



Feature Article

Effect of polymer architecture on the intrinsic self-healing character of polymers



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ABSTRACT

Intrinsic and extrinsic self-healing strategies can be employed to mitigate the effects of local damage in order to (partially) restore a lost property or functionality and to avoid premature catastrophic failure of the whole system.

It is well known that polymer architecture has a crucial influence on mechanical, physical and thermal properties. However, the effect of polymer architecture on the healing capabilities of self-healing polymers has not yet been studied in detail. This paper addresses the effect of polymer architecture on the intrinsic healing character of polymeric materials using different reversible chemistries and aims at highlighting the need for more studies on this particular topic.

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1. Introduction

Probably the most extreme case of natural self-healing or natural regeneration is the one observed in *Hydra. Hydra*

are fresh-water polyps capable of regenerating a totally new individual from small pieces of the original polyp by a mechanism known as morphallaxis, i.e. regeneration occurring in the absence of cellular proliferation and involving the transformation of existing body parts or tissues into newly organized structures [1]. Unfortunately, engineered self-healing systems are still far away from this

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extreme and not fully understood type of healing. However, the generic principles that govern the healing of *Hydra* can still be applied to intrinsic healing polymers. While *Hydra* require delay time, reorganization of tissue, continuous signalling, gradients of molecule concentration to provide positional information, adhesion of regenerating cells to permanent wall, and critical minimum tissue size a healing polymer requires damage detection, resting time, reorganization of chains, polymer integrity maintained during healing, and critical damage size. Despite these similarities with *Hydra*, self-healing engineering systems have reached a level of development that allows more straight forward conceptual comparisons with the healing mechanisms used by other natural systems such as plants. In order to implement repair of large scale damages, plants follow a two-step repair process consisting of self-sealing by liquid flooding and self-healing by hardening of the released liquid. This two-step model forms the basis for extrinsic self-healing approaches where the healing agent (generally liquid) is incorporated into the matrix as discrete entities such as capsules, natural systems can still be used as an inspiration to develop intrinsic self-healing systems [2]. In the case of intrinsic healing approaches, where the healing capability is intrinsically connected to the (chemically or compositionally tuned) matrix polymer architecture, the two-step process can be translated into a softening step leading to local mobility towards the damage followed by a hardening process leading to the restoration of the original properties as represented in Fig. 1 by the recovery of the local viscosity after the healing trigger (temperature) is removed.

While intentionally created self-healing behavior has become an active research topic in materials science in recent years examples of pseudo-engineered systems have been available since the appearance of natural building materials such as adobe and mortar around 4–5000 years ago. In these basic construction materials the healing process occurs due to sequential dissolution and re-precipitation of matter at micro-cracks promoted by cyclic changes in ambient humidity. Following the landmark works of Dry and White [3,4] the concept of self-healing has been implemented into all classes of engineering materials [5–8] leading to different development stages depending on the material and the application field. For instance, self-healing asphalt by induction heating [9] and self-healing concrete by bacteria [10] are already at a pre-commercialization level while self-healing metals [11,12] are still at their very infancy.

The research on engineered healing systems initially aimed at the recovery of mechanical properties after a drastic failure [4] but the field has evolved towards the healing of a broader spectrum of damage types and sizes [7]. Other functionalities potentially healable can be as diverse as color, hardness, adhesion, corrosion protection, brightness, hydrophobicity, wear resistance, reflectivity, electrical or thermal conductivity, stealth, ion selection, and liquid or gas barrier.

