Synthesis of cross-linked polyurethane with self-healing properties

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Abstract. Prepolymer synthesized from toluene-2,4-diisocyanate (TDI) (hard segment), and polypropylene glycol (PPG-2000) (soft segment) was end-capped with difurfurylamine groups. A new cross-linked self-healing polyurethane was obtained via Diels-Alder reaction of the en-capped prepolymer with N,N'-bismaleimido-4,4'-diphenylmethane (BMI). Thermal reversibility of the Diels-Alder reaction (DA-reaction) between terminal furanic rings of the polyurethane prepolymer and bismaleimide cross-linking agent designed to be responsible for self-healing. Polymers were characterized by NMR and IR spectroscopy and thermal analysis (DSC and TGA). Thermal reversibility of the DA-bonds in the cross-linked polymer was confirmed by DSC. The synthesized polymer has good processability and potential recyclability.

1. Introduction

Polyurethanes (PU) are widely used as elastomers, adhesives, covers, and foams due to their physical and mechanical properties [1, 2]. However, PUs are affected by the environment (mainly air moisture and light), mechanical and chemical influence, UV radiation and also with a combination of these factors causing microcracking and other structural defects [3]. Another disadvantage is that molded polyurethanes cannot be recycled as most thermosetting plastics and could pollute the environment.

Self-healing and recyclable resins are desirable materials that can reduce the major disadvantages of PUs. Self-healing properties could be realized in many ways such as encapsulation [4], hollow fibers with healing resins [5], microvascular networks [6], the addition of thermoplastic particles [7, 8] and e.t.c. All methods mentioned above demand incorporation of a healing agent and catalyst [9-11], and the number of self-healing attempts is limited with one or few. Internal healing based on reversible chemical interaction between functional groups in a polymer are more attractive due to unlimited mending cycles, but external stimulus such as heat or light must be applied [12-14]. There is a wide variety of internal self-healing approaches based on photoactivated [2+2]-cycloaddition [15], reversible formation of disulfide bridges [16] and hydrogen bonds [17], radical reactions [18], pH-dependent processes [19], Diels-Alder reactions [1, 20]. Diels-Alder (DA) reaction between furans and maleimides is a thermally reversible process [21]. Formation of bicyclic DA-adduct usually occurs at 40-70 °C and at higher temperatures (>100 °C) it undergoes cleavage (reverse DA-reaction, re-DA) which results in regeneration of starting components [21, 22]. A few examples of linear polyurethanes, prepared via DA-
based polymerization of difuranic oligomers and bismaleimides are known [1, 23-25]. We present here the synthesis of crosslinked PU based on tetrafuranic oligomer and bismaleimide. Tetrafuranic block (Fu2N-TDI-PPG2000) was prepared by the termination of NCO-ended oligomer (TDI-PPG2000) with difurfurylamine, and commercially available N,N'-bismaleimido-4,4'-diphenylmethane was used as maleimide linker. Difurfurylamine was synthesized by two-step route from furfural, an industrial byproduct of vegetable stock processing. Utilization of monomers obtainable from biorenewable sources allows to reduce using non-renewable stock sources as oil [26-28]; some furane-based resins are actively used as reactive diluents for epoxy and phenol-formaldehyde resins [28-30]. We present here the synthesis, spectroscopic characterization, and evaluation of self-healing abilities of these material.

2. Experimental

2.1. Materials and methods

Furfural (99.5%) was purchased from “Komponent-reactive” and purified by vacuum distillation. TDI (toluene-2,4-diisocyanate, 80%), sodium borohydride (98%) and BMI (1,10-(methylene-1,4-phenylene)bismaleimide, 95%) were purchased from Aldrich and used as received. PPG2000 (polypropylene glycol, Mn = 2000) was purchased from Aldrich and dried under vacuum at 110 °C prior to use. Hydrofuranimide was prepared by the common method [1] from furfural and ammonia. DMF (N,N-dimethylformamide) was purchased from Acros dried over CaH2 and distilled prior to use.

All NMR spectra were recorded by a Bruker Avance 600 NMR Spectrometer (600.1 MHz), using residual proton signal of deuterated solvent as a reference, chemical shifts were reported as parts per million downfield from tetramethylsilane (TMS). ATR-FTIR was performed on Nicolet iS10 spectrometer in the range of 4000 to 650 cm

-1 on a germanium crystal. The thermal behavior was examined by DSC, with a NETZH DSC 204 F1 Phoenix within a temperature range of 30 to 550 °C at the heating/cooling rate of 10 K min

-1 in an 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 the heating/cooling rate of 10 K min

-1 in an argon atmosphere.

