Polymer Testing 67 (2018) 110–121

Contents lists available at ScienceDirect

Polymer Testing

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

Material Characterisation

Structure-rheology relationship of fully bio-based linear polyester polyols for polyurethanes - Synthesis and investigation

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ARTICLE INFO

Keywords:
Bio-based poly(propylene succinate)
Macromolecular structure
Rheological behavior
MALDI-ToF mass spectrometry
Gel permeation chromatography

ABSTRACT

The synthesis of polyols from renewable substances as an alternative for petrochemical-based polyols play important matter in the polyurethane industry. In this work, the fully bio-based linear polyester polyols with different catalyst amounts were synthesized via two-step polycondensation method. The effect of various catalyst content on the structure and rheological behavior were established. Fourier Transform Infrared Spectroscopy, Nuclear Magnetic Resonance, Gel Permeation Chromatography and Matrix-Assisted Laser Desorption/Ionization Time-of-Flight mass spectrometry allowed confirming the impact of the catalyst amount during synthesis on the molecular structure of the resulted polyols. Through the hyphenation of these sophisticated polymer characterization techniques, information on the molecular weight distribution was obtained. Moreover, it was found that the obtained polyols are non-Newtonian fluids. According to conducted measurements, it was observed that the poly(propylene succinate)s prepared with the use of the 0.25 wt.% and 0.30 wt.% catalyst revealed the structures and selected properties the most akin to design.

1. Introduction

Currently, clearly visible is the growing interest of using biorenewables as a primary component at the polymer synthesis. This trend is determined by the unfavorable oil consumption forecasts when the increasing demand for the polymer materials utilization performs on the global market. Recently, the bio-components have become readily accessible which allow producing biopolymers, including polyester polyols even in 100% from bio-resources [1,2]. The biotechnological process consisting of the corn crops fermentation allow obtaining bio-based glycols and dicarboxylic acids. Such microorganisms as fungi, yeasts or bacteria [3–6] lead to the formation of the proper product during fermentation processes.

The major advantages which contribute to the increasing interest in the utilization of biorenewables in chemical syntheses [7] represent the reduction of energy consumption, the decrease of the greenhouse gasses production and CO_2 emission reduction. Moreover, the economic volatility reduction by the decrease in the fossil fuel stocks utilization and the decline in the production costs with increasing production scale made a contribution to develop the research on the biorenewables utilization.

The initial reaction, which leads to the polyester polyols obtainment, is a two-step polycondensation reaction. The first step constitutes the esterification or transesterification reaction between carboxylic acid or carboxylic acid esters, respectively, and the excess of the glycols. During the esterification, water or alcohols are formed, respectively, as by-products which hindered the main reaction. The capability of the by-product elimination from reaction mixture affected the reaction kinetics and productivity. After the by-product elimination, second step – polycondensation reaction, can be started [8].

It is characteristic for this type of polycondensation to run at high temperatures, sometimes exceeding 200 °C. However, the choice of temperature depends on the thermal stability of both substrates and the main product. The disadvantages of these methods are often the side reactions to which the oxidation reaction takes place. To prevent these reactions, polycondensation is carried out under inert gas (eg, nitrogen, argon) or under reduced pressure. In addition, the use of both reaction conditions facilitates the removal of the by-product from the reaction medium, thereby shifting the reaction to the main product. It is well-known that the reaction kinetics are also affected by the amount of the catalyst, the chemical structure of the catalyst and monomers, monomer concentration, by the temperature during both steps, reaction time, and removal rate of the low molecular by-products [9]. By manipulating these parameters, we can optimize the polycondensation process to accelerate the formation of the main product [10].

Among the industrial properties such as hydroxyl and acidic number and viscosity, the macromolecular structure has also a huge impact on the polyurethane synthesis and properties of resulted materials.

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https://doi.org/10.1016/j.polymertesting.2018.02.022
Received 12 January 2018; Received in revised form 15 February 2018; Accepted 17 February 2018
Available online 22 February 2018

Thereby, it is necessary to explore the macromolecular structure of the polyols before polyurethane material synthesis. Recently, the huge interest gained molecular weight distribution study with the use of Matrix-Assisted Laser Desorption/Ionization Time-of-Flight mass spectrometry [11–15]. This method allows obtaining information about absolute molecular weights, identification of mass-resolved polymer chains including intact oligomers, and simultaneous determination of end groups in a polymer sample. Many scientists have used this method to determine the molecular structure of the various type of polymers. Król and Pilch-Pitera [16,17] used this method for structure investigation of urethane oligomers for polyurethane elastomers. The researchers used this method to proposed the majority of molecular structure presented in the materials. They affirmed that not all of obtained bands could be identified in this method but the GPC findings could be confirmed.

One of the most important properties which verify polyols possibility to industrial processes is their rheological behavior. Furthermore, rheology can inform about the dynamic viscosity of the fluids, which is important properties during preparation at the used temperature and pressure. The rheological behavior and viscosity are also connected with the structure of the polymer chains [18]. Proposed rheological models, as an optimal individual function, described the fluids rheological behavior. There is two primary behavior delineated the liquids, namely, Newtonian and non-Newtonian. The Newtonian model characterizes the ideal fluids, which performed linear curve course in the rheograms, which show the shear stress via shear rate (dynamic viscosity stay constant for all point of the curve). This model is described by equation (1):

$$\tau = \eta * \gamma \quad (1)$$

Where: τ – shear stress [Pa], γ – shear rate [s^{-1}], η – viscosity [Pas].