The field of self-healing is thus aiming at the restoration of a lost functionality (property) of a certain material in a specific application in order to extend the service lifetime of the whole system. Fig. 2 shows a schematic of the basic

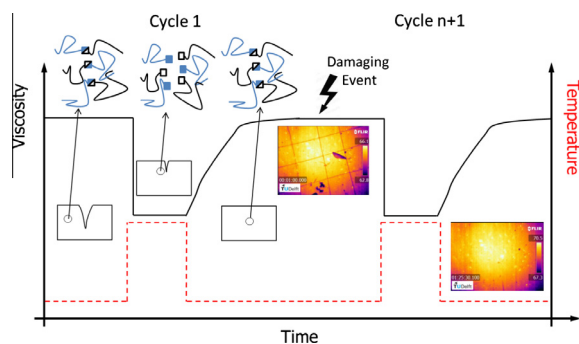


Fig. 1. General concept of matrix healing using intrinsic healing concepts. Figure shows a sudden drop in viscosity upon heating linked to local temporary network mobility necessary for flow and damage repair. Upon cooling the local properties (e.g. viscosity) are restored to initial values so the material can be further used. Figure also shows the multiple healing events possible with intrinsic healing concepts.

principle of lifetime extension by the implementation of healing concepts [13]. A traditional approach towards longer use of structures and systems is the development of more resistant and better materials than the original ones (curves a and b in Fig. 2). In the case of polymers, this is traditionally achieved by modifying the polymer architecture itself (e.g. crosslinking density, aromatic chains, crystallinity) or by introducing external agents such as exfoliated clays or graphene plates. While the traditional strategy of improving the initial properties leads to small developments due to the big advances reached so far, healing concepts offer an alternative strategy based on damage management rather than damage tolerance [5]. This new approach already led to very significant results despite the young age of the field. Curve c in Fig. 2 depicts an increase of service lifetime using one of the simplest self-healing approaches in which the initial properties have been partially recovered after damage. The most extreme case of lifetime extension would be one that allows multiple healing events with no loss of initial properties such as the one depicted in curve d in Fig. 2. Some polymeric systems capable of multiple healing events have already been developed [14,15] but the initial mechanical properties of these systems are far below those required in most of the

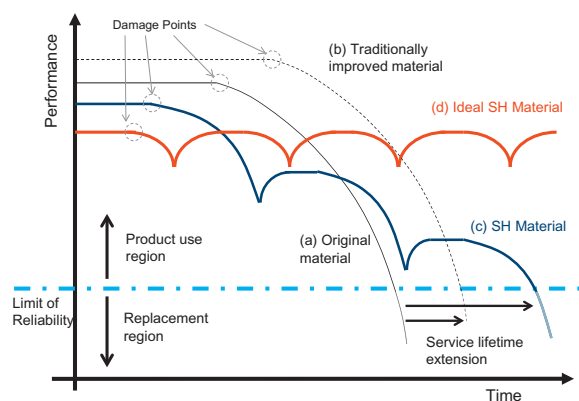


Fig. 2. Lifetime extension of engineered materials by implementation of self-healing principle.

potential applications of such materials. Despite the small amount of literature available, it becomes evident that further efforts to develop self-healing systems with high mechanical properties is a major step to be done in the field before systems using intrinsic healing concepts can be found in daily life materials. Hence, this paper aims at (i) highlighting the effect of polymer architecture on the balance between healing capabilities and mechanical properties by analyzing some reference study cases, and (ii) to increase the awareness of more studies needed in this particular relationship within intrinsic healing polymers so that the field can develop into its full potential.

2. Intrinsic healing

Intrinsic self-healing polymers are materials capable of repairing molecular and macroscale damages via a temporary local increase in mobility of the polymeric chains. Such behavior is generally based on specific molecular structures of the polymers that allow a marked step in (effective) inter-chain mobility upon the supply of modest amounts of energy (e.g. temperature, static load, UV) followed by a process of restoration of the chemical or physical bond strength upon stimulus removal (Fig. 1). The clearest advantage over extrinsic healing relies on the possibility of fully or partially repairing the initial properties multiple times. The intrinsic healing approach can be applied to both thermoplastic and thermoset polymers and elastomers.

