New reprocessable branched polyurethane from biorenewable sources

E O Platonova¹, A A Pavlov² and A V Polezhaev¹, ²*

¹N.E. Bauman Moscow State Technical University, 105005, Russia, Moscow, 2nd Baumanskaya str., 5/1
²A.N. Nesmeyanov Institute of Organoelement Compounds, 119334, Russia, Moscow, Vavilova str., 28
E-mail: ¹, ²*avp@emtc.ru

Abstract. Thermally-remendable and recyclable polyurethane was obtained via Diels-Alder reaction using branched glycol Voranol 3138 (glycerin-derived block-copolymer of polyethylene and polypropylene) as soft segment and toluene-2,4-diisocyanate (TDI) as hard segment subsequently functionalized by terminal difurfurylamine groups. By cross-linking via Diels-Alder reaction with N,N' -bismaleimido-4,4'-diphenylmethane (BMI) new self-healing branched polyurethane was obtained. Polymer structure was characterized by NMR and IR spectroscopy along with thermal analysis methods (DSC and TGA). Resulting material has good processability and opportunity for recycling.

Keywords: self-healing, Diels-Alder reaction, thermal remendability, polyurethane, furan, maleimide

1. Introduction

Polyurethane worldwide production is about worldwide production of around 20 million tons (2016) and most of this mass would not be recycled [1]. Today there is an obvious trend in polyurethane chemistry to design environmentally friendly materials. Indeed, the recycling process for PU is beneficial both in terms of the environment as well as from an economical point of view [2]. There are several approaches to PU recycling: advanced chemical and thermochemical recycling, mechanical recycling, energy recovery, and product recycling. Generally, PU may be recycled by either destructive or nondestructive methods. Linear polyurethanes can be simply reprocessed through the conventional molding process as other thermoplastics does. But thermoplastic polyurethanes are usually soluble in organic solvents and weak in modulus. Cross-linking with covalent bonds (vulcanization) is a standard solution to improve stiffness and solvent resistance but always resulted in materials that cannot be reshaped or repaired, and finally recycled when damaged once a cross-linked network is formed.

The introduction of covalent bonds which can reversibly dissociate upon extrinsic stimuli could substantially simplify material recycling. In particular, such covalent bonds that were developed by the Diels-Alder (DA) reaction between furan and the maleimide group are used for self-healing polymer systems [3, 4]. These furan-based polymers are biomass materials typically extracted from cellulose or hemicellulose [5, 6].

Using the branched furane-functionalized prepolymer and small molecule curing agent (BMI) we synthesized cross-linked PU. Properties of the material formed upon the Diels-Alder reaction between furan and maleimide groups are easy to tune varying the curing agent content. Since DA-reaction is a reversible process resulting material may be solved at the rDA-reaction temperature and then the solution casted again.
2. Experimental

2.1. Reagents and methods
TDI (toluene-2,4-diisocyanate, 80%), sodium borohydride (98%), BMI (1,10-(methylenedi-1,4-phenylene)bismaleimide, 95%) and BHT (2,6-di-tert-butyl-4-methylphenol, 99.0%) were purchased from Aldrich and used as received. Voranol 3138 (Mn = 3000) was purchased from Dow Europe GmbH and dried under vacuum at 110 °C prior to use. Hydrofuramide was prepared using published procedure [7] from furfural and ammonia. DMF (N,N-dimethylformamide) was purchased from Acros dried over CaH₂ and distilled prior to use.

NMR spectra were recorded by a Bruker Avance 600 NMR Spectrometer (600.1 MHz), using residual proton signal of deuterated solvent as reference, chemical shifts were reported as parts per million downfield from tetramethylsilane (TMS). ATI-FTIR was performed on Nicolet iS10 spectrometer in the range of 4000 to 650 cm⁻¹ on germanium crystal. The thermal behavior was examined by DSC, with a NETZH DSC 204 F1 Phoenix within a temperature range of -60 to 160 °C at heating/cooling rates of 10 K min⁻¹ in argon atmosphere. A sample weight of about 16 mg was used for the measurements. Thermogravimetric analysis (TGA) was performed on NETZH TG 209 F1 Libra within a temperature range of 30 to 550 °C at heating/cooling rate of 10 K min⁻¹ in argon atmosphere.

