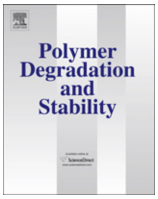
Polymer Degradation and Stability 96 (2011) 1497–1502

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab



Non-isothermal depolymerisation kinetics of poly(ethylene oxide)

Marlene J. Cran[a], Stephen R. Gray[a], John Scheirs[b], Stephen W. Bigger[a,*]

[a] Institute for Sustainability and Innovation, Victoria University, PO Box 14428, Melbourne 8001, Australia
[b] ExcelPlas Australia Limited, PO Box 2080, Edithvale 3196, Australia

ARTICLE INFO

Article history:
Received 23 February 2011
Received in revised form
14 April 2011
Accepted 11 May 2011
Available online 18 May 2011

Keywords:
Non-isothermal kinetics
Poly(ethylene oxide)
PEO
Depolymerisation
Lifetime prediction
Thermal degradation

ABSTRACT

The depolymerisation of low molecular weight poly(ethylene oxide) (PEO) under mild conditions was studied using a linear temperature ramped non-isothermal technique and the results compared with those obtained from a conventional isothermal technique. The analysis of the non-isothermal kinetic (NIK) data was performed using an original computer program incorporating an algorithm that systematically minimizes the sum of the squares of the residuals between the experimental data and the calculated theoretical kinetic profile in order to extract the kinetic parameters. The results revealed that the depolymerisation of PEO proceeds in accordance with the Ekenstam model and follows the Arrhenius equation over the temperature range of *ca.* 40–130 °C. The NIK analysis resulted in a two-dimensional convergence to produce a unique solution set for the kinetic parameters of $E_a = 89.4$ kJ mol^{-1} and $A = 9.6 \times 10^6$ h^{-1}. These data are consistent with the results obtained from the isothermal experiments. It is proposed that NIK analysis is a quick and reliable means of obtaining kinetic parameters relevant to lifetime predictions in polymers whose degradation behaviour can be considered to be close to ideal.

1. Introduction

1.1. Isothermal and non-isothermal kinetics

In the quest for the accurate prediction of polymer service lifetimes from data obtained in the laboratory under conditions of accelerated testing the need for robust kinetic models that hold over what is often considered to be a wide temperature range has long been recognized [1–3]. There currently exists an extensive body of literature on polymer degradation kinetics wherein the contributions typically describe a series of separate experiments, each conducted isothermally but at a different temperature across a wide range of temperatures, that are then used collectively in order to predict an expected outcome at a temperature typical of service conditions [1,3–15].

In many cases a series of such "isothermal experiments" have rendered reliable predictions of service lifetimes if the data have been treated appropriately. However, in conducting these experiments and making predictions based on the results one must always be aware of the possible pitfalls in the approach which include: (i) many service applications of polymers involve dynamic, or indeed cyclic, temperature variations and/or fluctuations and so a series of isothermal experiments may not adequately take this into account [3,5,16] and (ii) there may or may not be strict adherence to the Arrhenius equation over the temperature range of the study which can significantly affect the expected kinetics and which, in turn, may seriously affect the accuracy of any service lifetime prediction [8,12,16,17].

In an attempt to mimic the dynamic nature of temperature conditions experienced by polymers during their service lifetimes and, at the same time, reduce the experimental times required to produce meaningful lifetime predictions, some workers have adopted "non-isothermal" kinetics (NIK) techniques that usually involve the superposition of a (linear) temperature ramp on the kinetic experiment with a consequent distortion of the observed kinetic profile. In such experiments it can be argued that: (i) the dynamic temperature range will usually include kinetic data that lie within the service life conditions of the material of interest, (ii) the appropriate fitting of the distorted profile is a means by which such data can be accessed and (iii) the successful fit of the profile, in itself, provides some confidence in the reliability of the required data [18–21].

Although the concept of non-isothermal chemical kinetics was originally considered as long ago as the late 19th century [1], the number of such NIK studies pertaining to polymer stability determination reported in the literature is considerably smaller than the "isothermal" studies and non-isothermal studies are mainly confined to thermogravimetric (TG) analyses [22–24]. The

---

* Corresponding author. Tel.: +61 3 9919 2959.
E-mail address: stephen.bigger@vu.edu.au (S.W. Bigger).

0141-3910/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymdegradstab.2011.05.004

non-isothermal pyrolysis and TG analysis of plastic waste material in the search to produce new fuels [25] is one such example appearing in the polymer literature and the non-isothermal decomposition of inorganic salts [26,27] is representative of fundamental NIK studies that appear elsewhere in the literature. Data derived from non-isothermal pyrolysis techniques such as these, however, can in some cases produce seemingly high values of activation energies compared with other techniques [28]. It has also been suggested that reliable information on the degradation mechanism and kinetic parameters can only be obtained by the use of a set of TG curves recorded at different heating rates [16]. Other examples of NIK studies have included those cited in the chemical education literature [18,29,30], the performance of chemiluminescence experiments under imposed temperature ramps [31–35] and NIK studies of the thermal degradation of cellulose [19,21,36,37].

