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Review

Chemical and physical aspects of self-healing materials

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ABSTRACT

The concept of self-healing synthetic materials emerged a couple of decades ago and continues to attract scientific community. Driven primarily by an opportunity to develop life-like materials on one hand, and sustainable technologies on the other, several successful approaches to repair mechanically damaged materials have been explored. This review examines chemical and physical processes occurring during self-healing of polymers as well as examines the role of interfaces in rigid nano-objects in multi-component composites. The complex nature of processes involved in self-healing demands understanding of multi-level molecular and macroscopic events. Two aspects of self-healing are particularly intriguing: physical flow (macro) of matter at or near a wound and chemical re-bonding (molecular) of cleaved bonds. These events usually occur concurrently, and depending upon interplay between kinetics and thermodynamics of the processes involved, these transient relations as well as efficiency are critical in designing self-healing materials. This review examines covalent bonding and supramolecular chemistry in the context of molecular heterogeneities in repair processes. Interfacial regions in nanocomposites also facilitate an opportunity for supramolecular assemblies or covalent bonding which, if designed properly, are capable of self-repairs.

Contents

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1. Introduction

Living organisms are able to recover from injuries to resume active and reproductive functions. The ability to continue these metabolic processes determines the longevity of their existence. Synthetic materials are designed to be functional, but do not possess metabolic attributes. To prolong their lifespan, the concept of self-repairing has been explored and became the central topic of scientific interests and technological significance. Over the last decade, numerous successful approaches to repair mechanically damaged materials have been explored, and recent advances have been summarized in several review articles [1–6].

There are two events during self-repairing that are particularly critical: (1) physical flow of molecular segments at or near a wounded area and (2) re-bonding of cleaved bonds after mechanical damage. These events may occur continuously, depending upon interplay between kinetics and thermodynamics during these events. Ideally, one can envision diffusion of chain ends, followed by their re-bonding. The complexity in monitoring these interrelated events comes from the fact that reactivities of chain ends may not favor re-bonding. For example, when reactive free radicals are quenched immediately by atmospheric oxygen (O_2), water (H_2O), or other reactive groups, chemical re-bonding will not occur. However, if diffusion continues, segmental motion may still lead to inter-diffusion and repair. Consider these circumstances, repair will be determined by the kinetic energy of chains and entropic changes during the diffusion. As has been shown [5], these intrinsic properties will have significant impact on entropic contributions to the Gibbs free energy during repair. In contrast, when reactive chain ends are stable, but segmental mobility is limited, repairs will not occur at all, unless there is external energy input.

A critical factor to achieve desirable mobility of polymer chains is the presence of free volume [7–9]. Without 'voids,' the repeating units and segments forming longer macromolecular chains will be irresponsive. Thus, the well-known concept of "free" volume ought to describe an average chain mobility typically reflected in the glass transition temperature (T_g) that impact such properties as permeability, diffusivity, flexibility, and others [10]. Does this imply that all "soft", or low T_g, polymer networks are able to self-heal? If this was the case, all pressure sensitive adhesives (PSA) should offer self-healing properties. Experiments teach us that this is not the case. Thus, the question how to create "voids" that may facilitate segmental mobility and, at the same time, high T_g, remains open. One option is to create a polymer system that will be heterogeneous, which can be accomplished by either phase separation, or combining soft and hard segments into one network by utilizing copolymers that can phase separate or composite materials. Another alternative is to utilize shape memory polymers (SMP), which will facilitate restoration to original shape, thus aiding in self-repair.

Previous studies have shown that incorporating stimuli-responsive units into a copolymer backbone leads to endothermic stimuli-responsive transitions (T_{SR}) which are above the T_g, and require free volume distributions achieved by copolymerizing stimuli-responsive units into non-responsive functional backbone [10–12]. Fig. 1A depicts a heterogeneous network that consists of spatially distributed soft and hard domains, which, upon mechanical damage, are able to rearrange, thus facilitating repair. This is manifested by segmental mobility of chains into the voids or free volume areas. The most successful example of using this concept was to incorporate soft polyamide segments capable of forming H-bonds into rigid polystyrene (PS) chains, forming a heterogeneous polymer consists of a spherical PS phase within a polyamide matrix [13]. Analogous to liquid crystalline polymers, these networks can rearrange which is facilitated by the localized T_g variations, thus leading to spontaneous network rearrangements manifested by increased ΔS, and subsequent re-bonding. Excess free volume is also generated as a result of the void growth under external stress during mechanical damage [14], which may facilitate chain rearrangements and repair.

In designing self-healing systems, it is critical to realize the length scale of heterogeneities. As depicted in Fig. 1B, at Angstrom (Å) levels, self-healing will occur by reforming bonds at sites, where chain cleavage occurred. Block, branched, or star polymers forming nm-to-μm scale microphase separation will facilitate self-healing, and microcapsules or inorganic particles embedded in polymers will respond to larger wounds [15]. In essence, to rationally design self-repairing materials, it is important to (1) understand which chemical entities are capable of cleavage due to mechanical damage; (2) design networks to achieve localized segmental mobility upon mechanical damage; and (3) synchronize re-bonding dynamics with physical rearrangements of macromolecular reactive segments. These pre-requisites combined with network heterogeneities are typically a starting point in molecular design of networks that are responsive to macroscopic damages. The following sections outline the role of bond dynamics in the context of localized heterogeneities and network components that facilitate self-repair.

2. Chemistry of self-healing and heterogeneities

Due to limited chain mobility and a lack of bond reformation abilities, common polymers do not show self-repair attributes. The last decade resulted in the development of a