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Depolymerization of waste nylon 6 in [Bmim]Cl/water mixture

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Abstract: Depolymerization of nylon 6 (PA 6) to obtain caprolactam in the mixture of water and ionic liquid ([Bmim]Cl) was a environmentally benign and high efficient method. There are two reasons for the using of ionic liquid: first is that high H^+ concentration in the mixture and the other is that anions of ionic liquid can break the hydrogen bonding of PA 6. The products of depolymerization are analyzed by mass spectrometry and high-performance liquid chromatography and the main is caprolactam. The optimal conditions to obtain caprolactam are determined of reaction temperature 170 °C, IL/H_2O (w/w) 13.4%, and reaction time 8 h, and thus the yield of caprolactam 30.7% and degradation of PA 6 94.1%.

Introduction

With the development of plastic industry, plastic products are widely used in humans' daily life. Because of short using period, easily aging, stable chemical properties and difficulty to degrade under natural circumstance, waste plastics have caused serious environmental pollution [1], therefore, an effective method to treat waste plastic is very important. There are many physical and chemical methods to treat waste plastic [2]. The physical methods are mainly direct reusing waste PA 6 to produce some plastic products of poor quality, which cannot solve the pollution of waste plastics. The chemical method can recycle waste plastics to obtain chemical materials and as for the methods, the depolymerization to obtain corresponding monomer in sub- and super-critical water is undoubtedly very important owing to its green and efficiency.

Although sub- and super-critical water shows great potential for depolymerization of waste PA 6 [3, 4], many problems such as corrosion and the high temperature and pressure of the critical point of 374 ºC and 22.1MPa cause it very difficult to industrial utilization. To decrease temperature with addition some other solvent is an important direct owing to the cosolvent effect.

Recently, the room temperature ionic liquids (ILs) have attracted interest and been successfully used in many fields as environmentally benign solvents and catalysts due to their chemical stability, good solubility, nonvolatility, and low flammability [5, 6]. It reported that the mixture of water and ILs under mild conditions can exhibit high K_w values up to 3 orders of magnitude higher than pure water under ambient conditions [7]. The remarkably enhanced K_w is very important to depolymerize plastics, and thus, the addition of [Bmim]Cl to water was studied to depolymerize PA 6 in mild temperature.

Experimental

Nylon 6 powder of 33μm was obtained from Taizhou Luqiaosijia Biochemical Plastic Plant (Zhejiang, China). Caprolactam was purchased from Sinopharm Chemical Reagent Co., Ltd. (China). 1-n-Butyl-3-methylimidazolium chloride was purchased from Shanghai Cheng Jie Chemical Co. LTD (China). Distilled water was produced in the laboratory.

The different ratios of PA 6, water and IL were put in the hydrothermal vessel. After reaction, the hydrothermal vessel was put in ice water to cool to room temperature and then opened to take product for analysis.

Liquid-phase products were analyzed by mass spectrometry (MS) and high-performance liquid chromatography (HPLC). The MS instrument was a Hybrid Quadrupole-TOF system, Applied Biosystems, USA, and operated in the condition of electron spray ionization (ESI) of 4.5 kV and 573 K, a GS1 of 45.00, a GS2 of 30.00, a CUR of 10.00 μA, and an m/z range of 90-1000. The HPLC was an Agilent 1100 system, Agilent, USA and operated in the condition of a Zorbax SB-C18 chromatographic column (5 μm, 250 mm × 4.6 mm) with a UV-Vis detector at 200 nm, column temperature of 303 K, mobile phase of water/acetonitrile of 65/35 (V/V), flow velocity of 0.1 ml/min.

Results and discussion

3.1 Depolymerization products

The IR of solid residue shows that the two absorption peaks almost is the same. The peak of 3300 cm^{-1} is the N-H stretching vibration, 2950 and 2860 cm^{-1} are -CH_2 symmetric and asymmetric stretching vibration, 1648 cm^{-1} is the C=O stretching vibration, 1545 cm^{-1} results from the N-H vibration, and 1265 cm^{-1} is the C-N stretching vibration. The results indicate that the solid residue is the no completely depolymerization PA 6.

Except for the main liquid products of depolymerization of caprolactam and other oligomer similar to former study [5], there is an other product of N-methylcaprolactam (m/z=128.5 in Fig. 1) . These results indicate that PA 6 is depolymerized to caprolactam and subsequently the caprolactam may be alkylation to produce N-methylcaprolactam.

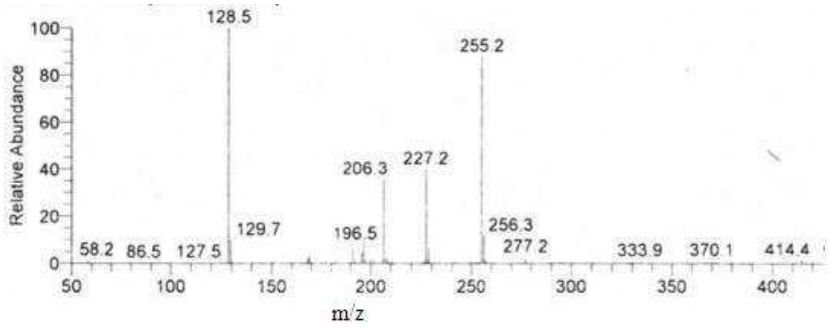

Fig. 1. Typical mass spectrum of liquid products about the N-methylcaprolactam (190 °C, 7 h, IL%=19.3%).