2.2. Synthesis and characterization
Synthetic approach of the self-healing polyurethane PU-DA showed in Figure 1. Detailed method according to reaction scheme described below.

2.2.1. Synthesis of PU-V0
Prepolymer PU-V0 was prepared using conventional two-step method. At the first step TDI (2.3 g, 13.4 mmol) reacted with Voranol 3138 (12.5 g, 4.2 mmol) in a 100 mL two-necked round bottom flask, equipped with magnetic stirrer and dropping funnel. The reaction was carried out at 60 °C under an argon atmosphere for 3 h. The reaction progress was monitored with IR-spectroscopy. At the second step reaction mixture was cooled to room temperature, diluted with DMF (3 mL) and difurfuryl amine (2.3 g, 13.0 mmol) dissolved in DMF (3 mL) was added dropwise into the isocyanate end-capped prepolymer solution in about 15 min. Reaction mixture was stirred at 60 °C under an argon atmosphere for 12 h. Yield: 21.0 g. 1H NMR (400 MHz, DMSO-d6, δ): 9.52 (s, 3H, –NH–CO–O–), 8.05 (d, JHH = 9.8 Hz, 3H, =HNC(O)NH–Ar), 7.61 (d, JHH = 6.9 Hz, 3H, =CHO– of furan ring), 7.44 (d, JHH = 6.4 Hz, 3H, –Ar), 7.26 – 7.12 (m,, 3H, –Ar), 7.04 (d, JHH = 5.3 Hz, 3H, –Ar), 6.41 (s, 6H, =CH–CH= of the furan ring), 6.32 (s, 6H, =CH–CH= of the furan ring), 4.54 (s, 12H, –N-CH2–), 3.71–3.62 (m, 5H, –O–CH2–CH(O)–CH2O–), 3.57–3.39 (m, 112H, –CH2– of polypropylene oxide and polyethylene oxide), 3.35–3.17 (m, 66H, –CH2–CH(CH3)–O–), 1.20 (s, 9H, CH3–Ar), 1.04 (d, JHH = 5.0 Hz, –O–
Advances in Composites Science and Technologies 2020 (ACST 2020) Journal of Physics: Conference Series 1990 (2021) 012045 IOP Publishing doi:10.1088/1742-6596/1990/1/012045

CH(CH3)–CH2–); 13C NMR (101 MHz, DMSO-d6, δ): 155.58, 153.68 151.91, 143.1 138.37, 138.23, 130.32, 123.13, 118.05, 110.93, 108.59, 75.04, 72.71, 42.81, 17.43; IR (ATR, neat, cm-1): 3315, 2971, 2931, 2895, 2897, 1728, 1672, 1600, 1531, 1506, 1453, 1374, 1343, 1296, 1225, 1103, 1012, 924, 868, 816, 737.

2.2.2 Synthesis of cross-linked PU
BMI (0.93 g, 2.5 mmol) and BHT (0.0057 g, 0.05 mmol, 1 %mol to the amount of prepolymer and crosslinker) as stabilizer were added to Fu2N-prepolymer PU-V0 (7.0 g, 1.7 mmol) in 6 mL DMF. The reaction mixture was heated to 60 °C for 3 h, then carried onto a glass surface and cured in an oven for 48 h to afford semitransparent polymer film.

3. Results and discussion
3.1. Characterization of PU-DA
Structure of the obtained polyurethane was characterized by NMR and IR spectroscopy. Figure 2 represents 1H NMR spectra of the initial monomer and resulting polymer.

