Composites Communications xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Composites Communications

journal homepage: www.elsevier.com/locate/coco

Bioinspired engineering of sacrificial bonds into rubber networks towards high-performance and functional elastomers

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ARTICLE INFO

Keywords:
Elastomer
Sacrificial bonds
Reinforcement
Functionalization

ABSTRACT

Elastomers with unique high elasticity are recognized as strategic materials. The development of elastomers with the combination of high-performance and functionality is of great importance. In recent years, inspired by the structural characteristics of natural materials, the concept of sacrificial bonding has been successfully applied in the design of elastomeric materials, aiming at significantly improving mechanical and functional properties. In this short review, followed by brief description of the principle of sacrificial bonding, we summarize the main progress of the design of the elastomers with sacrificial bonds, and the main performance characteristics. The sacrificial units, including the covalent and non-covalent sacrificial bonds, may be engineered in rubber chains or the interfaces of rubber nanocomposites. In addition, the mechanisms of sacrificial bonding in conferring the functionalities have been described. Several important functionalities, including shape memory effects, damping and self-healing capability combined with robustness, are introduced. Based on the state of the art of the elastomers with sacrificial bonds, the prospective and challenges of are accordingly presented and discussed.

1. Introduction

Rubbers, owing to their unique high entropy-elasticity, have been widely used in the tires, seals, and shock absorbers. However, most neat rubbers exhibit weak mechanical properties, which severely restricts their practical applications. The rubbers are commonly strengthened and toughened by incorporating various nanoparticles [1–4]. Generally, there are two ways to introduce nanoparticles into rubbers. One is directly to compound rubber with various nanoparticles, such as carbon black, silica, clays and carbon nanotubes, graphene etc.; The other is in-situ formation of nano-phases in rubbers through phase separation, such as rubbers reinforced by unsaturated metal carboxylates [5–7], elastomeric ionomers [8,9] and block copolymer-based thermoplastic elastomers [10]. However, the above-mentioned methods have several important limitations. Block copolymer-based thermoplastic elastomers suffer from high permanent set. Incorporation of metal carboxylates or ionic reinforcement is only feasible for some specialty rubbers. More importantly, tens or even more than one hundred parts of fillers are usually required for practical applications. This gives rise to additional challenges regarding to dispersion and interfacial regulation, which are known to play a vital role in determining the final performance of elastomers [3,11,12]. Furthermore, compounding with large numbers of fillers decreases elasticity of elastomers and increases energy consumption during processing [11,13]. In addition, due to the amorphous features and extremely low glass transition temperature, the rubbers, especially diene-based rubbers, have rarely been applied as functional materials. Therefore, it is significantly important, but always challengeable to seek novel yet effective strategies to prepare the elastomers combining high mechanical properties and functionalities.

In this regard, great efforts recently have been devoted to engineer bioinspired sacrificial bonds into rubber networks toward high-performance and functional elastomers. To date, essential progress has been achieved in this area. Herein, this short review focuses on the designs of sacrificial bonds in crosslinked elastomers and their effects on the performance of elastomers. The nature and the mechanism of sacrificial bonds are firstly introduced and interpreted. Then the progress of reinforcement and functionalization of elastomer by constructing sacrificial bonds are summarized. Finally, some important directions yet challenges for future research of elastomers with sacrificial bonds are discussed.

2. Bioinspired sacrificial bonds

Many biological materials such as spider silk, mussel byssus and bone are well known for their super strength and toughness as well as

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https://doi.org/10.1016/j.coco.2017.11.002
Received 30 September 2017; Received in revised form 1 November 2017; Accepted 3 November 2017

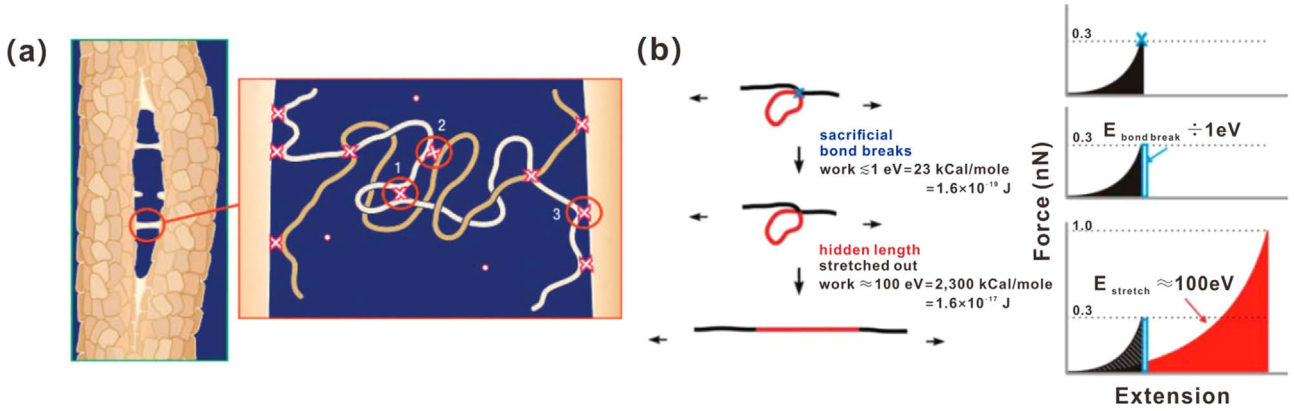

Fig. 1. (a) Possible kinds of calcium-mediated sacrificial bonds in bone. (Adapted with permission from Ref. [16]. Copyright 2005 Nature Publishing Group.) (b) Schematic diagram of the basic principle of the sacrificial bond-hidden length mechanism. (Adapted with permission from Ref. [19]. Copyright 2006 The Biophysical Society.).

