



Synthesis of fully bio-based and solvent free non-isocyanate poly (ester amide/urethane) networks with improved thermal stability on the basis of vegetable oils



Abdolreza Farhadian ^a, Abbas Ahmadi ^b, Ismail Omrani ^b, Ahmad Babaei Miyardan ^b, Mikhail A. Varfolomeev ^{a,*}, Mohammad Reza Nabid ^{b,**}

^a Department of Physical Chemistry, Kazan Federal University, Kremlevskaya str. 18, 420008, Kazan, Russian Federation

^b Department of Polymer and Materials Chemistry, Faculty of Chemistry and Petroleum Science, Shahid Beheshti University, G.C. 1983963411, Tehran, Iran

ARTICLE INFO

Article history:

Received 7 May 2018

Received in revised form

2 July 2018

Accepted 10 July 2018

Available online 11 July 2018

Keywords:

Non-isocyanate poly (ester amide/urethane) network

Vegetable oils

Biobased polymers

Environment-friendly synthesis

Thermal stability

Green chemistry

ABSTRACT

The purpose of this study is to synthesize non-isocyanate poly (ester amide/urethane) networks, based entirely on vegetable oil through a green method, i.e., without solvent and having any rigid and aromatic structures to improve their thermal stability. For this purpose, first, three amines were synthesized from castor oil and oleic acid. Second, carbonated sunflower oil (CSFO) was obtained by reaction of epoxidized sunflower oil with CO₂ at atmospheric pressure. In the final step, CSFO easily reacted with bio-based amines by melt-blending without catalyst to give corresponding non-isocyanate polyurethane (NIPU) networks. The Fourier-transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR), X-ray powder diffraction (XRD), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA) techniques were applied to characterize the structural, thermal and physical features of NIPU networks. In addition, to determine the environmental stability the water absorption amount and the degradation percentage were calculated in the deionized water and phosphate saline buffer, respectively. These NIPU networks showed an excellent thermal stability (T₅ wt% between 323 and 386 °C), low water absorption and degradation (4–10 and 1.04–1.40 wt% respectively). The results show the potential of this environmentally friendly strategy for preparing bio-based NIPU for high performances. Furthermore, the presence of an aliphatic ester group and their biodegradability nature may also make them proper for biological and/or biomedical applications.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

Isocyanate, phosgene, health, and environment are four words that come to our minds when we hear the name of polyurethanes (PUs). Since the introduction of polyurethanes to the realm of polymer chemistry in 1937, they have found many applications in the industry, academic research and in human's daily life. The reason behind this is their versatile properties, availability of raw material and mild and easy conditions for synthesis [1]. Despite all these advantages, polyurethanes also have disadvantages which pose a serious challenge to their use and application in the future. A

major drawback of polyurethanes is that their monomers are based on petroleum resources. As fossil resources deplete by the day, many chemists today are looking for bio-based precursors. Biomass such as lignin, polysaccharides or vegetable oils represents an interesting alternative for polymer production [2,3]. An excellent solution is using polyols as starting materials. Many researchers have focused on bio-based polyols to synthesize and use them in the preparation of polyurethanes since most of the final polyurethane weight is related to the polyol used in their synthesis [4,5]. Sensitivity to moisture is another important problem for isocyanate-functional materials; as they can react in presence of water at ambient temperature, and thus demand many safety precautions during storage, transportation, and production of polyurethanes. Moreover, traditional polyurethanes due to the presence of thermally labile biuret and allophanate groups in their structure show relatively low thermal stability [6]. But the biggest disadvantage of polyurethanes is that they are based on isocyanate.

* Corresponding author.

** Corresponding author.

E-mail addresses: mikhail.varfolomeev@kpfu.ru, vma.ksu@gmail.com (M.A. Varfolomeev), m-nabid@sbu.ac.ir (M.R. Nabid).