

Non-Covalent Interactions of Intrinsic Self-Healing Elastomers

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Self-healing elastomers refer to a class of synthetic polymers that possess the unique ability to autonomously repair from internal and external damages. In recent years, significant progress has been made in the field of self-healing elastomers. In particular, intrinsic self-healing elastomers have garnered a great deal of attention.

Keywords: self-healing ; elastomer ; intrinsic ; reversible bonds ; dynamic polymers

1. Introduction

Elastomers possess high extensibility and the capability to recover their original shape after the removal of external forces and are therefore extensively applied in various industries, including manufacturing, medical instruments, and automobile manufacturing. However, in practical applications, elastomers are often susceptible to environmental or external stresses which can lead to unexpected damage, cracks, and even macroscopic fractures, severely degrading their functionality and lifespan ^[1]. Self-healing elastomers, which have self-healing properties, can address these problems by fully or partially restoring in situ mechanical damages, thereby extending their service life and improving safety during use ^{[2][3]}. Consequently, self-healing elastomers have attracted tremendous attention over the past two decades as they can effectively alleviate environmental pollution, prolong the lifetime of products, and reduce costs ^{[4][5][6][7]}.

Self-healing can be divided into two kinds: extrinsic self-healing and intrinsic self-healing. Extrinsic self-healing elastomers rely on pre-embedded repairing reagents (e.g., microcapsules, hollow fibers, and microvascular networks) in the matrix ^[8] ^{[9][10][11][12]}. However, they are limited by the supply of healing agents, are incapable of multi-cycle repair and quick response, and may be affected by the outflow of healing agents ^[13]. On the other hand, the self-healing ability of intrinsic self-healing materials comes from the breakage and recombination of reversible chemical bonds ^[14]. Intrinsic self-healing elastomers do not require the addition of repair agents, thereby avoiding the above tough problems ^[15]. Since intrinsic self-healing elastomers not only possess superior elastomers properties but can also repair their mechanical properties themselves when physically damaged, they have become a kind of material with broad prospects ^{[16][17]}.

2. Hydrogen Bonds

Hydrogen bonds (H-bonds) have been widely used in self-healing elastomers since Cordier et al. first reported on them in 2008 ^[18]. The dynamic nature, tunable strength, responsiveness, and reversibility of hydrogen bonds could provide materials with significant mechanical strength and an excellent self-healing ability ^[19]. Low-molecular-weight polymers become robust and repairable when they are cross-linked by dense hydrogen bonds. For example, Aida et al. employed thiourea to form a less ordered hydrogen-bonded array without inducing unfavorable crystallization, and they also introduced a structural element to activate the exchange of hydrogen-bonded pairs ^[20]. They proposed four structural elements for the design of mechanically robust healable materials, including relatively short polymer chains for larger segmental movements, tight, cross-linked H-bonds for better mechanical properties, nonlinear (less ordered) H-bond arrays to prevent or reduce crystallization, and mechanisms for promoting the exchange of H-bonded pairs. Additionally, a biomimetic strategy was utilized to build polymer backbones with hierarchical (single, double, and quadruple) hydrogen bonding moieties ^[21]. The urethane, urea, and 2-ureido-4[1H]-pyrimidinone in the hierarchical hydrogen bonds endow transparent elastomers with super toughness (345 MJ m^{-3}) and high tensile strength (44 MPa) after self-healing. This may be attributed to the relatively low entanglement and the dynamic exchange of H-bond pairs. Generally, dynamic dense hydrogen bonding interactions contribute to extraordinary toughness and recoverability. On the other hand, Yoshie et al. demonstrated that entropy-driven strong H-bonds enabled the creation of a vicinal diol-functionalized polymer with mechanical robustness, along with functionalities based on the dynamicity of the H-bonds ^[22]. Furthermore, Konkolewicz et al. even suggested that only strong and dynamic H-bonds should be chosen for enhancing materials' performance ^[23].

