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Kinetics of hydrolysis of poly(ethylene terephthalate) wastes catalyzed by dual functional phase transfer catalyst: A mechanism of chain-end scission

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ABSTRACT

The dual functional phase transfer catalyst $[(CH_3)_3N(C_{16}H_{33})]_3[PW_{12}O_{40}]$ was used in the hydrolysis of poly(ethylene terephthalate) (PET) wastes and exhibited outstanding catalytic activity. In this work, the kinetic study about this reaction was carried out. The quantification of ethylene glycol (EG) formed in the hydrolysis was used to describe the reaction rate, which could result in more feasible and accurate kinetic analysis than terephthalic acid (TPA) formation or PET consumption used in traditional method. The results of kinetic analysis showed that the depolymerization reaction rate was first order to PET and catalyst concentration. This indicated that the ester linkages on the surface of the PET sequentially reacted with water to produce products. A mechanism for the reaction occurring on the polymer chain end section was proposed. Also the activation energy value was derived. Kinetic correlations provided a reliable mathematical reaction model for this recycling process, which is in agreement with the principles of sustainable development.

1. Introduction

Poly(ethylene terephthalate) (PET) exhibits excellent characteristic features, and with the rapid increase in consumption of PET, the amount of waste PET is growing rapidly [1]. PET does not generate a direct harm to the environment, but it is seen as a noxious material, hence its substantial fraction by volume in the waste and its high resistance to the atmospheric [2]. Therefore, PET recycling represents one of the most widespread examples of polymer recycling. The recycling of waste polymers including PET can be carried out in many ways [3–15]. Recently, there is a growing interest in hydrolysis for the chemical recycling of PET, since it leads to the formation of the monomers of terephthalic acid and ethylene glycol, from which the polymer is made of.

Our group has reported the hydrolysis of PET in the presence of dual functional phase transfer catalyst [16]. The dual functional phase transfer catalyst could behave as the efficient catalyst for the depolymerisation of PET. The excellent conversion of PET and yield of recovered product terephthalic acid (TPA) were obtained. Investigation into recycling of the catalyst showed that the catalyst could be reused without significant decrease of activity at least three cycles. This process provided an economically and convenient approach for the hydrolysis of PET waste bottles. In this work, based on our continuing interest in the depolymerisation of polyester PET, we carried out the comprehensively kinetic studies in order to further understand the process of dual functional phase transfer catalyzed hydrolysis. In spite of the widely proved feasibility, taking into account social, economic and environmental aspects of PET wasters by hydrolysis, relatively few works have been devoted to the kinetic description of PET hydrolysis [17–21]. Most published reports studied

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the kinetics by estimating the yield of TPA or the consumption of PET, however, this procedure involved a significant experimental error. The research neglected one important issue that the TPA recovered process included many steps which might resulted in the loss of product and in turn may affect kinetic calculations. Therefore, in this work three sets of data including TPA yield, ethylene glycol (EG) yield and PET conversion were recorded and compared to declare and afford accurate results. The specific objective of this study is not only to determine the kinetics of the catalyzed reaction in a batch reactor with dual functional phase transfer catalyst as catalyst, but also to provide a new pathway to study the kinetics in lab or under scale-up condition. Hence, integral kinetic analysis of the data was performed in order to establish the kinetic model and the kinetic parameters, which are necessary for developing the industrial process of depolymerisation of PET.

2. Experimental

PET flakes, dual functional phase transfer catalyst and water were charged into the reactor at room temperature and then heated to the selected temperature (115–145 °C) for conducting the hydrolytic runs. The mixture was allowed to react for some hours. Both temperature and pressure were kept constant during each experiment. In all kinetic studies, reaction time zero was taken to be the time at which the reactor temperature was the predetermined reaction temperature. After the required time interval for reaction was reached, the vessel was quickly removed from the heating mantle and immersed in an ice bath. The temperature of the vessel was quenched to room conditions so as to interrupt the progress of hydrolysis.

