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Process analysis of depolymerization polybutylene terephthalate in supercritical methanol

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Abstract

The characteristics of depolymerization of PBT in supercritical methanol were investigated in the range of 453–533 K by using a high-pressure reactor. Based on the qualitative and quantitative analyses of the products, a depolymerization–reaction model was proposed to explain the depolymerization and reaction mechanism, i.e. ester exchange reaction occurred randomly along the chain of PBT. It was suggested that the process of depolymerization consisted of subcritical region, transitional region and supercritical region. In the first region, PBT mainly showed a swelling process in the methanol with slow decrease in molecular weight and little conversion. In the second region, PBT dissolved quickly with high depolymerization rate. While in the third region, the molecular weight of PBT decreased quickly with a thorough depolymerization in few minutes. DMT and BG obtained from the depolymerization of PBT in supercritical methanol reached 98.5% and 72.3%, respectively.

Keywords: Polybutylene terephthalate; Supercritical region; Mechanism; Depolymerization

1. Introduction

It is estimated that the increment rate of PBT production will reach as high as 10–12% in the next 5 years because PBT is used extensively in the electricity, automobile, machinery and other fields. With the increasing PBT consumption, its recycling use has attracted wide attention for the preservation of resources and the protection of the environment.

Using supercritical techniques to resolve polyester plastics have interested many researchers according to its advantages. Sako et al. [1,2] firstly studied the characteristics of depolymerization of PET in supercritical methanol using a high-pressure reactor. PET could convert into monomer completely at 330 °C, 8.1 MPa for 45 min. Kim et al. [3] investigated the mechanism of alcoholysis of PET. Campanelli et al. [4] studied depolymerization of PET in the critical water under the condition of 523–553 K. Tagaya et al. [5] examined depolymerization of polycarbonic ether in subcritical and supercritical water. Chen et al. [6] also researched depolymerization of PET in supercritical methanol. The depolymerization of PET in supercritical methanol has been investigated deeply, while not many papers were published to report the alcoholysis of PBT. Linghui et al. [7,8] studied the alcoholysis kinetic of PBT in supercritical methanol and the effect of reaction temperature and pressure on decomposition of PBT, but changes of the polymer structure in the supercritical methanol have not been related with the depolymerization process. Shibata et al. [9] reported that the depolymerization of PBT in high temperature and high pressure was an effective method for the quantitative recovery of DMT and 1,4-butanediol, but the depolymerization and reaction mechanisms in the depolymerization process were not studied yet.

In this work, we studied the characteristics of depolymerization PBT in supercritical methanol by observing the change of polymer inner structure followed with different molecular weights. The products were mainly composed of liquid products and residues. The liquid products were identified by

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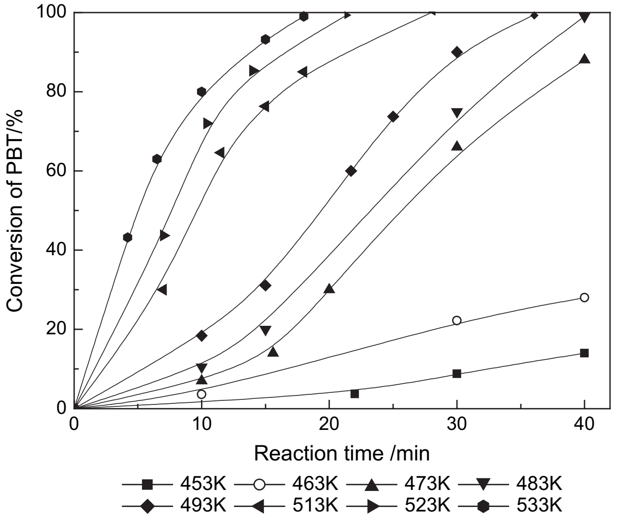

Fig. 1. Relationship between temperature and conversion of PBT.

