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Self-healing polymers

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Introduction

The main scope of this thesis is providing a review of the main self-healing polymers that have been developed. A relevant aspect in this technology is bioinspiration, not only on the technical side. The loss of contact with nature is a predominant factor which influences the habitudes of the modern mankind. This perspective can have a role on the psychology in which innovative concepts are incubated and may lead to an ethical discussion on what is the fulcrum of progress.

New scientific discoveries bring new hopes for our future. From Newton to Fleming, the natural world has been our first source of information, granting us more and more possibilities to understand it. That means, shaping it as we want. Today, mankind has a huge impact on the biosphere equilibrium and creates risks we shouldn't take. Considering a societal wealth based on technology[1], it is essential to acknowledge how to design it: more variables must be considered, such as environmental impact. Unravelling these aspects is a complex but unavoidable choice to maintain life as we know it: a fragile existence.

Polymers' field has undergone an exceptional development thanks to their low manufacturing costs and their tunable chemistry resulting in a wide spectrum of properties. Nevertheless, this rapid industry expansion emphasized one of the biggest quests of twenty-first century, which is how to efficiently manage waste. To extend the lifespan of a polymeric product, a self-healing function may play a crucial role. To implement this function various techniques were developed, leading to several categorizations. The ideal self-healing material is autonomous and can work multiple times, but it is not always the case. Remendable polymers need an external source of energy, and can be healed more than once. In contrast, the encapsulation technique provides an autonomous mechanism, but is limited to one healing cycle. The latter is an extrinsic healing method, since an healing agent must be introduced into the matrix. On the other side, intrinsic healing is achieved through the peculiar structure of the polymer without the need of an embedded phase.

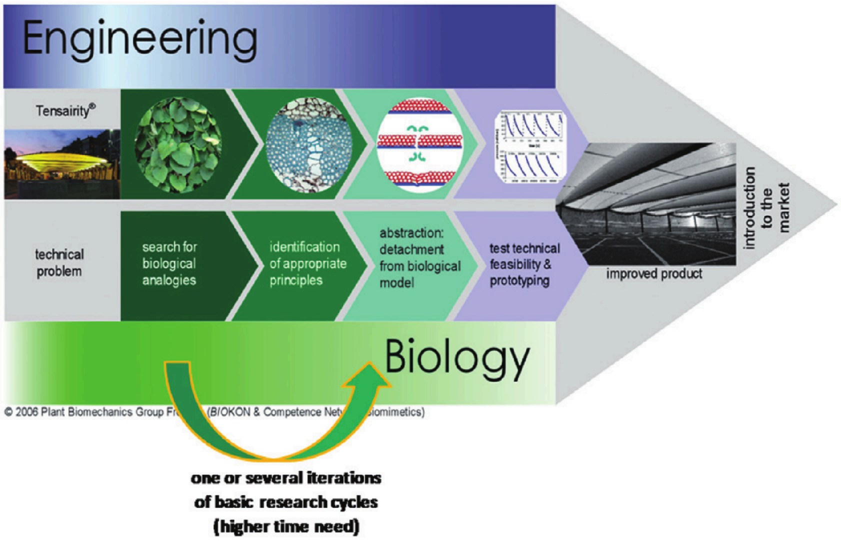
The first chapter of this thesis exposes the main concepts over which self-healing consolidates. Biomimetics are an important foundation for this strategy since they emulate the physical and chemical systems existing in nature to implement them in manufactured products. Another cornerstone of self-healing is the mitigation of anthropogenic negative influence on ecosystems synergistically combined with a reduced cost. Then, damage mechanics are approached in a somewhat historical point of view in order to give a wider scope of understanding. The second part presents the physical framework of polymers, starting from their structure and dynamics. It then pursues towards the idea of molecular interdiffusion, a central mechanism that occurs during healing when the wedge forms. The main chapter reveals the living core of this thesis, where several technologies, ranging from encapsulation to microvascularization, are discussed. A focus on the synthesis of irreversible and reversible covalent networks emerges, followed by a review of some intriguing supramolecular architectures. The fourth chapter deals with the characterization methods used to assess the healing performance for these novel class of materials. Firstly, visualization techniques using several instruments are discussed. Afterwards, a few mechanical tests are briefly introduced and finally diverse experiments are presented, such as thermomechanical and electrochemical analysis. The last chapter lists some interesting applications in which self-healing can have a major impact, such as coatings, composites, and in pneumatic structures.

I. Self-healing: an innovative and sustainable feature

1. Biomimetics

The design of new products in these last years is focused on the avoidance of damage by guaranteeing a minimum resistance over which existing flaws couldn't lead to a catastrophic failure. Great safety factors are incorporated in manufacture projects, and various quality assurances and norms synergically cooperate to establish an improved reliability of the outcome. But this vision needs to be supported not only by a constant, accurate maintenance of the man-made structures to preserve their efficiency during their lifetime. It also requires expensive processes to produce superior outputs.

Life has evolved over billions of years to adapt to extremely differing environments and situations. It is well known that forms of life are characterized by special features, for instance, homeostasis and adaptation. Intelligent organisms sense a variation in their steady state that triggers a reaction to re-establish the previous, optimal conditions. Dealing with damage is essential to survival, and almost all species possess self-repairing abilities. Hence observing and analyzing the hierarchical structures in nature can provide a deep insight into new extraordinary methods to solve relevant engineering problems. Self-healing materials must respond dynamically to an external stimulus to recover the lost properties. The main focus in literature is the reheabilitation of mechanical characteristics[2,3]. Nowadays, the focus is directed towards other domains, such as electrical, optical and corrosion properties. The biomimetic transfer process can be conducted in different ways: a top-down or a bottom-up approach. These are also called technology pull or biological push, respectively[4]. In the first case, the driver is the industry wanting to explore new material possibilities to ameliorate an existing product or to manufacture a new one. In the other case, a scientific discovery conducted by biologists and material scientists is the trigger to revolutionize specific sectors. The image below depicts in a simplified manner the developement of a self-sealing membrane (fig.1).



© 2006 Plant Biomechanics Group Fr (BIOKON & Competence Net iomimetics)

Fig.1 Example of top-down approach

2. Economic considerations and sustainability awareness

Creating more autonomous materials which are capable to manage their flaws during their lifetime could reduce the costs related to maintainance by delaying the necessity for manual intervention. Enhancing this aspect can also induce an average waste reduction: in many cases if a minor portion of a system is damaged, the whole structure has to be replaced. Esthetical criterions can be very tight, and , for example, a superficial scratch in a trasparent glass can abruptly decrease its extrinsic value. In some cases, a repair cannot be made without an important loss in marginal profit. Moreover, if the lifespan of polymeric manufacts is extended, less material will be used for its substitution.

Furthermore, our current economic model seems to be inadequate in view of a new set of objectives, in which the foremost quest is a viable technological progress. The perception of value is directly correlated to the cost of the object, and not with the energy used for its production. This erroneous understanding leads to an accelerated production of low-cost commodities which are abandoned as soon as they fulfill their brief function. In this context, self-healing materials can be harmonized in a circular economy which aims to minimize waste by combining their longer service life with recyclability.

3. Damage mechanics

Everything slowly degrades. Manufactured products degrade in specific ways because they are subjected to some kind of stresses related to their functionality. Mechanical solicitations, which can be static or dynamic, temperature gradients and electrical flows are just some of the events damaging a material. Polymers are particularly sensitive to temperature and UV radiation. Moreover, their mechanical behaviour is strongly time-dependent: the resulting strain is a function of the time during which the load has been applied. Not only the strain response is out of phase with the applied load, but there is a viscous component to take into account. Stress relaxation as well as creep take place, that's why they are viscoelastic. To analyze these physical properties different measurements can be made. Dynamic mechanical analysis links the stress response of the specimen to a controlled, forced cyclic deformation. A storage and a loss modulus are then extrapolated and are used to represent the viscoelastic characteristics of the material. Another method to profile those properties is through a thermoelectrical technique. In this case, the oscillating mechanical forces are replaced with an alternate potential, and the results are stored in the complex dielectric permittivity that has been calculated.

This peculiarity generates a high degree of complexity in the analytical description of damage mechanics. Actually, polymers' fracture can be brittle or ductile, since they can experience a brittle to ductile transition, even at room temperature. As it is well known, lower temperatures and higher strain rates, such as an impact, lead to a quasi elastic rupture. Viceversa, a slower load rate or a higher thermal motion promote material flow, allowing increased strain gradients.

Every breaking event starts from certain zones where stress is concentrated. Inhomogeneities can be geometric (grooves, holes, pores…) or compositional (segregation, contamination, interfaces…). They alter the distribution of internal forces and can generate local stresses much higher of the applied average stress. Over a certain value, the material starts to tear apart: a crack has nucleated and can propagate if the conditions are adequate.

One of the first rigorous papers which quantitatively determined how a hole can affect the tendency to break of an elastic material has been written by C.E. Inglis in 1913[5]. He found the mathematical solution of the stress at the tip A of an elliptic hole of length $2a$ with a radius of curvature ρ in an infinite plate subjected to a stress of magnitude σ_0:

$$\sigma_A = \sigma_0[1 + 2\sqrt{\frac{a}{\rho}}]$$

However, if the curvature is that of a perfectly sharp edge, the stress would be unsustainable for any relevant value of σ_0, since $\frac{a}{\rho}$ would tend to infinity.