From a mechanical and theoretical point of view 100% healing of an interface can only be obtained if the new interface has exactly the same properties as the bulk material. This means that the interfaces created by the damage event virtually disappear when healing takes place by formation of chain entanglements and chemical or physical crosslinks as strong as the bulk material. This process can be obtained by physical and chemical interactions and combination thereof. One of the most accepted theories leading to interfacial physical healing is the one proposed by Wool and O'Connor [16] based on molecular inter-diffusion leading to chain entanglements. This process can occur at temperatures above the bulk polymer glass transition temperature (T_g) [16] or after the application of a local external trigger such as a solvent and temperature beyond the melting point in thermoplastics (welding) [17]. It is remarkable that chain inter-diffusion has been observed also at temperatures theoretically below the bulk T_g which highlights the potential difference in T_g between the bulk and the surface in freshly damaged materials influencing the healing process [18].

Intrinsic healing has also been pursued by chemical principles in many dedicated studies leading to multiple chemistries susceptible to be used for macroscale healing. Based on their main molecular principle the existing chemistries can be grouped in two broad categories: (i) reversible covalent bonds [19] and (ii) supramolecular interactions [20]. Two other categories of intrinsic healing systems combining physical and chemical approaches can be included: shape memory polymers [21] and polymer blends [22] as recently highlighted in a review on self-

healing composites [8]. Moreover, the need to increase mechanical properties has pushed the field of research into the development of intrinsic polymer systems combining more than one chemical healing principle.

2.1. Reversible covalent bonds

This category comprises chemistries with reversible forming and breaking of covalent bonds. A dynamic dissociation and re-association of stress-bearing bonds allow for rapid conformational changes that ensure the healing action as reaction to damage. The success of the healing operation depends on the characteristics of the association, the overall flexibility of the molecule, and the environment of the system and, as will be discussed in this paper, the architecture. Current dynamic covalent systems comprise a wide range of well-known reaction types like ring-chain equilibrium and chain-exchange reaction as existing in the case of cross-linked poly(dimethylsiloxane) [23], retro Diels–Alder reactions [24–27], disulfide [28,29] and thiocarbonate exchange reactions [30], reversible hydrazone linkages [31] and alkoxyamines [32]. All these as well as diarylbenzofuranone [33] rely on a trigger/stimulus like thermal energy, but also other triggers for healing can be found in literature such as irradiation [34,35], pH-changes [31] or event catalytic additives. Of these, approaches using Diels–Alder/retro-Diels–Alder interactions (DA/rDA) and disulfide bonds are probably the best known. In the case of Diels–Alder chemical reactions several di-enes and di-enophiles can be used but the furan–maleimide interaction (healing temperature range of 100–150 °C) is the best known one [26,27]. Disulfide bonds have attracted a significantly growing attention due to their versatility and relative easy implementation in existing networks. The disulfide-promoted healing has been proven in conventional epoxy based thermosets using aliphatic disulfide containing chains with thiols as precursors [29,36,37] at mild healing temperatures (60–70 °C), in room-temperature elastomers based on aromatic disulfide metathesis [38] and in hybrid sol–gel based coatings [39]. It is remarkable to realize that although the reversible chemical principles of DA/rDA and disulfide bonds have been known for decades it has not been since relatively recently that these principles have been applied to produce self-healing polymers.

2.2. Supramolecular interactions

Supramolecular interactions impart the capability of self-assembly or self-organization using highly directional and reversible non-covalent interactions that dictate the overall mechanical properties of a material. These interactions, reversible by definition, are ideal to create self-healing intrinsic polymers. Probably the two most studied interactions so far are those found in ionomers for ballistic [40,41] and coating applications [42,43] and hydrogen bonding exemplified by the well-defined ureidopyrimidinone unit [14,44] and the use of randomly branched oligomers equipped with self-complementary and complementary hydrogen bonding groups [15,45].

