Research Progress of Self-healing Polymer Materials

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Abstract: According to the classification and repair principle of self-healing polymer materials,domestic and foreign research progress on self-healing polymer materials of intrinsic structure and synthetic structure was summarized. The intrinsic structure self-healing polymer materials included rupture spontaneous growth materials based on covalent bonds such acyl hydrazone bond,disulfide bond,nitrogen oxygen bond and Dieal-Alder,reversible non-covalent bond materials based on hydrogen bond type,super hydrophobic type, ionic reaction and coordination bond ;the synthetic self-healing polymer materials involved filling microcapsule type and bionic human vascular materials. Finally,the develop trend of self-healing polymer materials was prospected.

Keywords: self-healing polymer material ;mechanism ;functional material ;intrinsic structure ;synthetic structure

Polymer materials play a very important role in contemporary human production and life due to their high molecular weight, light weight, excellent mechanical properties and good insulation performance[1–3]. The properties of polymer materials vary widely, the structure is complex and varied, and the rich and varied materials bring considerable convenience to our production and life. Specific polymer materials can also have good optical properties, such as polycarbonate[4], polystyrene, etc.[5], functional polymer materials are related to biomedicine[6], weapons manufacturing [7], deep Empty exploration [8] is the sensor aspect of the high-precision field.

At present, the research results of polymer direction are numerous[9–12]. However, there are many reports of materials with single-sided superior performance, and there are few reports on functional polymer materials with outstanding functions in many aspects, and the development of their devices is rarely involved. In the field of self-repairing polymers, both intrinsic self-repairing polymer materials and composite self-healing polymer materials [13] have reported less self-repairing properties at room temperature, but temperature-sensitive self-repair The repair of polymer materials has been reported many years ago. There are two main methods for imparting conductivity to self-repairing polymer materials. One is to add in the polymer system [14]. The intrinsic conductive polymer self-healing material refers to self-repairing properties and electrical conductivity properties based on the polymer itself. Once this type of polymer material is prepared and stabilized, its properties are stable, and structural and performance changes are not easy to occur during use. However, the preparation process is generally cumbersome and complicated, costly, and difficult to improve. [15– 16]; another is a composite conductive polymer self-healing material, which refers to doping a repairable microcapsule in a polymer having conductive properties [17], or forming a conductive material in a polymer material having self-healing properties. The nanoparticles form a series of multifunctional and practical materials. Such materials are compounded from a variety of materials, and the corresponding materials can be separately produced in the industry for recombination, with a short production cycle and relatively high benefits.

The author analyzes the research progress of intrinsic self-repairing polymer materials and composite self-repairing

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polymer materials in recent years, in order to provide reference for the development of multi-functional self-repairing polymer materials.

1. Intrinsic self-repairing polymer material

The intrinsic self-repairing polymer material is a kind of material that can self-heal without any additional energy and force when the polymer matrix is damaged to some extent by external force or external energy. At present, relevant teams at home and abroad have carried out extensive research on self-healing materials [18]. The self-healing polymer materials developed are mainly divided into two types: self-repairing polymer materials with reversible covalent bonds; Covalently bonded polymeric material.

1.1 Self-repairing polymer material based on covalent bond-based spontaneous growth

Self-healing polymer material based on hydrazide bond type. The mechanism of the valence bond-based valence bond self-healing system is that the hydrazide bond formed by the reaction between the aldehyde group and the hydrazide can be self-generated. S. Bode *et al*. [18] developed a sol-gel system with a change in morphology with changes in p H , as shown in **Figure 1.** The system converts to a gel state when the p H value is greater than 4, when p H When the value is less than 4, the system will convert to the sol state, and the system can achieve self-repair by adjusting the p H value. The material is self-repairing polymer material under the condensation reaction mechanism by modifying dibenzoyl hydrazide at both ends of polyethylene glycol and then reacting with tris[(4-oxophenoxy)-methyl]ethane. When the p H value of the system changes within a certain range, the hydrazide bond will be broken and recombined, and the macroscopically manifests itself as the self-repairing behavior of the material.