Non-Newtonian fluids are described by a large number of models. This type of fluids does not show the linearity of the curve course in the rheograms. The non-Newtonian liquids exhibit the complex structure, and due to the various deformation effects, they can be characterized as pseudoplastic fluids, viscoplastic, dilatant or thixotropic liquids. There are several mathematical models which allow describing the information about the non-Newtonian fluids rheological behavior. There are three mostly applied models: Herschel, Bulkley, Ostwald-de Waele and Bingham models [19]. For the test analysis, two of them will be characterized.

The Herschel, Bulkley model, describe the fluids with a nonlinear rheograms. The model is expressed by equation (2):

$$\tau = \tau_0 + K * \gamma\hat{}n \quad (2)$$

Where: τ – shear stress [Pa], τ_0 – yield stress [Pa], γ – shear rate [s^{-1}], K – consistency index [−], which gives an idea of the fluid viscosity, n – flow behavior index [−], which should be similar to comparative study of the different fluids. The 'τ_0' and 'n' values give information about fluids behavior as follows:

$\tau_0 = 0$, $n = 1$ – means that the Herschel, Bulkley mathematical model describes the Newtonian behavior of the fluids;
$\tau_0 = 0$, $n > 1$ – the Herschel, Bulkley mathematical model describes the dilatant behavior (shear thickening);
$\tau_0 = 0$, $n < 1$ – the Herschel, Bulkley mathematical model describes the behavior of the pseudoplastic fluid (shear thinning);
$\tau_0 > 0$, $n = 1$ – the Herschel, Bulkley mathematical model describes the Bingham plastics, which are the fluids with the linear viscosity curve above the yield stress [19].

The Ostwald-de Waele describe the shear thinning fluids without a yield stress. The model is expressed by equation (3):

$$\tau = K * \gamma\hat{}(n-1) \quad (3)$$

Where: τ – shear stress [Pa], γ – shear rate [s^{-1}], K – consistency index [−] gives an idea of the fluid viscosity, n – flow behavior index [−] which give information about fluids behavior as follows:

$n < 1$ – pseudoplastic
$n = 1$ – Newtonian fluids,
$n > 1$ – dilatant fluids [19]

Schrock and co-workers [20] investigated the structure, thermal phase transition temperatures and viscosity of few polyester polyols prepared based on succinic acid, adipic acid and various glycols. Materials were synthesized with planned average molecular structure at ca. 1000 and 2000 Da. They explored that the poly(propylene succinate)s polyesters and co-polyester with other glycols revealed high viscosity even at elevated temperature. Schrock investigated that the viscosity value of pure poly(propylene succinate) at 80 °C revealed ca. 1000 mPas. Our work presents the impact of the catalyst employment during synthesis on the viscosity of poly(propylene succinate) and other properties.

In this work, the synthesis of fully bio-based poly(propylene succinate)s via well-known two-step polycondensation method is described. The polycondensation catalyst, tetraisopropyl orthotitanate TPT, was used to find the catalyst impact on the structure and rheological behavior. Six poly(propylene succinate)s were analyzed by Fourier Transform Infrared Spectroscopy and Nuclear Magnetic Resonance. The structure was also verified by Gel Permeation Chromatography, which characterizes the impact of the catalyst amount on the molecular weight distribution. Moreover, for more detailed investigation, the study of the molecular weight distribution was expanded about results of the Matrix-Assisted Laser Desorption/Ionization Time-of-Flight mass spectrometry. The influence of the catalyst amount on the rheological behavior was determined with the use of rotary rheometer. The choice of the measurements temperature ranges and shear rates were done due to the temperature conditions for industrial processes during preparation and production of polyurethane materials [18].

2. Materials and methods

2.1. Materials

The main components used in this study:

Bio-based succinic acid (SA) was obtained from BioAmber Sarnia Inc. (Ontario, Canada) as a solid-state component with purity in the range 98–100%. The molecular weight was 118.09 g/mol and relative density at 20 °C was 0.900 g/cm^3.

Susterra Propanediol (1.3-propanediol) was obtained from DuPont Tate&Lyle Corporation Bio Products (Loudon, Tennessee, USA) as a liquid component with purity ca. 99.98%. The molecular weight was 76.09 g/mol, and relative density at 20 °C was 1.053 g/cm^3. Moreover, water content by Karl Fischer equaled 12.1 ppm and a dynamic viscosity at 20 °C was 52 mPas.

Tetraisopropyl orthotitanate, Ti(O-i-Pr)$_4$ (TPT) was purchased from TCI Chemicals (India) as a liquid with the purity ca. 97% and the molecular weight: 284.22 g/mol and was used as a catalyst with four different amount.

For the analytical measurement methods, other materials and solvents were used of analytical grade.

2.2. Bio-based polyesters synthesis

Aliphatic bio-based polyester polyols – poly(propylene succinate)s, were prepared with the use of succinic acid SA and 1.3-propanediol PDO, both with a natural origin. Catalyst, tetraisopropyl orthotitanate TPT, was used as a glycol equivalent in five different amount, namely, 0.1 wt.% (PPS-0.10), 0.15 wt.% (PPS-0.15), 0.2 wt.% (PPS-0.20), 0.25 wt.% (PPS-0.25) and 0.30 wt.% (PPS-0.30). The reference sample