The FTIR spectra of the furan-terminated oligomer PU-V0 and film of crosslinked PU-DA are shown on Fig.2. A decreasing of the band at 741 cm⁻¹ associated with furan ring and appearance of the weak band at 1776 cm⁻¹ characteristic to a furan-maleimide Diels-Alder adduct in the spectrum of polymer PU-DA confirmed DA-adduct formation [8, 9]. However, the presence of two C=O bands stretches at 1707 cm⁻¹ may be assigned to partially unreacted maleimide groups. We speculate that incomplete behavior of the DA-reaction between prepolymer and BMI may be caused both rather high polymeric solution viscosity and steric reasons. A continuous heating of the sample did not change spectra so higher conversion of the starting material cannot be obtained with prolonger heating.

Obtained polymer (PU-DA) was not soluble in DMSO at r.t. and no leakage of BMI was detected with NMR after 12 h soaking of polymer in DMSO-d⁶ in NMR tube compared to PPG2000-based polymers that were perfectly soluble in DMSO. A prolonged heating at 100 °C was necessary to obtain a homogeneous solution required for 1H-NMR spectra registration. We believe that at least partial rDA reaction occurred during this process (Fig. 3). The 1H-NMR spectra of preheated sample showed residual furan ring signals at 7.62, 6.42 and 6.32 ppm and at the same time a new signal of DA adduct vinyl protons appeared at 6.52-6.26 ppm. Polymer proton NMR spectrum contained signals from crosslinking agent, which may be the result of DA-bonds cleavage caused by heating upon specimen preparation. The multiplet at 4.87 ppm corresponded to protons of N-C(O)-O-CH₂-fragment [10].

The thermal stability of PU-DA was investigated with TGA under an argon atmosphere (Fig. 4): the values of temperature at 5% mass loss (T5%) were 267 °C. Polymer sample showed a slow weight loss
of 19.0% in the range of 260-360 °C, suggesting its high thermal stability. Main weight loss of 85.9% occurs in the range of 370-450 °C. Thermal properties and DA-bonds reversibility of PU-DA were investigated by DSC (Fig. 5). The first heating curve (solid line) of polymer demonstrated two endothermic peaks: at 88 and 131 °C which can be assigned to rDA cleavage of endo and exo isomers, respectively [11]. Endo-adduct as kinetically-favored product has lower rDA-reaction temperature while exo-adduct as thermodynamically-favored product is frequently significantly thermally stable and has higher rDA-reaction temperature [11, 12]. DSC-curve of branched PU-DA was similar to DSC-curve of linear PUs, reported previously: thermograms had two endothermic peaks as well, and the rDA peak temperatures of 88-131 °C for branched materials were not very far from rDA peak temperatures of 124-136 °C for linear PPG-2000-based PUs [13].

![Figure 3. 1H NMR of PU-V0 and PU-DA](image)

**3.2. Reprocessability of PU-DA**

For reprocessing of the crosslinked PU a dissolution method was used. The pristine film was cut and dissolved in DMF at 100 °C, cast in PTFE mold, and cured for the 48 h at 60 °C. The same cycle was repeated five times and the mechanical properties of PU-DA specimens from every cycle are now under the investigation.

![Figure 4. TGA curve of PU-DA](image)  
**Figure 4.** TGA curve of PU-DA

![Figure 5. DSC curves of PU-DA](image)  
**Figure 5.** DSC curves of PU-DA
4. Conclusion
Via Diels-Alder reaction between bismaleimide and furan end-capped branched prepolymer new self-healing cross-linked polyurethane was synthesized. Self-healing properties and recycling possibility are now under the investigation.

Acknowledgements
This work was supported by Russian Foundation of Basic Research (RFBR) grants 18-29-18036 and 18-29-18037 and the Competence Center of the National Technological Initiative (NTI) "Digital Materials Science: New Materials and Substances" of the Bauman Moscow State Technical University.

