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Hydrolytic degradation of monomer casting nylon in subcritical water

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ABSTRACT

In contrast with the conventional physical methods, sub- and supercritical hydrolysis is not only a more environmentally friendly method to recycle the monomer casting nylon (MC nylon) wastes, but also a more feasible way to produce the corresponding monomer. In subcritical water, MC nylon was decomposed completely into water-soluble oligomers within 45 min at 345 °C and 9 MPa. Fourier transform infrared spectroscopy and X-ray diffraction were employed to characterize the chemical composition and crystalline form changes of the solid products obtained within 30 min of the degradation. Qualitative and quantitative analyses of liquid phase product were performed by liquid chromatography mass spectrometry and high performance liquid chromatography. The yield of the main degradation product ε-caprolactam largely depended on the hydrolysis temperature and reaction time. The maximum yield value reached 89.0% when the reaction time was 75 min. A hydrolytic degradation mechanism of MC nylon in subcritical water is proposed as well.

1. Introduction

Generally, polyamide materials can be recycled as normal thermoplastics by grinding, granulation or other mechanical methods without the decrease of the excellent performance [1]. It was reported that after 7 cycles of injection molding, the properties of nylon 6 essentially remained the same and the performance had not declined until the 10th injection cycles [2]. Thus the recycled polyamide wastes are mainly used to mix with new resins or directly reused as raw material to produce auto parts or other engineering parts.

As a special kind of nylon 6, the monomer casting nylon (MC nylon) is synthetized by casting method through the anionic ring-opening polymerization of ε-caprolactam. Plenty of unique performances such as the high strength, insulation, anticorrosive capacity and oil-resistance etc., make MC nylon having a wide range of applications as an engineering plastic [3]. However, the conventional physical recycling methods are not suitable for recycling MC nylon in some degree, because the molecular mass of MC nylon is up to $0.5–1.0 \times 10^5$ g/mol which leads to an entanglement between the molecules in the melting state and a particularly high melt viscosity.

Moreover, it is hardly possible to find any researches devoted to the decomposition of MC nylon, but some chemical methods for recycling regular nylon 6 have been developed which could provide some technical support [4–9]. The corresponding monomer ε-caprolactam is able to be recovered from the pyrolysis of nylon 6, in spite of that the energy consumption and the cost of the multi-component separation systems are relatively high. Other methods such as bio-degradation, photo-degradation and radiation degradation are time-consuming and incapable to obtain the valuable monomer. In comparison, catalytic hydrolysis or supercritical hydrolysis of nylon 6 is much more environment-friendly, and the monomer could be easily extracted from water after the hydrolytic reaction [10,11]. As a solvent and reaction medium, sub- and supercritical water has been found with increasingly wide utilization in the fields of catalysis, degradation, extraction and separation etc. [12–14]. Goto et al. [15] applied reactions in sub- and supercritical water to convert nylon 6 into its monomers. It was reported that the total yields of ε-caprolactam and the other monomer aminocaproic acid were about 100% for reactions at 300 °C in 60 min or at 330 °C in 30 min. Tomoko Iwaya et al. [16] discussed the influences of reaction temperature, time and water density on the degradation of nylon 6 in sub- and supercritical water; the reaction rate and the scheme were also investigated.

As compared with supercritical water, the reaction condition of subcritical water is much more moderate. Thus we selected the subcritical water to investigate the hydrolytic degradation of MC nylon wastes. The chemical composition of hydrolysis products,

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including the solid and liquid phases, and the influences of condition parameters on the product yields are examined. The discussion regarding the degradation of MC nylon in subcritical water is provided and a mechanism is proposed.

2. Experimental

2.1. Materials

MC nylon samples for this study were ivory MC nylon which was unmodified and collected as processing wastes. The samples were cleaned and crushed into small pieces. The water used in hydrolysis experiments was distilled water. Chromatographically pure ε-caprolactam and ε-aminocaproic acid were obtained from J & K (Beijing, China).

2.2. Decomposition in subcritical water

The reaction apparatus is shown in Fig. 1. The 90 cm^3 batch-type autoclave made of stainless steel was equipped with a pressure gauge and heated by an electric heating salt bath furnace with the mix of 0.45:0.55 (wt./wt.) $NaNO_2$ and KNO_3.

For the reaction, 1.0 g MC nylon sample was placed into the reactor, and then the water was added in a certain weight ratio. The liquid phase in the reactor was transformed into gas–liquid phase as the temperature rose and further raised the inside pressure. In this experiment, the pressure in the reactor with added water began to grow about 3 min after putting the sealed autoclave into the preheated salt bath and this time was defined to be start.

After the specified time at desired conditions, the reaction was quenched by placing the autoclave in an ice water bath quickly, cooling it to room temperature, then the pressure in the reactor dropped to ambient pressure. The products in the first 40 min of the reaction could be separated into solid phase and liquid phase while only liquid phase product existed after 45 min. After filtering and washing, the solid product was dried at 80 °C for 12 h. The liquid product was diluted and then filtered with 0.45 μm filter membrane for further analysis.