Arnold Alan Griffith, aware of Inglis' work, proposed a different approach, based on the energy balance during the propagation of a crack[6]. The energy strain accumulated per unit volume can be expressed as[7]:

$$U^* = \frac{1}{V}\int f\,dx = \int \frac{f}{A}\frac{dx}{L} = \int \sigma\,d\varepsilon$$

If the solid is purely elastic, Hooke's law is valid, and therefore this energy strain per unit volume is:

$$U^* = \frac{\sigma^2}{2E}$$

Considering a simple geometry as shown below (fig.2), the volume interested by the strain release is $V = \beta a^2$ if we consider thickness to be one. To adhere with Inglis' solution, in plain stress conditions $\beta = \pi$ and thus:

$$U = -\frac{\sigma^2}{2E}\pi a^2$$

The negative sign means that this energy is released into the system upon cracking, caused by the breakage of bonds and the formation of a new surface. The surface energy S needed depends on the surface energy γ as well as the length of the crack a:

$$S = 2\gamma a$$

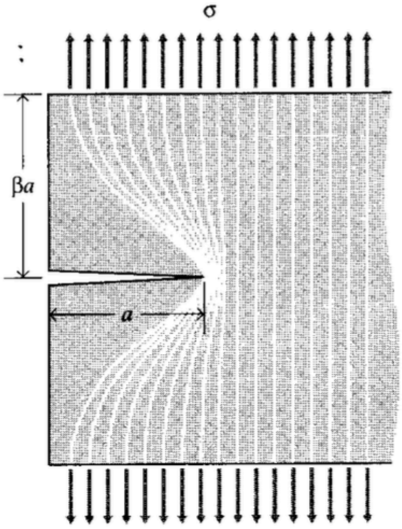


Fig.2 Idealized stress field

The maximum in the function $U + S$ will correspond to the critical length a_c after which the quadratic term in the strain energy dominates the linear surface term (fig.3). When $a > a_c$ the minimization of system's energy is achieved by increasing the crack's dimension: its propagation is energetically favorable. By calculating the derivative of the function, the failure stress can be obtained:

$$\frac{\partial(S+U)}{\partial a} = 2\gamma - \frac{\sigma_f^2}{E}\pi a = 0$$

$$\sigma_f = \sqrt{\frac{2E\gamma}{\pi a}}$$

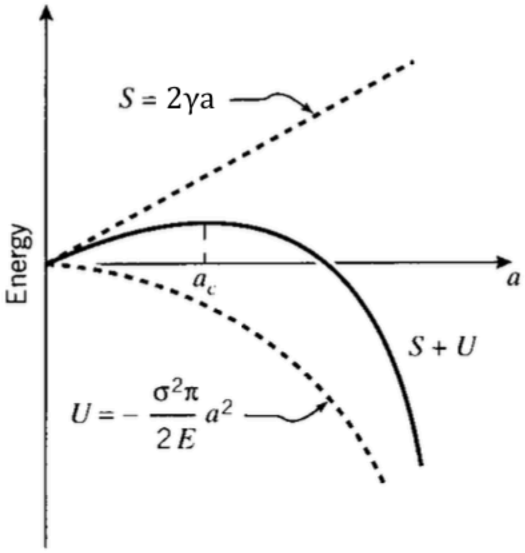


Fig.3 Schematic energy balance

As said, polymers possess a time-dependent response to mechanical stimulus, and a mechanism which dissipates the work done by external forces: plasticity. Therefore, the crack tip isn't so sharp, as it tends to blunt due to plastic deformation. But Griffith approach doesn't take it in consideration, as Orowan already noticed in 1954[8], observing that low carbon steel brittle fracture has a considerable amount of permanent distortion. He shed light on the correlation between the rate of propagation and the resulting fracture, explaining that a brittle behaviour may be due to a localized plastic deformation which exerts strong internal tensions in the material ahead of the crack tip. This phenomena creates multiple, tiny voids in the bulk that can coalesce very rapidly and speed up the propagation of the crack, causing a catastrophic fracture. Irwin[9] implemented this model by replacing the surface energy with a critical strain energy release rate G_c, which is characteristic of the material, in the fracture resistance formula, so that:

$$\sigma_f = \sqrt{\frac{EG_c}{\pi a}}$$

In practice, a critical stress intensity factor K_{Ic} is used during the design phase of a component. It depicts the magnitude of the stress distribution in a normal opening mode, called mode I (fig. 4). In plane stress conditions, the relation between K_{Ic} and σ_f is:

$$K_{Ic}^2 = EG_c$$

whereas in plain strain conditions

$$K_{Ic}^2 = EG_c(1 - \upsilon^2)$$

where υ is the Poisson ratio.

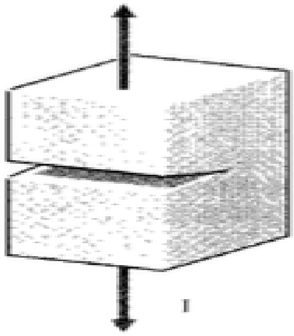


Fig. 4 Normal opening mode

Nevertheless, the plasticity of metals is neatly different from the viscous behaviour of polymers, the latter being dominated by dislocation motion and the former by chains sliding.
Semicrystalline polymers are made of spherulites, which in turn are constituted of lamellae, that are portions of ordered macromolecules, and amorphous regions. During a tensile test of a semicrystalline polyethylene (fig.5), the ordered structure is disrupted, and a considerable deformation occurs. Lamellae have a higher density compared to the interlamellar region, and provide a huge quantity of ordered polymer chains to be unfolded and straightened. A drop in the yield stress can be observed; in that region a strain softening occurs. In contrast, when PE is already highly strained, more stress is needed to withstand an increased strain: all the chains have unfolded and a strain hardening due to the orientation of the fibrillar network is obtained. The styrene group has a steric impedance that hinders chain mobility; furthermore, polystyrene is almost always atactic, so it cannot reach any level of crystallinity. Thus, deformation mechanisms cannot activate, and at low elongation values the material breaks.

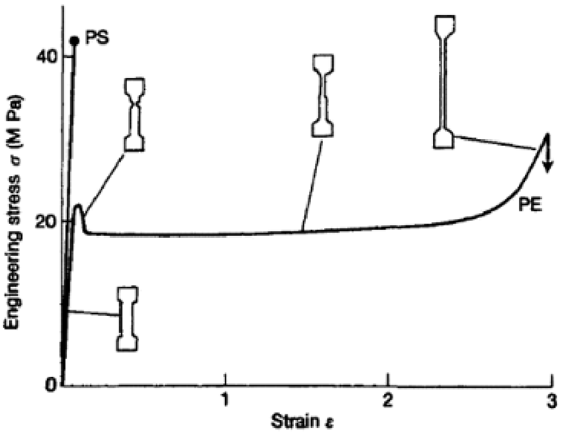


Fig.5 Stress-strain curves of two different polymers

Polymeric materials exhibit different types of yielding: crazing and shear bending. These are competitive mechanisms that are influenced by material properties, such as their glass transition temperature, strain and stress rates, geometry, and external conditions. The first typology often appears in rigid polymers, such as polystyrene or PMMA, and consists of a microcavitation process during which a fibrillar network is formed(fig. 6 and 7). Fibrils draw fresh material from the bulk to the surface or collapse under tension[10]. This void formation can also occur near the crack tip, since it is a region of high stress. Crazes form in planes oriented perpendicularly with respect to the applied force axis, and aren't as dangerous as voids, since the fibrillar network still bears some load.