Ionomers are polymer systems containing acid groups neutralized in the form of ionic metal salts bonded to the polymer backbone creating electrostatic interactions. As a result, ionic clusters are formed within the polymer structure, which have a positive effect on the mechanical and physical properties of the material [46]. The interest of such systems in terms of self-healing relies on the transitions and relaxations that the ionic clusters undergo under certain temperature ranges [47] although recent studies point towards the equally relevant effect of the non-neutralized acid groups in the healing capabilities at low temperatures [43].

The very inspiring work of Sijbesma et al. [14] using a strong reversible polymer system based on quadruple hydrogen bonding led to the first commercially available self-healing elastomer after a long-term collaboration between ESPCI and Arkema based on hydrogen bonds [15,48]. Other less studied supramolecular chemistries include metal coordination chemistry [49–52], or π – π stacking such as that reported between pyrene and polydiimide groups [53].

Despite the relatively broad amount of chemistries leading to intrinsic healing, the lack of studies that demonstrate that interfacial healing can be obtained purely by chemical approaches with no previous molecular inter-diffusion allows, for the moment, to establish that full interfacial healing cannot be obtained without the physical previous step of chain interdiffusion. The only possible exception would be a system where all the bonds of the polymer network were formed by reversible bonds so that when healed the polymer fracture would lead to the same amount and type of bonds as those in the bulk polymer. It is then possible to establish a generic healing process independent of the healing chemistry used and based on the physical model proposed by Wool and O'Connor [16] that consists of the following steps: (i) surface rearrangement and approach; (ii) wetting; (iii) chain inter-diffusion; and

(iv) randomization or/and chemical interactions. This observation highlights the interactions between polymer architecture and healing as will be discussed in the next section.

3. Influence of polymer architecture on healing

In traditional polymer research there are several parameters intrinsic to the formation of a polymer that can be modified in order to tune the physical and mechanical properties. For instance, molecular weight (M_w), crosslinking density, average intercrosslink molecular weight (\bar{M}_c), composition heterogeneity/homogeneity (polydispersity), crystallinity, chain entanglement, inhomogeneities in crosslink distribution, cluster size and distribution, free volume and its distribution, length of chain precursors and crosslinking molecules, degree of polymerization, monomer arrangement in copolymers, number of crosslink functionalities in a precursor/crosslinker, have a direct effect on T_g , T_m , stiffness, Young modulus, tensile strength and strain. Evidently the matter becomes even more complex when considering the effect of extrinsic parameters such as plasticizers, thermal history, polymer blends or inorganic reinforcements. Both the nature of the reversible chemistries as presented in Section 2 of this paper and the way the relevant entities are included in a polymer network should be taken into account when developing self-healing intrinsic polymers. However, partially due to the fact that most studies are still at their infancy and the lack of efficient and sensitive-enough healing-quantification techniques, most studies performed so far do not pay sufficient attention to the influence of polymer architecture (see examples in Fig. 3) on the healing capabilities.

Regardless of the chemistry employed, healing requires that local reversibility (i.e. bond forming-breaking reactions) is significantly faster than the global processes (e.g. polymer flow and macroscopic deformation) to avoid the