2.3. Analyses and characterization

The obtained solid products were examined by Fourier transform infrared spectroscopy (FTIR, NICOLET-Nexus 670, USA). The mass ratio of dried KBr and dried solid sample was about 100: 1.0–1.5. The mixture powder was ground and compressed into a disk under the infrared lamp. The FTIR spectra were acquired in the wave number range of 400–4000 cm^{-1} with the optical resolution of 2 cm^{-1}. Each sample was prepared and tested with 3 repetitions.

Wide-angle X-ray diffraction (WAXD, Empyrean) was employed to reveal the crystalline form changes of the solid products. Diffractograms were obtained from $2\theta = 10°–80°$ with a step size of 0.0131°.

Liquid chromatography mass spectrometry (LC-MS) and high performance liquid chromatography (HPLC) with gradient elution were used to analyze the liquid phase products. The LC-MS instrument was Hybrid Finnigan LCQ DECA XP MAX system with chromatographic column ASB-C18 (5 μm, 150 mm × 4.6 mm). The mass spectrometry used electrospray ionization (ESI) of 5.0 kV, 350 °C and positive ion mode with m/z range 50–1500. The mobile phase was water: acetonitrile = 90:10; the flow rate was 0.3 mL/min; sample size was 5 μL.

The HPLC apparatus was Agilent 1100 system with chromatographic column Zorbax SBC-18 (5 μm, 150 mm × 4.6 mm); UV detector read at 215 nm; the temperature of column was 30 °C. The mobile phase was the mixture of 0.1% acetic acid: acetonitrile = 90:10; velocity flow was 1.0 mL/min; injection volume was 5 μL.

3. Results and discussion

3.1. Analyses of solid phase products

In subcritical water, MC nylon decomposed completely into water-soluble oligomers without any gas phase product at 345 °C within 45 min, so the solid phase products existed only in the first 40 min of the hydrolytic reaction. The infrared spectra of unreacted MC nylon and the solid product obtained at 15 min of the degradation were investigated to study the chemical composition of solid hydrolytic product. The unreacted MC nylon gave the spectrum basically the same as typical nylon 6 (Fig. 2(a)). Fig. 2(b) obviously indicated that the solid phase product was the incompletely decomposed MC nylon. However a number of noticeable changes appeared in the intensity and area of some absorption bands.

Consequently, Figs.3 to 5 presents the specific infrared spectra of the solid residues obtained at 10, 20 and 30 min of the reaction to demonstrate the changes of solid phase products. The quantity of the solid product detected at 40 min was too small to be collected for further analysis.

The infrared absorption bands matched with CH_2 vibrations at 2861 cm^{-1}, 2933 cm^{-1} (symmetric and asymmetric stretching

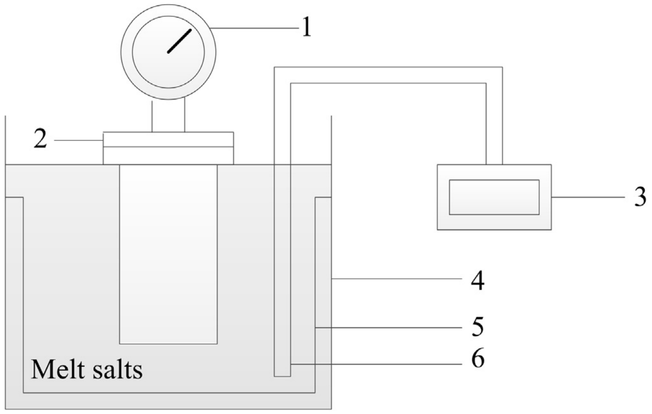

Fig. 1. Apparatus for the decomposition of MC nylon in subcritical water (1-pressure gauge; 2-autoclave; 3- thermometer; 4-salt bath furnace; 5-heater; 6-thermocouple).

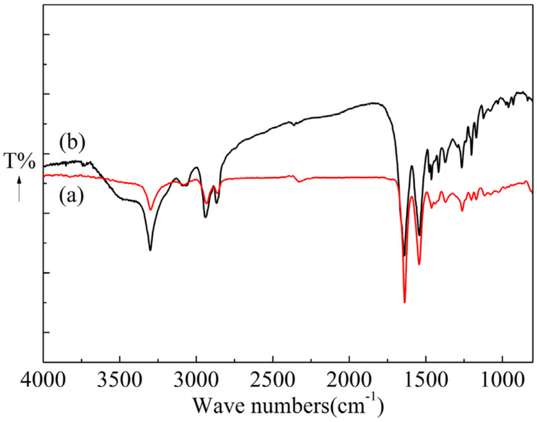

Fig. 2. FTIR spectra of (a) Unreacted MC nylon, (b) Solid product existed at 15 min of the hydrolysis reaction (345 °C, added water 30 g).