Polymer Testing 27 (2008) 675–678

Contents lists available at ScienceDirect

Polymer Testing

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

Short Communication: Analysis Method

Determination of hydroxyl number in aliphatic polyesters and polyethers using a colorimetric method

J. Padilha de Paula [a,*], P.V. Farago [a], P.B. Binhara [b], S.A. Silva [b], S.F. Zawadzki [b]

[a] Department of Pharmaceutical Sciences, State University of Ponta Grossa, Av. Carlos Cavalcanti, 4748, Ponta Grossa, Paraná 84030-900, Brazil
[b] Department of Chemistry, Federal University of Paraná, Centro Politécnico Jardim das Américas, Curitiba, Paraná 81531-990, Brazil

ARTICLE INFO

Article history:
Received 21 February 2008
Accepted 14 May 2008

Keywords:
Colorimetric method
Hydroxyl number
Polyesters
Polyethers
Polyols

ABSTRACT

Hydroxyl number quantification is an important tool used in polymer science and practice. However, the standard method recommended for polyols, *e.g.* polyesters and polyethers, uses noxious chemicals that occasionally can cause hydrolysis of the polymeric material. Therefore, further procedures have been investigated as alternative techniques that can be useful in the polymer laboratory as routine. The aim of this paper was to develop and validate a sensitive colorimetric assay for determination of hydroxyl number in aliphatic polyesters and polyethers. This study was carried out for all validation parameters established by the international guidelines. Validation results on linearity, specificity, accuracy and precision were effectively performed. The reproducibility presented a relative standard deviation of 0.81. The proposed method is a simple, low cost and easy handling approach for the quantitative determination of hydroxyl number in aliphatic polyesters and polyethers.

1. Introduction

The determination of hydroxyl number is a fundamental approach for polymer characterization. It is particularly used in quality control measurements for manufacturers and users of polyols, and as a strategy for the chemical monitoring of polyesterification reaction between dicarboxylic acids and diols [1,2]. According to the ASTM standard, the reference test for the determination of hydroxyl numbers in polyols is based on the esterification of the hydroxyl groups using a phthalic or acetic anhydride solution in pyridine with a final titration of the excess acid reagent by a previously standardized sodium hydroxide solution [3]. However, this procedure requires a substantial period of time and promotes the exposure of the operator to some chemicals of documented toxicity, in particular the pyridine solution [2].

Furthermore, some polyesters when evaluated by the standard method show easily broken bonds that can be hydrolyzed. This unexpected reaction can result in significant interference with the final result of the hydroxyl number quantification. This disadvantage was verified by our research group when the hydroxyl number of poly(lactic acid) was performed in pyridine/acetic anhydride medium. For this polymer, a depolymerization process occurred and lactic acid was released into the reaction medium, causing an error in the determined hydroxyl value.

Alternatives procedures for the hydroxyl number determination have been reported as mass spectroscopy, nuclear magnetic resonance, infrared spectroscopy and chromatography methods [4–6]. Hydroxyl number prediction in polyesters was investigated by infrared spectroscopy in association with mathematical tools, *e.g.* multivariate calibration approaches or artificial neural networks [7]. In spite of the reported advantages, these methods can show some limitations in respect of sensibility, versatility [6], availability of equipment and high cost.

The goal of this paper is to propose an alternative, low cost and easy handling method to determinate hydroxyl number in aliphatic polyesters and polyethers by

---

* Corresponding author. Fax: +55 42 32229966.
E-mail address: jopadilha@terra.com.br (J. Padilha de Paula).

0142-9418/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymertesting.2008.05.007

a colorimetric-based procedure. Also, the analytical validation was performed according to the literature [8].

2. Experimental

2.1. Materials

CAPA® 2043 [bifunctional caprolactone polyol, molecular weight (M_w) 400 g mol^{-1}, typical hydroxyl value 280 mg KOH g^{-1}] and CAPA® 2085 (bifunctional caprolactone polyol, M_w 830 g mol^{-1}, typical hydroxyl value 135 mg KOH g^{-1}) were kindly provided by Solvay (Warrington, United Kingdom).