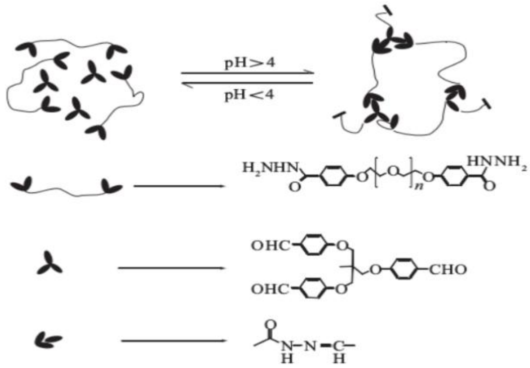

Figure 1. Self-healing mechanism diagram of hydrazide bond

Self-healing polymer material based on disulfide bond type

The reversible disulfide bond type self-healing polymer material is a weak covalent bond inside the polymer - the cleavage and recombination of a disulfide bond. Kyoto University of Japan reported a self-healing material with a disulfide bond type. The repair mechanism is shown in **Figure 2** [19]. The polymer material is broken and grown by S-H bond and S-S bond to realize the polymer. Macro self-healing performance. B. San dmann *et al*. used a PS inlaid copolymerization method and used a disulfide bond to bridge the inlaid copolymer. There is a terminal functional group at the end of the polymer, which affects the stability of the material. The polymer chain needs to be blocked, and the terminal blocking agent is ferric chloride.

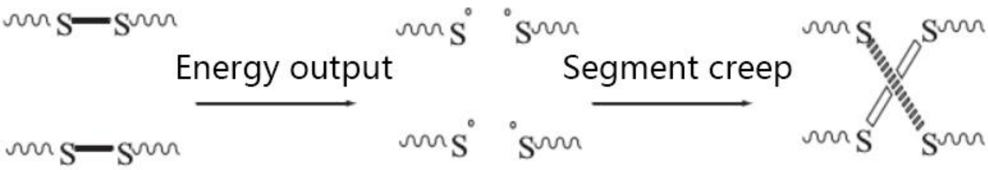

Figure 2. Self-repair mechanism of disulfide bond

Self-healing polymer material based on nitrogen-oxygen bond type

The N-O covalently bonded self-healing polymer material is similar to other covalently bonded polymers, and the macroscopic self-repairability of the material is achieved by the breaking and recombination of the N-O covalent bond. Y. Sakai *et al*. [20] innovatively introduced polymer materials in the C-O-N repeating unit, similar to block copolymers. Under the microscopic effect of the alkoxyamine group cleavage and recombination, Macroscopically, it shows the self-repairing behavior of the polymer. However, this material needs to be repaired at 126 ° C for 6 to 12 h. The application prospect of such self-repairing polymer is a big drawback.

Repair polymer based on Dieal-Alder (DA) type [21]

The excitation conditions of the reversible DA reaction are similar to those of the N-O bond, and both require external energy intervention to achieve self-healing performance. The mechanism of such self-repair is shown in Fig. 3 [21], which is a cycloaddition reaction of a conjugated double bond with a double bond or a triple bond, and the reaction is subjected to an addition positive reaction at a low temperature, and the reaction efficiency is high; When the temperature rises, the reaction equilibrium is broken, and the reaction direction changes 180°, moving in the opposite direction. M. Krogsgaard *et al*. synthesized furan and maleimide as raw materials to prepare a self-healing polymer matrix with DA self-healing effect. However, the self-repairing temperature of this substance is as high as 160 ° C, and the self-repair rate is only about 50%. Compared with other self-repairing polymers at normal temperature, the hardness and mechanical strength have great advantages.

