG, Germany. Ethanol, ethyl acetate, ammonium acetate, and glycerol were supplied by the Guangdong Guanghua Chemical Factory, China and used without any further purification.

### Synthesis of Ionic Liquid

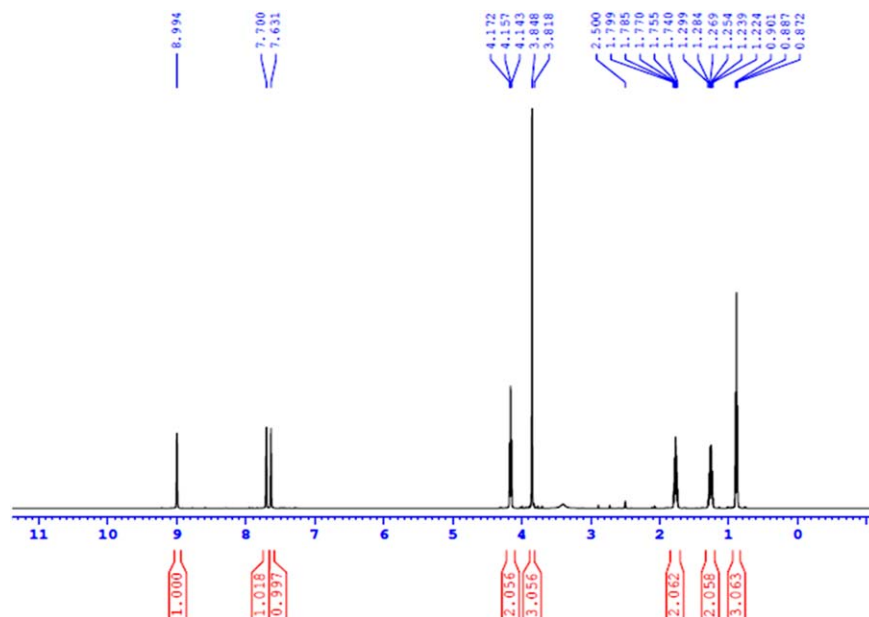
Equimolar amounts of 1-methylimidazol and 1-chlorobutane were added in a flask containing a magnetic stir bar. The flask was connected to a reflux condenser and immersed in an oil bath. The reaction mixture was stirred for about 100 h at 70 °C. Unreacted material was removed under vacuum at 110 °C. The residual ionic liquid was washed three times with ethyl acetate and then dried under vacuum at 110 °C. The ionic liquid obtained was characterized using FT-IR spectroscopy, MS, and NMR spectra <sup>1</sup>H-NMR, <sup>13</sup>C-NMR.

### Conversion of PET Waste to PE Polyol

**Transesterification of Soybean Oil with Glycerol.** The conversion of PET waste was performed in a three-necked-round bottom flask fitted with a stirrer, a reflux condenser, and a thermometer. For the transesterification, soybean oil, ionic liquid, and glycerol were introduced in the flask and the mixture reaction was stirred and heated at 180 °C in 8 h.



**Figure 2.** FTIR of synthesized [BMIM]Cl ionic liquid.

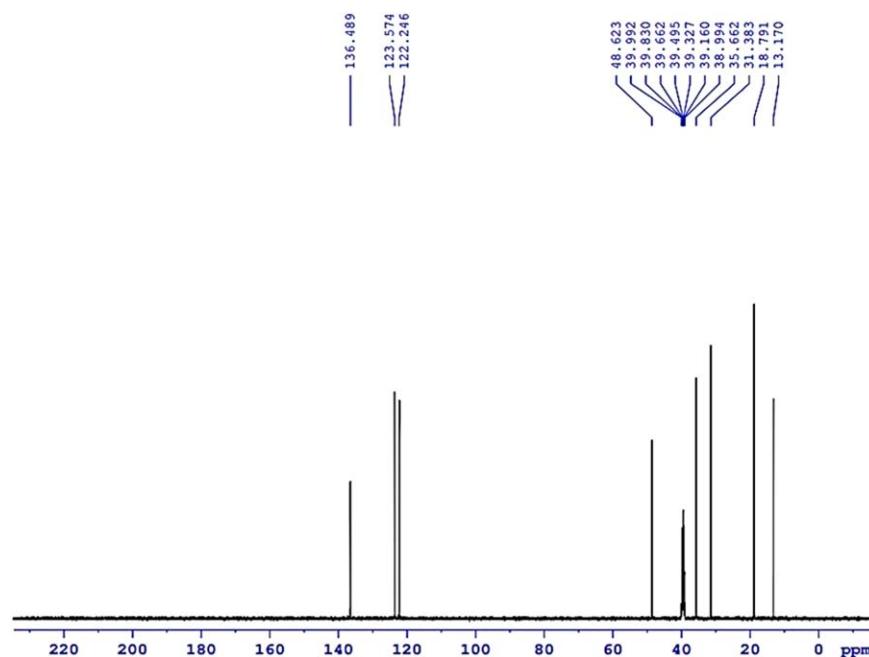


**Figure 3.**  $^1\text{H-NMR}$  of synthesized ionic liquid [BMIM]Cl. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

**Degradation of PET Waste to PE Polyol.** Then pretreated PET was added and the obtained mixture was stirred and heated during the reaction time. After the reaction time had ended, the reaction mixture was cooled to room temperature and dissolved in ethyl acetate. Ionic liquid and unconverted PET that stood in the lower layer was separated. The upper layer that contained product dissolved in ethyl acetate was heated and washed several times with hot water to remove oligomers of PET and unconverted glycerol. Then, the obtained liquid was heated under reduced pressure to remove ethyl acetate and trace water to get PE polyol.