The synthesis of dual functional phase transfer catalyst $[(CH_3)_3N(C_{16}H_{33})]_3[PW_{12}O_{40}]$, workup of hydrolysis and calculating of the conversion and yield were carried out following the procedure described in previous paper published by our group [16]. The ethylene glycol (EG) content was determined with the GC analysis by working curve method. Conversion of PET was calculated by following formula: Conversion of PET = $[(w_1 - w_2)/w_1] \times 100\%$. Yield of TPA = $(w_3/w) \times 100\%$, where w_1 is the original PET weight, w_2 is the undepolymerized PET weight, w_3 is the TPA product weight, w is the weight of TPA which should obtained theoretically.

3. Results and discussion

$$\begin{aligned}&[COC_6H_5COOCH_2CH_2O]_n\\&\quad + 2nH_2O \xrightarrow{\text{catalyst}} nHOOCC_6H_5COOH\\&\quad + nHOCH_2CH_2OH \qquad (1)\end{aligned}$$

PET flakes were hydrolyzed with water catalyzed by dual functional phase transfer catalyst to yield the TPA and EG [16]. The reaction of Eq. (1) was clean and high-yielding reaction, and the purity of recovered TPA was checked and analyzed by means of a number of analytical techniques (^{1}H NMR, FTIR and elemental analysis) and the results were the same as those corresponding to a commercial sample. Therefore, kinetic studies were carried out to evaluate the reaction orders, rate constants and activation parameters for mechanistic understandings. In the our published results, the dual functional phase transfer catalyst $[(CH_3)_3N(C_{16}H_{33})]_3[PW_{12}O_{40}]$ exhibited the best catalytic activity, therefore, an attempt to develop a kinetic model was made with it as a catalyst in this work.

A set of kinetic experiments were conducted in the 115–145 °C temperature range and varying PET: catalyst molar ratio 300:1 and 100:1. The regular depolymerisation and random scissions were two main form of polymer degradation. The results included in Fig. 1 showed that the TPA yield was proportional with reaction time. The yield at 145 °C lower than 100% might due to the uncompleted decomposition of PET. No depolymerisation conversion jump was observed, which suggesting that the reaction occurring on the polymer chain end section should be the major reaction. It is proposed a typical regular depolymerisation. This finding was in stark contrast with the hydrolysis mechanism observed for the microwave assisted hydrolysis [22]. The different heating method and reaction temperature might attribute to the huge difference of reaction mechanism. PET degradation into TPA was favoured with increasing temperature and catalyst concentration. The influence of temperature on yield was larger than that of the catalyst concentration. On the other hand, the molecular weights of unreacted flakes after reaction were measured. And the results showed that the molecular weight of remaining PET flakes was slightly decreased with an increase of the reaction temperatures and no significant change was observed. Therefore, the bulk phase of remaining flakes after the reactions was close to the fresh long chain PET. This suggested that the depolymerization of PET catalyzed by the dual functional phase transfer catalyst occurred on the external surface of PET flakes, and the flakes were lamellarly depolymerized.

Most reports regarding the hydrolysis of PET estimate the yield of TPA or the consumption of PET, and consequently the conversion of the process from the amount of TPA recovered after filtration followed by titration and dry. However, this procedure involves a significant experimental error, since the TPA recovered process included many steps which might resulted in the loss of product and in turn may affect kinetic calculations. In contrast, a quantification of EG formed after hydrolysis by GC can be lead to the more accurate kinetic data. Fig. 2 shows the comparison of conversion values calculated by three methods. Data included in this figure were recorded from numerous reaction runs performed under varying operation conditions in terms of temperature, reaction time and concentration of catalyst. From the figure, good correlation was found between the yields of EG after hydrolysis with PET conversions, however, the TPA yields were slightly lower than those of EG and PET conversions under the reaction conditions described in this work. The result indicated that a minor quantity of TPA would unavoidably not recoverable in this system. Moreover, it must be highlighted that the analytical method of EG formed would be likely to be employed under real conditions after a scale-up for the easy dealing process. Likewise, quantification of EG was more feasible and accessible than measurement of