2.2. Synthesis of Fu2N-TDI-PPG.

Fu2N-prepolymer was prepared using a conventional two-step method. At the first step, TDI (10.0 g, 57.4 mmol) was reacted with PPG2000 (57.0 g, 28.5 mmol) in a 100 mL two necked round bottom flask, equipped with a magnetic stirrer and dropping funnel. The reaction was carried out at 60 °C under an argon atmosphere for three hours, and the reaction progress was monitored by IR-spectroscopy. At the second step reaction mixture was cooled in an ice-water bath, diluted with DMF (3 mL) and difurfuryl amine (3.0 g, 16.9 mmol) dissolved in DMF (3 mL) was added dropwise into the isocyanate end-capped prepolymer solution in about 15 min. The reaction mixture was stirred at room temperature for two hours. Yield: 21.0 g. 1H NMR (400 MHz, DMSO-d6): 9.52 (s, 2H, –N=CH–O–), 8.05 (s, 2H, –HNC(O)N=Ar), 7.62 (s, 2H, =CHO– of furan ring), 7.53–7.40 (m, 2H, –Ar), 7.17 (d, JHH = 7.8 Hz, 2H, –Ar), 7.07–6.98 (m, 2H, –Ar), 6.42 (s, 4H, =CH–CH= of the furan ring), 6.32 (s, 4H, =CH–CH= of the furan ring), 4.96–4.77 (m, 2H, –CH(CH3)=O–), 4.62–4.46 (m, 4H, –N=CH2–), 3.82–3.78 (m, 32H, –CH2–CH2–O–), 1.27–1.14 (m, 6H, CH3-Ar), 1.04 (d, JHH = 5.7 Hz, –O–CH(CH3)=CH2–); 13C NMR (101 MHz, DMSO-d6): 155.45, 153.54, 151.84, 143.02, 138.27, 137.56, 130.33, 127.19, 127.09, 110.90, 108.42, 107.39, 75.14, 75.05, 74.94, 74.83, 74.70, 72.91, 72.72, 44.96, 44.88, 42.81, 17.76, 17.71, 17.36; IR (ATR, neat, cm

-1): 3304, 2970, 2930, 2895, 2869, 1727, 1673, 1600, 1531, 1506, 1453, 1373, 1225, 1102, 926, 868, 816, 751, 667.
2.3 Synthesis of cross-linked PU
BMI (0.88 g, 2.5 mmol) was added to Fu2N-prepolymer (7.0 g, 2.5 mmol) in 6 mL DMF. Reaction mixture was heated to 60 °C for three hours, then carried onto a glass and cured in oven within 96 hours to afford transparent polymer film.

3. Results and discussion
A synthetic approach for the self-healing polyurethane PU-DA is shown in Figure 1. Briefly, TDI reacted with oligomeric glycol yielding isocyanate-terminated preform which was further treated with difurfurylamine with the formation of the furan-terminated oligomer.

Figure 1. Synthesis of PU-DA.

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.

Both spectra demonstrate signals corresponding to hard segment: at 7.53-6.98 ppm corresponding to phenyl ring, and at 1.27-1.14 ppm corresponding to methyl groups of TDI [1] – and signals from protons of a soft segment: at 3.52-3.91 ppm corresponding to methylene groups, at 3.38-3.28 ppm – to methine protons of backbone chain, and a multiplet at 4.96-4.77 ppm complies to methine protons of the terminal PPG-2000 groups nearest to N-C(O)O-fragments. [2] In the polymer spectra (Fig. 2(b)) intensity of furanic ring signals (7.62, 6.42 and 6.32 ppm) is mainly smaller, which along with the appearance of multiplets in the range 6.52-6.26 ppm indicates completed reaction between monomer and bismaleimide and formation of the DA-adduct. [3]

All monomer and a resulting polyurethane were also characterized by IR-spectroscopy. An absence of the band at 2270 cm-1 in the Fu2N-TDI-PPG spectrum (Figure 3(a)) corresponding to isocyanate groups indicates completion of difurfurylamine addition reaction. A small intensity band at 1775 cm-1 in the
PU-DA spectrum (Figure 3(b)) corresponds to DA-adduct. [4] Also, a decreasing of 751 and 1012 cm⁻¹ bands intensity in the polymer spectrum indicates completion of Diels-Alder reaction.

The thermal behavior of PU-DA was characterized by TGA analysis. From the TGA curve, PU-DA shows a slow weight loss after 200 °C that is indicative of high thermal stability of PU-DA adduct (Fig. 4).

![Figure 3. IR-spectra of Fu₂N-TDI-PPG (a) and PU-DA (b).](image)

### 3.2 Self-healing properties of PU-DA.

Self-healing properties of the polyurethane were tested by DSC method using two-step heating-cooling cycle (Fig. 5). At the first heating curve, an endothermic peak at 98 °C appeared corresponding to reverse DA-reaction process (re-DA). An absence of this peak at the second heating suggests that material is lack of DA-bonds. Then the sample was placed to a thermostat at 60 °C for 48 hours and subsequent DSC-analysis observed pattern similar to the previous one: the first heating curve shows a peak of the reverse Diels-Alder reaction which is absent at the second heating curve.

![Figure 4. TGA curve of PU-DA.](image)  
![Figure 5. DSC curves of PU-DA.](image)

### 4. Conclusion

A new self-healing cross-linked polyurethane was synthesized via Diels-Alder reaction between bismaleimide and furan end-capped prepolymer. Self-healing properties of the resulting material were examined by DSC analysis.

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