

# Self-healing polyurethane-polypropylene oxide copolymers for the protection of carbon and glass fiber-reinforced composites

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**Abstract.** Polyurethane-polypropylene oxide block copolymers containing fragments of an adduct capable of self-healing by the Diels-Alder reaction mechanism have been synthesized and studied for the first time. All obtained polyurethane copolymers were characterized by IR spectroscopy. The temperature transitions and thermal stability of copolymer melts were determined by using the methods of differential scanning calorimetry and thermogravimetric analysis. The self-healing effect was confirmed using a thermal cycling procedure on pre-damaged samples of modified polyurethanes and surface morphology studies. The perspective of the work begun on the creation of self-healing protective polyurethane coatings are shown.

## 1 Introduction

Polymer composite materials have found wide application in various fields due to their outstanding performance properties, a well-developed theory of interaction between fiber and matrix, and the ability to adjust properties to various requirements, such as ensuring the minimum mass of structures, maximum strength and rigidity, reliability and durability [1-3]. The active introduction of carbon composites and glass composites into modern production of science-intensive products requires the development of protective coatings that prolong the service life of products based on them [4-8]. However, in order to protect carbon-reinforced and glass-reinforced composite products and structures, it is necessary to create specialized polyurethanes that would have high mechanical properties, barrier properties to water vapor and aggressive aqueous solutions, and would also have the ability to self-repair defects that occur during their operation [9-11]. Polyurethane coatings are one of the leaders in the market of protective coatings; they are widely used in the automotive and aviation industries, to protect pipes of gas and oil pipelines, as protective and chemical-resistant paints and varnishes [12-14]. The choice of these types of materials is related to their barrier and adhesive properties, which makes it possible to use polyurethanes as protective coatings for many materials [15, 16]. Polyurethanes based on polyethers,

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aromatic diisocyanates, and diols modified by the Diels-Alder reaction are characterized by a unique combination of high strength and hardness with elasticity, the ability to self-heal cracks, wear resistance, and other useful characteristics [17]. This specificity of polyurethanes is due to their multiblock structure, the presence of reversible covalent interactions, as well as a high concentration of urethane and other polar groups that form strong bonds of chemical and physical nature in the system [18].

In this work, new self-healing polyurethane (PU) block copolymers with a block ratio of 60:40 and 50:50 wt. % based on domestically produced polyether Polypropylene oxide 2000 (PPO-2000) and an adduct containing dynamic covalent bonds were obtained for further use as protective coatings for carbon and glass fiber-reinforced composites.

## 2 Experimental

### 2.1 Reagents and methods

Furfuryl alcohol (99.5%) ("Acros") and 1,4-BDO ("Component-reaktiv") were purchased and purified by vacuum distillation. Toluene diisocyanate (TDI) (toluene-2,4-diisocyanate, 80%, "Aldrich") and adduct of diphenylmethane-bismaleimide with furfuryl alcohol (BMFA) (1,10-(methylenedioxy 1,4-phenylene)bismaleimide, 95%, "Aldrich") [19] were used as received. Polypropylene oxide (PPO) ("Laprol 2000", "Macromer") was purchased and dried under vacuum at 110 °C prior to use. Dimethylformamide (DMF) (N,N-dimethylformamide, "Acros") was distilled before use.

ATI-FTIR was performed on Nicolet iS10 spectrometer in the range of 4000 to 650  $\text{cm}^{-1}$  on germanium crystal. The thermal behavior was examined by DSC, with a NETZH DSC 204 F1 Phoenix within a temperature range of -80 to 160 °C at heating/cooling rates of 10  $\text{K min}^{-1}$  in argon atmosphere. A sample weight of about 10-16 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  $\text{K min}^{-1}$  in argon atmosphere. The dynamics of the polymer film healing process was monitored using a Phenom Pro X scanning electron microscope (SEM) (accelerating voltage, 15 kV) before and after the healing process.

### 2.2 Synthesis and characterization

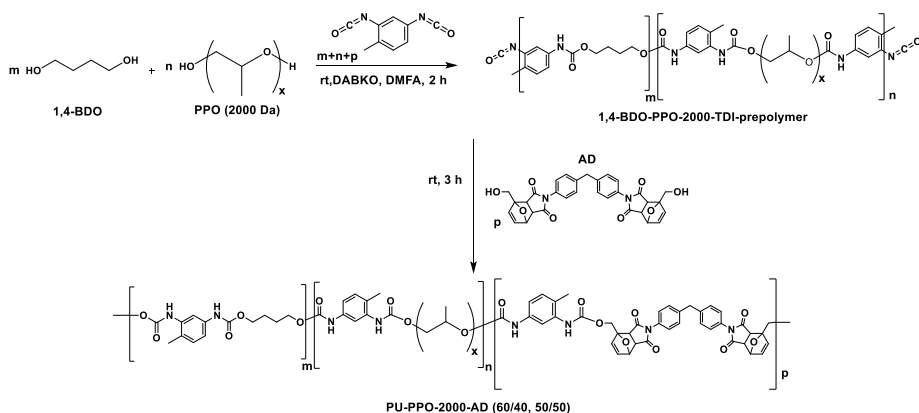
#### 2.2.1 Synthesis of PU-PPO2000-AD (60:40 wt.%) (PU-1)