The PE polyols obtained were characterized using FT-IR spectroscopy, MS, GPC, TGA, and DTA.

**Purification of Ionic Liquid and Calculation of Conversion and Yield.** The mixture of ionic liquid and unconverted PET (the lower layer obtained after dissolving) was dissolved in water. The residue, which is unconverted PET, was washed with water for several times, dried, and weighed for the calculation of PET conversion. The obtained liquor was heated under vacuum to remove water. The spent ionic liquid was characterized by FT-IR and reused for degradation of PET.



**Figure 4.**  $^{13}\text{C-NMR}$  of synthesized ionic liquid [BMIM]Cl. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

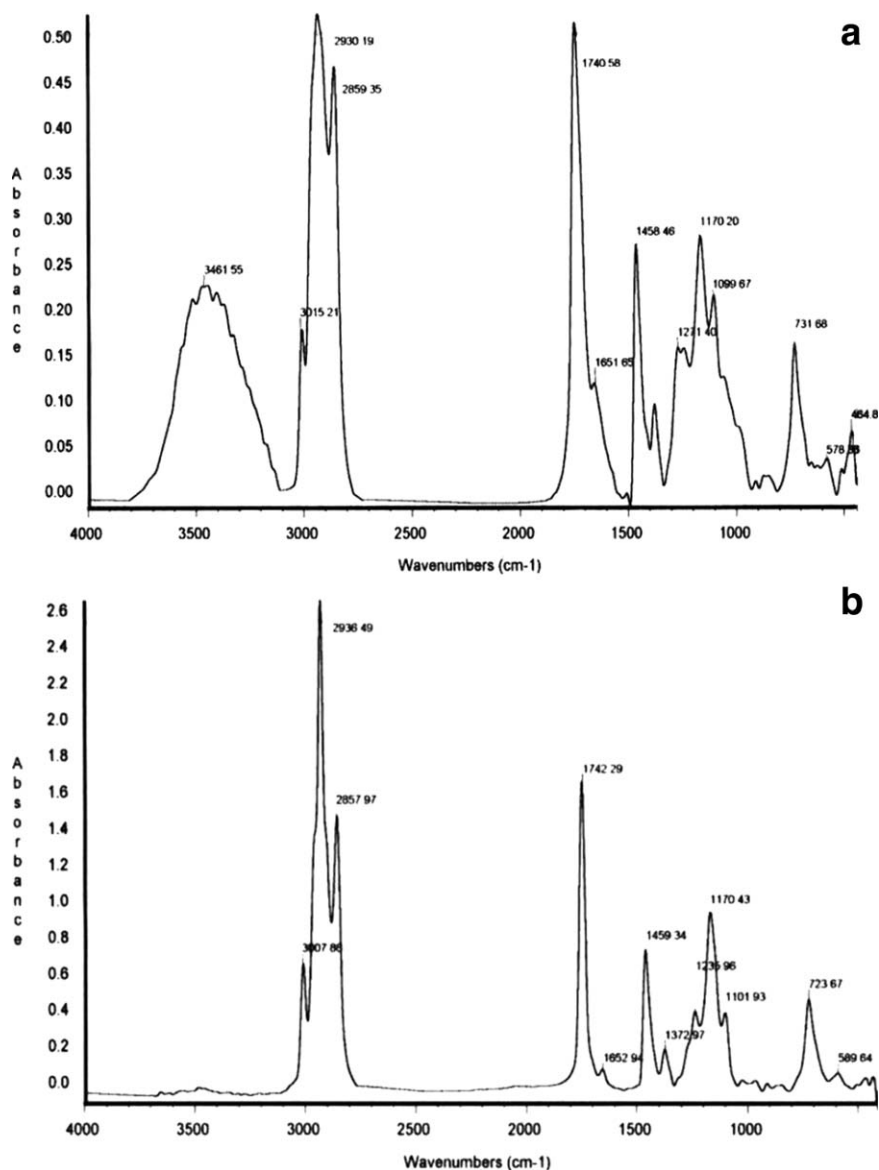


Figure 5. (a) FTIR of polyester polyol. (b) FTIR of soybean oil.

The conversion of PET can be determined by:

$$C_{\text{PET}} = \frac{W_1 - W_2}{W_1} \times 100\% \quad (1)$$

where  $W_1$  represents the initial weight of of PET and  $W_2$  represents the weight of residual PET.

### Characterization

**Spectroscopic Analysis of Ionic Liquid and Polymeric Products.** Infrared (IR) spectra of the prepared products were measured using an IMPAC 410 spectrometer (Nicolet). The samples were measured using the method of a KBr pellet. Mass spectra of the prepared products were measured by LC/MS/MS-Xevo TQMS, ESI (for PE polyol) and LC/MS/MS-Xevo, API-ESI (for ionic liquid) spectrometers in MeOH. TGA and DTA were performed using a Shimadzu TGA-504. NMR spectra  $^1\text{H}$ -NMR,

$^{13}\text{C}$ -NMR were measured using Bruker Avance in DMSO (for ionic liquid) and in MeOD (for PE polyol) solutions.