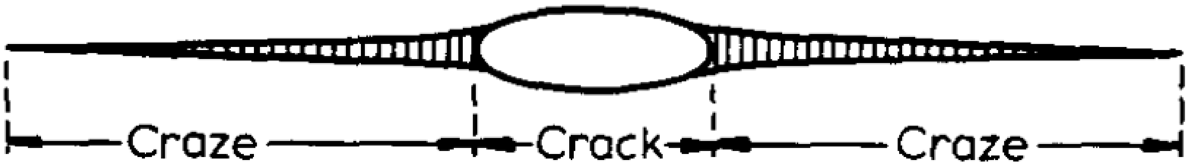


Fig.6 Schematic craze growth from crack tip

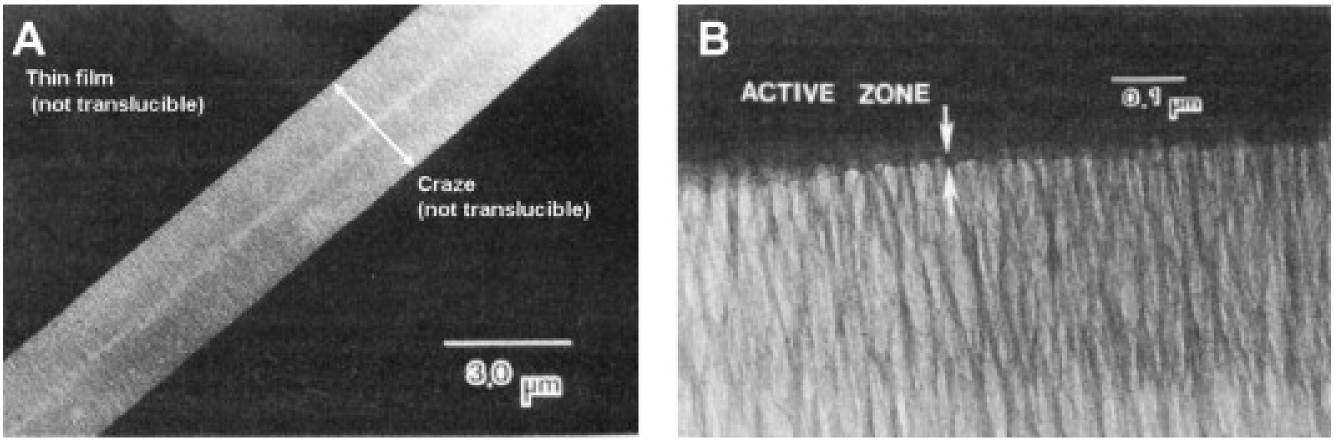


Fig.7 Crazing observed with TEM in polystyrene

On the other hand, shear yielding usually occurs at 45° from the tensile (or compressive) force's axis, where the shear stress is at its maximum. The material won't experience a change in its volume, but in its shape. No new surfaces are created, and two kinds of bands can grow. Coarse bands occurr at fast strain rates and low temperatures, while fine ones are prominent at lower rates and increased temperatures. In the former case, stress concentrators can trigger their initiation, which result in a fast, brittle fracture. In the latter, a ductile fracture is achieved by the multiplication of the finer bands which spread over a large portion of material[11]. In a real situation, all these mechanisms are superposed. The complex fracture behaviour is dependent upon different time and length scales that regulate numerous internal events.

II. Physical models and principles

Polymers are usually represented as random coils which structure is highly fluctuating, depending on brownian motion, chemical constituents and interactions. To study their dynamics, some instruments have been developed: small-angle neutron scattering (SANS) is a powerful characterization method to analyze their static configuration[12], while neutron spin echo technique has yielded important informations regarding segmental motions[13]. These extremely precise tools have grown a fertile database to compare empirical results with the simulations that have stemmed from the theories of these last years.

1. Polymer structure

One of the simplest model to represent the arrangement of a polymer chain is the freely jointed chain model[14]. It defines its path as a random walk (fig.8), and doesn't consider any monomer-monomer interaction. This latter condition is found in pratice in linear polymer melts and concentrated solutions, when the attractive and repulsive interactions between monomers are compensating: the polymer is in its θ-state. Several other systems which include the rotational nature of bonds have been developed, such as the freely rotating chain model or the rotational isomeric state model, but won't be presented.

The mean parameters are n, the number of units of the global chain, the bond vector $\vec{r_i}$, and the end-to-end vector (fig.8):

$$\overrightarrow{R_n} = \sum_{i=1}^{n} \vec{r_i}$$

Since the global properties are controlled by a massive amount of chains, these variables will possess a distribution since every single chain has a rather unique organisation. In this case, it is useful to introduce the average end-to-end vector, usually written $\langle \overrightarrow{R_n} \rangle$. In this specific model, the bond length l is constant and bond angles are independent from each other:

$$\langle \cos \theta_{ij} \rangle = 0 \qquad \text{for } i \neq j$$

where θ_{ij} is the bond angle between the bond vectors $\vec{r_i}$ and $\vec{r_j}$.

However, due to the stochastic characteristic of this representation, $\langle \overrightarrow{R_n} \rangle = 0$. To achieve a finite value, the mean square end-to-end distance is adopted to illustrate the volume in which the full chain is included. It can be easily calculated for this kind of ideal chain:

$$\langle \vec{R}_n^2 \rangle = \langle \vec{R}_n \cdot \vec{R}_n \rangle = \sum_{i=1}^{n} \sum_{j=1}^{n} \langle \vec{r}_i \cdot \vec{r}_j \rangle = nl^2$$

since $\vec{r}_i \cdot \vec{r}_j = l^2 \, \cos \theta_{ij}$.

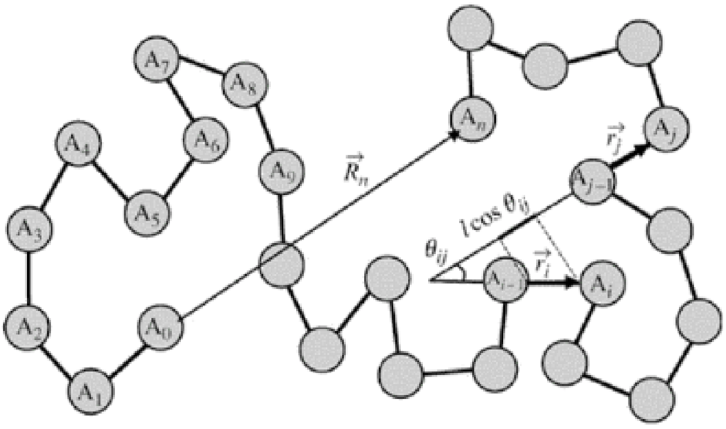


Fig. 8 Scheme of one possible conformation

This relationship yields an important consequence, that is, the size depends on the square root of the number of building blocks. Additionally, it can be proved that the sum

$$\sum_{j=1}^{n} \langle \cos\theta_{ij} \rangle = C'_i$$

so that

$$\langle \vec{R}_n^2 \rangle = l^2 \sum_{i=1}^{n} C'_i = C_n n l^2$$

where C_n is Flory's characteristic ratio, defined as the average value of the constants C'_i by Flory (fig.12).

Ignoring the interactions of monomers separated by many bonds will result in the saturation of C_n when n tends to infinity, as shown in the graph below (fig.9). Then, the mean square end-to-end distance can be approximated as:

$$\langle \vec{R}_n^2 \rangle \cong C_\infty n l^2$$

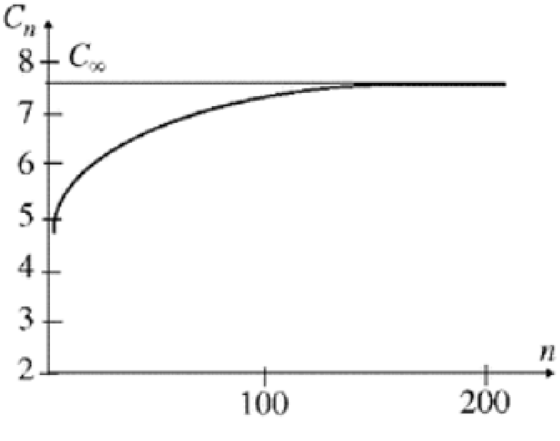


Fig. 9 Flory's ratio saturating at high n values

In case of perfect flexibility, $C_\infty = 1$. Highly-coiled polymers, then, assume low values of C_∞ (Polyisoprene, Polybutadiene) whereas loosened coils can have C_∞ values as high as 10 (PS, PMMA, double-stranded DNA). This new parameter incorporates the local stiffness of the chain. Nevertheless, in real polymers one particular bond has a direction which is greatly influenced by the surrounding neighbour bonds. Moreover, steric hindrance is not accounted in this simplified model, so bond angles can assume unrealistic values.

To avoid these difficulties, Kuhn has developed a model called the equivalent freely jointed model. The bond length is replaced by the so-called Kuhn monomer length b, represented by the dashed lines in the successive sketch (fig.10), and the random walk angles are restricted[15]. By grouping together a certain number of bonds m, the direction dependance is eliminated, if m is sufficiently large. This equivalent bond length is usually expressed as:

$$b = \frac{\langle \vec{R}_n^2 \rangle}{R_{max}} = \frac{C_\infty n l^2}{R_{max}}$$

where R_{max} is the length of the totally unfolded chain, or contour length. Above this statistical segment length, a real chain can be well described by the FJC model.

Fig. 10 2-D representation of a random walk with m=5 and angle bonds varying between $-\frac{\pi}{2}$ and $\frac{\pi}{2}$

Flory was the first to determine the probability to find the ideal chain end in an infinitesimal volume dV around a certain point of coordinates (x, y, z), while the other chain end is fixed at the origin of the cartesian system. This probability is calculated by a Gaussian distribution:

$$p(R) = \sqrt[\frac{2}{3}]{\frac{3}{2\pi \langle R_n^2 \rangle}}\, e^{\frac{-3R^2}{2\langle R_n^2 \rangle}}$$

This approximation is valid until $|\overrightarrow{R_n}| \ll R_{max}$.

In some cases, the definition of the mean square end-to-end vector is problematic. This description is well correlated to linear chains, but for closed or branched polymers the results aren't satisfying. The radius of gyration R_g is introduced to avoid any discrepancies in the definition of the previous parameters[16]. It designates the average square distance between monomers in a given conformation:

$$R_g^2 = \frac{1}{n}\sum_{i=1}^{n}\left(\vec{R_\iota} - \vec{R}_{cm}\right)^2$$

Here, $\vec{R}_{cm}$is the center of mass vector and R_i is the position vector.

