Polymer Testing 44 (2015) 1–7

Contents lists available at ScienceDirect

Polymer Testing

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

Property modelling

Novel theoretical and computer-assisted modeling of isothermal and non-isothermal depolymerization kinetics

Stephen W. Bigger [a], [*], Marlene J. Cran [a], Manfred A. Bohn [b]

[a] Institute for Sustainability and Innovation, College of Engineering and Science, Victoria University, PO Box 14428, Melbourne, 8001, Australia
[b] Fraunhofer-Institut für Chemische Technologie ICT, Postfach 1240, D-76318 Pfinztal-Berghausen, Germany

ARTICLE INFO

Article history:
Received 10 February 2015
Accepted 16 March 2015
Available online 23 March 2015

Keywords:
Non-isothermal degradation
Arrhenius
Depolymerization kinetics

ABSTRACT

A novel kinetic model accounting for the observed asymptotic approach of the degree of polymerization (DP) to a limiting value significantly greater than unity on prolonged degradation is derived and applied to the solid-state degradation of cellulose (Kraft paper) and poly(acrylic acid) (PAA) under isothermal and non-isothermal conditions. Experimental data were fitted using two iterative computer algorithms: one for isothermal DP data and the other for non-isothermal DP data obtained under a linear temperature ramp. The apparent activation energy for the solid-state recombination of chain radicals was found to be low in each case and was attributed to the proximity of free radicals being facilitated by restrictions imposed by the polymer matrix. The application of the model to non-isothermal DP yielded rate parameters that could be reconciled with those obtained from isothermal analyses, suggesting the novel approach has much merit for the future study of polymer degradation.

1. Introduction

The literature on polymer degradation kinetics and its application to in-service time prediction is extensive with a majority of individual experiments having been conducted under isothermal conditions. One example is the isothermal depolymerization of cellulose that has been of particular interest due its industrial applications [1–6]. A preponderance of isothermal degradation studies exists despite the fact that many, if not most, in-service applications of polymers involve dynamic or cyclic temperature variations and/or fluctuations. The considerably fewer non-isothermal studies [7–13] are concerned with mostly thermogravimetric (TG) analyses [14,15] commonly performed under a time-dependent temperature gradient. Examples of the latter include the non-isothermal degradation of cellulose in an inert atmosphere [16] as well as the non-isothermal pyrolysis and TG analysis of plastic waste material in the production of new fuels [17].

The study of polymer degradation kinetics either by isothermal or non-isothermal methods has generally invoked the assumption that a single Arrhenius relationship holds across the range of temperatures investigated. Although this assumption may sometimes be valid, there has been considerable evidence to suggest this is not always the case [18–20]. A review of this topic [21] has identified systems where departure from simple Arrhenius behaviour exists as a result of at least two kinetic processes that operate simultaneously. Often in such cases, one process predominates at lower temperatures whereas another may become more pronounced at higher temperatures. It is, therefore, important to be aware of the potential for departure from normal Arrhenius behavior when assessing the results from polymer degradation experiments, particularly if one is attempting to estimate expected in-service times from the analysis of the data.

---

[*] Corresponding author.
E-mail address: stephen.bigger@vu.edu.au (S.W. Bigger).

http://dx.doi.org/10.1016/j.polymertesting.2015.03.013
0142-9418/Crown Copyright © 2015 Published by Elsevier Ltd. All rights reserved.

In dealing with polymer degradation, non-isothermal experiments can inherently capture data that are collected under conditions close to those expected in service. In this way, non-isothermal techniques have the potential to deliver meaningful in-service time predictions provided appropriate methods and models are devised in order to interpolate the experimental data [22]. Non-isothermal experiments are also expected to deliver the required kinetic information in considerably shorter experimental times than isothermal techniques [22] provided meaningful conversions are reached, and this is possibly the main attraction of these methods.

A previous study [23] on the application of non-isothermal kinetics to the thermal degradation of cellulose demonstrated that kinetic parameters were obtained in a significantly shorter experimental time compared with standard isothermal experiments. It was also suggested that the thermal degradation of cellulose does not follow precisely a simple depolymerization mechanism, as evidenced by the observation that the degree of polymerization (DP) persists at *ca*. 200 after extended periods of time during isothermal degradation [24–28]. This phenomenon appears to have had little consequence on the accurate prediction of in-service time based on the non-isothermal experimental data, presumably because the fitting procedure [23] focused on the initial part of the DP profile that contained those data obtained under temperature conditions closest to the conditions encountered in service.