### Reversed Phase High Performance Liquid Chromatography of Transesterification Products.

Transesterification products were determined with a reversed-phase high-performance liquid chromatography (RP-HPLC) Aligent 1200 series. The chromatographic separation was carried out with a  $\text{NH}_2\text{C}_{18}$ (-Si-C18) column ( $250 \times 4.6$  mm). The effluent was monitored by a refractive index detector. Gradient elution was achieved by mobile phases A (acetonitrile:acetic acid = 99.95:0.05, v/v), B (dichloromethane), C (water), by volume. The course of the gradient was as followed: 0–2 min: 80% A and 20% C; 2–12 min: change to 100% A; 12–20 min: change to 70% A and 30% B; 20–26 min: maintain 70% A and 30% B; 26–35 min: change to 30% A and 70% B; 35–37 min: maintain 30% A and 70% B;

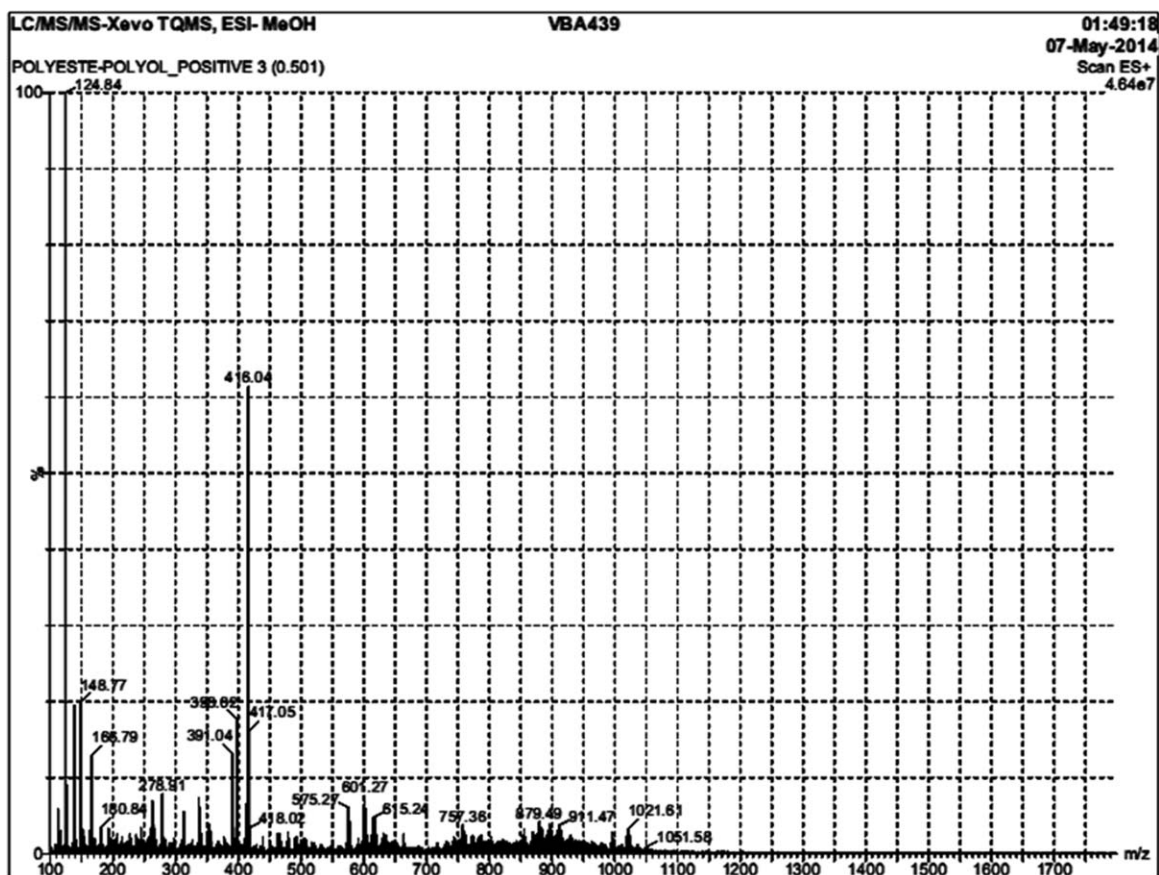


Figure 6. Mass spectroscopy of PE polyol.

37–39 min: change to 100% A; 39–42 min: maintain 100% A. The injection volumes of 10  $\mu\text{L}$  and the elution flow-rate of 1 mL/min were used in all experiments.

Compounds were identified by HPLC-MS ion trap Agilent 1100 with RP C18 column (250  $\times$  4.6 mm). The HPLC conditions were the same as described above.

