CATALYTIC DEGRADATION OF POLYETHYLENE EVALUATED BY TG

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Abstract

HZSM-5 zeolite was screened as catalyst for high density polyethylene degradation at 450°C, under nitrogen static atmosphere. Two different samples were studied in this condition: HDPE alone and mixed with HZSM-5. The reactor was connected on line to an HP 5890-II gas chromatograph. Sample degradation was investigated using a Perkin-Elmer Delta 7 Thermobalance, from room temperature to 800°C, with heating rates of 5.0, 10.0 and 20.0°C min^{-1}. From TG curves, the activation energies, calculated using an integral kinetic method, decreased 60.6% in the presence of the zeolite.

Keywords: catalytic degradation, kinetics, polyethylene

Introduction

Degradation of waste synthetic polymers has been the focus of increased attention because of their potential use as fuels or chemical resource [1, 2]. Besides, recycling of polymers from waste products can contribute to solve pollution problems. The use of suitable catalysts can enhance the thermal degradation of synthetic polymers [3, 4], which may be monitored by thermogravimetry [5, 6].

In this work the degradation of high density polyethylene (HDPE) was processed in the presence of HZSM-5 zeolite and the results of catalytic and thermal degradations were compared.

Experimental

The HZSM-5 was obtained exchanging ZSM-5 (synthesized by the hydrothermal method) with ammonium chloride and subsequent calcination at 550°C for 4 h.

High density polyethylene (HDPE), in powder form, was obtained from Balmman of Brazil as BM012. Blending of polymer and catalyst, previously activated at 450°C for 4 h, was carried out in a ball mill. The catalyst concentration was 10% (w/w). Polymer degradation was carried out in a quartz microreactor at 450°C, under static nitrogen atmosphere. The sample masses were of 1 g. Two different samples were studied in this condition: HDPE alone (PE1) and mixed with HZSM-5 zeolite (PE2).

The reactor was connected on line to an HP 5890-II gas chromatograph equipped with a flame ionization detector. It was used an HP-5 capillary column (30 m).

Sample degradation was also investigated using a Perkin-Elmer Delta 7 Thermobalance, from room temperature to 800°C, with heating rates of 5.0, 10.0 and 20.0°C min^{-1}. The thermogravimetric analysis were executed in dynamical atmosphere of nitrogen (30 cm^3 min^{-1}). 5 mg of sample was used for each experiment.

Results and discussion

Thermogravimetric analysis

Although reaction conducted in bulk involves more serious problems of heat transfer than those observed to the TG small samples, the influence of the catalyst on HDPE degradation could be readily explored by carrying out thermogravimetric experiments, allowing useful internal comparisons. Thus, the weight loss of the mixture (polymer + zeolite) was measured as a function of temperature up to 800°C, and the results were compared with that obtained without catalyst. Using differential TG curves it was possible to determinate T_i, T_m and T_f which refer to the temperatures corresponding to initial weight loss, maximum rate of weight loss, and final constant weight, respectively, reported in Table 1. It was observed that the presence of the HZSM-5 zeolite leaded to a marked lowering of the T_i, T_m and T_f values.

Table 1 Values of T_i, T_m and T_f observed in thermogravimetric analysis of HDPE carried out without and with catalyst, in dynamic nitrogen atmosphere of 30 cm^3 min^{-1}

Sample	T_i/°C	T_m/°C	T_f/°C
PE1	361.9	462.0	491.7
PE2	274.1	390.6	424.8

Degradation mechanism

Standard solutions from containing C_5–C_{30} n-alkanes were analysed on the same column and under the same conditions. The retention times (RT) of these hydrocarbons were used as references in order to group the degradation products. We designated as F5 the fraction containing all the products with RTs up to that of n-pentane. F6 represents the fraction containing all the products with Rts between those of n-pentane and n-hexane, and so on;

Chromatographic analysis showed that thermal degradation of HDPE without catalyst gave rise to products distributed over a wide range of carbon atom numbers (C_5–C_{26}) as reported in Table 2; the main fraction was C_{10}–C_{15} (60.2%). The catalytic reaction led to lighter products (C_5–C_{26}), predominantly C_5–C_9 (73.5%). This behavior may be due the strong acid sites of HZSM-5 zeolite, which can promote the polymer chains cracking.

Table 2 Product distribution (wt%) in the degradation of HDPE carried out without and with catalyst, in static nitrogen atmosphere

Fraction	PE1	PE2
F5	0.618	23.05
F6	6.60	16.94
F7	3.82	11.06
F8	4.11	11.81
F9	5.94	10.67
F10	8.70	8.41
F11	9.28	6.39
F12	9.30	4.84
F13	9.20	3.39
F14	9.26	2.07
F15	8.20	1.08
F16	6.21	0.290
F17	4.77	–
F18	3.32	–
F19	3.29	–
F20	2.72	–
F21	1.95	–
F22	1.20	–
F23	0.771	–
F24	0.502	–
F25	0.212	–
F26	0.027	–

Kinetic study

Reliable methods for determining the activation energy using dynamic integral TG curves at several heating rates have been proposed by Ozawa [7] and Flynn and Wall [8]. A software based on these methods was used to treat the TG data, allowing the evaluation of the apparent activation energy. A detailed mathematical procedure employed for better software comprehension is a given as follows.

