



Contents lists available at SciVerse ScienceDirect

European Polymer Journal

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

Characterization of polyurethane networks structure and properties based on rapeseed oil derived polyol

Anda Fridrihsone*, Uldis Stirna, Brigita Lazdiņa, Marija Misāne, Dzintra Vilsone

Polymer Laboratory, Latvian State Institute of Wood Chemistry, 27 Dzerbenes St., Riga, LV 1006, Latvia

ARTICLE INFO

Article history:

Received 11 July 2012

Received in revised form 1 March 2013

Accepted 11 March 2013

Available online xxxx

Keywords:

Rapeseed oil polyols

Polyurethane networks

Mechanical properties

Thermal properties

Cohesion energy density

Molecular weight between cross-links

ABSTRACT

Polyurethane (PU) networks were synthesized from rapeseed oil (RO) and triethanolamine (TEA) polyols, as well as from modified RO/TEA polyol with ϵ -caprolactone (CPL) and triethylene glycol (TEG) additives. The study was carried out to determine the impact of molecular weight between cross-links (M_c), urethane group concentration and dangling chain concentration on structure of PU networks, physical, mechanical and thermal properties. The M_c of PU networks was varied using isocyanates (4,4'-methylene diphenyldiisocyanate (MDI), polymeric MDI Suprasec 2651, a polymeric MDI Lupranate M20) separately or in a mixture; the functionality of isocyanates was changed in range from 2.0 to 2.7. Using The Fourier transform infra-red spectral analysis (FTIR-ATR) the impact of M_c and urethane group concentration on PU networks to form hydrogen bonds was determined. Hydrogen bonding index (HBI) was calculated using ratio $C=O_b/C=O_{free}$, parameter R was calculated using ratio NH_b/NH_{free} . It was found out that with increasing M_c of PU networks, HBI and R also increases. Glass transition temperature (T_g) of PU networks was determined using differential scanning calorimetry (DSC). Using model compound bis(2-hydroxyethyl)methylamine (MDEA) for PU networks synthesis, it was discovered that long dangling chains from RO/TEA are screening polar groups within PU networks, thus H-bond formation is interfered and as a result T_g and tensile strength decreases significantly in PU networks obtained from RO/TEA polyols. The volume contraction (Δv) during PU-forming reaction is determined by using experimental densities of PU and raw material additive densities. Higher Δv was for PU networks with higher urethane group concentration and higher M_c . The cohesion energy density (CED) and Van der Waals volume (V_w) was calculated for groups in PU networks structure. There is a correlation between CED and tensile strength of the obtained PU. The thermal properties of PU networks were characterized using thermogravimetric analysis (TGA). The initial weight loss (5 wt.%) occurs at lower temperature with increasing M_c and urethane group concentration.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

In recent years vegetable oils have attracted growing attention as raw materials for polyol synthesis for polyurethanes (PUs). PUs are well known and widely used because of their versatility. However, nowadays one of the prob-

lems PU industry is facing is their dependence on petroleum feedstock [1–3].

Many studies have been devoted to obtain PUs from renewable raw materials. In PU manufacturing, hydroxylated vegetable oils can be a potential replacement for conventionally used petroleum polyols. There are numerous publications about obtaining PUs from different vegetable oil based polyols. Vegetable oils such as soybean [4,5], sunflower and rapeseed oil [6], palm kernel oil [7], linseed oil [8] and castor oil [9]. To obtain PUs from renewable

* Corresponding author. Tel.: +371 67553063; fax: +371 67550635.
E-mail address: anda.fridrihsone@gmail.com (A. Fridrihsone).

vegetable oils there are some aspects that have to be considered – hydroxyl value, functionality, dangling chains and structure of polyol and their effect on properties of PU network.

The properties of PU are influenced by several features; all of which are interdependent to some extent. M_c is used to characterize the cross-linked polymer networks. Cross-linked polymers contain at least two bridges to another chain per any given chain. The value of M_c strongly depends on the PU network structure. If the structure of PU network is known, the M_c can be easily determined from the structure and functionality of the building blocks in the polymer synthesis. M_c is strongly related to cross-linking density in PU. If M_c increases then cross-linking density decreases and *vice versa*. Cross-linking formation in PU leads to a decrease in the molecular mobility and flexibility and causes an increase in modulus of elasticity (E) and tensile strength (σ_t), as well as increases T_g of PU, but on the other hand decreases elongation at break (ϵ). Cross-linking formation in PU can be altered by increasing isocyanate and polyol functionality, respectively the M_c decreases and it can be expected that tensile properties of PU will increase while elongation at break will decrease [5,10–12]. It has been found out that for PU elastomers M_c in range from 2100 to 4300 g/mol, σ_t decreases, but at M_c higher than 5300 g/mol σ_t increases. It is explained by the fact that with high cross-linking density the formation of intermolecular forces between polymer main chains are interfered [11].