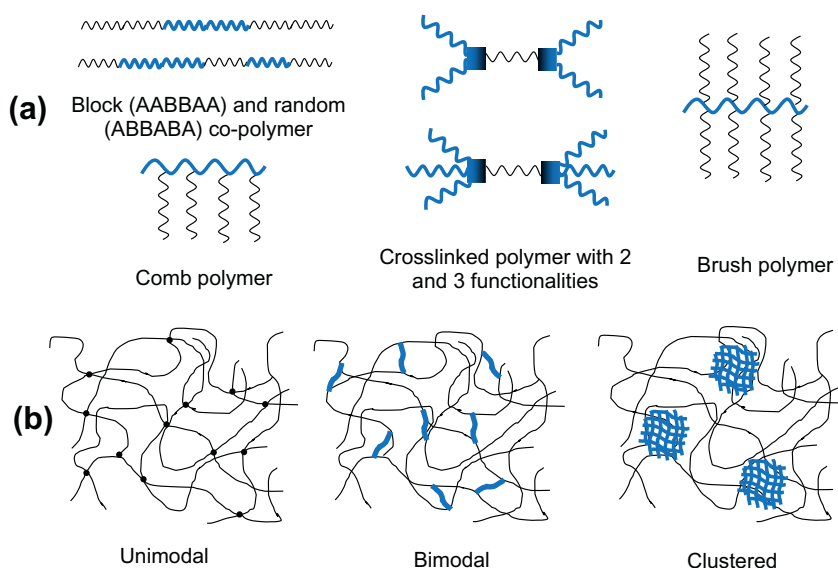


Fig. 3. Examples of polymer chain architectures (a) and polymer networks (b) with unimodal, bimodal and clustered topology.

total deformation of the material (shape loss) before healing. It may thus be that the design of strong networks with healing capabilities is based on hybrid architectures possessing both reversibly bonded regions (networks) as well as irreversibly bonded ones to overcome short-comings of an entirely reversible system formed by rather weak bonds. Such a requirement for hybrid architecture is the consequence of the introduction of increased mobility within the material which leads to generally lower mechanical properties. The formation of these hybrid polymers, as the hybrid sol–gel based polymer recently developed in our group [39], also allows evaluating the effect of the polymer architecture in the healing capabilities and mechanical properties. The effect of the polymer architecture on healing of fractured polymers (restoration of the interfaces created upon fracture) will be analyzed in the next subsections.

3.1. Chain stiffness and crosslink functionality

Generally speaking, to increase the lifetime of a polymer (such as coating) exposed to combined environmental and mechanical loads there are two opposite solutions: (i) increase of the crosslinking density leading to higher chemical resistance but also brittle fracture and lower scratch resistance; or (ii) increasing the flexibility of chains between crosslinks leading to higher elastic recovery but lower chemical resistance. However, a third alternative appears to be possible when considering self-healing concepts. In such an approach a network with high chain flexibility between crosslinks but a higher amount of physical reversible crosslinks could be explored. This polymer architecture would lead to a chemically resistant polymer with retarded elasticity to restore superficial scratches, described as delayed elasticity healing concept [7]. An example of chemistry versatile enough to allow this concept to be implemented is polyurethane chemistry. The main advantage of polyurethane chemistries when dealing with healing potential is the presence of hydrogen bonds between urethane groups (Fig. 4-a). A flexible network with high amounts of urethane linkages would then allow high barrier and initial plastic deformation. Since the physical crosslinks with hydrogen bonding are reversible and the network is flexible, mild temperatures beyond the polymer T_g would allow enough flow as to fully recover the surface

in a scratch healing process (Fig. 4-b), yet the coating would be rigid enough to prevent spontaneous sagging.

Another approach using the advantages of the chain flexibility was reported by Lafont et al. by changing the molecular weight between crosslinks in a polysulfide-based thermoset rubber [36]. For the same precursor, two different epoxidized polysulfides with different molecular weights (M_w) and chain rigidity were used (EPS25 and EPS70). It was found that a slightly shorter linkage but with higher flexibility (EPS25) would lead to lower T_g and faster healing at the same healing temperature independently of the thiol-based crosslinker used (Fig. 5). The authors suggest a critical parameter for healing based on the difference between the healing temperature and the T_g according to which the higher the difference the higher the healing kinetics. In the same work, the authors conclude that the use of a three thiol function (3SH) or a four thiol function (4SH) crosslinker also influences the healing kinetics even in the absence of a change in T_g . The authors propose that a faster healing process is obtained when four functional agents are used due to a higher probability of disulfide groups encountering each other.