For a gaussian chain it can be inferred that

$$\langle R_g^2\rangle = \frac{nl^2}{6}$$

In fact, the scattering experiments that are employed to deduce polymers' characteristic structure generally measure the radius of gyration of single polymers in solution or in a melt. However, this simple model isn't representative of all the hidden mechanics of polymers, because of the idealization of the chain. Mutual interactions between monomers are possible, and random walk statistics have to be modified into self-avoiding walks. This problem is typically known as the excluded volume effect. Idel chains, for this reason, are also called phantom chains.
Many scattering techniques can clarify polymers' structure: dynamic light scattering, X-ray diffraction, neutron scattering and others. SANS results are interpretated thanks to the static structure factor $S(Q)$, where Q is the scattering vector, that is, the norm of the difference between the incident and the scattered wave vectors. These empirical methods have allowed to discerne a somewhat universal power law between the size and the degree of polymerization N:

$$R \sim bN^{\upsilon}$$

where υ approaches $\frac{3}{5}$ if the solvent is good[17]. But this fact qualitatively shows that usually polymers aren't ideal at all, since $\upsilon \neq \frac{1}{2}$.

2. Polymer dynamics

Since many polymers' problems are analytically intractable, numerical simulations have helped the understanding of the underlaying physics, namely Monte-Carlo method and molecular dynamics[18]. One of the first useful theoretical model that has been ideated is the Rouse model[19] (fig.12). The latter wishes to describe the coarse behaviour of linear polymer in a newtonian solvent, and is usually illustrated by a series of beads and springs as depicted here (fig 11).

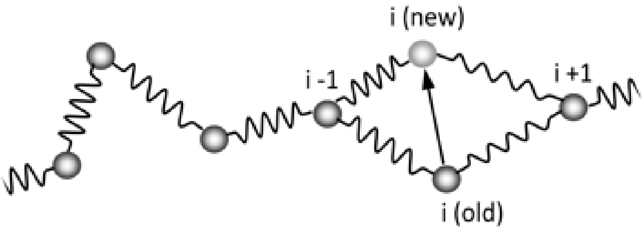


Fig. 11 Bead-spring model

Three main hypothesis are assumed to be true. The first is that each subunit is a Gaussian chain, and the net force transmitted by springs is of entropic nature. The spring constant κ can be calculated through a thermodynamic derivation[20]:

$$\kappa = \frac{3k_bT}{b^2}$$

In this relationship, N is the number of beads, k_b is Boltzmann constant, T is the temperature and b is the Kuhn length. Secondly, each bead represents a subsection of the polymer chain containing many Kuhn segments and is characterized by an intrinsic friction coefficient ζ. Additionally, any solvent can freely drain through the chain, and the brownian motion induces a random force on beads with a time length much smaller in comparison with polymer's dynamics[21].

By mean of Einstein's equation we can obtain the diffusion coefficient D_R of a Rouse chain:

$$D_R = \frac{kT}{\zeta_R} = \frac{kT}{\zeta N}$$

Further, it can be deduced a specific time length τ_R over which the chain movement can be attributed to a liquid-like behaviour:

$$\tau_R \approx \frac{R^2}{D_R} = \frac{\zeta N}{kT} R^2$$

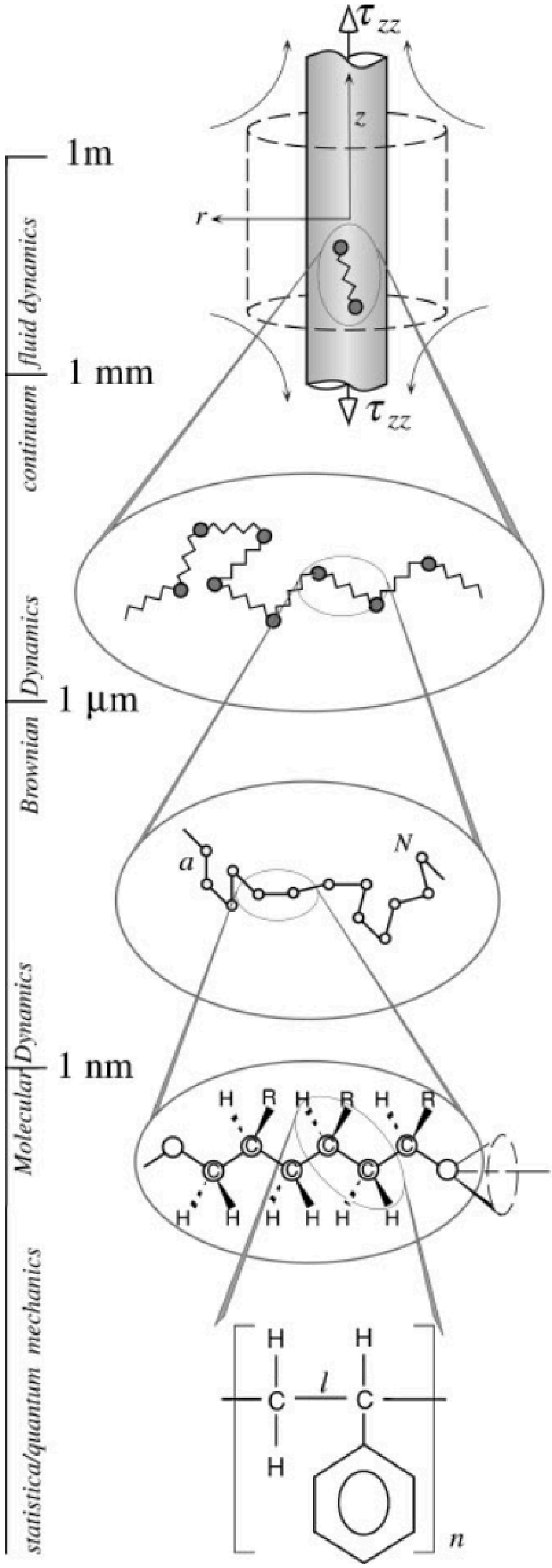
If the previous power law is introduced, for ideal chains with $\upsilon = \frac{1}{2}$ the Kuhn segment relaxation time τ_0 can be derived as:

$$\tau_R \approx \frac{\zeta b^2}{kT} N^2 \approx \tau_0 N^2$$

Any dynamic stimulus on time scales below τ_0 will lead to an elastic response of the chain. Thus, these two time parameters are fundamental for the separation of the viscous and elastic components of polymer viscoelasticity. Three years after Rouse's publication, Bruno H. Zimm[22] extended this theory by including hydrodynamic interactions between the beads.

The last half of the twentieth century has been a flourishing period, and many multiscale kinetic theories for polymers have been conceived, from the coarser FENE dummbbell model, which can be useful in fluid dynamics simulations, to the RIS model, elucidating molecular dynamics. This progressive focus on microstructural details and the concomitant refinement of technologies have enabled the construction of an intricated hierarchy of modelings, extending over many time and length scales (fig.13).

Fig. 12 From left to right: P.E. Rouse, P.J. Flory, P.-G. de Gennes



Finitely Extensible
Nonlinear Elastic model

Rouse model

FJC model

FRC or RIS model

Chemical structure

Fig.13 Microstructure modeling's hierarchy

Nonetheless, all the previously introduced models don't consider the rather complex topological interactions between the chains. These restricitons were embodied in Pierre-Gilles de Gennes(fig.12) reptation model[23], by representing a polymer P of mass M into a tridimensional network G (from gel). The choice for this name derives from an analogy with reptiles, in particular with snake's motion. In this model the chain is allowed to move just inside a tube, and many calculations are related to its dimensions. Furthermore, De Gennes exctracted some important reptation time dependances using the concept of "defects", which are foldings occurring along the chain, as depicted in figure 14.

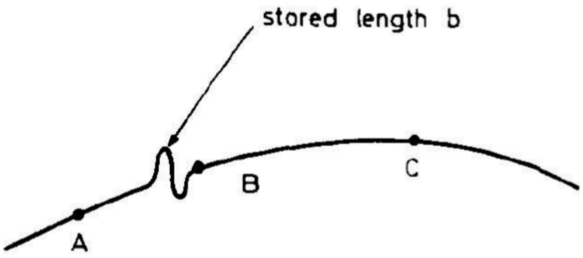


Fig. 14 A folding, or repton, along the ideal chain

By determining a certain conservation law, he deduced two sets of relaxation times: τ_d is correlated with the equilibration of defects, while τ_r , called renewal time, corresponds to the time required to disengage totally from the initial tube. This terminology can lead to some confusions with the Rouse time τ_R . Since it is a diffusive process, in literature τ_r is frequently replaced with τ_d whereas τ_d changes into τ_e , accentuating the equilibrium statement. The key results are:

$$\tau_d \propto M^3$$

$$\tau_e \propto M^2$$

Later, Edwards and Doi[24] refined this theory and extended it to rigid chains, using a similar tube model (fig 15). They represented the topological constraint of surrounding chains by a quadratic potential, and determined a primitive path coinciding with its minimum. The chain excursions from this line are dominated by thermal fluctuations and modulate the tube diameter a.