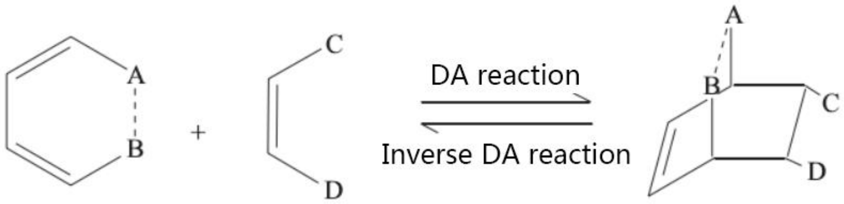

Figure 3. DA reaction self-repair mechanism diagram

1.2 Reversible non-covalent bond type self-repairing polymer material

Hydrogen-bonded self-healing polymer material

Hydrogen-bonded self-healing polymer materials are self-repairing polymer materials by introducing reversible hydrogen bonds into polymers. These materials have high molecular weight and fast repair efficiency, and are good in various fields. Application prospects. The hydrogen bonds are mainly H-F, H-N, and H-O. These three hydrogen bonds are reversible hydrogen bonds, and the reversible effect is better under heating conditions. S.Basak *et al*. [22] realized the hydrogen bond type self-repair by preparing a polymer matrix containing hydrogen bonds, and verified that the self-healing functional group is an amide ethyl group. The repair mechanism is shown in **Figure 4.** It is a copolymerization of ethylene and methacrylic acid to form a polymer elastomer rich in hydrogen bonds. The polymer elastomer is extremely sensitive to temperature and can be self-repaired under heating conditions.

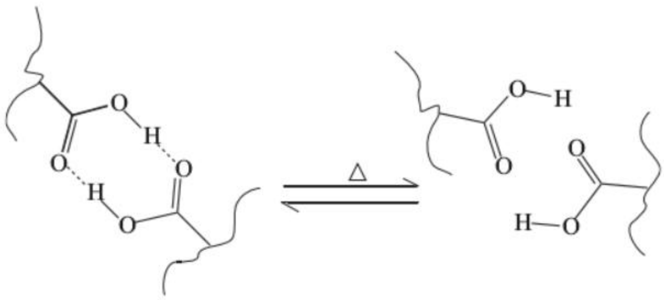

Figure 4. Hydrogen bond self-repair mechanism diagram

Superhydrophobic self-healing polymer material

Superhydrophobic groups are introduced in the polymer chain by grafting or molecular chain design, and the hydrophobic groups converge in an aqueous solution to form a three-dimensional network structure. When the material is broken by external force, the hydrophobic group It can move freely in the aqueous solution and form a new polymer three-dimensional network structure, which is macroscopically embodied as the self-repairing property of the polymer. P. Zheng *et al*. [23] copolymerized octadecyl methacrylate with acrylamide, and the synthesis reaction is shown in **Figure 5.** Octadecyl methacrylate has an ultra-high hydrophobic group, and acrylamide has an excellent hydrophilic group. The copolymerization of the two forms a gel-like self-healing elastomer. This elastomer has good properties. The self-healing function is excellent in terms of elongation at break, mechanical strength, and repeated self-healing rate.

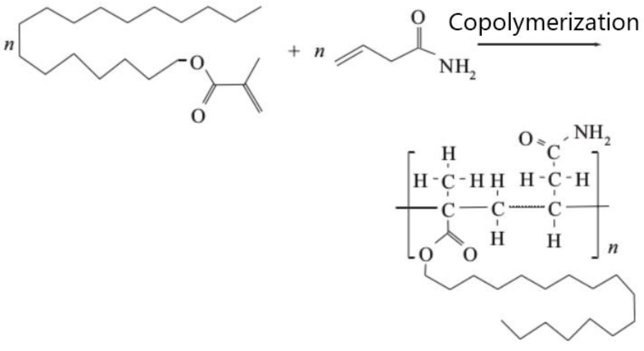

Figure 5. Super-sparing self-repairing polymer synthesis reaction

Self-healing polymer material based on ion action

The self-healing effect of ionic groups is the formation of valence bonds between ionic groups and polymers, and the linkage and cleavage between valence bonds is reversible [24]. Changes in ambient temperature have a large impact on the performance of this material, especially self-healing properties. The polymer matrix is modified by introducing metal ions into the polymer matrix, thereby obtaining self-repairing properties of the polymer material. DuPont's high-molecular copolymers prepared by copolymerization of ethylene and methacrylic acid have a standardized application in sportswear equipment, are highly commercialized, and have excellent wear resistance and elasticity.

