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Optimization of simultaneous thermal analysis for fast screening of polycondensation catalysts

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Abstract

Dynamic simultaneous thermal analysis was optimized to screen activity of different catalysts for polycondensation of bis-hydroxy ethylene terephthalate (BHET) to polyethylene terephthalate. Reactions were performed by heating BHET to 300 °C at a linear heating rate in 50 μl thermal analysis crucibles under inert gas purging. A sensitive and reproducible screening method was obtained after overcoming of critical problems such as monomer evaporation, catalytic activity of crucible material, and optimization of gas purging, monomer amount in the crucible and heating rate. Under the applied conditions mass transport limitations were absent and the reaction was controlled solely by chemistry. The temperature at which maximum reaction rate occurs was used as an index of catalytic activity. It was obtained from maximum differential scanning calorimetry signal together with the maximum derivative of thermogravimetry signal. Temperature at which the reaction starts was also applied as an activity index. It was obtained from the onset of mass loss. The value of these three indices was smaller for more active catalysts.

The optimized method was applied to study the activity of a new polycondensation heterogeneous catalyst based on hydrotalcite. This new catalyst was shown to be much more active than the conventional antimony catalyst under the applied conditions.

Keywords: Simultaneous thermal analysis; Poly(ethylene terephthalate); Catalyst screening; Hydrotalcite

1. Introduction

Poly(ethylene terephthalate) (PET) is an important polymer as reflected in its annual demand (37 million tons was the global demand for 2004) [1]. It is used as a commodity as well as engineering product for diverse applications. Its main end products are fibers, packaging articles, and films. PET has one of the fastest growing markets and will continue this trend in the future boosted by world economic growth and continuous development of new application fields. PET is nowadays synthesized mainly by esterification of purified terephthalic acid (PTA) with ethylene glycol (EG) followed by polycondensation of the esterification products, bis-hydroxy ethylene terephthalate (BHET) and its oligomers. Polycondensation rate is controlled by the removal of the by-product EG. The polycondensation stage occurs in a special type of reactor, which generates a large specific surface area. Antimony (Sb) in different forms, mainly oxide and acetate, is utilized to catalyze the polycondensation step in most of PET plants [2]. However, the presence of Sb as heavy metal in food packaging is a subject of increasing scrutiny. This, together with the search for a more active catalyst, is

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Abbreviations: BHET, bis(hydroxyl ethylene terephthalate); DSC, differential scanning calorimetry; DTG, first derivative of thermogravimetry; EG, ethylene glycol; HT, hydrotalcite catalyst; M_n, number average molecular weight (g/mol); M_w, weight average molecular weight (g/mol); PET, poly(ethylene terephthalate); Sb, antimony; STA, simultaneous thermal analysis; TG, thermogravimetry; TGA, thermogravimetric analysis; T_{max}, temperature at which maximum signal occurs (°C); T_o, onset temperature at which mass loss begins (°C)

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behind the ongoing research in many companies to replace Sb.

In 1978, Wolf et al. [3] applied dynamic differential thermal analysis to screen catalysts for polycondensation of BHET to PET. Bhatty et al. [4] introduced dynamic thermogravimetric analysis (TGA) as a catalyst screening aid in 1986. They used the temperature at which initial mass loss occurs (onset temperature T_o) as an activity index. Zimmerer et al. [5] studied the effect of crucible material on the polycondensation of pure BHET. They found that aluminium has a strong catalytic effect, which makes it non-favourable as a polymerization container material. On the other hand, these authors found that alumina has a negligible activity. Moreover, their experiments showed severe BHET evaporation, which was countered by developing a mathematical model that accounts for its effect of on thermal data evaluation.

The aim of this work was to optimize fast screening of polycondensation catalysts by simultaneous gravimetric and calorimetric thermal analysis (TG/DSC–STA). Application of STA for this aim would give a better panorama of the ongoing physical (monomer evaporation, crystallization, melting, etc.) and chemical (polycondensation) processes. The optimized method was used to study different recipes of a new heterogeneous catalyst based on hydrotalcite. To judge the new catalyst, its efficiency was compared to that of the conventional Sb compounds.

2. Experimental

2.1. Chemicals

BHET (>93%) was purchased from TCI, EG (>99%) from Merck, antimony triacetate from Atofina, hydrotalcite (HT) catalyst from Sasol GmbH. All the applied chemicals were used without further purification.

2.2. Preparation of different polycondensation recipes

Due to technical limitations it was not possible to weigh an amount of catalyst corresponding to 200 ppm in 10 mg of BHET (2×10^{-3} mg of catalyst). For this reason a larger amount of HT–BHET mixture was prepared by mixing of the desired amount of HT and 1 g of BHET at 40 °C as slurry in 25 ml EG for 3 h. After this homogenization process, EG was evaporated at 40 °C under high vacuum overnight. In order to prepare Sb–BHET mixtures, antimony triacetate was completely dissolved in EG by heating it at 60 °C for 1 h and then for another hour at 97 °C. Given amounts of this solution were mixed with BHET at 40 °C for 3 h before drying under high vacuum overnight.

2.3. Isothermal polycondensation

All isothermal runs were done on a STA 220 from Seiko because of its excellent applicability under isothermal conditions. The STA oven was evacuated and refilled with nitrogen at 1 atm pressure before each run to prevent product oxidation.

Pure BHET was heated at 20 K/min to 120 °C where they were held at constant temperature for 60 min before heating them to 280 °C at the same scanning rate where they were held for 240 min. Uncovered crucibles made of aluminium, platinum and alumina were used as polycondensation reactors. The diameter of these crucibles was 4 mm. Nitrogen was applied as purging gas at 50 ml/min. Catalyst was not added in these experiments. These runs were repeated under the same conditions except for 30 min at 280 °C instead of 240 min and another time for 240 min at 200 °C instead of 280 °C. Different amounts of pure BHET were also polymerized in uncovered aluminium crucibles isothermally at 208 °C.

2.4. Dynamic polycondensation

STA 409 PG from Netzsch was applied to perform all dynamic runs as this instrument is very efficient for this type of runs. Various Sb–BHET mixtures and HT–BHET mixtures were condensed by heating to 300 °C at 10 K/min under 50 ml/min nitrogen purging. All these runs were done in aluminium crucibles of 6 mm diameter covered with centrally holed lids. The STA oven was evacuated and refilled with nitrogen at 1 atm before each run. Polycondensation of 200 ppm Sb–BHET and 350 ppm HT–BHET mixtures were performed by changing the following parameters:

(1) monomer amount,
(2) nitrogen purging rate,
(3) lid/without lid, and
(4) heating rate.

2.5. Molecular weight determination

Molecular weight of resulting polymers was measured by gel permeation chromatography (GPC) on an Agilent 1100 system.

3. Results and discussion

The reaction scheme of BHET polycondensation is shown in Fig. 1. Since EG is removed as it is formed, the reaction is considered irreversible. Condensation of 1 mol of BHET produces 1 mol of EG. For complete conversion of free ester

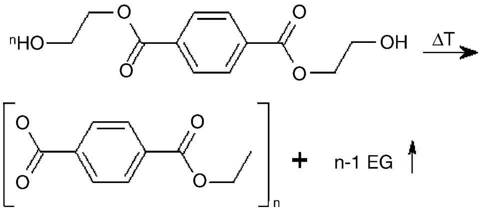

Fig. 1. Reaction scheme of BHET polycondensation to PET.