STUDY ON METHANOLYSIS OF WASTE POLY(ETHYLENE TEREPHTHALATE) IN IONIC LIQUID

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Abstract: The methanolysis of poly(ethylene terephthalate) (PET) was studied using ionic liquid 1- n-butyl-3-methylimidazolium chloride as solvent and zinc acetate as catalyst. The effects of reaction temperature, time, dosages of solvent and catalyst on methanolysis results were examined. The obtained optimum reaction conditions were reaction temperature 160℃, reaction time 3h, m(solvent):m(PET)=2:1, m(zinc acetate):m(reaction mixture)=1:20. Under above conditions, the conversion of PET could reach 100%. After easily separated from the product, the system of solvent and catalyst could be reused 8 times without obvious decrease in conversion of PET. Therefore, an environmental friendly approach for methanolysis of waste PET was developed.

1. Introduction

Over the last decades, polyester (PET) consumption has tremendously increased due to its ever-increasing use in fiber manufacturing and packaging. With the rapid increase of production and consumption of PET, the problem about the treatment of waste PET is now an important issue in the world [1-2]. For the purpose of chemical recycling of waste PET, there have been reported a number of degradation methods [3-6], among which methanolysis of PET is an important one. However, due to the insolubility of PET in methanol, the methanolysis of PET require severe conditions such higher temperature and pressure [7-8] or even under supercritical conditions[9-10]. Therefore, its application is limited. it is necessary to explore a new approach for methanolysis of PET.

The room temperature ionic liquid, a kind of environmental friendly solvent and catalyst, due to its adjustable physical and chemical properties, got broadly attention of scholars from various fields such as synthesis, catalysis and separation [11-13]. But to the best of our knowledge, no article about ionic liquid used in hydrolysis of PET has been published. In this paper, we prepared several ionic liquids (Fig. 1) and used them in methanolysis of PET. The results showed that 1-butyl-3- methylimidazolium chloride was a good solvent for methanolysis of PET.

2. Experimental

2.1 Chemicals and instruments

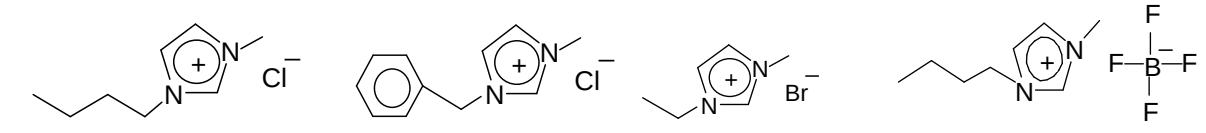
PET powder of 0.1-0.3mm was prepared from commercial PET pellets (Ø2.5x3mm, Mw=30000). n-Methylimidazole (MIM, 99%), n-butylchloride and other chemicals (AR) were commercially available and used without further purification. The IR spectra were recorded by a Nicolete 510P FT-IR spectrometer in the range of 4500-400cm^{-1}.

2.2 Synthesis Procedure for Synthesis of [Bmim][Cl]

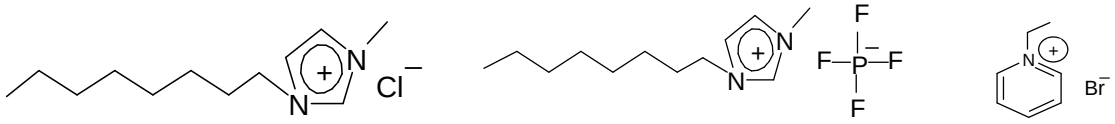
A mixture of 1-methylimidazole and n-butylchloride in a 1:1.2 molar ratio was reacted with stirring at 70℃ for 72 h. The mixture was washed by ethyl acetate for three time to remove the unreacted starting materials and then distilled at 70℃ under reduced pressure (10 mmHg) over 2 h to obtain [Bmim][Cl](yield 95%). [Bymim][Cl], [Omim][Cl], [Emim][Br] and [Epydin][Br] were prepared with a similar procedure. [Bmim][BF_4] and [Omim][PF_6] were synthesized according to the references[14-16].

2.3 Metholysis of PET

Weighed amounts of PET (w_1), methanol and ionic liquids were added in an autoclave with a stirrer and a thermometer. The mixture was heated up to the given temperature for certain time. The reaction mixture was filtered to remove the unreacted PET (w_2). The obtained filtrate was diluted with an equal volume of water and a precipitate was obtained and filtered. The obtained filtrate was distilled under vacuum to remove water and ethanediol, the residue which is mainly composed of ionic liquid and catalyst was reused directly as solvent and catalyst. The filter cake which is mainly composed of dimethyl terephthalate(DMT) was dried to obtain DMT product (w_3). Conversion of PET and yield of DMT were calculated by following formula: Conversion of PET = $[(w_1–w_2) / w_1]$ x 100%. Yield of DMT = (w_3 / w) x 100%, where w is the weight of DMT that should obtained theoretically.



[Bmim][Cl] [Bymim][Cl] [Emim][Br] [Bmim][BF_4]



[Omim][Cl] [Omim][PF_6] [Epydin][Br]

Fig. 1 Structures of ionic liquids prepared and used in this paper

3. Results and Discussion

3.1 Effect of ionic liquid solvent on metholysis results of PET

Tab. 1 Effects of different ionic liquids on methanolysis reaction. [a)]

Entry	Ionic liquids	Dosage(g)	PET conversion(%)	DMT Yield(%)
1	-[b)]	0	30.1	20.2
2	[Bmim][Cl]	6.0	100	88.7
3	[Bmim] [BF_4]	6.0	59.3	51.4
4	[Bymim][Cl]	6.0	58.3	49.9
5	[Omim][Cl]	6.0	91.8	83.4
6	[Omim][PF_6]	6.0	36.5	28.8
7	[Emim][Br]	6.0	94.1	88.6
8	[Epydin][Br]	6.0	37.7	30.1

[a)] PET 3g, CH_3OH 12g, $Zn(Ac)_2$ 1g, t=3h, T= 160 ^oC; [b)] Using another 6g CH_3OH instead of ionic liquid.

