

Advances in the Diels-Alder Reaction in Self-Healing Polymeric Materials

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Abstract. Polymeric functional materials are widely used in all aspects of everyday life. However, they are subject to a variety of environmental influences such as chemical attack, mechanical abrasion or impact and thermal decomposition, resulting in a significant shortening of the service life of polymer materials. Using traditional repair methods, the damaged part of the material is only reattached or reinforced at a macro level. Currently, more and more research is focused on smart composite materials with self-healing properties. This eliminates hidden problems in the use of the material, thereby extending its service life and broadening the range of applications. The Diels-Alder (DA) reaction is a [4+2] cycloaddition reaction between a conjugated diene and a substituted alkene. It has become a hot research topic in the field of self-healing due to its mild reaction conditions and lack of catalyst. In this paper, the progress of research on self-healing polymeric materials is reviewed with a focus on applications in DA reactions. The research progress in this field is reviewed based on the chemical structures of the prepared DA reaction-based polymers, and the development of DA reaction based self-healing polymers is investigated. Finally, the development of self-healing polymers based on DA reactions is given as an outlook.

1 Introduction

With the continuous progress of science and technology and the rapid development of industrialisation, organic polymers have become indispensable and important materials in various fields. Whether in daily life, food, clothing, housing and transport, or in the high-tech field of highly sophisticated equipment, organic polymer materials have a wide range of applications. However, over time, these materials can suffer from fatigue, ageing and damage, leading to a decline in performance and even failure. Therefore, it is necessary to find a way to enhance the durability of these materials.

In this context, self-healing polymer materials have emerged. Compared to ordinary polymers, self-healing polymers are more durable. This is because they can automatically repair and restore their original properties after damage. This ability can effectively extend the life of the material and improve its reliability and stability.

Therefore, the study of self-healing polymer materials has become an important direction in the field of scientific research today. Through continuous research and experimentation, new self-healing polymer materials are being developed to meet the needs of different fields. These new materials offer higher self-healing efficiency, better mechanical properties and a wider range of applications.

There are various approaches to obtain self-healing polymers, such as hydrogen bonds, coordinate bonds and covalent bonds. In organic chemistry, the Diels – Alder reaction is a chemical reaction between a conjugated diene and a substituted alkene, commonly termed the

dienophile, to form a substituted cyclohexene derivative [1]. The D-A reaction has the following characteristics: (1) it can be carried out under mild conditions and generally does not require a metal catalyst; (2) the reaction can be reversed up to a certain temperature, so that the polymer synthesized by this reaction can be easily decomposed to the original monomer under heated conditions, which facilitates the regeneration of the polymer; (3) the reaction is highly selective [2].

Therefore, the D-A reaction can be chosen as the mechanism of self-healing polymers [3]. Today's research is based on the repair of single-substance polymers such as thermally reversible self-healing polyurethane, self-healing epoxy resins, etc. A cross-sectional comparison of self-healing polymers using the D-A reaction is lacking.

The aim of this study is to conduct a literature review of various self-healing polymers using the D-A reaction, so as to screen out the materials with excellent performances and compare their self-healing properties, material structure, reaction mechanism and other factors. By comparing the studies, the aim of this study is to reveal the material properties and performance of self-healing polymers and their advantages and disadvantages in various applications.

Firstly, this study will review the current status of research on D-A reactive self-healing polymers, including research methods, reaction conditions, material properties and their self-healing properties. Based on this, a method and evaluation criteria for cross-sectional comparison of research will be proposed to identify key factors and optimisation directions for the self-healing

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performance of polymers. Secondly, this study will use literature research for comparative analysis in order to compare the strengths and weaknesses of various self-healing polymers in terms of durability, self-healing ability, toughness, stiffness and mechanical properties, and to summarise their respective strengths and weaknesses [4]. At the same time, the material properties that affect the self-healing ability and their formation mechanisms are investigated by comparing the structure and reaction mechanism of the materials. Finally, in view of the shortcomings of the existing research and the prospects for future research, this study will propose improvement proposals and directions for further research, to provide new ideas and directions for the development of self-repairable polymers.