Metal-organic self-repairing polymer material based on coordination bond

In the polymer material, many of the outer layers of the atom have electron pairs that are unpaired. If a metal is introduced to form a coordination bond between the metal and the polymer, a polymer material having theoretically infinite self-repairing ability can be synthesized. Based on this assumption, P. Sollich *et al*. [25] used terpyridine and divalent iron ions to form a coordination copolymer. The mechanism is shown in Fig. 6. The self-healing polymer material can be obtained by a solution of terpyridine in which diethyl ethane is attached and dissolved in a ferrous chloride solution in an amount of the same substance. The addition of hydroxyethyldiaminetetraacetic acid trisodium salt (HEDTA) to the system results in a better self-healing effect.

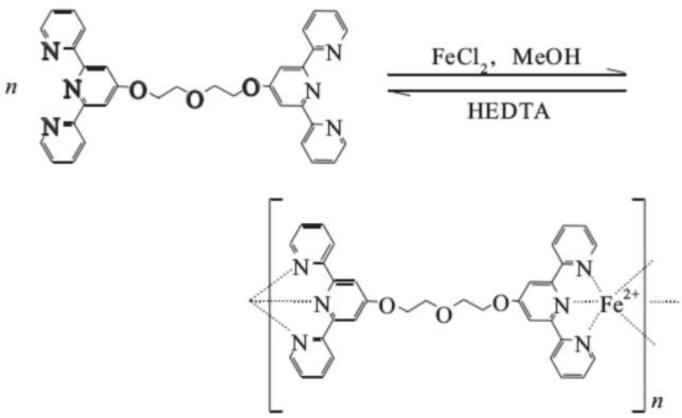

Figure 6 Coordination mechanism diagram of coordination key

2. Composite self-healing polymer material

Unlike the intrinsic self-healing polymer material, the composite self-healing polymer material achieves a self-healing effect by rapidly curing the position of the crack by adding a curing agent to the polymer matrix. There are many ways to add a curing agent. Two of them are more common and easy to operate: one is to directly embed microcapsules in a polymer matrix; the other is to add a biomimetic structure such as a bionic human blood vessel to a polymer matrix, when the polymer matrix When the impact is broken, the bionic blood vessel ruptures and the curing agent flows out to repair itself at the rupture.

2.1 Filled microcapsule type self-healing material

The microparticles enclosing the repairing liquid are hidden in the polymer matrix. When the polymer matrix is subjected to impact rupture, the microparticles are broken together, the repairing fluid flows out together, and finally the secondary cross-linking reaction is carried out at the fracture surface of the polymer. The real self-repair of the polymer is achieved, and the mechanism is shown in **Figure 7.** When the self-repairing matrix ruptures, the microcapsules rupture and release the repairing liquid. After the repair, the repairing fluid is also used up to become a hollow sac, so the second rupture cannot be repaired, and the number of repairs is limited.

