



Synthesis and characterisation of polyurethane elastomers with semi-products obtained from polyurethane recycling

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ARTICLE INFO

Article history:

Received 8 August 2016

Received in revised form 28 September 2016

Accepted 30 September 2016

Available online 1 October 2016

Keywords:

Chemical recycling

Crude glycerine

Semi-products

Polyurethane elastomer

ABSTRACT

In this work polyurethane elastomers were synthesised by using different mixtures of a petrochemical and glycerolysate polyols and 4,4-diphenylmethane diisocyanate (MDI). Glycerolysate polyol was produced from polyurethane foam decomposition using crude glycerine as a decomposition agent. The structure and thermal properties of obtained semi-product were similar to the polyol used in the synthesis of original foam. Glycerolysate polyol was incorporated into polyurethane formulation as soft segment (SS). Since polyol is one of the major component in polyurethane system (>70%) introducing recycled components leads to lowering of consumption of petrochemicals and valorisation of recycled products. Polyurethane elastomers containing up to 16.4 wt.% of glycerolysate polyol were synthesised, soluble in dimethylformamide (DMF) up to ca. 12 wt.%. The effect of glycerolysate polyol content on the structure and properties was analysed by Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA) and mechanical tests. Thermal properties did not worsen after using glycerolysate into polyurethane formulation. A slight increase in glass transition temperature is observed with the incorporation of glycerolysate polyol. Elastic modulus, tensile strength and hardness of polyurethane elastomers increased with recycled polyol content. Moreover they showed high elongation at break values.

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1. Introduction

Plastics production is increasing yearly on the level of 9.9%. Such high growth is connected with their diversity, low-cost of production and an ability to replace conventional materials such as metal, glass or wood. However, this growing trend causes also huge amount of waste which needs to be managed that may not spread on the landfills. Therefore in the recent years to prevent the environmental damage, the international regulations were introduced. In accordance to European Directive 2008/98/EC, the waste management should be in order of importance as follows [1,2]:

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1. Prevention,
2. Reuse,
3. Recycling,
4. Other recovery as energy recovery,
5. Disposal.

When the first two principle are not suitable for specific plastic waste, recycling is a suitable option after which useful products can be received. Recycling can be divided into two main groups (excluding energy recovery): mechanical recycling and chemical recycling [3,4]. During mechanical recycling the polymer waste is very often subjected to the following procedure: collection, separation, purification, shredding, melting, extrusion and re-granulation. This option is mainly suitable for thermoplastic polymers such as polyethylene (PE), polypropylene (PP) or polystyrene (PS), while for thermoset polymers i.e. polyurethanes (PUs) mechanical recycling is limited to changing its physical form and instead of re-granulation can be used as fillers, bonded with adhesives, hot pressed or extruded in order to reduce the molecular chain to obtain thermoplastic material [5]. Chemical recycling allows to depolymerise polymers to starting monomers or into basic oil and hydrocarbons [1,6]. Thus, the majority of research on polyurethanes recycling describes methods of chemical recycling due to the possibility of obtaining starting substrates [3,7–9]. Thereby the reduction of plastic waste (recycling) remains and it helps to conserve commercially used substrates by production reduction (prevention).

Growing interests of polyurethane chemical recycling is related with their increasing production (currently is on the level of 15 million tonnes [10]) and quite expensive starting substrates which translates to their higher price in comparison with more conventional polymers as PE, PP. Success of polyurethanes in the plastic market is associated with their variable structure and broad spectrum of forms (rigid, elastic, viscoelastic foams; elastomers; sealants; adhesives; coatings) and hence wide range of application starting with mattresses sponges, shoe soles, paints, insulating materials, adhesives and even in medical application [7,11].

In a view of chemical variety, chemical recycling of PUs can be carried out in different ways that starting substrates can be received. The idea of PUs chemical recycling it to treat PU waste at increased temperature with a decomposing agent which allows to break the biuret, urea and urethane bond [12]. As a decomposing agents, in the literature, were used substances as follows: water [13], glycols [14], pure and crude glycerines [15,16], alcohols [3], acids and amines [3]. Very well and broad described method of polyurethane recycling is glycolysis [12,17,18]. In general, glycolysis carries out in the reaction with glycols at high temperatures, ca. 200 °C and the PU structure is decomposed in a transesterification reaction [19]. As the main idea of this process is to recover constituent polyols, many researchers surveyed on valorisation of that intermediates in synthesis of polyurethanes because they show similar properties to original, commercial substances [20]. Hence, the concept to implement semi-products obtained from the chemical recycling looks like a good way of managing recycled substances and simultaneously reducing the usage of petrochemicals and the cost of material production. Recycled polyol (in the case of glycolysis known as glycolysate) can be introduced to polyurethanes system to obtain rigid [21–23] or flexible [24,25] foams, elastomers [26,27] and adhesive [28]. Most of the works are concerned with the application of recovered polyol in the synthesis of flexible and rigid polyurethane foam synthesis. In the work of Beneš et al. [29], rigid high density polyurethane foams were synthesised using 100% recycled polyol obtained from PU decomposition by fish oil-based polyol. Recovered and purified polyol from glycolysis of PU was used to prepare flexible polyurethane foams replacing 25 and 50% of origin polyol [30]. In another three works of Simón et al. [31–33], the upper and bottom phase of recovered polyol were incorporated into flexible and rigid polyurethane foam synthesis, respectively. The concept of using recovered polyol in polyurethane elastomer synthesis was proposed by Datta and Haponiuk [34]. Synthesis was carried out by a one-step method in which polymeric 4,4-diphenylmethane diisocyanate, the selected glycolysate, polyol (an elongation agent) and phosphoric acid (an inhibitor of side reactions) were mixed. Materials were thermally stable up to 300 °C and tensile strength was in the range of 3.6–5.4 MPa.

With respect to the “green chemistry” trend, oil industry also became interested in renewable resources and tries to replace crude oil with i.e. biodiesel which is created in a transesterification reaction of vegetable oil or animal fat with methanol (mostly) in the presence of catalyst. Besides the ester phase, the by-products in the form of glycerol phase are obtained. The crude glycerol is separated from esters, which are in sequence purified from catalyst and methanol. Crude glycerine can be purified and then used in pharmaceutical, chemical industry and also in alkyd resins, cellulose coatings, but the cost of purification and refining are high and the use of crude glycerine has been less exploited [15,35].

In this study crude glycerine was used in flexible polyurethane foam decomposition, as a reactant agent in the transesterification reaction, to obtain valuable semi-product – glycerolysate. Glycerolysis was performed in the “split-phase” condition resulting in two phase semi-product, viz. upper phase (liquid one, considered as a re-polyol) and bottom phase (solid one, residues from the disrupted urethane bond). The semi-product was tested by Fourier transform infrared (FTIR) spectroscopy, and gel permeation chromatography (GPC) and differential scanning calorimetry (DSC). The main goal is to demonstrate the feasibility of incorporate the obtained glycerolysate in standard polyurethane elastomer as a part of polyol system. The glycerolysate was used to replace commercial polyol up to ca. 26% in new polyurethane elastomers synthesis. The synthesis was carried out in a two-step bulk polymerisation process without catalyst. The effect of glycerolysate content on synthesised polyurethanes physicochemical, mechanical and thermal properties was studied, using FTIR, DSC, TGA, DMA and mechanical testing.

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