References
[1] Akindoyo J O, Beg M D H, Ghazali S, Islam M R, Jeyaratnam N and Yuvaraj A R 2016 Polyurethane types, synthesis and applications – a review RSC Advances 6 pp 114453-114482.
[2] Howard G T 2002 Biodegradation of Polyurethane: A Review. International Biodeterioration & Biodegradation International Biodeterioration & Biodegradation 49 pp 245-252.
[3] Chen X, Dam M A, Ono K, Mal A, Shen H, Nutt S R, Sheran K and Wudl F 2002 Autonomous healing materials based on epoxidized natural rubber and ethylene methacrylic acid ionomers Science 295 pp 1698-1702.
[4] Zhong Y, Wang X, Zheng Z and Du P 2015 One-component Diels-Alder based polyurethanes: A unique way to self-heal J. Appl. Polym. Sci. 132 pp 48047-48053.
[5] Zeng C, Seino H, Ren J, Hatanaka K and Yoshiie N 2013 Bio-Based Furan Polymers with Self-Healing Ability Macromolecules 46 pp 1794-1802.
[6] Nayak L and Mishra S P 2016 Prospect of bamboo as a renewable textile fiber, historical overview, labeling, controversies and regulation Fashion and Textiles 3(2) pp 1-23.
[7] Akindoyo J O, Beg M D H, Ghazali S, Islam M R, Jeyaratnam N and Yuvaraj A R 2016 Polyurethane types, synthesis and applications – a review RSC Advances 6 114453-82.
[2] Howard G T 2002 Biodegradation of polyurethane: a review International Biodeterioration & Biodegradation 49 pp 245-252.
[3] Chen X, Dam M A, Ono K, Mal A, Shen H, Nutt S R, Sheran K and Wudl F 2002 A Thermally Re-mendable Cross-Linked Polymeric Material Science 295 pp 1698-1702.
[4] Zhong Y, Wang X, Zheng Z and Du P 2015 Polyether–maleimide-based crosslinked self-healing polyurethane with Diels–Alder bonds J. Appl. Polym. Sci. 132.
[5] Zeng C, Seino H, Ren J, Hatanaka K and Yoshiie N 2013 Bio-Based Furan Polymers with Self-Healing Ability Macromolecules 46 pp 1794-1802.
[6] Nayak L and Mishra S P 2016 Prospect of bamboo as a renewable textile fiber, historical overview, labeling, controversies and regulation Fashion and Textiles 3:2.
[7] Hunter D H and Sim S K 1972 2,4-Diazapentadienes. I. Prototropy, Cyclization, and Addition–Elimination Can. J. Chem. 50 pp 669-677.
[8] Goussé C, Gandini A and Hodge P 1998 Application of the Diels–Alder reaction to polymers bearing furan moieties. 2. Diels–Alder and Retro-Diels–Alder Reactions Involving Fur an Rings in Some Styrene Copolymers Macromolecules 31 pp 314-321.
[9] Petrova T V, Solodilov V I, Kabantsvea V E, Karelina N V and Polezhaev A V 2019 Furfurylglycidyl ether: a new effective active diluent for epoxy resins from bio-renewable raw materials IOP Conference Series: Materials Science and Engineering 683 pp 012070-012077.
[10] Arshad M, Saied S and Ullah A 2014 PEG–lipid telechelics incorporating fatty acids from canola oil: synthesis, characterization and solution self-assembly RSC Advances 4 pp 26439-26446.
[11] Froidevaux V, Borne M, Laborbe E, Auvergne R, Gandini A and Boutevin B 2015 Study of the Diels–Alder and retro-Diels–Alder reaction between furan derivatives and maleimide for the creation of new materials RSC Advances 5 pp 37742-37754.
[12] Cuvelier A, Verhelle R, Brancart J, Vanderborght B, Van Assche G and Rahier H 2019 The influence of stereochemistry on the reactivity of the Diels–Alder cycloaddition and the implications for reversible network polymerization Polymer Chemistry 10 pp 473-485.
[13] Platonova E O, Vlasov E, Pavlov A A, Kireynov A, Nelyub V A and Polezhaev A V 2019 Self-healing polyurethane based on a difuranic monomer from biorenewable source *J. Appl. Polym. Sci.* 136 pp 47869-47877.