However, this mean-field theory is quite rigid[25]: a is constant, even if these constraints are generated by other reptating chains, thus continually mutating their spatial conformation and the exerted constraining force. So, a certain constraint release can influence the dynamics of the network. Also, the contour length fluctuations (CLF) aren't assessed; both of these simplifications underestimate the exponent correlating the renewal time, also named terminal time, to the mass (or the degree of polymerization). Indeed rheological experiments gather a 3,4 exponent: Doi[26] consistently showed that a relaxation process faster than reptation occurs, that is the stretching and contraction of the chain. Many efforts have been made to incorporate these effects with a high degree of accuracy, trying to estimate the massive amount of errors that could be introduced both by mismatching formalisms and approximations. Likhtman and McLeish[27] have developed a good model which take all these aspects in consideration.

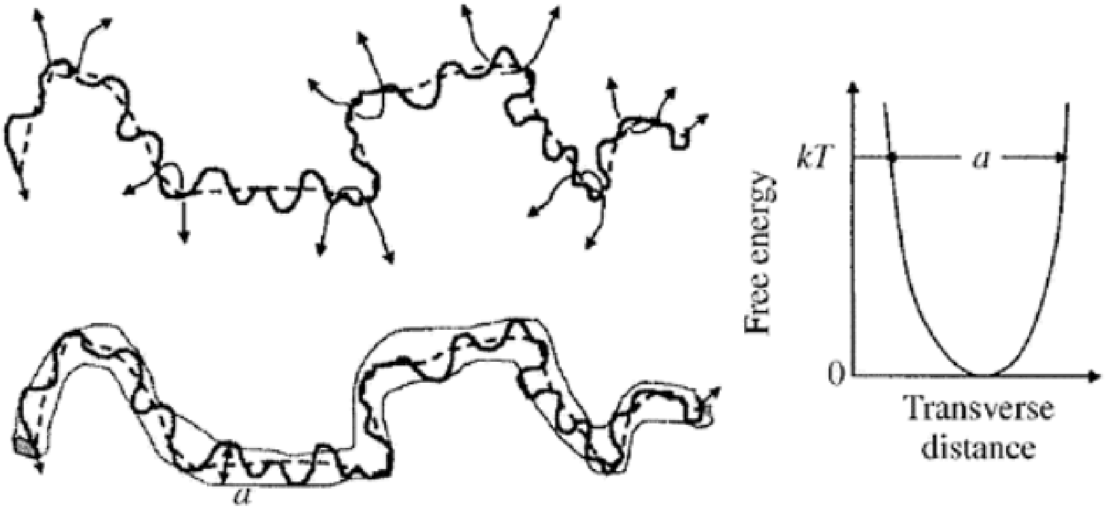


Fig. 15 Scheme representing the topological restrictions imposed by other chains and the energy potential function. The primitive path is the dashed line.

3. Molecular interdiffusion

In microscopic terms, healing is achieved through a number of physical and chemical phenomenons which control the mobility and reactivity of the polymer chains.

One of the best understood physical principles is molecular interdiffusion; in 1981 Wool and O'Connor[28] proposed a five stage mechanism to represent it (fig.16).

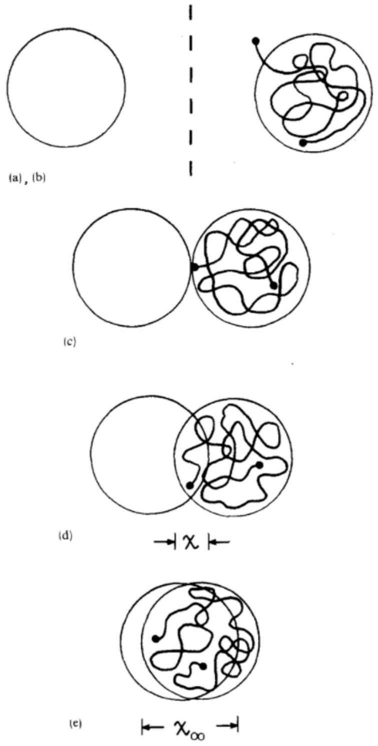


Fig. 16 Wool and O'Connor five stage mechanism

The sequential steps are: surface rearrangement (a), surface approach (b), wetting (c), diffusion (d) and randomization (e).

Damages form new surfaces with different kind of morphologies, i.e. the crack interface is more or less rough. With increasing roughness the surface area is higher, thus enhancing healing mechanisms. However, polymer surfaces possess a higher energy than bulk, and restructure to minimize it[29], sometimes inhibiting physical entanglements. To obtain a significant recovery the chains near the interface must reposition in a favourable way. In this case, they should form new entanglements with the opposite polymer surface to recreate a new network. For these reasons the first step is crucial to the initiation of self-healing, and a diffusion initiation function has been tailored to describe its influence.

Surface approach is often taken for granted in many empirical approaches, but is in fact the most important phase, since the molecular interdiffusion cannot exist without contacting surfaces. Two pieces of polymer can be pressed together at a specific temperature, often above the T_g to accelerate the process, and self-healing can be observed. This can be convenient to analize some self-healing potential, for instance by measuring the recovery strength with known pressure, temperature, and other fixed variables. But in real situations it can be tremendously complicated applying pressure to a certain portion of the material while in use; accordingly, different methods have been developed to resolve this problem, such as the CTH scheme[30].

The wetting stage consists in a molecular interplay of surface potentials; to quantify the attractive forces existing between two surfaces different methods exist, the simplest being the contact angle measurement. The surface energies of different phases can then be extrapolated thanks to Young's equation. Moreover, wetting has a temporal character which can be incorporated through a spreading coefficient. This stage allows the contact of two different surfaces; only after this diffusion can start.

In this fourth stage the damage can be successfully healed: the segmental mobility of the chains is the fulcrum of any possible entanglement event to regenerate the polymer matrix. Chains near the interface are less bonded than chains in the bulk, and this condition leads to an enhanced mobility which contributes to diffusion bonding, even at temperatures below T_g[31]. Finally, the loss of memory interface is achieved by a randomization process: the properties are completely regenerated through chain relaxation.

The recovery ratio R is an essential parameter to standardize the effectiveness of a self-healing material; it is the ratio of the recovered property over the virgin property, which is denoted by the subscript ∞. This can be the fracture stress σ, the elongation at break ε, or some spectroscopic measure I:

$$R(\sigma) = \frac{\sigma}{\sigma_\infty}$$

$$R(\varepsilon) = \frac{\varepsilon}{\varepsilon_\infty}$$

$$R(I) = \frac{I}{I_\infty}$$

R has also been defined by the authors through the convolution of two functions, namely, $R_h(t)$ and $\phi(t)$. These are the intrinsic healing function and the wetting distribution function, respectively. To compute the effective recovery it must be considered that all stages of healing can occur at the same time, i.e. healing starts at different times in different regions of the interface. By considering X a domain in the crack interface and τ the time variable, the problem can be equated as follows:

$$R = \int_{\tau=-\infty}^{\tau=t} R_h(t-\tau)\frac{d\phi(\tau,X)}{d\tau}d\tau = R_h(t) * \phi(t)$$

where the symbol $*$ implies convolution. It is then evident that wetting and diffusion play a central role in the recuperation of the mechanical properties at the interface, and the separation of roles is helpful in the resolution of the problem. Indeed, the stress transmitted at the interface σ is assumed to be composed by σ_0, the component due to surface attraction (i.e. wetting), and σ_d, due to the interpenetration of the random coils dominated by diffusion:

$$\sigma = \sigma_0 + \sigma_d$$

This last-mentioned concept is supported by the reptation model of a chain in a tube, introduced previously. By employing the reptation diffusion coefficient D_c, Wool and O'Connor correlated the interpenetration distance χ with time t:

$$\chi \propto t^{1/4}$$

A specification must be made:

$$t \leq t_\infty$$

where t_∞ is the time to achieve the equilibrium interpenetration distance χ_∞.
An intuitive assumption has been made, that is, the strength of the healed interface due to diffusion linearly depends on χ and on the number of entanglements n:

$$\sigma_d = qn$$

where q is a constant.
Using the number of constraints per unit volume n_0 the last equation may be rewritten:

$$\sigma_d = qn_0\chi$$

with $\chi < \chi_\infty$.

Then

$$\sigma_d = Kt^{1/4}$$

where

$$K = qn_0(2D_c)^{1/4}$$

Wetting and diffusion can occurr almost instantaneous if the compatibility and the mobility are sufficient, but can also be time dependent. In the first case, $\dot{\phi}(t) = \dot{\psi}(t) = \delta(t)$; the upper point represents the time derivative and $\delta(t)$ is the Dirac delta function. Otherwise, the function must be chosen appropriately to correspond with the specific situation.
$\psi(t)$ is the diffusion initiation function which correlates σ_d with the effect of the rearrangement period from fracture to effective wetting:

$$\sigma_d = Kt^{1/4} * \dot{\psi}(t)$$

R is then obtained when dividing σ by σ_∞:

$$R(\sigma, t) = \left[R_0 + \left(\frac{K}{\sigma_\infty} t^{1/4} * \dot{\psi}(t)\right)\right] * \dot{\phi}(t)$$

with

$$R_0 = \frac{\sigma_0}{\sigma_\infty}$$

This approach clarifies the cascade interactions occurring during molecular interdiffusion of polymers, by dividing and analyzing the multiple facets of a variegated physical problem. Experiments have validated several behaviours happening during healing, but the randomness governing diffusion still hides the details of this complex mechanism[32]. For example, the formation of diffused fractal structures at polymer interface is of primary importance since it affects its properties, and has been studied intensively[33, 34].

