



# The changes of crosslink density of polyurethanes synthesised with using recycled component. Chemical structure and mechanical properties investigations

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## ARTICLE INFO

### Keywords:

Polyurethanes  
Chemical recycling  
Crosslink density  
Thermal properties  
Mechanical properties

## ABSTRACT

This paper aims at the utilisation of glycerolysate (Gly) obtained in polyurethane recycling process by means of crude glycerine, which has in its structure hydroxyl end groups that allow for further processing. Polyurethanes (PUs) were synthesised using prepolymer method with the mixture of neat polyol and glycerolysate, in different ratios, with 4,4-diphenylmethane diisocyanate (MDI). The prepolymer was subsequently extended using 1,4-butanediol (BD). The incorporation of glycerolysate caused the crosslinking of obtained polyurethane materials. The crosslink density was calculated from swelling measurements by means of Flory and Rehner equation. The effect of recycled component content on the structure, thermal and mechanical properties were investigated by Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA) and mechanical tests, respectively. Morphology was also analysed by atomic force microscopy (AFM). As the content of recycled component increased, the swelling ratio decreased and simultaneously crosslink density increased, resulting in the increase of glass transition and storage modulus at room temperature. Thermomechanical stability, tensile strength, elastic modulus and hardness of PUs also increased with the incorporation of glycerolysate. Although elongation at break decreased, the recoverable deformation increased with the content of glycerolysate. Morphology reveals the transition from a microphase-separated microstructure to an interconnected hard segments domain structure with the incorporation of glycerolysate. These materials can be applied as protective coatings.

## 1. Introduction

Polyurethanes (PUs) are versatile materials with different properties and thus applications closely dependent on the used components. The main components for polyurethane formation are polyols, isocyanates, short chain extenders and catalysts. The structure and properties can be also changed by additives such as blowing agents, fillers, antioxidants, components containing ionic groups, etc. The primary reaction goes between hydroxyl groups (OH) of polyol and isocyanate group (N=C=O) of the isocyanate compound forming urethane linkages, and the reaction is an addition polymerisation [1]. The structure depends on the relative ratios of the main compounds. Due to those wide possibilities, polyurethanes can be obtained in the form of rigid or flexible

foams, thermoplastics, CASE (coatings, adhesives, sealants and elastomers) and waterborne dispersions [2,3]. Polyurethane coatings are particularly recommended for application to surfaces subject to high levels of wear-and-tear, because they combine outstanding resistance to solvents and chemicals with good weather stability and they exhibit very good mechanical properties and provide the ideal balance of hardness and flexibility, even at low temperatures [4]. Such broad range of forms and properties result in a high interest from industry in these materials and nowadays are placed in 5th in European plastics demand [5] with CAGR (Compound Annual Growth Rate) of 7% from 2016 to 2025 [6]. Global PU market demand in 2013 was 15 million tons and it is expected to reach over 22 million tons by 2020. With such high production, there exists a problem of produced waste from PUs. Therefore a lot of recycling methods are developed for an accurate treatment route [7–9]. Moreover, there is a pressure on the plastic industry for implementing eco- or bio-based products [10]. Hence a lot of research

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works in polyurethane area concern on the usage of natural oils or fatty acids for the production of bio-based substrates [11–13]. The usage of different biobased, synthesised from vegetable oils, polyols on the properties of PU coatings were studied [14]. Another method for sustainability in polyurethanes is recycling, that can prevent from usage crude oils and reuse already produced articles and materials. In most methods of PUs chemical recycling, usually, the polyol can be recovered and further used in new polyurethane formulation, what was presented in the literature [15–17]. Similar topic to this paper was presented by Rane et al. [18]. They prepared polyurethane-urea coatings with usage a recycled component obtained from aminolysis of polyurethane foam.

The advantages of polyurethanes recycling are related to both, economic and environmental issues. Firstly, due to the recycling, the amount of polyurethane waste (and their volume) from the landfill is reduced and the costs of such disposal are minimised. Secondly, the recovered intermediates aren't waste, these are valuable components that can be used as raw chemicals in a new synthesis, reducing simultaneously the cost of usage of petrochemical components (even by partial replacement) and saving natural resources as polyols are made from gas and oil. Moreover, reducing landfilling of polyurethanes also contribute to the reduction of harmful substances emissions into the environment by reducing groundwater pollution, air and morbidity of civilization diseases.

As it was mentioned before, polyurethane properties can be tailored by changing the composition: either by means of substrates or varying the molar ratio of the components. Moreover, PU properties strongly depend on the crosslinking of the polymer chains and it can be modified by the crosslink density. The crosslinking can have dual origin namely physical or chemical crosslinking. Physical crosslinking is a result of the hydrogen bonding in hard domains of segmented polyurethanes. Hydrogen bonding causes relatively strong interactions and therefore the polar nature of the hard urethane segments causes a strong mutual attraction leading to domain formation [19]. Physical crosslinking disappears above their melting point and are restored under cooling. When the material is chemically crosslinked it cannot be easily destroyed by heating as in the case of physical crosslinks [20]. Chemical crosslinking can be obtained by using the following combination:

- Using polyols with  $f > 2$
- Substitution of glycols chain extender with polyfunctional alcohols or amines
- Using isocyanates with  $f > 2$
- Using NCO:OH ratio  $> 1$  (the excess of isocyanate can lead to forming of allophanate or biuret bonds causing branching and chemical crosslinking)
- Introducing of a crosslinker or crosslinking nodes in the form of rings of isocyanurate [21,22].