**GPC of PE Polyol Products.** The molecular weights of PE polyols were determined using the GPC technique with a Perkin Elmer GPC 50Plus–Varian at 30  $^{\circ}\text{C}$  using a mesopore 7.5  $\times$

**Table I.** Structures of the Product from PET Degradation with Soybean Oil and Glycerol (180  $^{\circ}\text{C}$ ; 16 h; Soybean Oil/Glycerol Mass Ratio = 2; Soybean Oil/PET Mass Ratio = 2.1)

$m/e$	$\Delta m/e$	Ion fragments
1051.58		
1021.61	29.97	$-\text{C}_2\text{H}_5$
757.36	264.25	$\text{R}-\text{C}(\text{O})-$
601.27	156.09	$-\text{C}_6\text{H}_4\text{C}(\text{O})\text{O}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}-$
575.27	28.00	$-\text{C}=\text{O}$
416.04	159.23	$-\text{CH}_2\text{OC}(\text{O})\text{C}_6\text{H}_4\text{C}(\text{O})-$
398.02	16.02	$-\text{O}-$
278.91	119.11	$-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{OC}(\text{O})-\text{CH}_2-$
124.84	154.07	$-\text{C}_6\text{H}_4-\text{C}(\text{O})\text{O}-$

300 mm column with integrated refractive index detector. Tetrahydrofuran was used as mobile phase at a flow rate of 1 mL  $\text{min}^{-1}$ . Polystyrene standards with weight-average molecular weights ( $M_w$ ) of 500, 1000, 3000, and 10,000 were used for calibration.

## RESULTS AND DISCUSSION

### Characterization of Synthesized Ionic Liquid

The ionic liquid was formed in an approximately 86% yield. It was characterized by FT-IR,  $^1\text{H}$ -NMR,  $^{13}\text{C}$ -NMR, and mass spectra. The structure of the butyl methyl imidazolium chloride ionic liquid is given in Figure 1.

**FTIR Spectroscopy.** The FTIR spectroscopy of synthesized ionic liquid is shown in Figure 2. The bands of wave numbers at 2939  $\text{cm}^{-1}$  and 2869  $\text{cm}^{-1}$  are the aliphatic asymmetric and symmetric (C–H) stretching vibrations due to methyl groups. A broad band in the range 3392–3450  $\text{cm}^{-1}$  comes from the quaternary amine salt formation with chloride. C=C and C–C stretching is shown by wave numbers 1635  $\text{cm}^{-1}$  and 1570  $\text{cm}^{-1}$ . The band at wave number 840  $\text{cm}^{-1}$  is due to the C–N stretching vibration.

**$^1\text{H}$ -NMR,  $^{13}\text{C}$ -NMR, and Mass Spectra.**  $^1\text{H}$ -NMR data are shown in Figure 3 in ppm ( $\delta$ ) from the internal standard (TMT, 0.0 ppm), chemical shift (multiplicity, integration).  $^{13}\text{C}$ -NMR data are shown in Figure 4 in ppm ( $\delta$ ) from the internal standard (TMS, 0.0 ppm).



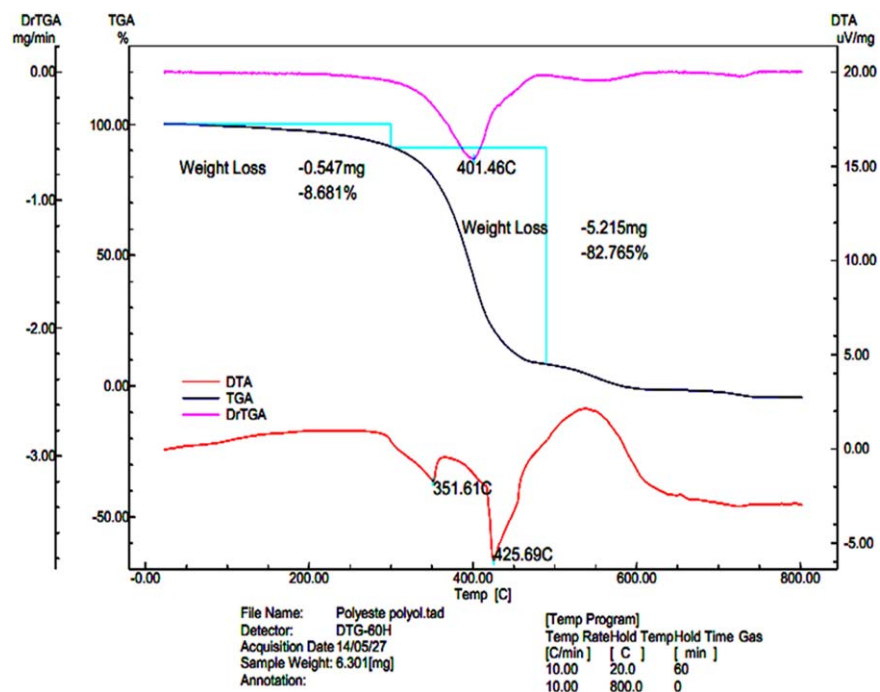


Figure 7. TGA and DTA of PE polyol. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

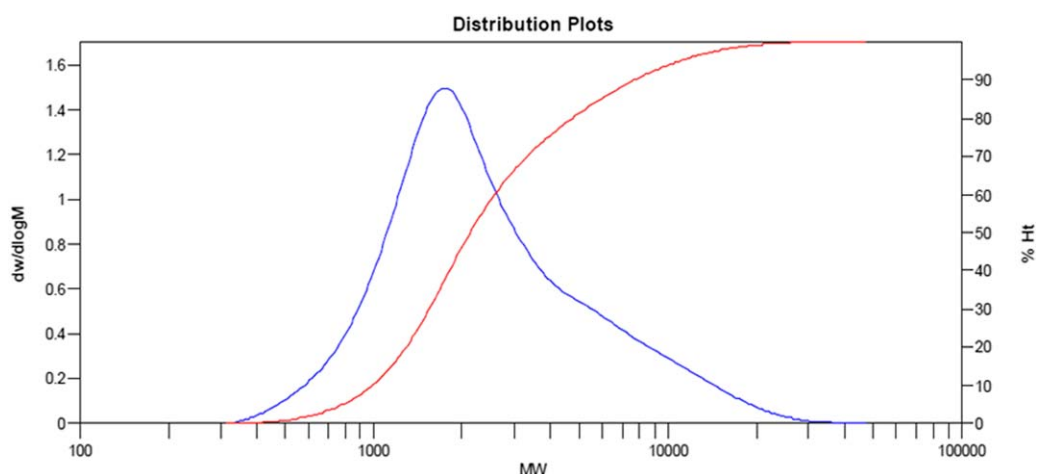


Figure 8. The molecular weight distribution of product polyester polyol (by GPC). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