3. Ionic Interactions

An ionic cluster is a small cluster of several to several hundred atoms or molecules with special physical and chemical properties which exist in ionomers, polyelectrolytes, and polyampholytes. Ionic clusters are associated with a comparatively long lifetime responsible for enhanced flexibility, toughness under dynamic load, and potential self-healing functions derived from sufficient molecular mobility [13]. Furthermore, ionic elastomers with dispersed ionic clusters also benefit from the variable network density of reversible aggregates. Typically, ionic interactions can be introduced into commercially available rubbers through ion–dipole interactions. A simple method that converts widely used rubbers into elastomers with extraordinary self-healing properties is replacing conventional fillers with reactive materials and constructing a reversible supramolecular hybrid network. For instance, zinc oxide (ZnO) can be blended with styrene–butadiene–styrene (SBS) or natural rubber (NR) to obtain ionic cross-links in the rubber matrix through in situ neutralization reactions [24][25]. By melt-mixing with 1-butyl imidazole, imidazolium-modified bromo-butyl rubber (bromine-modified isoprene–isobutylene copolymer, BIIR) can form a cross-linked network via ionic association [26][27]. Another strategy is to fabricate biomimetic self-healing ionic elastomers. Zhao et al. developed a type of bottle-brush elastomer with a terminal bromine atom in each side chain, resulting in the formation of a supramolecular ionic network [28]. The bottle-brush elastomer is capable of mimicking the typical features of skin by regulating the densities of branch chains and cross-linking points. It exhibits a shear modulus of 46 kPa and a self-healing efficiency of 98% at room temperature. A class of self-healing strengthening elastomers (SSEs) that becomes strengthened during the healing process has also been reported [29]. This is because of the larger and denser ionic aggregates resulting from the disruption of kinetic stability under heat or an external force. These ionic self-healing elastomers hold great potential for artificial skin, wearable devices, smart soft robots, and so on [30].

4. Metal-Ligand Coordination

Metal–ligand coordination refers to the moderate bonding energy between low hydrogen bonding energy and high covalent bonding energy, providing both self-healing capacity and certain mechanical properties. The most common coordination is between the ligand and iron ions. Han and Filippidi et al. reported that reversible catechol-Fe³⁺ coordination bonds could serve as effective cross-linking points to amplify the effect of nanoscale domains and provide bonds as strong as those of covalent bonds [31][32]. Pyridine-containing ligands with Fe³⁺ can readily break and reform while the iron centers remain attached to the ligands, enabling reversible unfolding and refolding of the polymer chains [33]. Metal-coordinated polyurethane with an optimized monomer ratio and Fe²⁺ content shows a high tensile strength of 4.6 MPa (Strain ≈ 498%) and a high Young's modulus of 3.2 MPa. Chen et al. introduced Fe³⁺-pyridine coordination bonds to rubber chains in commercially available epoxidized natural rubber (ENR) via a ring-opening reaction between epoxy groups and aminopyridine [34]. The Fe³⁺-pyridine coordination bonds can be readily broken and re-formed under moderate conditions. A sample with a molar ratio of Fe³⁺ to pyridine of 1:4 showed excellent healing efficiency with a tensile strength of 87%. Meanwhile, the Fe³⁺-pyridine coordination bonds can also act as cross-linking points, which increased the mechanical properties of the fabricated rubbers 18 times more than the original sample in terms of tensile strength. On the other hand, an Fe-triazole interaction can also achieve a healable efficiency of over 90% [35]. In addition to iron ions, Co²⁺ and Zn²⁺ have been utilized to form kinetically labile coordination bonds, endowing cross-linked polymer hydrogels, nitrile rubber (NBR), and polydimethylsiloxane (PDMS) with self-healing abilities [36][37][38][39][40]. In addition, multiple metal–ligand coordination with various metal ions can form weak or strong coordination bonds to modulate different properties of elastomers, leading to optimal self-healing efficiency and superior mechanical properties [41][42][43].

5. Other Non-Covalent Systems

Compared with the non-covalent interactions illustrated above, cyclodextrins (CDs) have emerged as promising host monomers that can construct reversible cross-linked network in elastomers via host–guest interactions [44]. For example, permethylated cyclodextrins (PM-CDAAmMe) used in the bulk polymerization of liquid acrylate monomers and guest monomers can fabricate highly flexible, self-healing, and tough elastomers [45]. In particular, the incorporation of CDs into polyurethane has demonstrated outstanding self-healing efficiency, including in waterborne polyurethane, thermoset polyurethane, and thermoplastic polyurethane, resulting in a high healing efficiency of 98.54% and nearly 100% repair after scratches [46][47][48].

Other than the host–guest interaction, shape memory has also been verified to facilitate self-healing since physical damage usually occurs during the deformation process. In blended polymer complexes, polycaprolactone (PCL) can act as a healing agent capable of diffusing and rearranging between cracks during the annealing process to heal scratches at 80 °C for 30 min as well as a semicrystalline thermoplastic [49]. It is worth mentioning that shape memory must assist self-healing with external stimuli such as thermal, magnetic, or light stimuli or a combination thereof [50]. By tailoring polymer

chains, shape-memory polymers can simultaneously achieve high elasticity, excellent shape recovery, and repeatable thermal-assisted healing [51].

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