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Polymer Testing

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TESTING

Material Behaviour

Novel cast polyetherurethanes based on dispersed polymeric polyols

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ARTICLE INFO

Keywords:

Polymeric polyols
 Polyetherurethane synthesis
 Chemical structure
 Thermal stability
 Mechanical properties

ABSTRACT

Our study was focused on obtaining polyetherurethanes synthesized with using polymeric polyether based polyols differing in dispersed copolymer content (10, 20 and 40 wt%). The polyetherurethane materials were synthesized via two step method. The influence of different polymeric polyether based polyols on the chemical structure, morphology, mechanical and thermal properties of the obtained polyetherurethanes was investigated. The Fourier transform infrared spectroscopy (FTIR) was used to analyze and confirm the chemical structure of synthesized materials. Analysis of thermal stability by thermogravimetric method (TGA) of polyetherurethanes indicated that the decomposition of all materials carried out in two steps. The results of the thermomechanical analysis (DMA) showed that the polyetherurethanes synthesized with using polymeric polyols containing 10 wt % of the copolymer characterized by the highest storage modulus of all materials. The same materials have got also the highest tensile strength value.

1. Introduction

Polymeric polyols (known as filled polyols) are defined as a polymer or copolymer dispersion in a flexible polyether polyol matrix. These kinds of polyols are often used as “reinforced polyols” for polyurethane foam synthesis (soft and semi-rigid foam) [1,2]. Polyether polyols containing polymers as fillers are a class of polymer polyols and are produced in a large industrial scale because they are one of the most important group of polyols used for high-performance flexible polyurethane (PU) foam and PU elastomers. Polymeric polyols are divided, by the nature of the polymer finely dispersed in the polyether matrix, into the following categories: graft polyether polyols also known as dispersion polymer or as dispersant polyol; polyurea dispersion - PHD polyols; polyisocyanate polyaddition PIPA polyols (polyurethane dispersion) and other polymeric polyols (epoxy or aminoplast dispersion) [3].

Commonly, the styrene/acrylonitrile copolymer dispersion (SAN) in the base polyether polyol is used. The polyether polyols technology based exclusively on ACN are commercialized because of the high glass transition temperature (T_g) of the polyacrylonitrile solid fraction. The disadvantage of this example of polymeric polyols is the higher cost of SAN in comparison with the cost of alternative polymers such as polyethylene and polypropylene. The methods of polymeric polyols preparation have been described in many patent applications. Process

for preparing a stable dispersion of a preformed polymer in a polyol in a single mixer. A preformed polymer is mixed under sufficient heat and shear to reduce its particle size to the desired size in the presence of a polyol. The effect of the type, concentration and monomers ratio, the polyol - monomer ratio, of the chain transfer agent concentration, reaction temperature, the initiator type, reaction time on the polymerization system dispersion stability was described [1,2].

Generally, copolymer polyols are produced by polymerizing one or more ethylenically unsaturated monomers dissolved or dispersed in a polyol (carrier polyol) in the presence of a free radical polymerization initiator to form a stable dispersion of solid polymer particles in the polyol. Carrier polyols like can be both feedstock which are added to the reactor before and/or during the polymerization of the solid particles. and diluent polyol which is added to the feedstock polyol after this polymerization. The low viscosity polyol allows to increase the solid content when making the polymer polyol from the said polyol, keeping viscosity similar to other polymeric polyols [4]. Another potential approach to manufacturing polymer polyols is to polymerize the discontinuous phase polymer separately, and then disperse the polymer into the polyol [5,6].

Polymeric polyols, as stated earlier, can be used in polyurethane synthesis [7]. Polymeric polyols compositions, which are used in the preparation of polyurethane foams are based in known materials and were first disclosed in US Patents [8,9]. Such polymeric polyols are

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prepared by polymerizing one or more unsaturated monomers (styrene monomer, acrylonitrile, etc.), dissolved in the base polyol in the presence of a free radical catalyst. Thus, the produced polymer particles are stably dispersed in polyol liquid, and polyurethane foams prepared from this kind of polymeric polyol present higher hardness and greater physical properties compared to polyurethane foams prepared from conventional polyols [7]. In order to manufacture polyurethanes having further improved physical properties, several efforts to improve the properties of polymeric polyols have been made. Particularly, in order to prepare low-viscosity polymeric polyols, having high polymer content together with high dispersion stability, a method of introducing a reactive NAD (nonaqueous dispersant) stabilizer was suggested. The NAD stabilizer serves to introduce a small amount of unsaturation into polyol and contributes to increase the dispersion stability of solids, which are produced in the preparation of polymeric polyols [7].

Methods of preparing polymeric polyol composition and the grafted polyol-polyacrylate are also provided to have a low viscosity as well as high stability and may be prepared with high level of dispersed vinyl polymer and high styrene: acrylonitrile ratios in the dispersed vinyl polymer. This polymeric polyol composition is useful for the preparation of polyurethanes, particularly polyurethane foams and comprises a continuous phase, a disperse phase within the continuous phase and as a dispersant to enhance the stability of the polymer polyol a grafted polyol-polyacrylate dispersant comprising an isocyanate vinyl monomer/ethylenically unsaturated monomer random copolymer and a polyoxyethylene polyether which are connected through at least one urethane graft site [10].