It is, therefore, evident that the simple Ekenstam model [29,30] is unable to account for the often experimentally observed persistence of the DP at a value significantly greater than unity after a prolonged period of isothermal degradation. It is also apparent that there is potential for the use of non-isothermal methods to efficiently deliver kinetic data for depolymerization processes. In view of these observations, this paper: (i) proposes a model that describes the isothermal depolymerization of polymers that exhibit a persistence in their DP after extended periods of isothermal degradation, (ii) describes the application of an arithmetic computer algorithm that can be used to fit isothermal experimental data using the model and (iii) describes a computer-based arithmetic technique in which the derived theoretical model can be applied to non-isothermal kinetics in order to demonstrate the potential of such a technique in the convenient determination of kinetic parameters. The isothermal and non-isothermal degradation of cellulose (Kraft paper) and poly(acrylic acid) are investigated.

2. Experimental section

2.1. Non-isothermal depolymerization of cellulose

The data on cellulose degraded under non-isothermal conditions were obtained from transformer-grade insulation paper (Kraft paper, ImatranVoima OY, Finland) and its characterization has been reported elsewhere [23]. The paper was aged by immersion in naphthenic oil (Nynas 10GB) commonly used in electrical transformers. In the first experiment, 1.0 g of Kraft paper was aged in 100 mL of aerated oil in a sealed 150 mL glass vessel at 1.0 atm of air [6]. In the second experiment, 1.0 g of Kraft paper was aged in 100 mL of nitrogen-purged oil in a sealed 150 mL glass vessel at 1.0 atm of nitrogen [31]. The sealed vessels were dynamically heated in a fan-forced, programmable oven from room temperature to 200°C at 1.0 K h^{-1} with samples being removed at *ca*. 10 h intervals, starting from the time when the temperature reached 70°C. Following Soxhlet extraction with chloroform to remove residual oil and dissolution in a cupric ethylenediamine solution, the DP of the cellulose was measured by viscometry with a Cannon-Fenske viscometer [32].

2.2. Thermal depolymerization of poly(acrylic acid)

Poly(acrylic acid) (PAA, DP = 1800) was obtained from Sigma Aldrich (Australia). Samples were aged in an air-circulating oven (Labec model TWM24/J459) equipped with a programmable temperature controller (model 2416). In the isothermal experiments, samples were degraded for up to a maximum of *ca*. 670 h at 105, 135, 150 and 175°C. For the non-isothermal experiments, samples were degraded at heating rates of 0.5, 1.0 and 2.0 K h^{-1} over the range 40 to 180°C. In all experiments, samples were taken periodically and prepared for rheology measurements as 5% (w/w) aqueous solutions in 0.1 M phosphate buffer at pH = 7.

The viscosities of the PAA solutions were measured using an Anton Paar Physica MCR Rheometer (model MCR 301) with a cone and plate accessory (model CP-501). The intrinsic viscosity was calculated and the viscosity average molecular mass, M_η, determined using the Mark-Houwink equation with associated parameters [33]. Samples of PAA (M_w = 1,250 − 130,000 Dalton, Sigma Aldrich Australia) were used for calibration.

3. Theoretical considerations

3.1. Equation for depolymerization kinetics

The traditional kinetic model for polymer depolymerization assumes that a first-order random scission process occurs [4,30,34–36] and predicts that the DP will asymptotically approach unity after prolonged degradation. This approach does not account for the possibility of chain recombination which often manifests itself in crosslinking and gel formation, resulting in a persistent DP significantly greater than unity.

Eq. (1), whose derivation is given in the Supplementary Material, describes the time dependence of the DP during degradation in which "back" reactions such as cross-linking are allowed:

$$1/\nu = (1/\nu_0)\mathrm{e}^{-(k_1+k_2)t} + [(k_1 + k_2/\nu_0)/(k_1 + k_2)] \times \left[1 - \mathrm{e}^{-(k_1+k_2)t}\right] \quad (1)$$

where ν is the DP at time $t = t$, ν_0 is the DP at $t = 0$, k_1 and k_2 are the first-order rate constants for the forward (chain scission) and reverse (chain recombination, etc.) processes respectively.