For a given solid state thermo-degradation reaction

$$A_{(s)} \rightarrow B_{(g)} \qquad (1)$$

where $A_{(s)}$ is the polymer without or with catalyst and $B_{(g)}$ represents the degradation products. The reaction rate can be expressed by [5, 9]

$$\frac{\partial C}{\partial t} = f(C)k \tag{2}$$

$$k = \frac{\partial C}{\partial t f(C)} \tag{3}$$

where C is the polymer fraction decomposed in a time of reaction t and k is a constant depending on the absolute temperature T.

According to the Arrhenius equation

$$k = A \exp\left(-\frac{E}{RT}\right) \tag{4}$$

where A is the pre-exponential factor, E is the activation energy and R is the gas constant.

Assuming a linear heating rate β, so that

$$T = T_0 + \beta t \tag{5}$$

$$\frac{\partial T}{\partial t} = \beta \tag{6}$$

Applying Eq. (2) in Eq. (4)

$$\frac{\partial C}{\partial t f(C)} = A \exp\left(-\frac{E}{RT}\right) \tag{7}$$

Substituting Eq. (6) in Eq. (7), we obtain

$$\frac{\partial C}{\partial T} = \left(\frac{A}{\beta}\right) f(C) \exp\left(-\frac{E}{RT}\right) \tag{8}$$

Supposing that: A, E, $F(C) \neq g(T)$ and A, $E \neq h[f(C)]$, then the variables can be separated and Eq. (8) can be integrated

$$F(C) = \int_0^C \frac{\partial C}{f(C)} = \left(\frac{A}{\beta}\right) \int_{T_0}^T \exp\left(-\frac{E}{RT}\right) \partial T \tag{9}$$

$$F(C) = \left(\frac{AE}{\beta R}\right) \left[\frac{\exp(-E/RT)}{E/RT} + \int_{-\infty}^{-E/RT} \frac{\exp(-E/RT)}{E/RT} \partial T\right] \tag{10}$$

$$F(C) = \left(\frac{AE}{\beta R}\right) P \frac{E}{RT} \tag{11}$$

or in the logarithmic form

$$logF(C) = log\left(\frac{AE}{R}\right) - log\beta + logP\left(\frac{E}{RT}\right) \qquad (12)$$

Doyle [11] observed that, when $E/RT >= 20$, $logP(E/RT)$ can be obtained by the expression

$$logP\left(\frac{E}{RT}\right) \cong -2.315 - 0.457\frac{E}{RT} \qquad (13)$$

So Eq. (12) becomes

$$logF(C) \cong log\left(\frac{AE}{R}\right) - log\beta - 2.315 - 0.457\frac{E}{RT} \qquad (14)$$

Differentiation of Eq. (14) at a constant conversion rate gives

$$\frac{\partial log\beta}{\partial 1/T} \cong -\frac{0.457}{R}E \qquad (15)$$

and, inserting the R value 8.314 J mol^{-1} K^{-1}, an expression obtained for E

$$E \cong -4.35 \frac{\partial log\beta}{\partial 1/T} \qquad (16)$$

It is thus possible to calculate the activation energy related to thermal degradation of a polymer, using the slope of the logarithmic heating rate curves as a function of reciprocal temperature.

This method has been used for evaluating rigid polyurethane thermal stability [9] and in studies about coke thermoxidation for solid catalysts regeneration [10, 11].

The activation energy observed for the polymer degradation without catalyst was 170.2 kJ mol^{-1} against 67.0 kJ mol^{-1} in the presence of HZSM-5 zeolite. This results indicate that zeolite may have acted as a cracking catalyst for HDPE, enhancing the generation of light products of potential industrial use.

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References

1 W. Kaminski, J. Janning and H. Sinn, Eur. Rubber J., 15 (1979) 161.
2 R. C. Poller, J. Chem. Tech. Biotechnol., 30 (1980) 152.
3 A. Lucchesi, G. Maschio and P. Giusti, Poliplasti, 288 (1981) 73.
4 G. Audisio, A. Silvani, P. L. Beltrame and P. Cartini, J. Anal. Appl. Pyrol., 7 (1984) 83.

5 Y. Uemichi, Y. Kashiowaya, M.Tsukidate, A. Ayame and H. Kanoh, Bull. Chem. Soc. Jpn., 55 (1983) 2768.
6 Y. Uemichi, Y. Kashiowaya, A. Ayame and H. Kanoh, Chem. Lett., 1 (1984) 41.
7 T. Ozawa, Bull. Chem. Soc. Jpn., 38 (1965) 1881.
8 J. H. Flynn and W. A. Wall, Polym. Lett., 4 (1969) 323.
9 V. J. Fernandes Jr., DSc. Thesis, Universidade de São Paulo, 1991.
10 V. J. Fernandes Jr. and A. S. Araújo, Química Nova, 18 (1995) 11.
11 V. J. Fernandes Jr. and A. S. Araújo, Thermochim. Acta, 255 (1995) 273.