PEG 400 (bifunctional polyethylene glycol, M_w 400 g mol^{-1}, typical hydroxyl value 150 mg KOH g^{-1}) was purchased from Delaware (Porto Alegre, Brazil). PET 1 and PET 2 were synthesized by the transesterification of poly(ethylene terephthalate) (PET), respectively, as pellets (Rhopet® S80, Rhodia, São Paulo Brazil) (1 mol from PET-mer unit) and as post-consumer recycled PET (colourless soft drink bottles) (1 mol from PET-mer unit), with diethylene glycol (5 mol). These reactions were carried out at 210 °C for 5 h using zinc acetate (0.01 mol) as catalyst. Purification was performed by washing with Milli-Q® water to remove diethylene glycol excess. Products were dissolved in acetone, filtered and dried to obtain PET 1 and PET 2. PET 1 and PET 2 (polyol-PET copolymers) showed M_w 972 g mol^{-1} and M_w 1074 g mol^{-1}, respectively. VORANOL® 2110 (bifunctional polypropylene glycol, M_w 1300 g mol^{-1}, typical hydroxyl value 55 mg KOH g^{-1}) was obtained from Dow Chemical (Midland, USA). Other chemicals were analytical grade. Purified Milli-Q® water (Millipore, Bedford, USA) was used throughout the study.

2.2. Procedures

2.2.1. Jones reagent

The hydroxyl end-groups in the chemical structure of the indicated polymers were initially submitted to a modified Jones reaction, a general assay for primary and secondary alcohols. Jones reagent [9] was obtained as a saturated solution of potassium dichromate in sulfuric acid (25 g $K_2Cr_2O_7$/25 mL H_2SO_4 and 75 mL Milli-Q® water).

2.2.2. Standard solution

The standard polymeric solution was obtained from CAPA® 2085 with a hydroxyl value of 136.6 mg KOH g^{-1}, previously determined by the ASTM standard [3]. A mass of 1.2 g of CAPA® 2085 was accurately weighed and transferred to a volumetric flask of 100.0 mL. The volume was made up with acetone to achieve a concentration of 1.6392 mg KOH mL^{-1}.

2.2.3. Preparation of the standard solution and modified Jones technique

From the standard solution, 10 different dilutions corresponding to hydroxyl values ranging from 0.16392 mg KOH mL^{-1} to 1.6392 mg KOH mL^{-1} were exactly obtained in acetone to perform a volume of 5 mL. In each glass vial, 300 μL of the Jones reagent was added and the reaction medium was kept into an ultrasonic bath (Elma, Transonic Digital, Singen, Germany) for 1 min at 25 °C. Then, 2 mL HCl 3 mol L^{-1} was poured into the vial which remained in the ultrasonic bath for 30 min.

2.2.4. Colorimetric measurements

The samples prepared as mentioned above were analyzed at 600 nm in a Perkin–Elmer Coleman Junior® III Spectrophotometer (Perkin–Elmer Corp., Model 6|8, Waltham, USA). The absorbance measurements were obtained in a Coleman® glass tube (1 cm optical path length). The absorptions data were plotted in the Origin® software (MicroCal Software, version 7.0, Northampton, USA) to acquire an analytical curve.

2.2.5. Analytical validation

Analytical validation was performed according to the international guidelines [8]. The linearity was established from three different standard solutions of CAPA® 2085 (1.6392 mg KOH mL^{-1}) that resulted in three analytical curves as previously described. Absorbance values were plotted and the correlation coefficient was determined for each curve. Also, an average analytical curve was carried out to calculate the detection and quantification limits using Eqs. (1) and (2), respectively.

$$\mathrm{DL} = \frac{3.3\sigma}{S} \tag{1}$$

$$\mathrm{QL} = \frac{10\sigma}{S} \tag{2}$$

where DL is the detection limit, QL is the quantification limit, σ is the standard deviation of the responses and S is the slope of the analytical curve.

The precision was estimated by the repeatability and the intermediate precision (reproducibility) parameters. Under the same conditions, *e.g.* day and analyst, nine different sample solutions divided into three groups containing 0.53274 mg KOH mL^{-1}, 0.90156 mg KOH mL^{-1} and 1.27038 mg KOH mL^{-1} were assayed by the colorimetric method at 600 nm. For the intermediate precision, nine sample solutions containing 0.90156 mg KOH mL^{-1} were prepared and separated into three groups. On three non-consecutive days, each group was colorimetrically determined by different analysts. The repeatability and intermediate precision results were evaluated from the obtained relative standard deviations (RSD).

For accuracy, nine sample solutions divided into three groups with 0.53274 mg KOH mL^{-1}, 0.90156 mg KOH mL^{-1} and 1.27038 mg KOH mL^{-1} were prepared. A known weight of CAPA® 2085 equivalent to 0.08196 mg KOH mL^{-1} was added to each solution, resulting in three groups with 0.6147 mg KOH mL^{-1}, 0.98352 mg KOH mL^{-1} and 1.35234 mg KOH mL^{-1}. The absorbance values were obtained by colorimetric measurements at 600 nm and the percentage recovery was calculated.

2.2.6. Sample analyses

The investigated sample solutions were obtained from the polymers CAPA® 2043, PEG 400, PET 1, PET 2, and VORANOL® 2110. Considering the labeled and/or previously