1,4-BDO (1.364 g, 15.16 mmol), Polypropylene oxide 2000 (3.680 g, 1.84 mmol) and DABCO catalyst (0.060 g, 0.54 mmol) was added to a two-necked flask under argon flow, then DMF (10 ml) was added, and the solution was stirred for 30 minutes for complete homogenization. Then, an excess of the TDI (3.434 g, 19.74 mmol) was added to the flask in a counterflow of argon, and the solution was stirred at room temperature for 2 hours. At the second stage, the solution of the BMFA adduct (1.522 g, 2.74 mmol) in DMF (5 ml) was added to the reaction mixture and stirred at 25°C for 3 hours. The progress of the reaction was monitored by IR spectroscopy (disappearance of the  $\text{N}=\text{C}=\text{O}$  band at 2277  $\text{cm}^{-1}$ ). The polymer solution was poured into a Petri dish preliminarily coated with an antiadhesive layer and dried at 70°C for 72 hours.

### 2.2.2 Synthesis of PU-PPO2000-AD (50:50 wt.%) (PU-2)

1,4-BDO (1.023 g, 11.35 mmol), Polypropylene oxide 2000 (4.599 g, 2.29 mmol) and DABCO catalyst (0.060 g, 0.54 mmol.) were added to a two-necked flask under argon flow, then DMF (10 ml) was added and stirred solution for 30 minutes for complete homogenization. Then, an excess of the TDI (2.856 g, 16.39 mmol) was added to the flask in a counterflow of argon, and the solution was stirred at room temperature for 2 hours. At the second stage, the solution of the BMFA adduct (1.522 g, 2.74 mmol) in DMF (5 ml) was added to the reaction mixture and stirred at 25°C for 3 hours. The progress of the reaction was monitored by IR spectroscopy (disappearance of the N=C=O band at 2277 cm<sup>-1</sup>). The polymer solution was poured into a Petri dish preliminarily coated with an antiadhesive layer and dried at 70°C for 72 hours.

Synthetic approach of the self-healing polyurethane PU-PPO2000-AD showed in Figure 1.

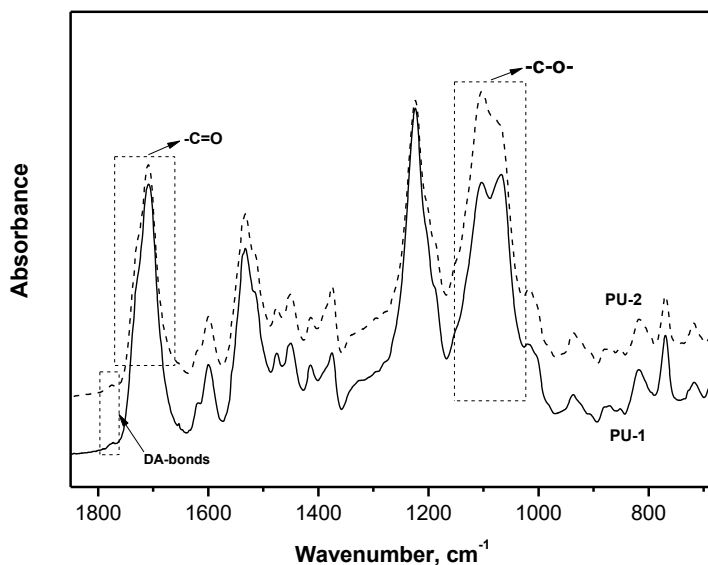


**Fig. 1.** Synthetic process of polyurethane copolymers PU-PPO2000-AD.

## 3 Results and discussion

### 3.1 Characterization of PU-DA

Structure of the obtained polyurethane was characterized by FTIR spectroscopy.

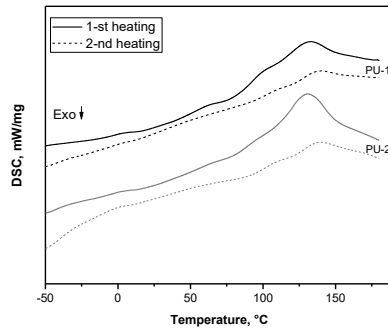


**Fig. 2.** IR-spectra of PU-1 (solid line) and PU-2 (dashed line).

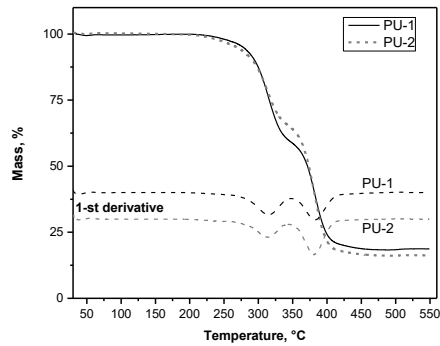
The FTIR spectra of the PU-PPO2000-AD samples are shown in Figure 2. The appearance of the weak band at  $1776\text{ cm}^{-1}$  in the polymer spectrum confirms the formation of a DA adduct [20, 21]. The C–O band was observed in the range of  $1000\text{--}1100\text{ cm}^{-1}$  in the spectra of both samples which refers to the polyether component of the obtained polymer. The presence of the band at  $1706\text{ cm}^{-1}$  corresponds to vibrations of the C=O group of the urethane bond [22].