3.2 The effect of nylon 6 decomperization

3.2.1 Reaction temperature

Five different reaction temperatures were examined at 150, 170, 190, 210, 230°C (Fig. 2). The ratio of IL/H_2O (w/w) was 13.4 %. The reaction times were 5 h.

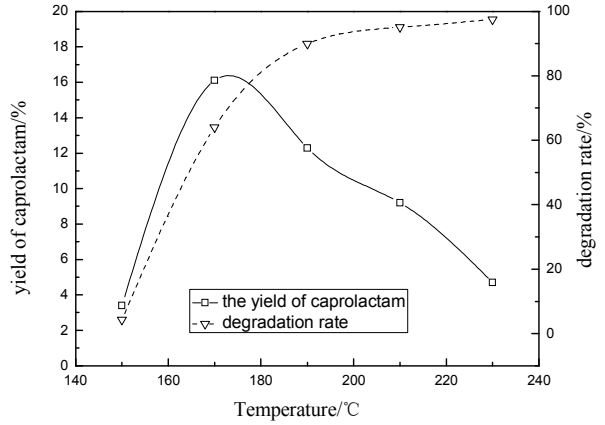

Fig. 2. The effects of temperature on the depolymerization of 5 h and IL/H_2O (w/w) of 13.4%.

Fig.2 shows the degradation of PA 6 increases with increasing temperature, but as for the temperature higher than 190 °C, the degradation of PA 6 are all 90%. Whereas, there is transition for the yield of caprolactam, that is, with increasing temperature, the yield of caprolactam first increases, but when in higher temperature, it decreases. When the temperature is higher than 170 °C, the yield of caprolactam decreases owing to its degradation, therefore, the temperature should not be too higher than 170 °C.

3.2.2 Appropriate amount of IL

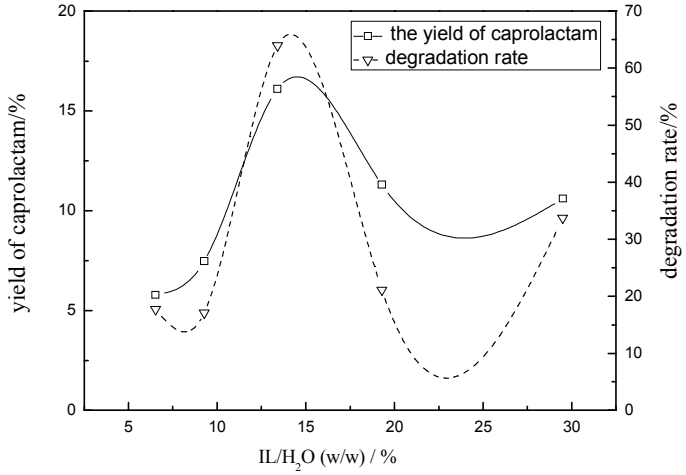

Fig. 3. The effects of IL/H_2O (w/w) on the depolymerization of 170 °C and 5 h.

The effects of IL/H_2O (w/w) on the depolymerization are given in Fig.3. It shows that both the yield of caprolactam and degradation obtain highest of 13.4% IL/H_2O (w/w). The result may be because that there is the highest H^+, and which is favor of PA 6 degradation to produce caprolactam.

3.2.3 Reaction time

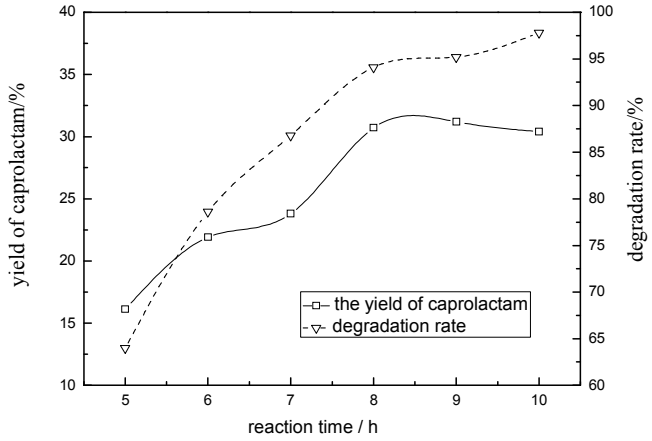

Fig. 4. The effects of time on the depolymerization of 170 °C and IL/H_2O (w/w) of 13.4%.

Fig.4 shows the yield of caprolactam and degradation of PA 6 with increasing time. With increasing time, the degradation increases, but the change is very little longer than 8 h. Furthermore, the yield of caprolactam almost obtains highest value at 8 h, and it will degrade to cause its yield decreases. Therefore, the optimum time should be 8 h.

Conclusion

The ionic liquids and water binary mixture is indeed a feasible way to decrease the temperature for waste polymer degradation to obtain useful chemical material. As for the waste PA 6, the ionic liquid of [Bmim]Cl can play better effect to decrease temperature in water. With [Bmin]Cl/H_2O of 13.4, the optimal conditions to obtain caprolactam are of 170 °C, reaction time 8 h, and the yield of caprolactam and degradation of PA 6 can obtain 30.7% and 94.1 respectively.

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