Probably the most studied healing chemistry in terms of architecture is the DA/rDA. One of the latest published studies shows how the healing kinetics using the

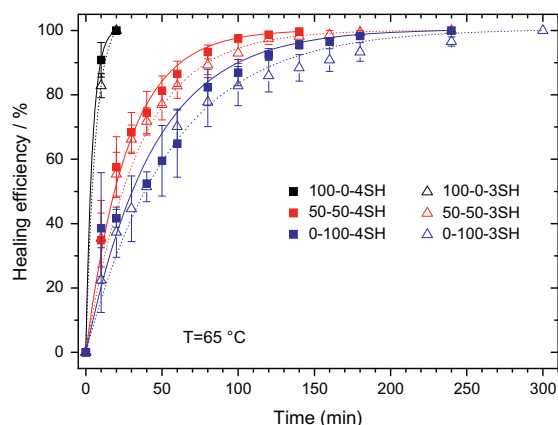


Fig. 5. Effect of crosslinker functionality in the healing capabilities of a disulfide based polymer. (Adapted with permission from [36]).

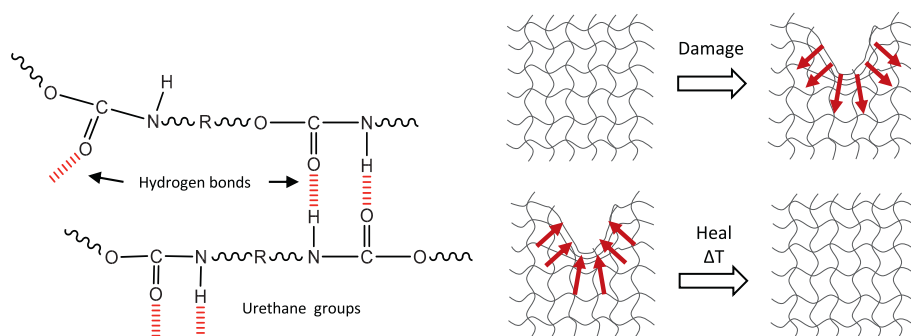


Fig. 4. Polyurethane network with H-bonds in urethane linkages (left) and network deformation and healing based on delayed elasticity concept (right).

well-studied furan–maleimide reaction depends on the rigidity of the chain of the maleimide used as well as its concentration [54]. Scheltjens et al. reported on the behavior of flexible Diels–Alder networks with varying spacer lengths of the furan and maleimide units [55]. Sheridan and Bowman on the other hand directly addressed the polymer architecture influence on the healing capabilities using Diels–Alder reactions [56] by changing the effective functionality of the monomers from 3 to 3.5. In their work they show and conclude that both healing time and the interaction between healing time and composition are key factors to understand healing performance becoming this one of the first studies of its kind. In the search for new architectures using Diels–Alder moieties, Schubert et al. have recently developed one-component reversible polymers where both moieties are pending from the same polymer backbone. In this work the authors also highlight the possibility of adding a third alkyl branch (apart from the Diels–Alder moieties) in order to increase the mobility (reducing the T_g) to obtain better healing possibilities finding that the type of pending chain also influences the healing properties [57].

The influence of polymer architecture on the healing capabilities has also been approached for a healing system that does not aim at interface mechanical strength but at surface properties restoration (i.e. hydrophobicity) by means of surface segregation using dangling chains [58]. In this study the authors show how a polymer surface can restore its hydrophobicity after surface material removal by adding dangling chains containing different fluorine amounts and different spacer chain lengths. The surface restoration was observed for both low T_g polymers and high T_g ones upon temperature trigger highlighting the need for chain mobility and surface segregation. Although the authors did not compare the observed segregation phenomena to mechanisms in other intrinsic healing systems, the mechanism proposed could be very much related to the very successful intrinsic healing system using hydrogen bonding presented by Leibler et al. [45] for which the surface state of the freshly cut sample is a key parameter to obtain healing.