The thermal depolymerisation of cellulose can be modelled to a very good approximation by assuming first-order kinetics [38–41] out of which can be derived the familiar Ekenstam [40] equations of which one such version is:

$$\ln(1-1/\mathrm{DP}) - \ln(1-1/\mathrm{DP}_0) = k(T)t \tag{1}$$

where DP is the degree of polymerization, DP_0 is the initial DP, and k is the rate constant which is a function of the temperature, T. This model predicts that after prolonged degradation the DP of the polymer will asymptotically approach zero. Unfortunately, this is not what is observed in the case of, say, cellulose which forms stable oligomers after prolonged degradation and the DP tends towards a persistent value of *ca.* 200 corresponding approximately to the crystallite size [19,42–46].

In order to study in further detail the applicability of NIK techniques where Eq. (1) can be applied it is necessary to identify a polymer whose behaviour can be described adequately by this equation at all stages in the thermal depolymerisation process. To this end, polyethylene oxide (PEO) can be identified as a polymer with a wide range of commercial, scientific and industrial uses including applications in cosmetics and pharmaceuticals [47] whose behaviour during thermal depolymerisation conforms closely to the Ekenstam model. The structure of PEO, its relatively low degree of thermal stability and its simple mechanism for degradation makes it an ideal candidate to trial. The structure of PEO is simple and a wide range of molecular weights (MW's) can be prepared for various applications. The thermo-oxidative depolymerisation of PEO proceeds *via* β_1 and β_2 scissions to produce a range of intermediary products [48].

This paper investigates further the application of the NIK technique described previously [19] to PEO, a polymer that is "well behaved" in terms of its thermal depolymerisation kinetics, with a view to drawing conclusions in regard to: (i) the potential savings in experimental time of the NIK technique compared with "isothermal" methods to deliver a result of similar reliability and (ii) whether the computer-based analysis technique used previously [29] delivers a two-dimensional convergence to produce a unique solution of the Arrhenius A-factor and activation energy kinetic parameters from a given set of input data.

1.2. Data analysis

A previous study on the NIK analysis of the degradation of cellulose [29] described an original computer program that utilized an algorithm based on a variation of Eq. (1). In the presence of a linear temperature ramp, the first-order rate constant, $k(T)$, varies in accordance with Eq. (2):

$$k(T) = A \times \exp[-E_a/R(T_0+\beta t)] \tag{2}$$

where A is the Arrhenius A-factor, E_a is the activation energy, R is the ideal gas constant, T_0 is the initial temperature, β is the heating rate and t is time.

An original computer program was written that iteratively calculates the theoretical DP profile in accordance with Eqs. (1) and (2) over a set range of A and E_a values. During each iteration the program calculates the goodness of fit of the theoretical curve to the input experimental data, expressed in terms of the sum of the squares of the residuals (SSR's) existing between the theoretically calculated data and the experimental data. The SSR values obtained in each iteration were calculated in accordance with Eq. (3) and were stored for comparative purposes along with the corresponding kinetic parameters:

$$\mathrm{SSR} = \sum_{n=1}^{n}[F(t_i) - \mathrm{DP}(t_i)]^2 \tag{3}$$

where $F(t_i)$ is the computer-generated non-isothermal DP function, $\mathrm{DP}(t_i)$ is the experimental DP at time t_i and n is the number of experimental DP data.

Clearly, the optimum fit of the experimental data is identified by the minimum SSR value where a set range of A and E_a values are systematically scanned in the iterations. These calculations enable the testing of whether or not a two-dimensional convergence of the A and E_a values occurs to render a unique value of the minimum SSR. Such a condition indicates that the analysis produces a unique set (A, E_a) of the kinetic parameters that pertain to the given analysis. The inherent applicability of the derived kinetic parameters over the entire non-isothermal process is evidenced by the goodness of fit of the theoretically calculated kinetic profile to the experimental data. This, in turn, infers a high level of confidence in the applicability of the kinetic parameters, particularly at lower temperatures that are usually of primary interest in service lifetime prediction calculations.

2. Materials and methods

A sample of PEO powder (MW = 8000 Da, average M_v) was obtained from Sigma Aldrich (Sydney, Australia). Samples were aged in an air-circulating oven (Labec model TWM24/J459) with programmable temperature controller (model 2416). In the case of the isothermal experiments, samples were degraded for up to 40 days at 60, 70, 80 and 90 °C. For the non-isothermal experiments, two sets of samples were degraded at different heating rates, namely 0.10 $^\circ\mathrm{C\,h^{-1}}$ over the range 52–130 °C and 0.04 $^\circ\mathrm{C\,h^{-1}}$ over the range 40–100 °C. In the case of both the isothermal and non-isothermal experiments, samples were taken periodically and prepared as 5% (w/w) aqueous solutions in 0.1 M phosphate buffer at pH = 7 ready for rheological measurements.

The viscosities of the degraded PEO solutions were measured using an Anton Paar Physica MCR Rheometer (model MCR 301) using a cone and plate accessory (model CP-501). The intrinsic viscosity was calculated and the MW was determined using Eq. (4), the Mark–Houwink equation [49]:

$$[\eta] = KM^a \tag{4}$$

where $[\eta]$ is the intrinsic viscosity, M is the MW and K and a are the Mark–Houwink constants. Samples of PEO (MW = 500 to 20,000 Da, Sigma Aldrich, Sydney, Australia) were used to determine the constants K and a, which were found to be 0.074 $\mathrm{mL\,g^{-1}}$ and 0.71 respectively. These parameters are in agreement with those reported elsewhere which range from 0.5 to 0.82 for the exponent, a, [50–52] and 0.072 $\mathrm{mL\,g^{-1}}$ for the constant, K [51].