Several researchers have studied the properties and structures of PU networks obtained from different vegetable oil polyols and have concluded that the structure of networks, mechanical and thermal properties depend on the cross-linking density [2,14–17]. Carme Coll Ferrer et al. [15] have characterized and compared PU networks obtained from vegetable derived polyols and synthetic based networks. As discussed before, the increase in cross-linking formation leads to higher T_g . From another point of view it is well known that the T_g of polymers decrease significantly when plasticizers are added [12].

The secondary weak forces or intermolecular forces between polymer chains play very important role in PU properties. The intermolecular forces (attractions) are H-bonding, London dispersion forces, permanent dipole interactions, ionic bond interactions and Van der Waals forces. They can be expressed as CED. As a rule, high CED leads to higher mechanical properties. Polyol structure has a very significant effect on a value of CED of PU networks [10,11].

PU obtained from vegetable oil polyols can contain short, average or very long dangling chains depending on the chosen method of polyol synthesis. Dangling chains and their structure significantly impact the properties of PU networks. N-substituted diethanolamides were employed as chain extenders in the synthesis of segmented PU having the structure of comb shaped copolymers [18]. He et al. has reported that incorporation of short dangling chains in semi-rigid polymer system is an effective way to reduce crystallization [13]. Stirna et al. [19] has studied comb shaped segmented PU properties when glycerol monostearate, D,L-3-octadecyloxy-1,2-propanediol, 3-

tert-butoxy-1,2-propanediol and 3-benzyloxy-1,2-propanediol are used as a chain extender. In segmented PU the impact of dangling chain CED and their V_w on stress-strain and thermal properties, as well as on formation of H-bonds is determined.

It is known that PU networks obtained from castor oil and polyols from epoxidized vegetable oils contain short dangling chains [2]. It is found out that short dangling chains favor intermolecular plasticization, decrease T_g of polymer, increase hydrophobicity of polymer. But PU networks obtained from vegetable oil monoglycerides or alkanolamines contain long C12–C22 dangling chains [20,22]. The impact of long dangling chains on PU networks and segmented PU elastomers which are derived from vegetable oil polyols or monoglycerides, has been little studied [15,21,22].

Overall it can be concluded that many studies have been carried out based on different factors, for example, cross-linking density, urethane group concentration or dangling chain impact on PU networks' structure and properties. There are few studies in which impact of all previously mentioned factors on PU networks structure and properties are characterized.

The goal of our research was to obtain polyurethane networks from polyol obtained from RO using transesterification with TEA, as well as to obtain RO polyol modifications with CPL and to obtain RO polyol system TEG to see variation in hydroxyl value, respectively, in urethane group concentration. In this work, an attempt to correlate the properties of PU network with their structure has been made. To explain and characterize the relationship between PU structure and mechanical, physical and thermal properties, the impact of CED, urethane group concentration, M_c and dangling chain content in PU network have been studied.

2. Experimental

2.1. Materials

RO (specifications: iodine value = 117 I₂ mg/100 g sample, acid value = 2.1 mg KOH/g sample, saponification value = 192 mg KOH/g sample) was obtained from Iecavnieks & Co., Ltd., Latvia and was used without further purification. TEA (99.5%, $M = 149$ g/mol) and MDEA (98.5%) from BASF, TEG (99%), CPL (99%) and toluene anhydrous ($\geq 99.7\%$) from Sigma Aldrich were used as purchased. 4,4'-methylene diphenyldiisocyanate (MDI) (NCO = 33.6%, $f_n = 2.0$, $M = 250$ g/mol) from Sigma Aldrich, a polymeric MDI Suprasec 2651 (NCO = 31.8%, $f_n = 2.3$) from Huntsman, a polymeric MDI Lupranate M20 (NCO = 31.5%, $f_n = 2.7$) from BASF were used as purchased. The catalysts stannous octoate (95%) and zinc acetate dehydrate ($\geq 98\%$) from Sigma Aldrich were used as purchased.

2.2. Preparation of RO/TEA esters and polyol systems

RO/TEA esters were synthesized by transesterification using TEA. The reaction was carried out in a three neck 1.0 L thermo resistant glass reaction flask submerged in a

Download English Version:

<https://daneshyari.com/en/article/10609503>

Download Persian Version:

<https://daneshyari.com/article/10609503>

[Daneshyari.com](https://daneshyari.com)