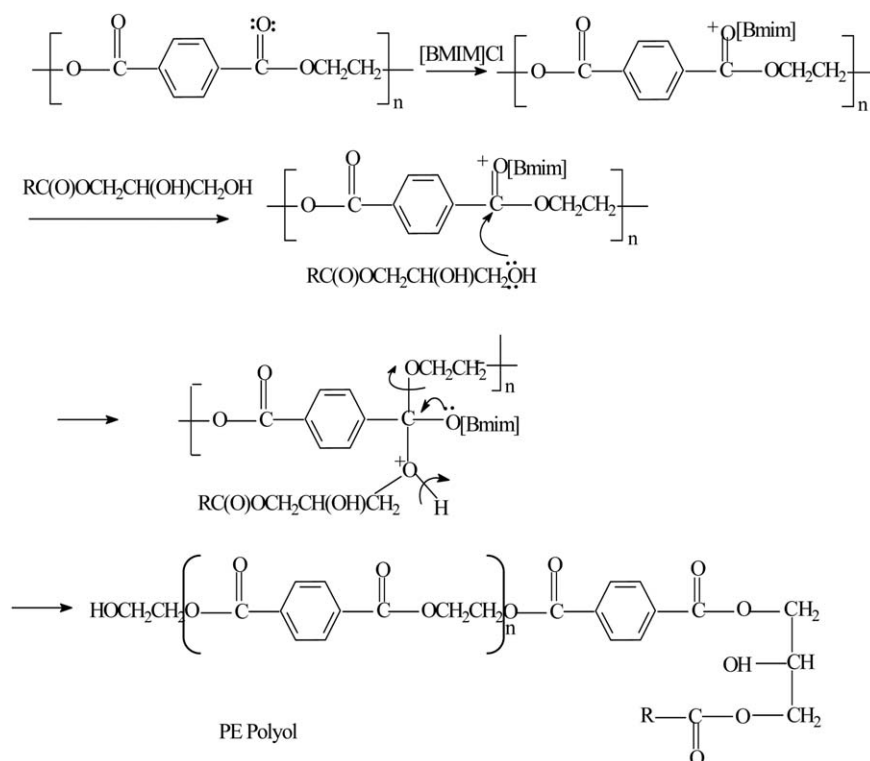
The results of  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  analysis of [BMIM]Cl are given as follows:

$^1\text{H-NMR}$  (500 MHz, DMSO- $d_6$ )  $\delta$  (ppm): 8.994 (1H, s, C(2)H), 7.7 (1H, m, C(4)H), 7.631 (1H, m, C(5)H), 4.143–

4.172 (2H, t, N(1)–CH $_2$  (C7)), 3.848 (3H, s, NCH $_3$  (C6)), 1.740–1.799 (2H, m, NCH $_2$ CH $_2$  (C8)), 1.224–1.299 (2H, m, N(CH $_2$ ) $_2$ CH $_2$  (C9)), 0.872–0.901 (3H, t,  $J = 7.3$  Hz, N(CH $_2$ ) $_3$  CH $_3$  (C10)).

Table II. The Molecular Weight Distribution of Product Polyester Polyol Determined by GPC

Number average molecular mass of polymer ( $M_n$ ), Da	Weight average molecular mass ( $M_w$ ), Da	Polydispersity index (PD = $M_w/M_n$ )	Z average molar mass ( $M_z$ ), Da	Viscosity average molar mass ( $M_v$ ), Da
1856	3418	1.84	7209	3056



**Scheme 1.** Transesterification of soybean oil with glycerol.

$^{13}\text{C}$  NMR (125Mz, DMSO)  $\delta$  (ppm): 136.489 (C2), 123.533 (C4), 122.267 (C5), 49.340 [N(1)— $\text{CH}_2$  (C7)], 35.714 [(N(3)— $\text{CH}_3$  (C6)], 31.319 [N(1)— $\text{CH}_2\text{CH}_2$  (C8)], 18,791 [N(1)— $\text{CH}_2\text{CH}_2\text{CH}_2$  (C9)], 13,170 [N(1)— $(\text{CH}_2)_n\text{CH}_3$  (C10)].

The mass spectrum showed the fragment of  $m/z$ : 139 [BMIM] $^+$ . Based on FT-IR, NMR, and mass spectra, it was determined that synthesized IL is [BMIM]Cl.