3.2. Crosslinking density and content of reversible groups

In intrinsic self-healing polymers the healing process takes place at temperatures either above their T_g or above the activation temperature of the main reversible chemistry. Not many systematic works can be found in literature on the relation between crosslinking density and T_g and healing efficiency. Sijbesma et al. [59] showed that the preemptive healing capabilities of polyester–polyurethane networks can be modified by varying the content of dimers of quadruple hydrogen-bonding ureidopyrimidinone (UPy) without significantly affecting the T_g while increasing the toughness of the resulting polymers. At the same time, the works on self-healing elastomers using hydrogen bonding led by ESPCI and Arkema [60] resulted in commercial self-healing elastomers with different mechanical and healing capabilities by modifying the polymer architecture while using the same reversible groups [48].

Although most work on the relation between T_g and healing efficiency has focused on DA/rDA and hydrogen

bonding, we studied the relationship between crosslinking density and the mechanical properties and healing capabilities of a disulfide based healing polymer [39]. In this study a new hybrid sol–gel based intrinsic healing polymer was developed using a permanent organic network (epoxy–amine) and a reversible inorganic network (bis[3-(triethoxysilyl)propyl]tetrasulfide (BS) and 3-aminopropyltrimethoxysilane (APS)) and tetrathiol as precursor. The BS and the tetrathiol are the main players in the healing process leading to damage healing up to 500 μm wide cracks upon application of mild temperatures and pressure without losing the mechanical integrity of the polymer thanks to the non-reversible organic network in the hybrid. In order to evaluate the effect of the crosslinking density on the healing efficiency the crosslinking of both the organic and the inorganic networks was modified without varying the amount of reversible groups. In both cases it was observed that a decrease of the crosslinking led to a significant decrease in the Young modulus and T_g (e.g. around 400 MPa and 20 °C in the case of the organic network modification). At the same time a significant increase of the healing kinetics was observed (Fig. 6a): after 10 min healing at 70 °C the healing efficiency (crack closure) is doubled when a less crosslinked network is used. At longer times 100% healing efficiency (when crack is fully closed) was possible for all systems suggesting that the T_g has a direct effect on the crack closure kinetics but does not seem to control the long term gap closure. The polymers after gap closure and sealing showed similar water diffusion kinetics as the bulk although the mechanical properties were slightly reduced. In the same study it was found nevertheless that the content of reversible groups can be increased without affecting the T_g (Fig. 6b). A minimum content of reactive groups was necessary to obtain 100% healing although the kinetics of these systems were also affected by the disulfide content. Based on these studies it seems that the content of reactive groups is the controlling factor to obtain 100% healing although once this critical factor is reached the degree of crosslinking on the network controls the kinetics of damage closure.

3.3. Cluster content

While the content of ionic clusters (or pseudo-crystals) has been reported as the main governing factor of the healing efficiency under ballistic tests [61,62] in another not yet published study of our group we report the as-relevant influence of the free carboxylic group content in the healing at low temperatures and static healing conditions [43]. It appears that in ionomers the temperature transition in the ionic morphology even with high contents of ionization is not translated into macroscale movement and hence healing at temperatures above the order–disorder. On the other hand the presence of higher contents of free carboxylic groups leads to an increase of the healing efficiency independently of the content of ionic morphologies [43].

3.4. Multiphase polymers

The effect of the polymer network architecture on healing can be systematically studied using copolymers or