extraordinary self-healing capability. Their fascinating performances have been proved to originate from their complex hierarchical structures involving sacrificial bonds, such as unfolding of domains within the protein titin [14], calcium-mediated bonds in bone [15,16] (Fig. 1a) and the organic component of nacre [17]. Sacrificial bonds are defined as bonds that rupture prior to the broken of main structural link (often the covalent molecular backbone) [18]. Both of covalent bonds and noncovalent bonds, such as hydrogen bonds, metal-ligand coordination bonds, ionic bonds, etc., can be acted as sacrificial bonds. The hidden length is the part of the molecular segments that is constrained from stretching by the sacrificial bond [19]. Fantner et al. [19] and Wang et al. [20] demonstrated that sacrificial bonds and hidden length greatly increased the fracture toughness of biomaterials by providing a reversible, molecular-scale energy-dissipation mechanism, which is uncovered by atomic force microscopy (AFM) and model simulation. Under external loading, the sacrificial bonds preferentially rupture prior to the rupture of covalent bonds, which maintain the polymer backbone intact and material integrity. Once the sacrificial bonds are broken, the hidden lengths will be released that allows for increased polymer elongation. A substantial amount of energy is needed to reduce the entropy and increase the enthalpy of the system. Consequently, enormous mechanical energy is dissipated during loading while the material integrity is preserved. Noteworthy is that it takes much more energy to stretch hidden lengths than to break a bond (Fig. 1b). Moreover, sacrificial bonds are found to be reversible in most of biological materials, which additionally endows the materials with self-healing properties.

Inspired by these natural materials, the concept of sacrificial bonding has widely been introduced into artificial polymeric materials, aiming to achieve biomimetic properties. Super tough hydrogels with sacrificial bonds, like double-network (DN) hydrogels, have been extensively studied [21–24]. Generally, DN hydrogels are prepared by immersing the first network in aqueous solution of monomers that subsequently polymerize to form the second network. The first network is rigid and brittle, composed of short chains and densely crosslinked, whereas the second network is soft and stretchable, composed of long chains and loosely crosslinked. The first stretched and brittle network, serving as sacrificial bonds, is preferentially fractured under large deformation, dissipating much energy, while the second network maintains the elasticity, which allows it to return to its original configuration after deformation. Consequently, the fracture energy of the DN is much higher than those of either of the corresponding single networks. The DN strategy has been applied not only to double- or multiple-network systems, but also to single-network systems in which a dual-crosslinking structure can be constructed as long as they have sacrificial bonds and a permanent network that can retain the integrity of the materials [23]. In such cases, the sacrificial bonds are usually noncovalent bonds, such as hydrogen bonds [25,26], metal-ligand coordination bonds [27,28] and ionic bonds[29,30], etc. For instance, Sun et al. reported a dual cross-linking structure that composed of polyampholytes carrying opposite charges randomly distributed on the polymer chains [29]. The randomness makes ionic bonds with a wide distribution of strength. The strong bonds serve as permanent crosslinks maintain the whole elasticity while the weak bonds act as sacrificial bonds, continuously dissipating energy. Such a unique structure endows the physical hydrogels with super high toughness and self-recovery/healing functionalities. In comparison with the noncovalent sacrificial bonds, the covalent sacrificial bonds have the advantages of high bond energy and low sensibility to temperature and the rate of deformation, but they generally cannot be recovered once broken.

3. Reinforcement of elastomers by engineering sacrificial bonds

Reinforcement of elastomers is essential for most of practical applications. Although significant reinforcement of elastomers by conventional nanofilling has been demonstrated, there are several drawbacks, such as difficulties in dispersion/interfacial regulation and processing. Recently, bioinspired sacrificial bonds have been introduced into elastomers to simultaneously improve the strength and toughness of elastomers. In an elastomer with sacrificial bonds, besides the energy dissipating mechanism caused by the rupture of sacrificial bonds, the orientation of polymer chains also plays an important role in improving the mechanical properties [31–33]. It is believed that the preferential rupture and dynamic feature of sacrificial bonds will prevent local stress concentration on a molecular level throughout the network, which facilitates the chains to slide and orientate when deformation is applied. In the below sections, the design of sacrificial bonds and their reinforcement effects on elastomers are illustrated in detail.

3.1. Sacrificial covalent network

Although the principle of DN in hydrogels can also be introduced in non-hydrated elastomers, it is much more challengeable. Firstly, due to the lack of polyelectrolyte forms, it is difficult to form an DN or dual-crosslinked structure in elastomers. Secondly, elastomers usually have high molecular weight and viscosity, and are normally processed via mechanical shearing, which is not favor of forming double network elastomers [23]. Nevertheless, inspired by the principle of DN hydrogels, the elastomers with DN structure have been developed successfully.

Ducrot et al. designed and prepared a DN elastomer by swelling the first crosslinked network with a second monomer followed by polymerization. Further the triple-network (TN) elastomer was also obtained through repeating the above polymerization procedure [34]. The first network chains account for a small fraction of weight and are