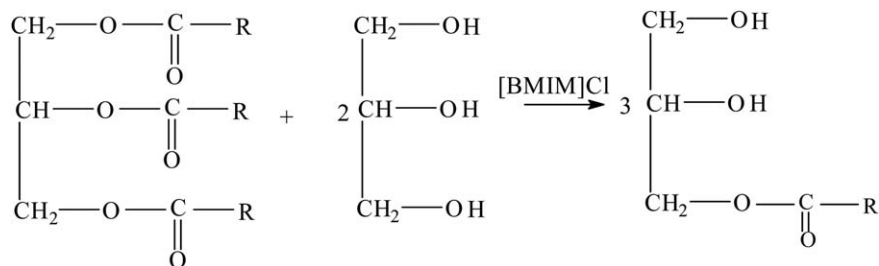
### Characterization of Products

**FTIR Spectroscopy.** PE polyol formation by reaction of waste PET and glycerides of soybean oil fatty acid in the presence of glycerol was confirmed by FT-IR spectra analysis [Figure 5(a)]. A sharp band at  $1742.29\text{ cm}^{-1}$  confirms the polyester formation. A band at  $1154.98\text{ cm}^{-1}$  shows the presence of a C—O bond in an ester group. The band at  $3436.04\text{ cm}^{-1}$  is due to the presence of free hydroxyl groups in the polyols. This can be directly compared with the soybean oil FT-IR spectra which does not contain any band around  $3436.04\text{ cm}^{-1}$  [Figure 5(b)].

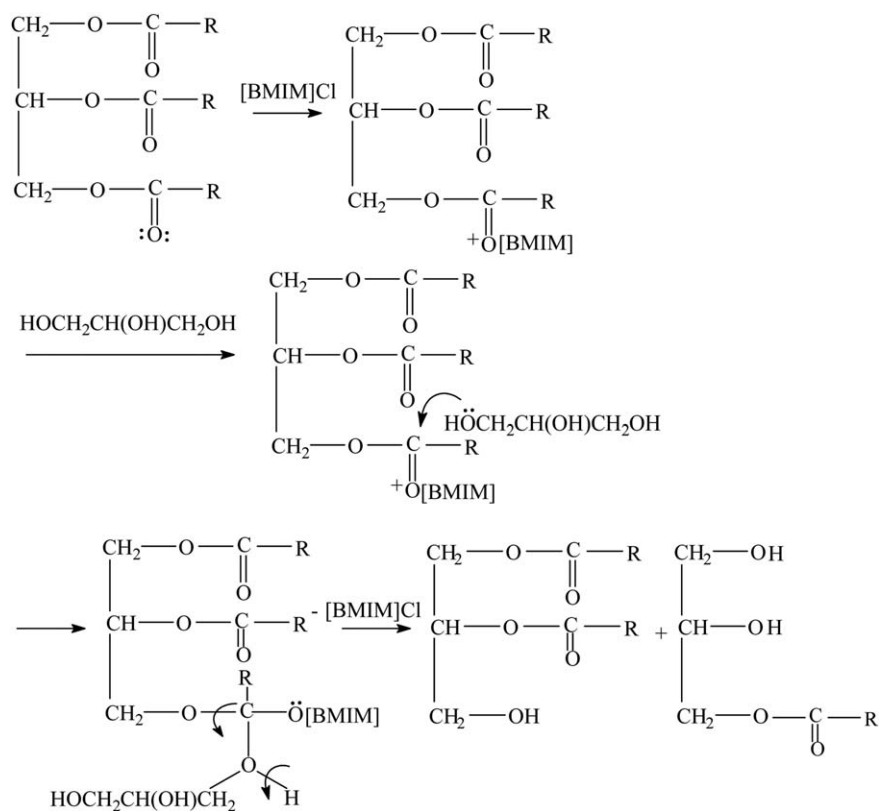
Similar results were reported by Patel *et al.*<sup>33</sup> in the PE polyol FT-IR spectra such as a sharp band at  $1736\text{ cm}^{-1}$  (confirming the polyester formation) and the band at  $3435.8\text{ cm}^{-1}$  (due to the presence of free hydroxyl groups).

**Mass Spectroscopy.** Figure 6 and Table I show the mass spectroscopy of the resulting PE polyol. The found fragments in the spectroscopy show the presence of groups of atoms that should be included in PE polyol. Especially noteworthy, the fragment  $m/z = 264.25$  shows the presence of an R—C(O)— group in linoleic acid which exists at a level of 49% in fatty acids of soybean oil.

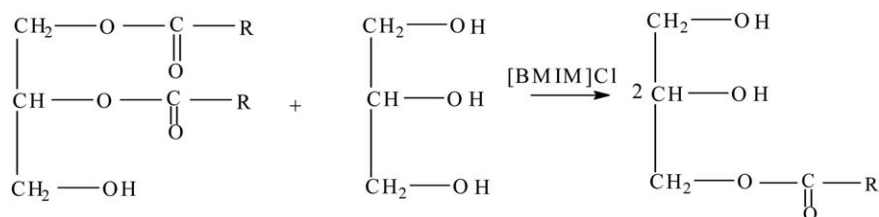
**TGA and DTA.** TGA and DTA results for the PE polyol are given in Figure 7. The trough in the DTA curve shows an endothermic process during the heat exchange. This endothermic phenomenon is mainly due to the degradation of the PE polyol, and may include contributions from the evaporation of the volatile substances such as ethyl acetate and water. The TGA curve shows two temperature ranges in which the PE polyol sample



**Scheme 2.** Reaction detail between soybean oil and glycerol.



**Scheme 3.** Transesterification of monoglyceride of soybean oil with glycerol.



**Scheme 4.** The formation of PE polyol.

lost weight. The loss of weight started around 80 °C where the PE polyol lost 0.547 mg corresponding to 8.681% by weight. The loss may be due to the evaporation of ethyl acetate or water products. The main weight loss began around 351.61 °C with the maximum loss rate at 425.69 °C due to the degradation of PE polyol. About 82.765% by weight of the PE polyol was lost during this temperature range. The weight loss continued to about 600 °C. The bottom of the DTA curve at 401.46 °C shows

that the maximum endothermic process occurs at this temperature, indicating the formation of more volatile compounds during the decomposition of PE polyol.

