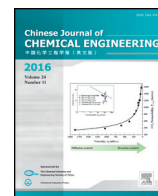




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Article

High-efficiency acetaldehyde removal during solid-state polycondensation of poly(ethylene terephthalate) assisted by supercritical carbon dioxide

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ABSTRACT

The concentration of acetaldehyde (AA) is the main quality index of poly(ethylene terephthalate) (PET) used in food and drink packaging. A new method for AA removal has been developed by using supercritical carbon dioxide (scCO₂) during the solid-state polycondensation of PET. The influence factors of AA removal including the temperature, pressure, reaction time and the size of pre-polymer particles are systematically studied in this work. The results indicate that it is a highly efficient way to obtain high molecular weight PET with relative low concentration of AA. Correspondingly, the polymerization degree of PET could increase from 27.9 to 85.6 while the concentration of AA reduces from 0.229×10^{-6} to 0.055×10^{-6} under the optimal operation conditions of 230 °C, 8 MPa and size of 0.30–0.45 mm. Thermodynamic performance tests show the increasing extent of PET crystallinity due to the fact that the plasticization of scCO₂ is not obvious with extended reaction time, therefore the increasing crystallinity has no significant influence on AA removal. SEM observations reveal that the effects of scCO₂-induced plasticization and swelling on PET increase significantly with the decrease of prepolymer size, and the surface of PET becomes more loose and porous in favor of the AA removal.

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1. Introduction

Poly(ethylene terephthalate) (PET) is a thermoplastic aromatic polyester with excellent thermodynamic and mechanical properties and has been widely used in fiber industry as well as in food and drink packaging [1]. With the rapid development of beverage and beer packaging, the demand for bottle-grade PET increases by double digits per year in recent days. The polymerization degree (Pn) of bottle-grade PET is higher than that of standard fiber products, usually more than 100 in industry. The concentration of acetaldehyde (AA) is the main quality index of PET, especially in bottle-grade PET for food and drink packaging. The residual AA can easily change the taste, color and thermophysical properties of PET, that will adversely affect the quality and application of final products and even cause the environmental and health hazards. Besides, strict regulations have been enacted to establish maximum permissible levels of AA, which is required to be lower than 1×10^{-6} in bottle-grade PET as listed in the national standard GB17931-2003.

For bottle-grade PET with relatively high molecular weight (MW), there are usually two ways to efficiently increase the polymerization degree of PET: the melt polycondensation [2–4] and the solid-state polycondensation (SSP) [5–7]. For melt polycondensation, the polymerization degree of polymer is increased by prolonging the reaction time

in a specially designed high-viscosity polycondensation device. But the viscosity of bulk melt increases rapidly with the raise of MW resulted in a dramatic growth of agitation power and great difficulty for devolatilization. The problems mentioned above limit the growth of Pn, which can only increase to about 100 after melt polycondensation. On the other hand, the long reaction time at relatively high temperature will increase seriously the thermal degradation, which leads to increasing AA concentration up to 100×10^{-6} . For SSP, although it can effectively inhibit the thermal degradation reaction to obtain PET with high Pn and lower concentration of AA by using a SSP tower coupled with a downstream dealdehyder, there are still many problems especially the usage of a lot of normal nitrogen for devolatilization and a long operation time with high energy consumption.

The utilization of supercritical fluids in polymers processing has attracted much attention over the last two decades, such as the crystal transition of syndiotactic polystyrene in supercritical CO₂-containing solvent [8–12], foaming of polypropylene [13–16] and PET [17–20] with scCO₂, extracting impurities from polymers, etc. [21,22]. Currently, environmentally benign fluids such as scCO₂ and ethyl alcohol (C₂H₅OH) are attractive alternatives as physical agents due to their unique properties such as non-toxic, quick dissolving, and good solvent characteristics. With relatively low critical temperature and critical pressure ($T_c = 31.1$ °C, $P_c = 7.38$ MPa), scCO₂ in general is one of the most widely used and studied solvents in the extraction process [23, 24]. During the saturation process, scCO₂ can quickly diffuse into the free volume between polymer chains and improve the motion ability

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of long molecule chains to a certain extent. In addition, many volatile impurities with small molecular weight also can be dissolved into scCO_2 because of the solvent effect. A recent research [25,26] indicated that the SSP of PET was promoted significantly with a periodical scCO_2 renewing strategy, and the Pn of PET increased from 100 to 150 only at 6 h, while it takes nearly 20 h in the industrial SSP process of PET. Therefore, it can be expected to remove the by-product of AA in PET via SSP process assisted by the periodical scCO_2 renewing strategy which has not been reported to date.

In this work, the SSP process of PET had been carried out assisted by periodical renewal of scCO_2 [26]. The effects of operation conditions, including the temperature, pressure, reaction time and the size of prepolymer particles, on the molecular weight and the corresponding AA concentration of PET were investigated experimentally by intrinsic viscosity testing and headspace gas chromatography, respectively. Correspondingly, the thermodynamic properties and morphology characteristics of PET samples were characterized by differential scanning calorimetry (DSC) and scanning electron microscopy (SEM), respectively. This work may provide a new method of SSP without AA removal tower to get high molecular weight PET with low concentration of AA.