2 Introduction and comparison of self-healing polymers

Among the self-healing polymers using the D-A reaction, the D-A reaction between furan groups and maleimide groups to achieve self-healing is the most common system [5]. Therefore, this section will focus on the mechanism, reaction conditions and self-healing capacity of self-healing polymers in this system. Of course, the rest of the reaction systems will also be mentioned.

2.1. The thermally reversible self-healing epoxy resin

According to Figure 1, the thermally reversible self-healing epoxy resin was created. Xia He et al. used a two-step method to synthesize DGFA, an epoxy resin precursor containing a flavonoid ring, which was then reacted with bismaleimide to produce Thermo-reversible epoxy resin (EP-DA), an epoxy resin with good thermo-reversible properties. EP-DA specimens were prepared and reacted at 70 °C for 48 h. After demoulding, rectangular EP-DA specimens were obtained [6].

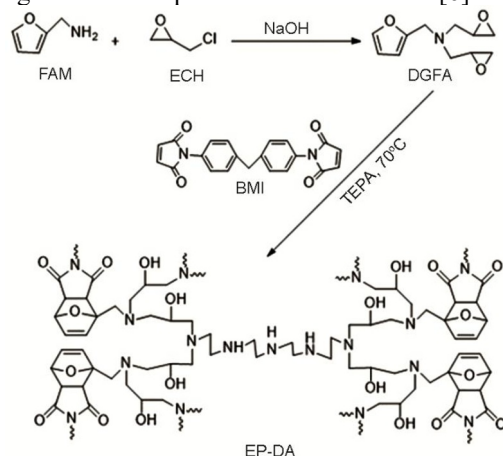


Fig. 1. Synthetic routes of EP-DA [6]

Source link: <https://www.cjmr.org/article/2019/1005-3093/1005-3093-33-8-635.shtml>

In self-healing polymers, EP-DA decomposes through the rD-A reaction, which can be broken down at higher temperatures into two monomers, which then

each undergoes thermal movement. Subsequently, after cooling and then the D-A reaction, the whole is remodelled and cracks and defects are self-healed [7] (Figure 2).

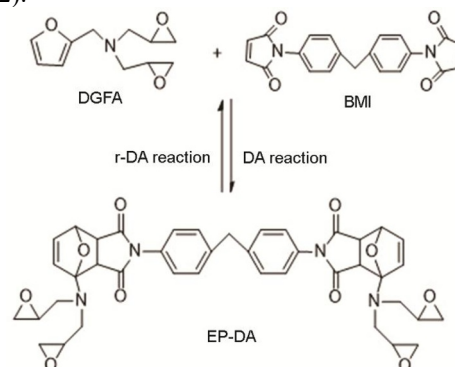


Fig. 2. rD-A reaction of EP-DA [7].

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Self-repair performance was investigated by qualitative observation of circular specimens and quantitative determination of bending loads on rectangular standard specimens: (1) a 30 mm diameter steel ball was dropped from a height of 15 cm and the impacted specimens were heat-treated at 110, 120 and 130 °C to observe the healing of impact cracks; (2) EP-DA standard specimens were prepared, butt-jointed after complete fracture and treated at 130 °C, subjected to a three-point bending test to determine the optimum repair time and characterised by the bending load recovery rate for self-repair efficiency [6].

The heat treatment temperature and time have a significant effect on the mechanical properties and repair ability of EP-DA. Its bending load gradually increased with the reaction time, and its bending displacement also gradually increased. This indicates that at 70 °C, the epoxy resin was gradually cured by the reaction between DGFA and TEPA. On the other hand, the DA reaction between DGFA and BMI produced DA adducts, which gradually increased the flexural strength and toughness of the resulting EP-DA. In addition, the strength and toughness of EP-DA obtained at 70°C for 48 h were very similar to those obtained at 36 h. This indicates that the curing of EP-DA and the D-A reaction had been completed at 70 °C for 48 h [6].

However, the load of the specimens decreased instead as the heat treatment time continued to increase. This indicates that the D-A reaction was already relatively adequate at 30 min r treatment at 130 °C and that the D-A reaction occurred again after a further 48 h treatment at 70 °C, resulting in a good repair of the cracks leading to an increase in the strength of the material [6]. If the treatment time at 130 °C is longer than 30 min, the prolonged high temperature heating causes the self-polymerisation of the bismaleimide molecules containing dienophiles in the end groups and the amount of D-A bonds formed decreases, resulting in a poorer repair of the cracks and a decrease in mechanical properties.