The TGA and DTA experiments show that PE polyol is thermally stable, an important fact for coating and composite applications.

**Table III.** influence of Glycerol Content (Used in Transesterification Step) on PET Conversion (180 °C; 8 h; Soybean Oil/PET Mass Ratio = 2.1)

Run	Mass of soybean oil (g)	Mass of glycerol (g)	Soybean oil/glycerol mass ratio	PET conversion (wt %)
1	12.5	1.7	8	30.6
2	12.5	3.4	4	52.8
3	12.5	5.3	2	87.3

**Table IV.** Influence of Degradation Time on PET Conversion (Soybean Oil/PET Mass Ratio = 2.1)

Run	Temperature (°C)	Time (h)	Soybean oil/glycerol mass ratio	PET conversion (wt %)
1	180	6	2	63.3
2	180	7	2	76.4
3	180	8	2	87.3
4	180	9	2	90.5



**Table V.** Influence of Degradation Temperature on PET Conversion (Soybean Oil/PET Mass Ratio = 2.1)

Run	Temperature (°C)	Time (h)	Soybean oil/glycerol mass ratio	PET conversion (wt %)
1	160	8	2	63.6
2	170	8	2	74.6
3	180	8	2	87.3
4	190	8	2	90.4

**RP-HPLC Analysis.** The RP- HPLC results show that the transesterification products are mixtures of monoglycerides, diglycerides, and triglycerides. Almost glycerides of fatty acids in soybean oil are detected. The products contain 51% monoglyceride, 49% of diglycerides and triglycerides.

**Gel Permeation Chromatography.** The molecular weight distribution of the PE polyol product synthesized at optimum condition is shown in Figure 8 and Table II. The GPC shows that the high molecular weight PE polyols were the predominant species. The number average molecular mass of polymer ( $M_n$ ), the

weight average molecular mass ( $M_w$ ), and the polydispersity distribution ( $PD = M_w/M_n$ ) were as follow:  $M_n = 1856$  Da,  $M_w = 3418$  Da, and  $M_w/M_n = 1.84$ .

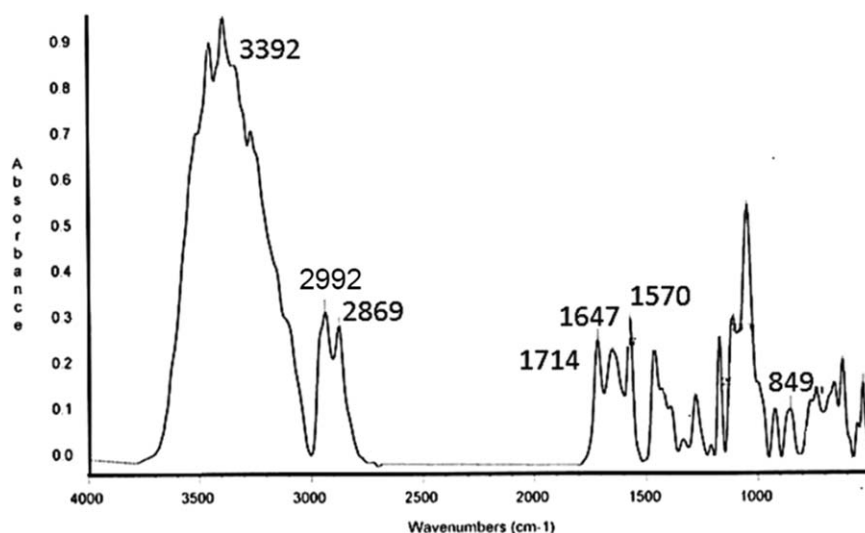
### Proposed Process Reactions

The reaction scheme for the degradation of PET waste is proposed as follows:

Firstly, the transesterification of soybean oil with glycerol could be acidic catalyzed by [BMIM]Cl (Scheme 1).

The details are as follows: soybean oil and glycerol react with a 1:1 ratio (Scheme 2).

The cation [BMIM]<sup>+</sup> would attack the carbonyl oxygen and thus make the carbonyl group more susceptible to nucleophilic attack. Meanwhile, the attachment of the oxygen atom of glycerol onto the carbonyl carbon of the ester of soybean oil is easier. Next is the removal of the [BMIM]<sup>+</sup> cation. Then the intermediate product transfers to diglycerides and monoglycerides of fatty acid. It could be that the diglyceride product can react further with a glycerol molecule to form two molecules of monoglyceride  $\text{OHCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OCOR}$  (Scheme 3). This can occur because the molar ratio of glycerol to soybean oil is about 4:3.