2. Experimental

2.1. Materials

Phenol (analytical reagent, purity $\geq 99.0\text{wt}\%$) was purchased from Sinopharm Chemical Reagent Co. Tetrachloroethane (analytical reagent, purity $\geq 99.0\text{wt}\%$) was purchased from Shanghai Lingfeng Chemical Reagent Co. Acetaldehyde (gradient grade, purity $95.5\text{wt}\%$) and Ethanol (analytical reagent, purity: $99.8\text{wt}\%$) were purchased from Shanghai Titan Scientific Co. CO_2 (purity: $99.9\text{wt}\%$) was purchased from Shanghai Chenggong Gases Co, China. H_2 (purity: $99.99\text{wt}\%$), air, N_2 (purity: $99.99\text{wt}\%$) were commercially available from Shanghai Shenzhong Industrial Gases Co. All gases and reagents were used without any further purification. The PET prepolymer (Pn = 27.9, [AA] = 0.299×10^{-6} , crystalline = 53.59%) used in SSP was provided by Sinopec Shanghai Petrochemical Co.

2.2. Experimental method

As shown in Fig. 1, the experimental set-up for the SSP of PET carried out in scCO_2 was consisted of five elements: the high-pressure autoclave with internal volume of 115 ml, the agitation equipment, the oil bath,

the pressurization system and the temperature control system. A two-layer stainless sample cell (5) with 4 cm^2 square bottom was used to load prepolymers. The pressure of the autoclave was maintained by the pressurization system (2) with a pressure sensor with accuracy of $\pm 0.1\text{ MPa}$. One thermocouple was attached to the temperature control system.

In the SSP process of PET, the system loading with 1.50 g prepolymer was swept by low pressure CO_2 several times. Subsequently, the autoclave was heated to the reaction temperature in about 5 min and then pressurized to the desired pressure with CO_2 . After the system reacting 1 h, the pressure was relieved within 2 min, and then the autoclave was re-pressurized to the desired pressure again. The pressurization and depressurization operations, namely periodic renewal of scCO_2 , were repeated every 1 h [25,26]. After the SSP process was completed the system was depressurized to ambient pressure and the autoclave was then cooled down quickly. Finally, the samples were taken out for the subsequent analysis.

The operating conditions of SSP reaction process were carried out as follows: temperature $200\text{--}230\text{ }^\circ\text{C}$, pressure $0\text{--}10\text{ MPa}$, pre-polymer size $0.30\text{--}3.00\text{ mm}$, and reaction time $1\text{--}14\text{ h}$.

2.3. Analytical methods

2.3.1. Headspace gas chromatography

The concentration of AA in a PET sample was tested by headspace gas chromatography, and the headspace sampler was Agilent 7697A while GC was Agilent 7890A (with hydrogen flame ionization detector (FID)). The chromatographic column was Agilent HP-PONA Methyl Siloxane $50\text{ m} \times 0.20\text{ mm}$. The conditions of chromatography were as follows: N_2 was used as carrier gas while H_2 was as combustion gas, the column temperature was $150\text{ }^\circ\text{C}$, and the detector temperature was $200\text{ }^\circ\text{C}$. The analysis procedure through gradient elevation of temperature was: staying at the constant temperature of $50\text{ }^\circ\text{C}$ for 2 min and then raising the temperature from $50\text{ }^\circ\text{C}$ to $70\text{ }^\circ\text{C}$ in 5 min with a flow rate of N_2 at $2\text{ ml} \cdot \text{min}^{-1}$.

Additionally, the pure AA was also tested by headspace gas chromatography to obtain the standard curves of AA. The concentrations of prepared AA standard solutions and the corresponding standard curves of AA were shown in Table S1 and Fig. S1, respectively (see ESI†).

2.3.2. Ubbelohde viscometer

Intrinsic viscosity (IV) of PET sample was measured with an Ubbelohde Viscometer using the mixture of phenol and

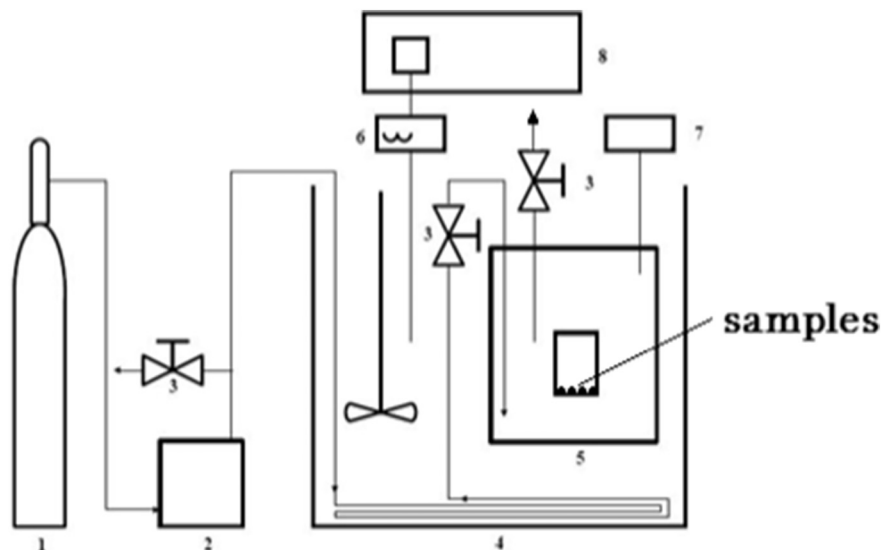


Fig. 1. Experimental setup for PET SSP and AA removal. 1 – gas cylinder; 2 – pressurization system; 3 – high-pressure ball valve; 4 – oil bath; 5 – high-pressure autoclave; 6 – temperature sensor; 7 – pressure sensor; 8 – temperature control system.

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