In the EP-DA repair mechanism of self-healing polymeric materials, it was found that repair time and repair temperature have a strong influence on their repair effectiveness. The effect of repair temperature, in particular, is more significant. When the repair temperature is appropriate, the EP-DA repair mechanism can complete the self-repair of cracks and debris in a relatively short period of time, thus effectively improving the durability and reliability of the material. However, too high or too low repair temperatures can adversely affect the repair results and even lead to repair failure. Therefore, in practice, the appropriate repair temperature and time needs to be selected according to the specific situation in order to achieve the best repair results.

2.2. The self-healing polyurethane (PU-DA)

Wan Liying et al. obtained self-healing polymer PU-DA based on thermoreversible DA dynamic covalent bonds. PTMG was reacted with FGE-FA to give linear polyurethanes with a tetrauran structure at the end group. It was then cross-linked and cured with 1,8-BMI to give a netted cross-linked self-healing PU-DA containing reversible DA dynamic covalent bonds. With the introduction of DA dynamic covalent bond

15.4 g of FGE and DMF were added, and the mixture was heated to 60 °C in a 100 mL flask. Over 30 minutes for 8 hours, 9.7 g of FA was gradually introduced dropwise to the FGE. To remove the remaining solvent, the system was distilled at low pressure, and the product FGE-FA was produced. As solvents, 10 g of PTMG-1000, 5 mL of anhydrous DMF, and IPDI were added. By adding 0.01 g of TBTDL and increasing the temperature to 75 °C for 1 hour, the reaction was continued. Then a product, IPDI-PTMG, was produced when the solvent was removed.

0.02 mol of FGE-FA and 0.02 mol of IPDI-PTMG were added to 10 mL of anhydrous DMF and then stirred for 10 min at room temperature. Then this system was warmed up to 80 °C for 3 h and then 0.01 g of TBTDL was added and the reaction continued for 3 h. The step b product, Pre-PU, was obtained.

6.08 g of 1,8-BMI was added to the Pre-PU in a 250 mL beaker, and the mixture was agitated in a water bath at 55°C until the 1,8-BMI was completely dissolved. The reaction was then carried out at 70 °C for 30 min to ensure that the D-A reaction occurred at a constant temperature. To create the polymer PU-DA, the product was poured into a mold and heated to 70 °C for 24 hours [8]. Figure 3 depicts the above-described synthetic method.

