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Thermal degradation of high density polyethylene in a reactive extruder

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Abstract

The thermal degradation of high density polyethylene was conducted in a reactive extruder at various screw speeds with reaction temperatures of 400 °C and 425 °C. The residence time of the extruder was estimated and the molecular weight distribution of the fed plastic and reaction products was analysed using gel permeation chromatography. A continuous kinetic model was used to describe the degradation of the high density polyethylene in the reactive extruder. The breakage kernel and the scission rate model parameters were estimated from the experimental data for a variety of cases. It was found that purely random breakage and a scission rate which had a power law dependence on molecular size of 0.474 best described the experimental data.

Keywords: HDPE; Thermal degradation; Reactive extruder; Continuous kinetics

1. Introduction

Feedstock recycling of waste plastic has been a topic of great interest in both the academic community and industrial research and development. This is primarily due to an increase in environmental awareness and an acknowledgement that the depletion of natural resources requires more efficient utilisation of resources. The advantage of feedstock recycling over mechanical recycling is the ability to accept unsorted or contaminated plastic waste streams. The numerous feedstock recycling literature including current demonstration projects, patents and industrial processes have been reviewed previously [1–3].

The degradation of plastic in a variety of different reactor types has been investigated at various processing scales [2]. Reactive extruders have shown to be a flexible and useful reactor design for the degradation of plastic. Some examples of reactive extruders used for plastic degradation include, thermal and catalytic degradation of polyethylene for the production of liquid fuel [4,5], co-processing polyethylene with lubricating oil [6] and as a moving bed reactor that conveys both sand and polypropylene for fuel gas production [7]. However, most investigations fail to characterise the reactor with sufficient detail to be used as a basis for a kinetic model of the system.

The degradation of polyethylene in particular has been widely studied in the literature due to both its prevalence in solid municipal waste and simple structure. Kinetic studies of the thermal degradation of polyethylene have been reviewed previously [8,9] and they show a wide variety of values for reaction constants as well as differing approaches used in the development of kinetic models. The complex nature of the thermal degradation, along with differences in both reactor configuration and starting material makes comparison and validation of kinetic models difficult [9]. Modelling approaches range from simplistic *n*th order reaction kinetics to detailed models that extrapolate kinetic rate behaviour from that of small model molecules.

The majority of kinetic studies of polyethylene degradation are carried out in a thermogravimetric analyser and report lumped kinetic rate constant of the material [10]. The excessive

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Nomenclature

τ	residence time of reactive extruder (min)
$\dot{m}$	mass flowrate of reactive extruder (g/h)
t	time (s)
x	molecular size (g/mol)
y	dummy variable for integration
$P(x,t)\mathrm{d}x$	molar concentration of polymer with molecular weight in the range of x to $x+\mathrm{d}x$ at time t
$n(x,t)$	normalised number of molecules with molecular weight in the range of x to $x+\mathrm{d}x$ at time t
$\Omega(x,y)$	breakage kernel
$s(x,t)$	rate of scission of molecules of size x at time t
k_r	reaction rate constant ($\mathrm{s}^{-1}\,(\mathrm{g/mol})^{-p}$)
E_r	activation energy (kJ/mol)
A_r	pre-exponential factor ($\mathrm{s}^{-1}\,(\mathrm{g/mol})^{-p}$)
T	temperature (K)
p	rate of scission parameter
v	breakage kernel parameter
$B(v,v)$	beta function
x_i	grid point i
L_i	lumping function for lump i
N_i	normalised number of molecules in lump i
S_{x_i}	rate of scission of molecules of size x_i
$n_{i,k}$	lumped breakage kernel
$I_y(v,v)$	incomplete beta function
$F_1(x)$	B-spline of the cumulative mass fraction data
M_n	number average

simplification of the reaction mechanism generally used in interpreting thermogravimetric analysis (TGA) data results in a wide range of reported reaction rate constants [8–10]. A full description of the complex free radical mechanisms by which polyethylene degrades would require many different rate constants that are both difficult to estimate [11] and require very detailed experimental data [9].

A balance between complexity and robustness of the kinetic model must be found. The modelling of polymer degradation using continuous reaction kinetics has been shown to be an effective way to describe the size reduction of the entire distribution of molecular sizes [12–14]. The advantage of using continuous kinetics is that the essential dynamics of the system is captured with a small number of model parameters. The prediction of the entire molecular weight distribution is useful for calculating liquid and gas yields as well as other thermodynamic behaviour of reacting fluid. Therefore once the kinetics of a reaction is captured it can be used to predict yields in different reactor configurations by imposing the particular conditions of the new system. This is not possible with simple weight loss or lumped models.

This article reports on our kinetic modelling of the thermal degradation of high density polyethylene conducted in a reactive extruder. The article is organised as follows: the first section gives a brief outline of the reactive extruder, experimental procedures used and characterises important process variables of the extruder such as mass flowrate, residence time and the temperature–time profile; the next section develops a continuous kinetic model that describes the molecular weight distribution of the polymer in the reactive extruder; results of the model are then compared to the experimental data and the validity of the kinetic model discussed.

2. Experimental

2.1. Reactive extruder

Experiments were carried out in a 20 mm diameter constant depth, constant pitch single screw extruder as shown in Fig. 1. The extruder had five controllable heating zones as shown in Fig. 1; upper hopper (T1), lower hopper (T2), barrel feed (T3) directly below hopper; first reaction zone controlled by thermocouple T4 with two temperature indicators T4A and T4B and second reaction zone controlled by thermocouple T5 with two temperature indicators T5A and T5B. All thermocouples embedded into the barrel and hopper walls were used to approximate reactor temperature without interfering with the flow patterns of the reactants. The six barrel thermocouples were distributed 7 cm apart down the length of the 48 cm barrel.

The hopper components included two heaters controlled by thermocouples T1 and T2, inlet and outlet valves and a removable lid with a gasket. The lid of the hopper was fitted with a glass window to allow for visual inspection of hopper contents during the reactor operation. A nitrogen gas supply was fitted to the hopper inlet valve and a pressure indicator and purge line to the outlet valve. This allowed nitrogen to be flushed over the hopper contents during normal operation. At the end of the barrel the dye (L shaped 20 mm tube) was heated to ensure that products could easily flow into a glass condenser that was immersed in an ice bath.

2.2. Procedure

A typical experiment commenced with loading high density polyethylene (HDPE) into the hopper. All experiments used

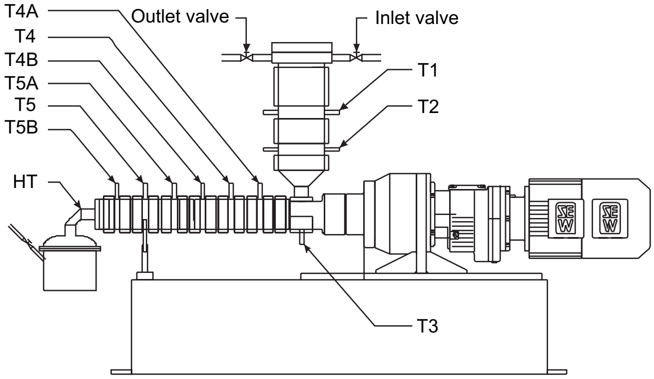

Fig. 1. Reactive extruder (HT = heating tape; T1, T2, T3, T4, T5 = control thermocouples; T4A, T4B, T5A, T5B = measurement thermocouples).