Recent progress in self-healing polyurethanes based on Diels-Alder reaction

A S Borodulin¹, P F Ponomareva¹, E O Platonova¹, V A Pavlova²

¹Intersectoral Engineering Center «Composites of Russia» of Bauman Moscow State Technical University, FSAEI HE «Bauman Moscow State Technical University». 2-d Bauman str., 5. 105005, Moscow, Russia

E-mail: asb@emtc.ru, verapavlova@general.chem.msu.ru

²Lomonosov Moscow State University, Chemistry Department, Leninskie gory, GSP-1, str.3. 119991, Moscow, Russia

Abstract. This review examines the latest advances in the synthesis and application of polyurethanes that have a self-healing effect due to the thermally reversible Diels-Alder reaction. A classification of strategies for improving the parameters of the final polymers is proposed, which includes the division into polyurethanes with a flexible organic linker, composites with nanoparticles, and systems with a dual self-healing mechanism both due to the Diels-Alder reaction and the reaction of the formation of a disulfide bonds from thiols. The possible applications of the obtained materials and the assumption about the further development of the field are considered.

1. Introduction

Thermoplastic polyurethanes (TPU) are an important class of industrial polymers and are characterized by high flexibility, strength and a wide range of methods for manufacturing products [1-3]. Classical TPU is obtained by the reaction of diisocyanates with diols of different nature, which form a multiblock copolymer consisting of alternating so-called soft and hard segments.

Depending on the type and percentage of different segments, a microphase separation could be formed, which allows varying the mechanical and thermal properties of the final polymer [4]. Thus, TPUs with programmable properties, such as biocompatibility [5], conductivity [6] and optical transparency [7], etc., can be obtained.

Inspired by nature, self-healing materials are able to restore their original properties both in the presence of external stimuli and completely independently [8]. Thermally reversible Diels-Alder reaction is the most popular method of self-healing, since it leads to the greatest strength due to the formation of strong covalent interactions in the material [9]. In recent years, significant progress has been made in obtaining various self-healing materials based on different polymers and using different self-healing mechanisms, which is reflected in a large number of reviews on this topic [10-13]. This paper focuses on the achievements over the past 5 years in the field of self-healing polyurethanes based on the Diels-Alder reaction and reveals new strategies for improving the time and degree of recovery of the material, as well as ways to impart specific properties.

2. Self-healing polyurethanes based on Diels-Alder reactions

Diisocyanate-free methods of synthesis of polyurethanes have not yet been introduced into the industry, so the most common method for producing PU is the reaction of diols with diisocyanates (Fig. 1a).
Figure 1. a) scheme of polyurethane formation by reaction of diisocyanates and diols; b) chemical structures of typical diisocyanates; c) chemical structure of typical diols for soft segments

The most commonly used diisocyanates are hexamethylenedisocyanate (HDI), 4,4’-diisocyanatomethylendicyclohexane (HMDI), isophorone diisocyanate (IPDI), methylene diphenyl disocyanate (MDI) and toluene diisocyanate (TDI) (Fig. 1b). Typical structures of diols are shown in Figure 1c. Polyethylene glycol (PEG), polypropylene glycols (PPG), and polytetramethylene glycols (PTMG) of various lengths are used as flexible soft segments, and bisphenol A and other aromatic diols are used as rigid hard segments.

To achieve self-healing properties, fragments that can participate into a thermally reversible Diels-Alder (DA) reaction are included in the polyurethane structures both in main and side chains [10,11]. The most common couple for DA reaction is furan-maleimide due to their availability and possibility to obtain from natural sources (Fig. 2).

Figure 2. Scheme of Diels-Alder reaction and retro-Diels-Alder reaction of furan and maleimide derivatives

2.1. Chemical design of PU

The rapid development of the field of self-healing materials, which is expressed in the emergence of many new applications, has led to the emergence of additional properties of polyurethanes [13]. Therefore, new strategies are needed to control the properties of this class of polymers.