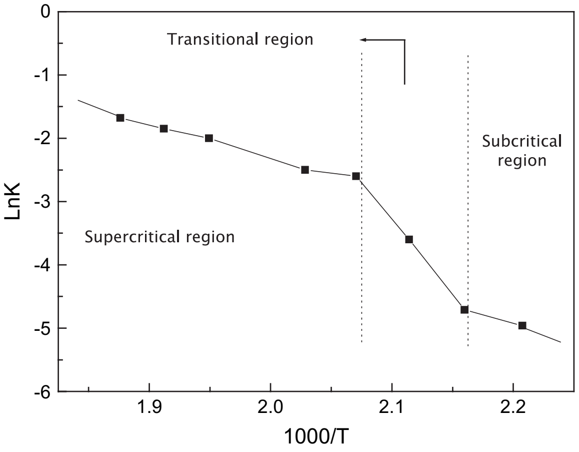

Fig. 2. Relationship between degradation rate and temperature.

GC/MS and quantitatively determined by GC, and the residues were detected by IR, SEM and viscometer. Based on the experimental results, we proposed the mechanism of depolymerization and reaction PBT in supercritical methanol.

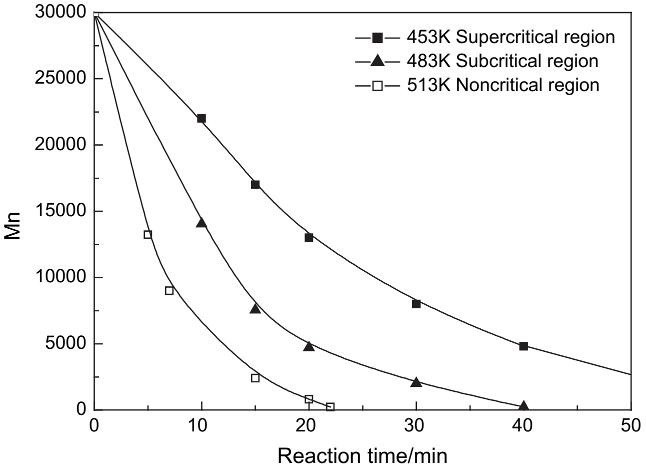

Fig. 4. Relationship between time and molecular weight of PBT.

2. Experimental

2.1. Material and solution

The PBT used in the experiments was commercial slice with average molecular weight 29,700 produced by the Shanghai polyester fiber factory. The solutions used in the experiments including DMT and methanol were all of chromatography grade.

2.2. Apparatus and procedure

The experimental apparatus composed of stainless steel reactor with a volume of 20 cm^3. The reactor was heated by melting salts (KNO_3 and $NaNO_2$). The temperature was maintained by a temperature controller in conjunction with a thermocouple immersed in the melting salts. To avoid the effect of air on the depolymerization of PBT, the air in the reactor was extracted by a vacuum pump after 0.988 of PBT was fed, and then 12.5 ml of solvent was inputted by the negative pressure. The reactor was immersed into the melting salts, and the thermocouple and pressure indicator were used to detect the temperature and pressure of the reaction system. When the reaction ended, the reactor was taken out of the melting salt

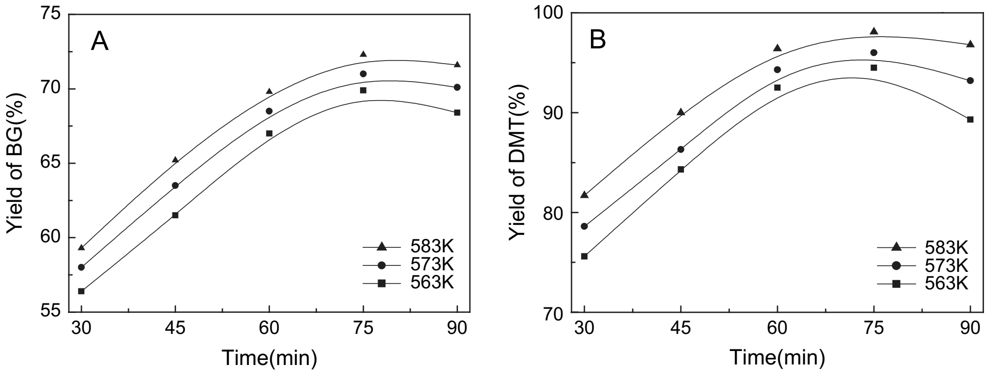

Fig. 3. Relationships between reaction time temperature and the yields of DMT and BG.