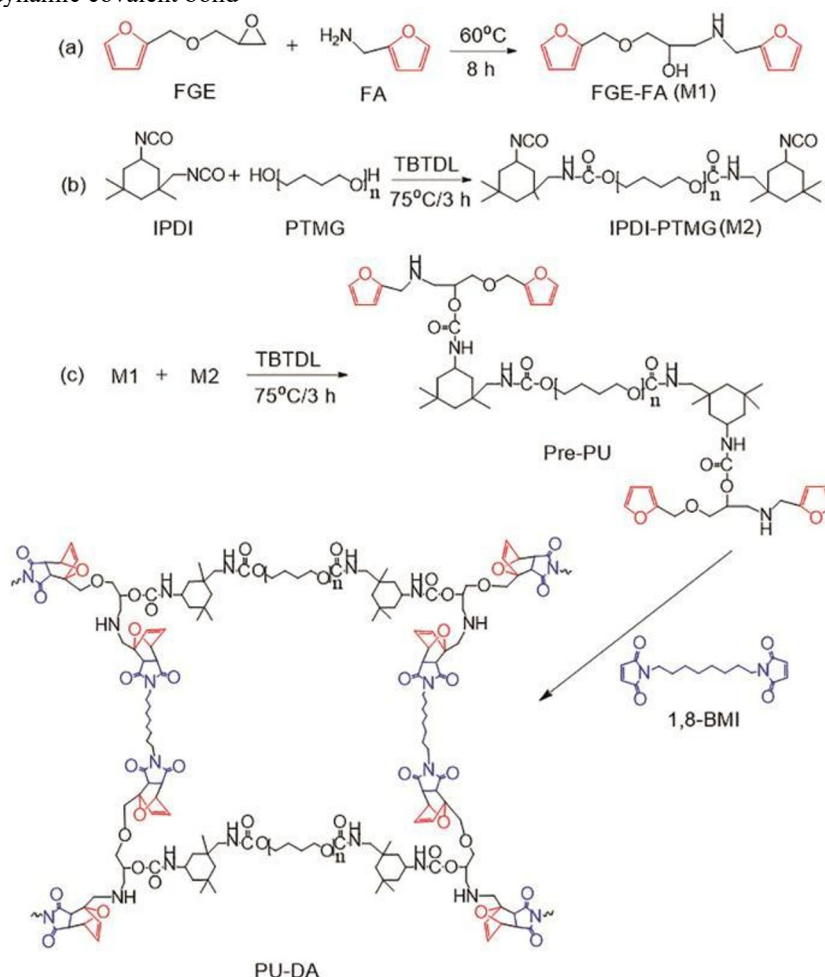


Fig. 3. Synthetic routes of PU-DA [8]

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Then, the PU-DA specimens were fixed by putting them in a 70 °C oven. The impact of the repair duration

on the mechanical characteristics and repair rate of the specimens was then examined. The first PU-DA specimens had a tensile strength of 4.20 MPa and an elongation at break of 305.59%. After being repaired at 70 °C for two hours, the specimens' tensile strength and elongation at break were 2.27 MPa and 225.14%, respectively. Only 54.1% of the repairs were successful. The recorded tensile strength was 3.98 MPa and the elongation at break was 298.98% with a repair rate of 94.8% when the repair duration was increased to 4 h. The repair rate increased to 96.9% once the repair period was increased to 8 hours. These results show that the longer the repair time, the higher the mechanical properties and repair rate of the specimens.

2.3. Other self-healing polymers

Wang et al. firstly used the thiol-olefin reaction to graft furfuryl groups onto butadiene rubber, and used furfuryl-functionalised multi-walled carbon nanotubes (MWCNT-FA) as reinforcing agents to obtain covalently bonded and reversibly cross-linked rubber composites through the DA reaction between bifunctional maleimides and furfuryl groups, achieving self-healing of general-purpose rubber. In this system the modified MWCNT-FA plays a dual role of reinforcing and aiding repair at the same time [9].

Shi et al. similarly prepared modified thermoplastic elastomer styrene-butadiene-styrene block copolymer (SBS) hybrid materials based on reversible cross-linking by the DA reaction. The method grafted furan groups onto SBS molecular chains via the thiol-ene click reaction, and then used the DA-reactivity of carbon nanotubes to construct carbon nanotubes reversibly cross-linked modified SBS composites. The structural features of the reversible cross-linking enabled the composites to have self-healing and editable shape memory behaviour [10].

3 Conclusion

In this study, it was found that the repair time and repair temperature affect the repair effect of self-healing polymers using the D-A reaction. If the repair temperature is too low, the activity of the repair reaction will be reduced and the self-repair effect will be affected; if the repair temperature is too high, the reverse reaction of the D-A reaction will occur and the repair effect will be affected. The repair time also directly affects the repair effect of the self-repairing polymer. If the repair time is too short, the repair reaction will not be sufficient to fully repair the defects and damage on the surface of the material, resulting in unsatisfactory repair results, while too long a repair time will waste time and resources and may result in an excessive repair reaction that will affect the performance of the material. In conclusion, by controlling the repair time and repair temperature, the repair effect of self-healing polymers can be maximised, thereby extending the life of the material and improving its performance.

Current research has the disadvantage of analysing a single condition of breakage when studying the self-healing of individual substances. A wide range of damage, such as abrasions, tears, scratches, fractures, and heavy pressure, is not considered in the study. And there is not much mention and analysis of the practical application aspects. Future research should be based on the current study and discuss the classification of self-healing under multiple damage, and ultimately the best repair solution. At the same time, damage simulations from similar studies can be used for cross-sectional comparisons. Secondly, the best repair solution should be followed by a reasonable discussion and analysis of the actual application scenarios and the simulation of damage caused by the actual application scenarios under certain conditions.

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