Summing up the achievements over the past 5 years, we can distinguish the following ways of developing polyurethane foam: 1) introduction of specific organic linkers 2) introduction of nanoparticles 3) creation of systems with a binary healing mechanism (Fig. 3).
2.1.1. Flexible organic linkers/species

Silicon organic compounds are most often used as a specific linker due to their flexibility. In recent study [14] polyurethane functionalized with pendant furan moiety was prepared using furfurylamine and furfuryl glycidyl ether. This PU was grafted with maleimide functionalized with polyhedral oligomeric silsesquioxanes via Diels–Alder reaction. The resulting polymers showed water contact angle 141.3°, but there is no data about mechanical properties of obtained polymers. In other work a silicone-based polyurethane with 2-ureido-4[1H]-pyrimidinone and amphiphilic pendant chains can form hydrogen bonds with various substrates with adhesion strength (0.9–3.0 MPa), which is higher compared with the PDMS elastomer (0.3–0.4 MPa) [15]. However, the poor mechanical properties of silicone-containing PUs (mechanical strength) limit their use as coatings, rather than as the main material of the composite.

2.1.2. Inorganic particles

The creation of composite materials has always made it possible to give the desired properties to the polymer matrix. To create thermally active composites, ceramic aluminum-containing particles were incorporated into the polyurethane structure [16]. The thermal resistance of obtained PUs was 0.48 K/W by a thermal transient test. The thermosetting composite was recycled via the retro DA reaction. In other core-shell copper nanowire were incorporated in healable polyurethane to achieve sufficient conductivity for production flexible electronics [17]. PU with furan rings was cross-linked with N,N'- (4,4'-methylendiphenyl) dimaleimide via a Diels-Alder reaction to form the healable network polymer. Obtained nanocomposite conductor exhibits a sheet resistance of 22.3 Ω·sq\(^{-1}\), 66.5% transmittance at 550 nm. The self-healing could be achieved up to 98% in 3 min at 120 °C. Other way for obtaining of electrically conductive polyurethanes was published recently [18] and related with incorporation of graphene oxide and silver nanowires into the polymer matrix. Self-healing properties was improves by functionalization of graphene nanosheets with DA group which could activate a self-healing property under NIR. however, the introduction of nanoparticles is an expensive technology and involves their aggregation under different temperature conditions.

2.1.3. Dual self-healing mechanism with disulfide bounds.

It is a great challenge to design a materials with complex integration of stretchability, transparency, healability and fast healing abilities. One of the recent strategies is synthesis of dual covalently reversible

![Figure 3. Ways for obtaining task-specific polyurethanes](image)
dynamic bond-based polymers that could integrate two types of covalent reversible dynamic bonds, Diels–Alder and disulfide bonds. PU based on cystamine, 1,6-diaminohexane, and 4,4′-diaminodiphenylmethane was synthesized and demonstrated high stretchability, fast healing abilities (60 °C, 5 min), skin adhesion, recyclability, high transparency, and tactile sensing abilities [19]. In other work PU based on functional diol having furfuryl and disulfide functionality, polycaprolactone (PCL) diol and 4,4′-methylenebis (phenyl diisocyanate) [20]. This dual functional PU elastomer was cross-linked using a bismaleimide via the Diels–Alder reaction with the furfuryl pendant group in PU. This dual functional PU having thermoreversible DA linkage and disulfide linkage showed excellent tensile strength (σ = 39.5 MPa) and good self-healing characteristics Eσ ≈ 97% after 3 cycles.

2.2. Application of PU
The most popular applications of self-healing polyurethanes is construction materials [10-13, 19, 20, 21]. However, due to the complexity of the balance of speed and degree of recovery, as well as the possibility of giving new properties to polymer composites, new areas are emerging such as hydrophobic [14] and anti-fouling coatings [15], applications related to the development of flexible electronics [16,17] and artificial skin [18], as well as bio-applications [22].

3. Conclusion and outlook
This brief overview focuses on the latest trends in self-healing polyurethanes over the past five years. It should be noted that this article is not a comprehensive review, but a brief analysis of this field focused specifically on polyurethanes with reduction by the thermally reversible Diels-Alder reaction. However, developing the most effective self-healing systems remains a big challenge. The three aspects must be balanced: 1) the self-healing efficiency is close to ideal both in the degree and in the number of recovery cycles; 2) mechanical properties that allow the use of PU as structural materials (including modulus of elasticity, tensile strength and viscosity); 3) soft healing conditions. In addition, the existing difference is in determining the effectiveness of self-healing. A universal recovery measurement methodology needs to be developed, as it is difficult to compare different self-healing materials based on different measurement standards. And the characteristics of self-healing TPU in a particular application should be checked, such as fatigue resistance, long-term stability of thermal and electrical conductivity, recirculation time. With the development of synthetic chemistry and supramolecular chemistry, there will be huge opportunities in the creation of thermoplastic healing polyurethane elastomers.

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