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Healable supramolecular polymer solids

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ABSTRACT

The reversible nature of non-covalent interactions between constituting building blocks permits one to temporarily disassemble supramolecular polymers through the application of an appropriate external stimulus “on command”. This framework has recently emerged as a general design strategy for the development of healable polymer systems. The approach exploits that the temporary disassembly decreases the molecular weight and in the case of cross-linked polymers the cross-link density, and thereby causes an increase of the chain mobility and a reduction of the viscosity of the material. The transformation thus enables the disassembled material to flow and fill defects, before the original supramolecular polymer is re-assembled. Focusing on recent progress in the area of healable supramolecular polymer solids based on hydrogen-bonding, metal-ligand and π–π interactions, as well as supramolecular nanocomposites, this review article summarizes the development and current state of the field.

Contents

1. Introduction

Healable or self-healing polymers, in which defects can be repaired or which heal autonomously, are of great technological interest, as such materials can improve product functionality, dependability, and lifetime. Consequently, the development of healable materials is receiving growing attention from researchers around the globe [1–9]. In principle, the most straightforward approach to eliminate defects in thermoplastic polymers involves heating the damaged area or exposing it to a plasticizing solvent, so that the material forms a melt or solution [10]. However, since the rates of polymer chain diffusion and re-entanglement are inversely proportional to the molecular weight, thermal

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or solvent-induced healing in high-molecular-weight polymers is generally slow and not very efficient [11], except in the case of polymer gels, where an abundance of solvent increases the mobility of free macromolecules [7]. In the last decade, a range of approaches to overcome this problem have been devised. One early idea is the incorporation of monomer-filled microcapsules and a suitable catalyst into a polymer matrix [12–14]. The microcapsules are designed to rupture and release the monomer when the material is damaged. Once this liquid “healing agent” is released from the protective shells, it can fill defects such as small cracks and cuts, before the contact with the catalyst triggers polymerization. A very different strategy relies on the possibility to temporarily disassemble structurally dynamic polymers [1]. In this approach, an external stimulus is utilized to shift the equilibrium of the polymer-forming reaction to the monomer side [3,7]. This triggers a reduction of the molecular weight and in the case of polymer networks of the cross-link density, and thereby causes an increase of the chain mobility and a decrease of the viscosity of the material. The disassembled material can then flow and fill defects, before the original supramolecular polymer is re-assembled. In the first embodiment of this idea [15], a Diels–Alder reaction was used to form a reversible thermally re-mendable cross-linked polymeric material with mechanical properties that were similar to those of commercial epoxy resins. The ability to mend the resin was based on the fact that the cross-link density could be temporarily reduced by heating the polymer and triggering a retro-Diels–Alder reaction. In the meantime, many follow-up studies have led a plethora of healable materials that rely on a rather broad range of dynamic covalent chemistries [3,7].

As an alternative to reversible covalent bonds, dynamic supramolecular motifs can also be used as basis for the creation of healable polymers. The first demonstration of a supramolecular system exhibiting polymer-like properties [16–21] was built on initial work on hydrogen-bonded monomer units [22], and the studies of main-chain supramolecular polymers based on simple hydrogen bonding motifs [23,24]. The properties of this material were accounted for by the comparably high dimerization constant of the ureidopyrimidinone (UPy) motif employed, the use of telechelic building blocks, and phase segregation effects. Since this discovery, a plethora of studies have reported the successful use of various types of non-covalent interactions, such as H-bonding [25], π–π stacking [26,27], or metal-ligand coordination [28], for the assembly of supramolecular polymeric materials with a broad range of structures and properties [29]. While one of the original driving forces for research on supramolecular polymers was to gain access to structures that could otherwise not be made, it was eventually recognized that the dynamic nature bestows supramolecular polymers with stimuli-responsive properties [30,31]. For example, the ability to reversibly disassemble supramolecular motifs in a controlled manner upon application of external stimuli has been exploited to develop materials that respond to changes in temperature [32] or pH [33], exposure to UV light [34], or application of mechanical stress [35] with a range of useful effects such as changes in optical properties [35], recovery of a memorized shape [36], or on-demand adhesive (de)bonding [37]. The possibility to exploit the reversible and dynamic nature of non-covalent interactions to create thermally [38–41] or optically healable materials [42] can in principle be inferred from the early work on re-formable supramolecular polymers. However, it was only in 2008 when the self-healing ability of hydrogen-bonded polymer networks was reported that the idea to exploit supramolecular motifs for this purpose became widely popularized [39]. Many examples of healable or self-healing polymers have been demonstrated since. With the objective to complement several excellent reviews on this subject [43–48], the present article seeks to summarize the recent progress and current knowledge in this domain. Based on prominent examples from the literature, the most important design approaches and materials characteristics are presented and the development and current state of the field are discussed. The examples focus on *solid materials* and are primarily organized according to the nature of the supramolecular motif: hydrogen-bonding, metal-ligand, and π–π interactions. The burgeoning field of healable supramolecular gels is generally omitted and the reader is referred to several recent reviews on this topic [7,49–55], with the notion that many of the chemistries and concepts discussed herein are applicable (or have in fact been applied) in the context of healable polymer gels. On account of the large solvent content (healable) gels are typically much softer and weaker than the solid materials discussed here, but the high solvent content also causes a very high degree of mobility of the disassembled polymer (fragments), which often translates in excellent healability. This review also omits ionomers, as the clusters formed in such materials are often not well-defined and the definition of a supramolecular material is in many cases not met. Nevertheless, it shall be mentioned here that ionic polymers displaying autonomous healing have been recently synthesized [56,57]. A special section is devoted to supramolecular nanocomposites, which represent an emerging class of healable materials with intriguing mechanical properties.

2. Hydrogen-bonded polymers

The fact that hydrogen bonds play a key role in many important biological processes [58], such as DNA replication, molecular recognition, or protein folding, is related to the reversibility of these interactions. The use of hydrogen bonds in the development of synthetic polymers has focused much interest as a versatile approach to reach novel functionality [31]. Hydrogen-bonded polymers display very attractive features and offer high tunability through the vast number of available hydrogen-bonding motifs. Indeed, H-bonding motifs cover a broad range of association constants K_a ranging from <100 M^{-1} to >10^6 M^{-1} and thus cover binding characteristics that span from highly dynamic to quasi-covalent [25]. As will be discussed in this section, self-healing polymers can be made if highly dynamic H-bonds are used, although such materials usually exhibit very low mechanical strength and stiffness. On the other hand, polymers built with strongly binding H-bonds can approach the mechanical properties of