4. Welding

Molecular interdiffusion plays a role in every joining process and is influenced by several variables which concurr in the formation of a strong weld. Tipically thermal energy is the driving force which promotes chain migration and the subsequent restoration of mechanical properties in a ruptured volume. The laser welding technique is a precise method to assemble plastic pipes as well as microfluidic devices[35], and is readily available on the market, but other welding systems are abundant.

It must be noted that thermoset polymers normally aren't thermally welded, since they would degrade. However, due to their higher mechanical features and the proliferation of thermoset composites, many researches have been conducted to solve the matter. A solution to reduce the negative effect of temperature is that heating times can be decreased[36] by employing rapid operations, such as ultrasonic welding.

Welding is a specific process in which molecular interdiffusion occurs: the welding temperature, pressure, and the surface properties of the two components influence the resulting weld strength. The ensued recovery in a healed material depends on it, and diverse strategies can be implemented to achieve the wanted properties.

Solvents can improve the chain mobility by entering the strand network to swell the polymer, taking advantage of its free volume. This happens relatively easily with thermoplastics, in contrast with thermosets, that need extreme conditions to incorporate solvents[37]. To avoid the encountered problems with thermoset welding, a new class of polymers possessing dynamic covalent bonds[38] have been object of study[39]. These peculiar bonds can rupture under specific conditions without penalizing the mechanical properties due to the strong characteristic interlinkage of thermosets. The reversibility of these reactions is an attractive feature for self-healing materials, and in the next section, another approach will be taken to explore the manifold chemical systems able to generate a new network upon fracture.

III. Self-healing technologies and reactions

Self-healing polymers have gained success through the years thanks to the versatile chemistry yielding a variety of products which differ significantly. The healing paths can be chosen to optimize the timing, amplitude and effectiveness of the recovery. The ideal self-healing polymer should be able to sustain multiple healing cycles without any need of manual intervention. But this case is still far from reality: most of the time autonomous self-healing systems are capable of a single cycle of healing, or just a few, whereas multiple healing typically requires intervention. Several technologies have been developed in concomitance with chemical systems, to optimize the recovery efficiency and uncover innovative ways to smarten up polymers. In figure 17 are illustrated various mechanisms of polymers that can engender a new network if adequately stimulated. Anyway, it should be noted that this categorization is not strictly valid, due to the nuanced world of self-healing chemistries and systems.

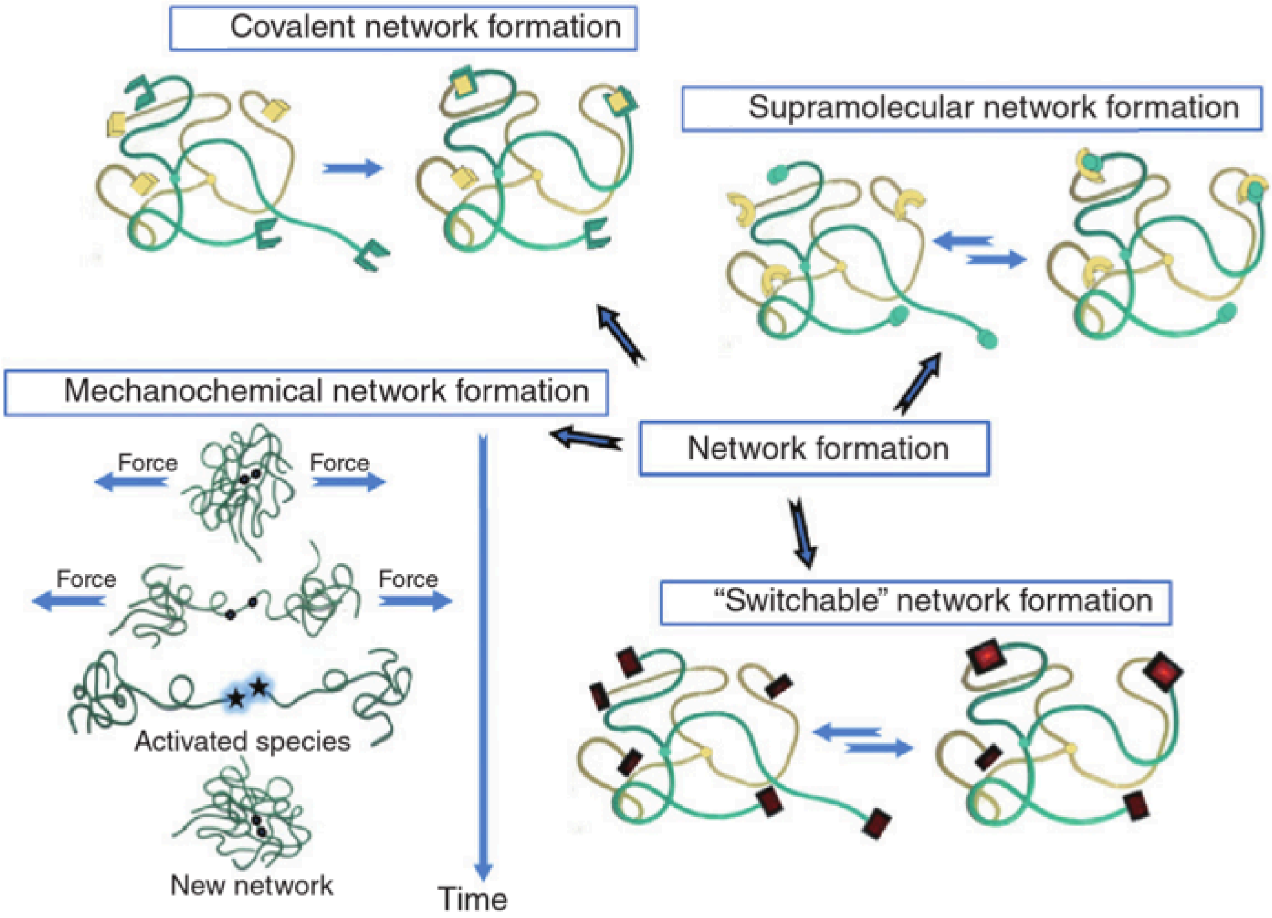


Fig.17 Typologies of healing mechanism

1. Irreversible covalent network formation

1.1 Self-healing technologies

1.1.1 Encapsulation techniques

Microencapsulation has been one of the first techniques that have been adopted to introduce a healing agent in a polymer matrix. In 2001 White *et al.*[40] published one of the first papers regarding the autonomous healing of polymer composites through encapsulation. A ring opening metathesis polymerization (ROMP) was the driving reaction to obtain a new covalent network where the crack occurred. The encapsulated healing agent has a low viscosity that allows its flow into the crack plane and consequently wets the engendered free surfaces, where polymerization can initiate due to the embedded catalyst. This method is attractive since it doesn't imply the molecular modification of the matrix and is a well implemented technique in industry. Nevertheless, several parameters must be taken in consideration to create a useful healing system. First, the shell material must share some compatibility both with the filler and the matrix, to reach a good adhesion between the two surfaces, thereby guaranteeing the rupture of the capsule and the deliver of the healing agent. Moreover, the shell must provide an efficient protection from the ambient, to reduce the probability of unwanted reaction, and must sustain the processing phase, in which the applied loads and temperatures could potentially damage the capsule. The selected material must thereby have a sufficient thermal stability and fracture strength; however, the latter must not exceed a certain value, over which the crack wouldn't break the shell. Another important parameter is related to its interaction with the healing agent: it must be inert, and the permeation rate through it has to be sufficiently low to maintain the healing's effectiveness over long periods of time. The evolution of this method generated various types of healing systems, as schematized in fig. 18. The simpler is a single capsule containing the healing agent which, upon release, starts the polymerization without any need for a catalyst (A). Nonetheless, to achieve an adequate healing response, catalysts are often required (B). In certain approaches, one component is encapsulated whilst the other is phase separated into the matrix (C). Otherwise, multicomponent healing systems are often integrated into the matrix by a double capsule system: one contains the hardener while the other the monomer (D). Finally, there are two types of all-in-one systems, where the healing components are integrated in a layered multishell envelope (E) or in a single capsule storing several smaller shells containing the healing agents. All of these techniques present various problems; for instance, when solid particles (i.e. the catalyst) are embedded in the matrix, they can aggregate and form clusters that could act as stress concentrators. The dispersion of the various components is critical in every approach; the last proposed method, that is, the spherical reactor, has complications due to the major complexity of its assembly. Various synthesis paths can be followed to achieve the desired capsule. In situ polymerization is one of the most prominent type of emulsion polymerization. In this way, Brown *et al.*[41] synthesized poly(urea-formaldehyde) (PUF) capsules carrying dicyclopentadiene (DCPD) as reactive healant for an epoxy resin. The diameter of the obtained spherical shells ranged between 10 and 1000 microns, while the shell thickness lied between 160 and 220 nanometres; the capsule size variation was due to different setups and is mainly related to the agitation rate acting during the polymerization. Due to the poor thermomechanical properties of PUF, other studies tried other types of shell material, such as poly(melamine-formaldehyde)[42] and polyphenylene oxide[43]. An interesting approach related to the recovery of electrical properties using microencapsulation has been conducted by Caruso *et. al*[44], by filling capsules with a suspension of carbon nanotubes.