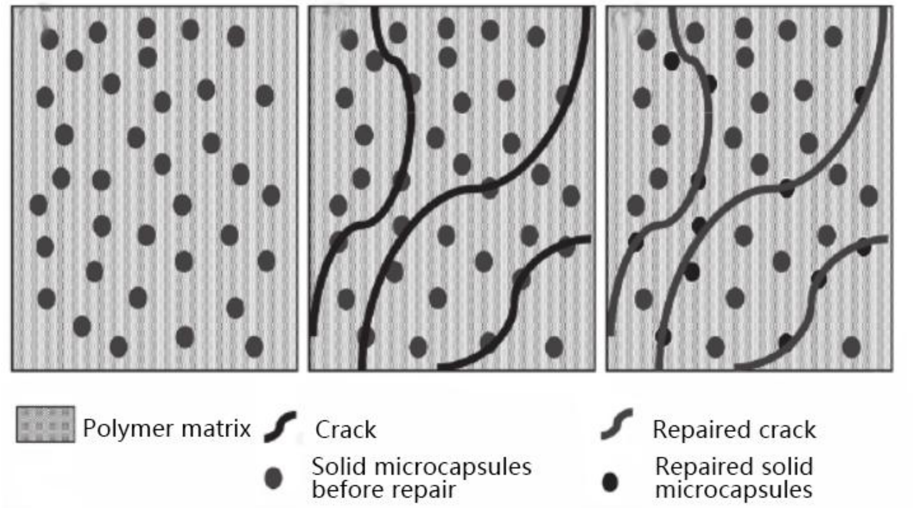

Figure 7. Self-repair mechanism of microcapsule self-repairing polymer

Inspired by such techniques, Li Haiyan *et al.* [26] implanted hollow long straight pipes in the polymer matrix. These pipes are about 10 cm in length, but the volume is as small as 1 × 10–10 L. It is filled with a repair solution that can further chemically react with the polymer-related groups. When the polymer matrix breaks, these solutions will flow out, allowing the material to self-heal. The repairing solution is a bisphenol type epoxy resin having an epoxy group at both ends and having a two-component repairing effect. When the crack occurs, the epoxy resin flows out to form a curing reaction, and at the same time, the crack is blocked. It is difficult to spread the polymer cracks, and the path of microcrack propagation is blocked to some extent, so that the destruction of the polymer material is blocked inside the body.

2.2 Bionic human vascular self-repairing polymer material

The bionic self-healing matrix is similar to the fine capsule implanting system, and is solidified by the solidifying agent liquid to prevent further cracking of the polymer material. Based on the principle of human bionics, a hollow tubular network similar to human vascular tissue structure is implanted in the polymer material, and a self-healing filler is filled in the network. When external impact or shear force acts, the curing agent is applied. Will flow along the crack, cross-linking curing reaction at the crack - that is, self-repairing behavior, making the crack expansion slow or stop expanding, the mechanism is shown in **Figure 8.** Compared with the microcapsule-type repairing body, the self-healing polymer of the bionic vascular type has considerable advantages. When the area of the fracture surface is quite large, the fine particles of a single system can only be blocked by a limited amount of solidified filling, and large-area wounds seem to be powerless, but the blood vessels of the human body bionic structure can repair the inside of the polymer through a well-connected pipeline network. The agent is delivered to the wound and the curing reaction is continued until the wound is completely repaired.

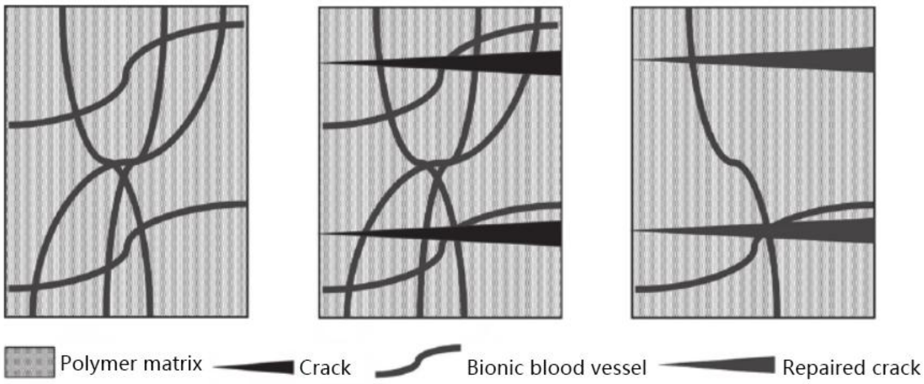

Figure 8. Schematic diagram of self-repair of bionic blood vessels

Sun TL *et al* [27] have reported that the liquid used in the tube is dicyclopentadiene resin, the resin is buried in the bionic blood vessel, and the vascular system is inserted into the epoxy resin polymer matrix while being polymerized. A catalyst that contributes to the curing of the epoxy resin is added to the solution, and the system is finally made into a self-healing coating. After testing and evaluation, the self-healing effect of the coating is remarkable, and multiple self-healing treatments can be performed, and the repair rate is as high as 50% or more, and the repetition times are more than 7 times.

3. Outlook

Self-healing polymer materials have broad application prospects in various high-end industries such as biomedicine, deep space exploration, and weapon manufacturing, but most of the research currently has a long way to go from practical applications. The most close to practical is the composite doped self-repairing polymer material, but its excessive impurities will affect the number of repairs and performance. It is believed that in the near future, some scholars will develop self-healing polymer materials with simple process and excellent performance.

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