The thermal stability of crosslinked polyurethanes is proved to be higher and depends more on crosslink density than on molecular weight. Not only the crosslink density influence on polyurethane properties but also cure conditions. It happens because more thermal energy is needed to break the additional bonds with increasing crosslink density before the breakdown of the total network takes place [21]. The molecular weight between crosslinks ( $M_c$ ) can be used to characterise crosslinked PU as it is the parameter characterising macromolecule architecture [23]. The glass transition of polyurethanes (regardless their chemical composition) depends on the polyol hydroxyl number and hence crosslink density. The higher molecular weight in PUs which poses branched and/or crosslinked structure also gives the result in improvement of mechanical properties. However, chemical crosslinking can have various effects on tensile properties according to the network chain molecular weight compared to the molecular weight between crosslinks [20].

The application of new, recycled component into polyurethane synthesis was investigated. The aim of this work was to apply the

recycled polyurethane component in solvent-free polyurethane coating synthesis. Firstly, polyurethane foam recycling was carried out by means of crude glycerine, where a homogenous intermediate (glycerolysate) was obtained. In this one reaction, two types of waste, polyurethane foam and crude glycerine, will be utilised to obtain valuable components for further usage. The goal was to examine the effect of crosslinking occurring due to the presence of glycerolysate on the thermal and mechanical properties of synthesised materials. The crosslink density was estimated through swelling properties and using Flory-Rhener equation. The crosslink density was in accordance with DMA results. Obtained materials exhibit properties suitable to act as protective coatings [24].

## 2. Experimental

### 2.1. Polyurethane synthesis

Polyurethane materials were synthesised by solvent-free, two-step bulk polymerisation. In the first step the prepolymer was obtained by the reaction of difunctional poly(ethylene-butylene)adipate diol (Polios 55/20 macrodiol, Purinova,  $\text{OH}_{\text{number}} = 58$ ,  $M_w \sim 2000$ , information given by the company) and recycled glycerolysate component ( $\text{OH}_{\text{number}} = 369.7 \text{ mg KOH g}^{-1}$  in accordance to standard ASTM D 4274-99) with 4,4'-diphenylmethane diisocyanate (MDI, Desmodur 44, Bayer). The reaction was carried out at  $80^\circ\text{C}$  for 5 h under a nitrogen atmosphere in a three-necked glass reactor equipped with mechanical stirrer and nitrogen inlet. In the second step, the chain extender 1,4-butanediol (BD, Sigma-Aldrich) was added and stirred for 10–15 min in order to homogenise. The molar ratio of NCO to OH was kept constant for all PUs, 1.05. Finally, the viscous mixture was poured into a mould and pressed at  $100^\circ\text{C}$  under 50 bar for 10 h. Polyurethanes with different molar ratios of glycerolysate and macrodiol were prepared, as a polyol part of the system. However, the polyol part: diisocyanate: chain extender molar ratio of the system was kept constant at a ratio of 1:3:2 (polyol part: MDI: BD). Polyurethanes were coded as PU0 to PU5, where the number determines the percentage of glycerolysate in PU. The two-step synthesis reaction scheme of polyurethanes obtained with glycerolysate was presented in our previous research [25].

Glycerolysate was obtained in the chemical recycling process of polyurethane foam, which was originally prepared from a trifunctional polyol. The foam was reacted with crude glycerine in 3 to 1 weight ratio at  $220^\circ\text{C}$ . The used catalyst was potassium acetate. A detailed procedure was described in a previous paper [26].

### 2.2. Characterisation techniques

#### 2.2.1. Fourier transform infrared spectroscopy (FTIR)

FTIR was used to identify glycerolysate and polyurethane characteristic functional groups. Spectra were recorded using a Nicolet Nexus FTIR spectrometer, equipped with a MKII Golden Gate accessory (Specac) with diamond crystal at a nominal incident angle of  $45^\circ$  and a ZnSe lens. The spectra were obtained after 32 scans in a range from  $4000$  to  $750 \text{ cm}^{-1}$  with a resolution of  $2 \text{ cm}^{-1}$ .

#### 2.2.2. Equilibrium swelling properties and crosslink density

The crosslink density and swelling parameters of obtained polyurethanes were determined by employing the equilibrium swelling method according to the procedures described in the literature [27–29]. The rectangular specimens with average dimensions  $10 \times 10 \times 1.4 \text{ mm}^3$  were immersed in dimethylformamide solvent (DMF, purchased from Chempur). The equilibrium point was obtained after 72 h. When the samples reached equilibrium, they were removed from the solvent, patted with paper and weighted again. The crosslink density ( $\nu_c$ ) ( $\text{mol cm}^{-3}$ ) and average molecular weights between the chains ( $M_c$ ) were estimated using following equations, which were introduced by Flory and Rhener Eq. [30].

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