Tab.1 shows the effect of ionic liquid solvent on methanolysis results of PET. According to Tab.1, using ionic liquids [Bmim][Cl], [Emim][Br] or [Omim][Cl] as reaction medium (entries 2, 5 and 7), the conversions of PET were much higher than that of without ionic liquid as solvent (Tab.1 entry 1). Especially, [Bmim][Cl] exhibited an outstanding performance for methanolysis of PET. This is because the ionic liquids can improve the dissolubility of PET in the reaction system. It is difficult for PET to dissolve in methanol, so the reaction result was poor when no ionic liquid solvent was used. Moreover, we can see from Tab.1 that the cations and anions of ionic liquids have significant effect on hydrolysis results of PET.

3.2 Effect of PET particle size on hydrolysis results

Tab. 2 Effect of PET particle size on methanolysis results[a]

Particle size of PET	**PET Conversion (%)**	**DMT Yield (%)**
Ø2.5x3mm	77.7	69.3
0.40 mm	89.8	80.1
0.15 mm	100.0	88.7

[a)] PET 3g, CH_3OH 12g, $Zn(Ac)_2$ 1g, t=3h, T= 160 ^oC

Tab. 2 shows the effect of PET particle size on methanolysis results. According to Tab.2, the size of PET particle was of a significant influence on methanolysis results. With decreasing of the particle size, both the PET conversion and DMT yield increased greatly. Under the given conditions, when the particle size was Ø2.5x3mm, PET conversion only 77.7%. However, when the particle size became 0.15mm, the methanolysis of PET almost finished and DMT yield reached to 88.7%. This is because PET is a macromolecule and the

dissolving of PET in reaction mixture was very slowly. That is to say, the solubility of PET is the methanolysis reaction rate determining step. Therefore, the smaller the particle size of PET is, the more quickly the dissolving and methanolysis of PET are. On the other hand, PET with decreased particle size has increased surface area available for the reaction. Thus, the reaction rate is increased and greater PET conversion and DMT yield can be obtained.

3.3 Effect of temperature and solvent dosage on methanolysis results of PET

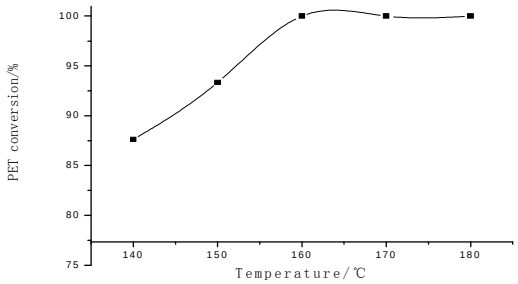


Fig. 1 Effect of reaction temperature on PET methanolysis results

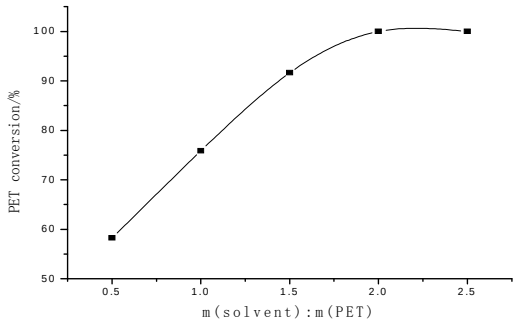


Fig. 2 Effect of solvent dosage on PET methanolysis results

The influences of reaction temperatures and solvent dosage on methanolysis results were examined and shown in Fig.1 and Fig.2. A great increase in PET conversion with increasing reaction temperature was observed (Fig.1). When temperature is 140℃, the PET conversion is only 87.5% after 3h. However, under the given conditions, when the temperature was increased to 160℃, the methanolysis of PET almost finished. It can be seen that with the increasing of [Bmim][Cl] dosage, PET conversion was gradually increased. Under the given conditions, when m([Bmim][Cl]):m(PET) =2:1, the methanolysis of PET almost finished.

3.4 Reusability results of system of solvent and catalyst

Tab. 3 Reusability results of system of solvent and catalyst [a)]

Cycle	1	2	3	4	5	6	7	8
PET conversion (%)	100	100	100	100	100	100	100	100
Yield of DMT (%)	88.9	88.0	88.8	87.9	88.7	88.7	88.1	88.6

[a)] PET 3g, CH_3OH 12g, $Zn(Ac)_2$ 1g, t=3h, T= 160 ^oC

The system of solvent and catalyst was easily separated from the reaction mixture and reused directly as solvent and catalyst. The reusability of the system of solvent and catalyst

for the methanolysis of PET was examined and the results were showed in Tab.3. The results showed that the system was reused for 8 times without obvious decrease in PET conversion and DMT yield. Therefore, the system of solvent and catalyst has excellent reusable performance in the methanolysis of PET.

4. Conclusion

The kind of ionic liquids used as solvent was of a significant influence on methanolysis results of PET. Among the ionic liquids examined, [Bmim][Cl] is an excellent reaction medium. A great increase in PET conversion was observed with increasing of [Bmim][Cl] dosage and reaction temperature. Under the optimum conditions of reaction temperature 160℃, reaction time 3h, m(solvent):m(PET)=2:1, m(zinc acetate):m(reaction mixture)=1:20, the conversion of PET and the yield of DMT were almost 100% and ≥88% respectively. After easily separated from the product, the system of solvent and catalyst could be reused 8 times without obvious decrease in the conversion of PET and yield of DMT.

Acknowledgements

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