Glycolysis of flexible polyurethane waste containing polymeric polyols can be conducted and recovered polyol can partially replace the commercial polyols in the novel process of polyurethanes synthesis. Influence of SAN content on the glycolysis processes kinetic rate was studied. It was found that lower SAN content caused increasing in rate of glycolysis reaction progress [11].

Polymer blends based on thermoplastic polyurethanes and poly-styrene-co-acrylonitrile have different properties which derived from individual properties of a single polymer. This multicomponent composition leads to join different, usually contrary, properties of various polymers [12]. Vatalis et al. noted that SAN, as a polymer blend component, promotes microphase separation between hard segment (HS) and soft segment (SS) in polyurethanes materials. The microphase separation of PU/SAN blend was studied by differential scanning calorimetry (DSC), dielectric relaxation spectroscopy (DRS) and thermally stimulated depolarization currents (TSDC) [13]. The addition of SAN copolymer enhances mobility of hard segments (HS) at their microdomains region, visible as a decreasing of ΔC_p [14].

The aim of this study was to investigate the influence of different SAN copolymer content in polyol used to the polyetherurethane synthesis on structure, morphology, thermal, thermomechanical and mechanical properties of produced materials. The aforementioned properties and parameters were determined by means of spectroscopy, and thermal methods and mechanical testing under static and dynamic conditions.

2. Experimental

The polyetherurethanes (PU) were synthesized by the prepolymer method. The prepolymer was prepared from diisocyanate 4,4'-diphenylmethane diisocyanate, MDI (BorsodChem, Hungary) and a polymeric polyol based on polytetrahydrofurane (PTHF, 2000 g/mol, BASF, Germany) containing dispersed copolymer SAN particles in an amount of 10, 20 and 40 wt % (Castilla La Mancha University, Spain). This reaction was conducted at 80 °C for 1 h. During the second step, the prepolymer chains were extended by using 1,4-butanediol (Brenntag, Poland) with 0.3 wt% of 1,4-diazabicyclo[2.2.2]octane (DABCO, Merck, Germany) as a catalyst. The molar ratio $[NCO]_{\text{prepolymer}}/[OH]_{\text{chain extender}}$ was equaled 1.05:1. All samples were molded by

gravity casting to the forms and then cured at 100 °C for 24 h. Segmented structure of synthesized cast polyurethanes as a graphic scheme is presented below.

3. Measurement

3.1. FT-IR spectroscopy

The Fourier transform infrared spectroscopy (FTIR) of cast polyetherurethanes was carried out using a FTIR Nicolet 8700 spectrophotometer (Thermo Electron Corporation) and ATR technique; a Specac Heated Golden Gate single reflection diamond ATR accessory was used. Spectra were registered at room temperature for the wavenumbers ranging from 500 to 4500 cm^{-1} at 4 cm^{-1} nominal resolution. Each spectrum was an average of 64 independent scans.

3.2. SEM analysis

The microscopic analysis was conducted on the cross section of samples using a Phenom G2 PRO (Phenom- World) scanning electron microscope, with accelerating voltage of 5 kV.

3.3. DMA

Dynamic mechanical analysis of cast polyetherurethanes was performed using a DMA Q800 Analyzer (TA Instruments). The measurements were taken under the nitrogen atmosphere, at a temperature range from –100 to +100 °C, at an operating frequency of 10 Hz, with a heating rate of 4 °C/min. The values of storage modulus, loss modulus and glass transition temperature were also recorded. Rectangular samples with dimension 17.6 × 9.7 × 2.9 mm (length x width x thickness) were used to the measurement.

3.4. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed with the use of NETZSCH TG 209F3 analyzer. Samples about ca. 6 mg were measured in the temperature range from 35 to 700 °C with the heating rate of 20 K/min. Measurements were carried out under the nitrogen atmosphere. Thermogravimetric (TGA) and differential thermogravimetric (DTG) curves for each cast polyetherurethane were plotted. The temperature of mass loss 5, 10 and 50% were given as $T_{5\%}$, $T_{10\%}$ and $T_{50\%}$ respectively, while the maximum of rate decomposition temperature of the each stage were described as $T_{\text{max I}}$ and $T_{\text{max II}}$.

3.5. Mechanical analysis

3.5.1. Tensile test

The tensile strength (TSb) and elongation at break (Eb) were measured under static pressure by using a Zwick Z020 tensile-testing machine, in accordance with the EN ISO 527-1:1996 and EN ISO 527-2:1996 standards. The dumbbell-shaped samples of standard dimensions were tested at a rate of 100 mm per minute. The original gauge length (l_0) was equal 25 mm. The measurements were performed at room temperature.

3.5.2. Cyclic compression tests

The compression test were carried out by using a Zwick Z020 tensile-testing machine, in accordance with the EN ISO 604:2006 standards. The compression cylindrical shape specimens were measured 10 ± 0.5 mm in diameter and about 25 ± 1 mm in height. The cyclic compression tests consist of achieving three load-unload loops continuously up to the strain value of about 40% and successively up to 10% of the strain in order to calculate hysteresis. The samples were tested at a compression rate of 5 mm per minute. The measurements were performed at room temperature.

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