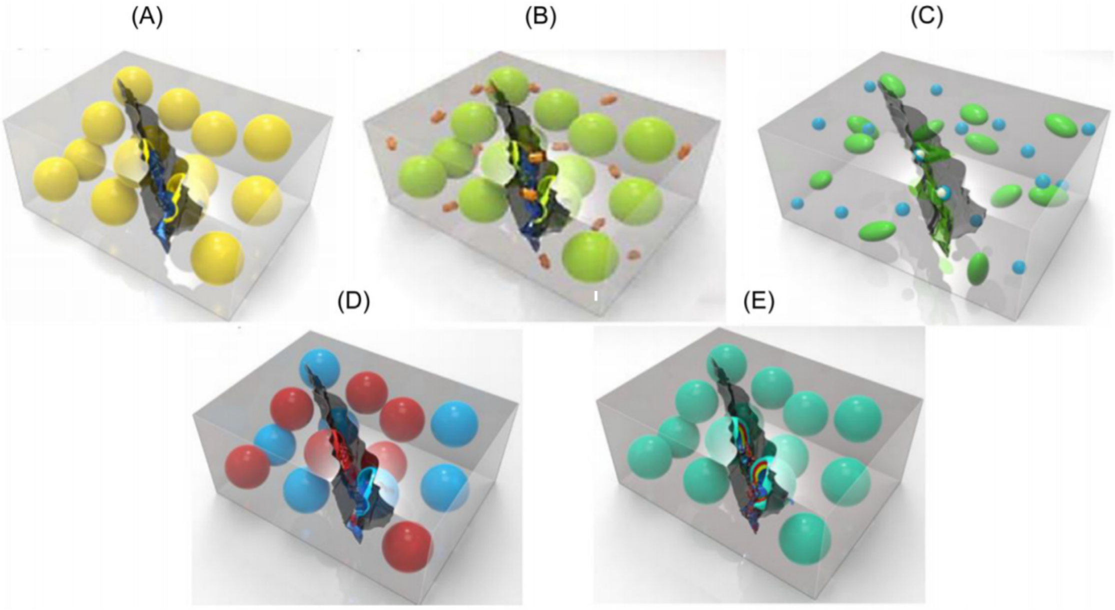


Fig. 18 Encapsulation approaches

Interfacial polymerization is another captivating technique in the fabrication of microcapsules. Usually, two types monomers are used: one is dissolved in the continuous phase, i.e. the solvent, while the other is soluble in the core material. By emulsifying the latter, the polymerization will occur near the organic-aqueous interface, and both the dispersed and continuous phases take part in the reaction, which will proceed faster in comparison with in situ polymerization. This fast reaction is often a condensation between an amine and a proper reactant group, such as isocyanates. For instance, Liu *et al.* encased an epoxy monomer, finely dispersed in an aqueous medium, thanks to the reaction with the water-soluble ethylenediamine[45]. Many other methods exist to attain an encapsulated system, using a Pickering emulsion template, miniemulsions, sol-gel reactions, layer by layer assembly, or exploiting phase separation. An intensive research is progressing toward the understanding of the optimization of capsule-based healing systems, assessing how the different parameters modify the recovery efficiency. Besides microscopy, which can verify the integrity, roughness and size of the capsules, other measurements such as differential scanning calorimetry and thermogravimetric analysis can be employed to extrapolate their thermal stability[46].

1.1.2 Hollow fibres

Another healing technique is the integration of hollow glass fibres in composite panels[47]. Hollow fibres, in contrast with spherical shells, can distribute a superior quantity of healing agent, and can do it homogeneously over various lengths, depending on the fibre's size. Sandwich fibre-reinforced structures notoriously suffer from fatigue and impact degradation, which cause hardly detectable and repairable defects. Upon rupture of the brittle fibres, a new network could substitute the crack to increase the cross-section resistance and prevent further delamination (fig. 19). These fibres could also act as structural reinforcement, even if most of the experiments show a reduction of mechanical properties, probably due to the large size of the fibres that can locally amplify the stress field. Reducing their diameter would not only diminish the storage capacity, but also hinder the fluid delivery because of the greater capillary forces. Furthermore, polymerization kinetics must meet a strict rule: the liquid healing agent must flow and wet the internal flaws completely before solidifying. To decrease the resin viscosity and enhance the viscous contribute of the healing agent solvent can be previously added to the uncured thermoset, or temperature can be raised. Both of these two procedures entail some issues that hamper practical application.

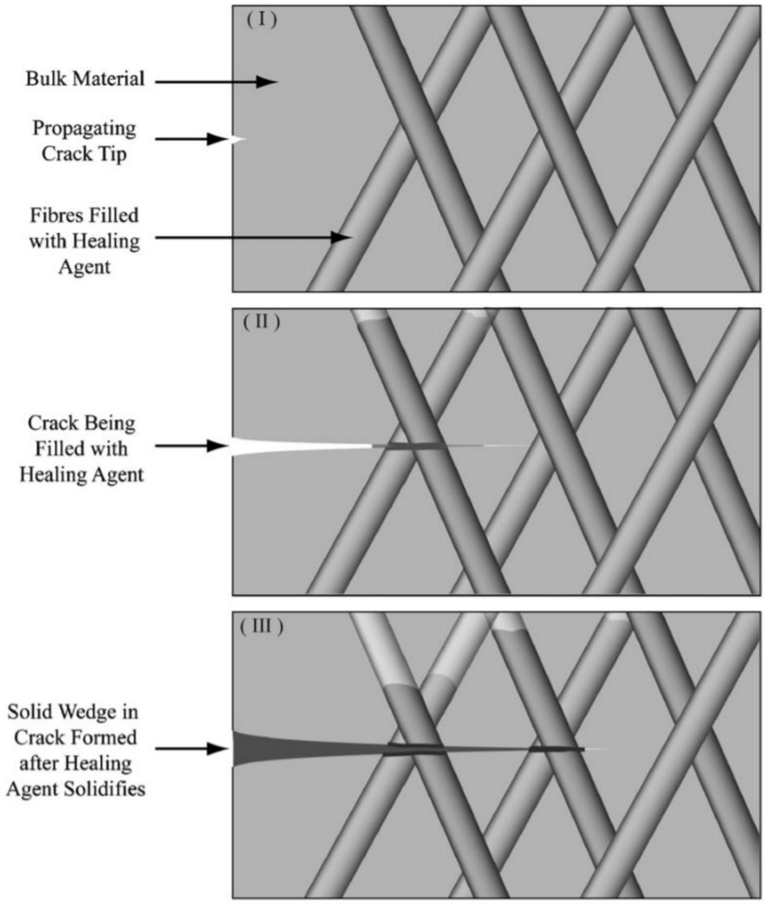


Fig. 19 Self-healing by hollow fibres integration

1.1.3 Microvascularization

A fascinating aspect in self-healing polymers is the possibility to emulate natural systems when prototyping healing technologies. It is in fact well known that biological beings often possess a complex vascularization system, capable of distributing nutrients, maintaning optimal conditions (i.e. homeostasis), and autonomously repairing itself. Generally, those kind of networks include three main elements: a pump, a pathway, and a fluid. The difficulty of reproduction of complex geometries, the integration of a pumping system connected to a reservoir engender, and the optimization of a system with a large parametere space hinder the production of a viable healing product, but efforts have been made to disentangle this laborious quest, focused on several aspects. Biological circulatory patterns are hierarchical and try to minimize the work needed for fluid displacement. Murray[48] studied how the vascular system transporting blood is precisely designed to fulfill a maximum economy of work, and using the Hagen-Poiseuille equation for laminar flow, he obtained a mathematical equation relating the thickness of a mother branch to the size of its daughter branches. The most semplificated version states that, for a parent branch or radius r bifurcating into two smaller branches of radii r_1 and r_2:

$$r^3 = r_1^3 + r_2^3$$

This simple yet powerful equation improved the design for bioinspired materials with optimal mass transport properties, crucial in some applications like photocatalysis, gas sensing and as lithium-ion battery electrode[49]. Application to self-healing has already been completed by Toohey *et al.*[50] utilizing the previously mentioned chemistry system to heal a coating. Grubbs' catalyst was dispersed in the coating, while the substrate contained the microvascular network, fabricated by direct-write assembly of a fugitive organic ink[51], as represented in the image below (fig. 20).