**Figure 9.** FT-IR of recycled ionic liquid [BMIM]Cl.**Table VI.** Wave Numbers of Typical Peaks in FT-IR Spectra of Ionic Liquids (soybean Oil/PET Mass Ratio = 2.1)

Wave numbers of typical peaks ( $\text{cm}^{-1}$ )			
Synthesized [BMIM]Cl	Recovered [BMIM]Cl	[BMIM]Cl in Ref. 35	Groups
3392-3450	3390-3450	3330-3450	quaternary amine salt
2993 and 2869	2990-2866	2973-2870	(C-H) in methyl group
	1714		C=O
1635	1647	1635	C=C
1570	1571	1600	C-C
840	849	840	C-N

**Table VII.** Reusability of [BMIM]Cl Catalyst in Conversion of PET to PE Polyol (Soybean Oil/PET Mass Ratio = 2.1)

Number of IL recycling	Temperature (°C)	Time (h)	Soybean oil/glycerol mass ratio	PET conversion (wt %)
0	180	8	2	87.3
1	180	8	2	86.4
2	180	8	2	85.9
3	180	8	2	84.8

Next  $\text{OHCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OCOR}$  could react with waste PET following a similar mechanism to previous steps and also acidic catalyzed by [BMIM]Cl (Scheme 4).

### Influence of Some Factors on PET Conversion

**Influence of Glycerol Content (Used in the Transesterification Step).** The influence of glycerol content on PET conversion is summarized in Table III. PET conversion increases with increasing glycerol concentration. The results show that PET conversion reaches 87.3% when the mass ratio of oil:glycerol is 2:1, which is expected based on the stoichiometry of the proposed mechanism, as described below.

Glycerol is used to supply  $-\text{OH}$  groups to soybean oil through transesterification. The lower content of glycerol results in a smaller amount of  $\text{OHCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OCOR}$  formed (Scheme 3) and a high content of obtained diglyceride and unconverted soybean oil in the first step, which leads to lower PET conversion because there is not enough  $\text{OHCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OCOR}$  substance for PET cleavage in the second step (Scheme 4).

When the glycerol concentration is increased, there is a concomitant increase in the concentration of  $\text{OHCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OCOR}$  which in turn promotes the cleavage of PET. However, since glycerol is itself a PET cleaving agent,<sup>7</sup> excess glycerol leads to glycolysis of PET catalyzed by the ionic liquid [BMIM]Cl to form oligomers of PET other than PE polyol.<sup>29</sup> Furthermore, unconverted glycerol impedes the recovery of ionic liquid [BMIM]Cl. For these reasons, the soybean oil:glycerol mass ratio was maintained at 2:1 in this study.

**Influence of PET Waste Degradation Time.** In this work, the degradation time was varied from 6 to 9 h. The results from Table IV show that PET conversion increases with increasing degradation time. PET conversion changed from 63.3 to 87.3% when the degradation time was increased from 6 to 8 h. However, if the degradation time is extended to 9 h, a slight reduction in the amount of produced PE polyol was observed. This is because cleavage of PET increases with time to form shorter chain compounds (oligomers or dimers), which can dissolve in hot water during refining of the products.

**Influence of PET Waste Degradation Temperature.** The influence of degradation temperature (160–190 °C) on PET conversion is summarized in Table V. The results show that the degradation temperature on PET conversion has similar characteristics of reaction temperature on glycolysis PET<sup>29</sup> using the same ionic liquid [BMIM]Cl. The temperatures for PET conver-

sion using ionic liquid in both these cases (160–190 °C) are lower than those when metal salt catalysts are used (220–250 °C).<sup>7</sup> Clearly, high reaction temperature enhances the degradation of PET to form PE polyol. The PET conversion increases from 63.6 to 90.4% when raising the reaction temperature from (160 to 190 °C). However, it appears that there is no benefit to having degradation temperatures of 190 °C or higher because ionic liquids are unstable at these temperatures. Furthermore, the PET conversion increased only slightly from 180 to 190 °C.

### Reusability of [BMIM]Cl

After separation and refining products, the ionic liquid was recovered from the aqueous solution by evaporation of the volatile compounds under reduced pressure. The recovered [BMIM]Cl was characterized by FT-IR spectra (see Figures 2 and 9) to confirm its structure with published spectra of [BMIM]Cl.<sup>35</sup> The recovered [BMIM]Cl spectra shows that all peaks responsible for the presence of typical groups were found (Table VI). Note that the presence of band at  $1714\text{ cm}^{-1}$  in the recovered ionic liquid spectrum shows that the recovered ionic liquid does become contaminated by a small amount of oil.

The catalytic activity of the recovered [BMIM]Cl was also investigated. After the reaction time had ended, the product was separated and ionic liquid was recovered and reused. This procedure was repeated three times. The results in Table VII show that the PET conversion was slightly reduced after each reaction cycle, suggesting that after every run a small amount of ionic liquid should be added to compensate for the decrease in catalytic activity.

## CONCLUSIONS

This article demonstrates that low price, renewable, and readily available soybean oil and glycerol can be used as effective reagents for the degradation of waste PET. This process produces the depolymerization of the PET chain. The ionic liquid [BMIM]Cl was found to be an efficient catalyst. A long degradation time leads to significant PET decomposition into oligomers. Nevertheless, great attention must be paid to the precise control of the degradation temperature. The optimal temperature range for PET degradation is from 180 to 190 °C, which is lower than the degradation temperature used for other catalysts (220–250 °C). The high reusability of the ionic liquid helps to reduce the cost and environmental pollution, making ionic liquids preferred over currently used metal salt catalysts.

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