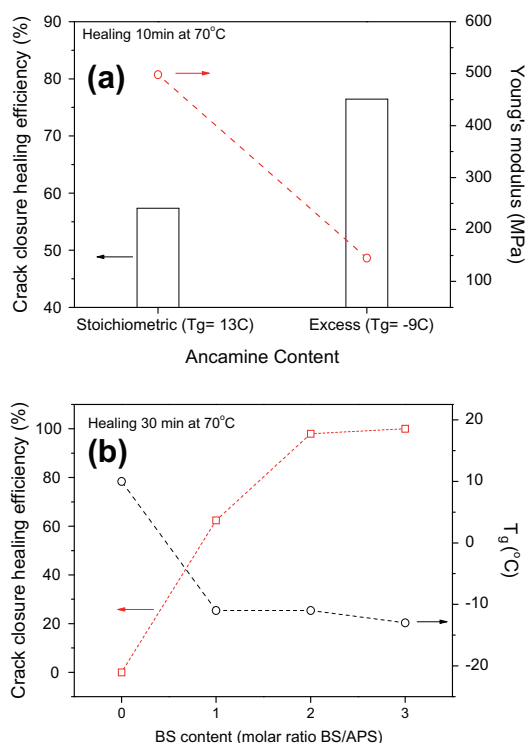


Fig. 6. Effect on the crack closure healing of a hybrid sol-gel based intrinsic healing polymer of the: (a) crosslinking density (by modifying crosslinker content ancamine) after 10 min healing at 70°C ; and (b) content of reversible groups (bis[3-(triethoxysilyl)propyl]tetrasulfide (BS) as ratio BS/APS) after maximum healing time of 30 min at 70°C . (Adapted from [39]).

other multiphase systems. Copolymers with incorporated self-healing capabilities have been reported in hydrogels where ionic crosslinking is used in conjunction with a physically associated triblock copolymer network [63]. This study showed how gels containing ionic crosslinks with weaker bonds (e.g. Ca^{2+} vs. Zn^{2+}) are less stiff but show the energy dissipation recovery needed for fatigue resistance. Guan et al. designed low temperature-to room temperature self-healing elastomers based on hard-soft multiphase networks with dynamic healing motifs in the soft phase [64,65]. On the one hand a polystyrene hard polymer backbone with polyacrylate-amide brushes as soft phase was synthesized [64] while on the other hand the self-healing network was achieved by implementing reversible well-defined quadruple hydrogen bonding UPy units in the soft phase of a block copolymer [65]. Self-healing copolymers have also been designed by implementing either reversible crosslinks by Diels–Alder moieties [66] or foldamers where reversibility is possible due to the hydrogen bonds folding the structure [67].

In order to find a better balance between base mechanical properties and some healing capability, hence increasing the applicability of self-healing polymers, polymer blends have been proposed. Hayes et al. developed a single phase blend by dissolving thermoplastic linear molecules in a conventional thermoset matrix [68] while the inclusion of melt processable thermosetting epoxy particles in a stable and rigid polymer matrix showed healing of cracks

by local melting and reaction [69]. Finally, studies with ionomer blends have reported on the effect of phase morphology on healing of ionomers [70]. Notwithstanding these studies, the effect of multiphase structure and morphology in healing is yet at its infancy and it is expected that studies to come will reveal clear design principles for more efficient healing polymers with better tuned mechanical properties.

As a conclusion it is clear that despite the advances realized in the field more systematic research is required to establish the generic rules that correlate polymer network architecture containing healing groups and healing efficiency and kinetics as was previously done to describe the relation between polymer architecture and mechanical, chemical and physical properties.

4. Final remarks

Many different chemistries have been proposed and are being developed in order to create intrinsic self-healing polymers nevertheless the relationship between healing and polymer architecture has not yet been studied sufficiently being normally considered a secondary factor. Fortunately, some early attempts are being made towards performing systematic studies where the main factor is the polymer architecture and its influence in the healing capabilities. It can be foreseen that future research in the field will not only consider the chemical reactions and conditions at which healing takes place but will also consider the effect of the mechanics and structure of the polymer network itself. Preliminary results highlight the crucial relevance of both the physics and the chemistry to obtain very efficient intrinsic self-healing systems. The difference between the properties (e.g. T_g) at the surface in for instance a crack plane and the bulk seem to be crucial to obtain full restoration of the properties at the interface. On-going and future developments in the field suggest it will be possible to use traditional polymer architecture and multilayer concepts to obtain an intrinsic healing polymer with high mechanical properties that acts as a fully dynamic system as *Hydra*.

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