The thermal stability of PU-PPO2000-AD was studied by the TGA (Figure 3): all polyurethanes synthesized in this work have typical two-stage degradation. The first stage of decomposition refers to the hard segments of PU: the reverse Diels–Alder reaction proceeds with the formation of furanurethane and bismaleimide, followed by further decomposition of the hard phase [23, 24]. Samples PU-1 and PU-2 showed approximately the same mass loss by 40% and 35% in the range of  $260\text{--}360^\circ\text{C}$  at the first stage of decomposition. Next, the second degradation step, caused by the soft segments, in the range of  $370\text{--}450^\circ\text{C}$  with a weight loss of 40% (PU-1) and 50% (PU-2) [23, 24].

Thermal properties and reversibility of DA bonds were studied by DSC (Figure 4). The first heating curve (solid line) of the polymers demonstrated two endothermic peaks: at  $100$  and  $132^\circ\text{C}$  for samples PU-1 and PU-2 which can be attributed to rDA cleavage of endo- and exo-isomers, respectively [25]. However, the second heating curve (dashed line) showed two effects characteristic of endo- and exo-isomers, which indicated that the rDA reaction did not proceed completely: the DA reaction did not occur on the cooling curves.



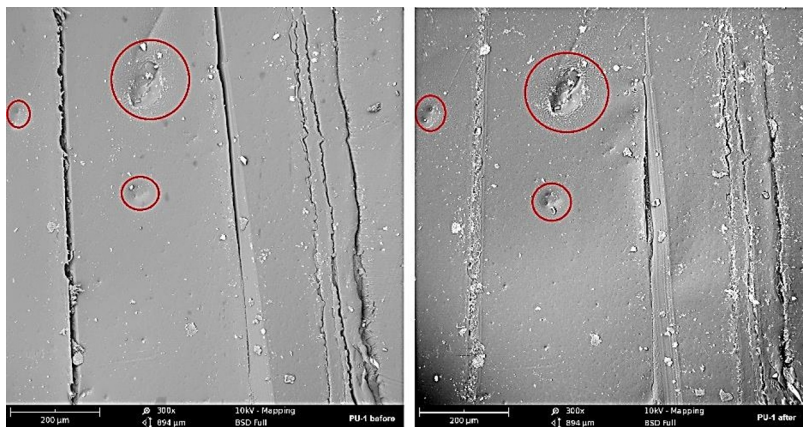
**Fig. 3.** TGA curve of PU-1 and PU-2

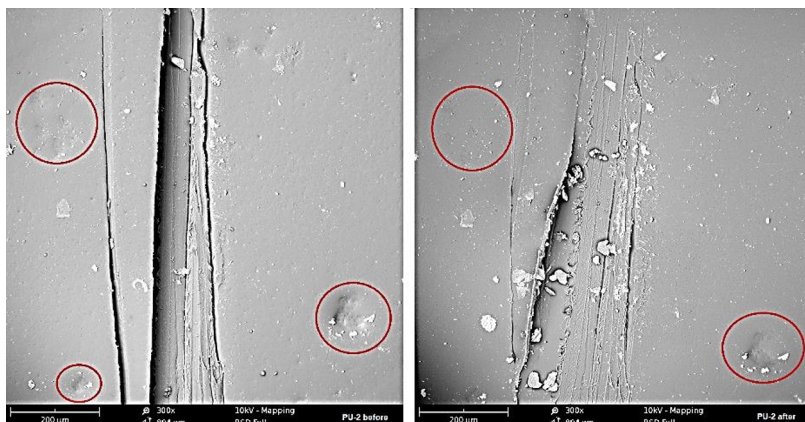


**Fig. 4.** DSC curves of PU-1 and PU-2.

### 3.2 Self-healing efficiency

To study the self-healing ability the samples were damaged in the middle with a blade. Damaged samples were subjected to thermal treatment: 1 h at 100 °C and 48 h at 60 °C. SEM-images were obtained before and after the healing process (Figure 5). It is obvious, that partial healing of defects is observed in the case of samples PU-1 and PU-2.





**Fig. 5.** SEM-images of PU-1 and PU-2

## 4 Conclusion

Polyurethane-polypropylene oxide block copolymers containing fragments of an adduct capable of self-healing by the Diels-Alder reaction mechanism have been synthesized and studied for the first time. It was found that they have the effect of self-healing of defects when film samples are heated according to the regime of 1 hour at 100°C and 48 hours at 60°C. The perspective of the work begun on the creation of self-healing protective polyurethane coatings are shown.

## 5 Acknowledgements

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