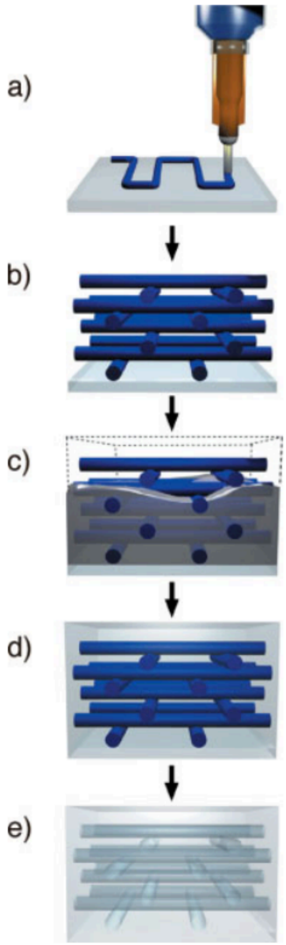


Fig. 20 Layer by layer assembly of a three-dimensional microvasculatory network

This additive manufacture method is relatively simple and is based on the layer-by-layer deposition of an organic ink (a) to obtain a solid scaffold (b). The structural material such as an epoxy is then infiltrated (c) and let solidify at ambient temperature (d). Finally, the sacrificial ink is removed (e) by heating under a light vacuum. The typical channel diameter depends on the syringe employed for the deposition; hundreds of microns are a typical order of magnitude. Substractive manufacturing processes such as electrostatic discharge machining have also resulted in 3D networks, as proved by Huang et *al.*[52]. This procedure forces an electric current through a substrate by the mean of an electron beam irradiation, which implants a high level of electric charge in the polymer, which is then rapidly transferred to the grounded point. The vascular morphology can be controlled by choosing the point of discharge, that can be a conductive electrode in contact with the polymeric material or a superficial defect. The local vaporization generated by the electron flow produces a peculiar vascular pattern, sometimes called Lichtenberg figures, and is a hierarchical network. The channels' thicknesses range between 500 and 10 microns, and the analysis conducted on the bifurcations concluded that this architecture followed a modified Murray's law, with an exponent between 2,1 and 2,3. By varying the number of discharges, the implanted charge, and the location of nucleation sites different patterns can be achieved, even interlocking ones, as depicted in fig. 21. This fast technique could be envisaged for mass production of vascularized bulk polymers.

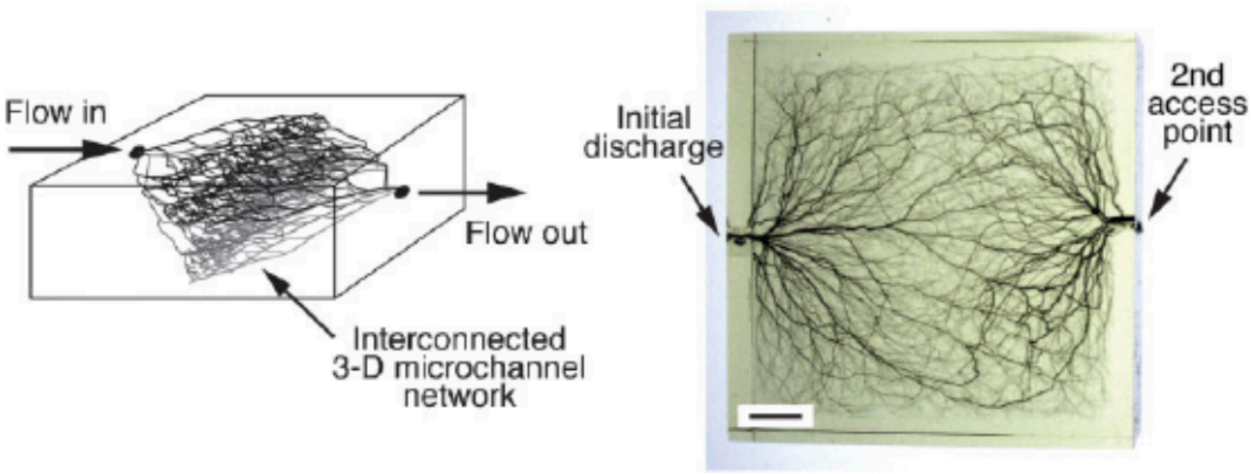


Fig. 21 Two irradiation and discharge cycles resulting in an interdigitated network. Scheme on the left and photo on the right, where the scale bar is 1 cm.

Microvascular-based self-healing polymers are at the forefront of materials innovation, but many aspects are still unsatisfactory. The pump and tank system are not considered, yet, to completely exploit this technology potential, one must investigate this critical aspect. Furthermore, some strategies are not prone to multiple healings: the previously presented coating contains Grubbs' catalyst, which is depleted after each healing cycle. New chemical reactions, based on dual epoxy systems for example, could pave the road for a better design. Other typical problems of these structures are the occlusion and the rupture of the channels, which could lead to a loss of functionality. Therefore, manifold progresses must be realized to develop a maturer technology encompassing some crucial steps that are missing.

1.2 Self-healing reactions

1.2.1 Ring-opening metathesis polymerization

A number of chemical reactions are in the focus of self-healing. As previously cited, the ROMP reaction is the most well-known since it has been the first that has been proved to be successful in terms of availability of the components, reaction rate, and cross-link density of the newly formed material. This chemical system comprises DCPD and Grubbs' catalyst, as depicted in the figure below (fig. 22), and is a kind of heterogeneous catalysis which rapidly generates a covalent network involving chains with regular *trans* double bonds. This type of polymerization is energetically favourable since it relieves the ring strain of the monomer. For this reason, not only DCPD but also other ring precursors can be selected, such as norbornene[53]. However, Grubbs' catalyst is expensive and susceptible to degradation at epoxide processing temperatures. Moreover, curing agents can interact with the solid catalyst, which must be extremely well dispersed in the matrix, and consequently deactivate it.

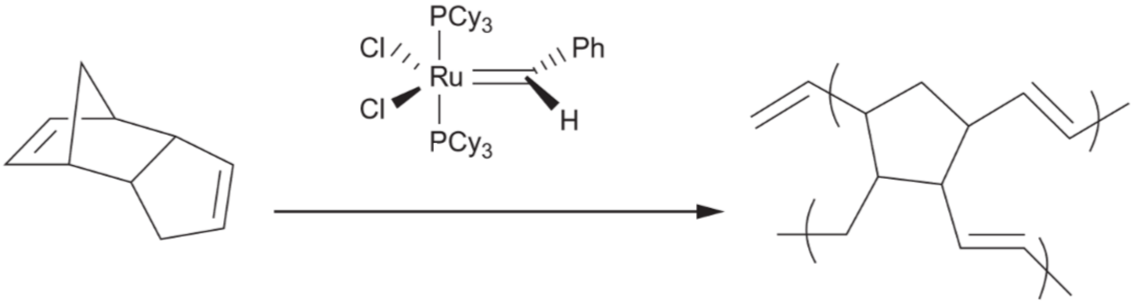


Fig. 22 ROMP reaction of DCPD catalyzed by ruthenium-based Grubbs' catalyst

1.2.2 Siloxanes polycondensation

This traditional synthesis opened the way to other numerous healing reactions, trying to be as cost-saving end efficient as possible. Polymeric structural components are generally made by epoxide resins, but also vinyl esters. In this case the polycondensation of siloxane groups is attractive for a healing function[54]. Hydroxyl end-functionalized polydimethylsiloxane (HOPDMS) and polydiethoxysiloxane (PDES) are incorporated into the matrix via phase separation, and the organotin compound is stored in a polyurethane microcapsule. HOPDMS is sufficiently fluid to permeate the generated crack, and the catalyst promotes the cross-linking through bridging oxygens. The advantages of this reaction is the minor cost of the tin-based catalyst and the selectivity of the reaction, that is, almost no side reactions occur. Additionally, thanks to the hydrophobic nature of the two healing agents and to the stability of the embedded catalyst, the reaction is not perturbated by humidity nor oxygen.

1.2.3 Epoxy and latent hardener systems

An ideal candidate for a further reaction is the epoxide group itself, which can undergo rapid coupling with hardener, commonly possessing an activated hydrogenò. By encapsulating the liquid epoxy and homogeneously distributing a latent hardener, good healing recovery can be achieved[55]. The anionic ring-opening polymerization occurs when the latent hardener dissociates into $CuCl_2$ and imidazole: the latter reacts with the epoxide ring through its reactive hydrogen and propagates the reaction, illustrated here in figure 23.
This complex is soluble in epoxy, and it is then easily dispersed and its ring group is incorporated into the cured polymer, giving to the established network good mechanical properties. However, its dissociation occurs at 130-170°C, so the healing material must be heated to recover. To circumvent this matter other chemistries have been proposed, such as a dual capsule approach, one containing a modified aliphatic amine while the other a diluted epoxy monomer[56]. The tested sample has been set aside for 48 hours at ambient temperature after fracture, and showed an excellent flexural strength recovery. Nevertheless, performing optical microscopy after several thermal treatments revealed the leakage of the amine component through the capsule, demonstrating a poor thermal stability at 121°C.

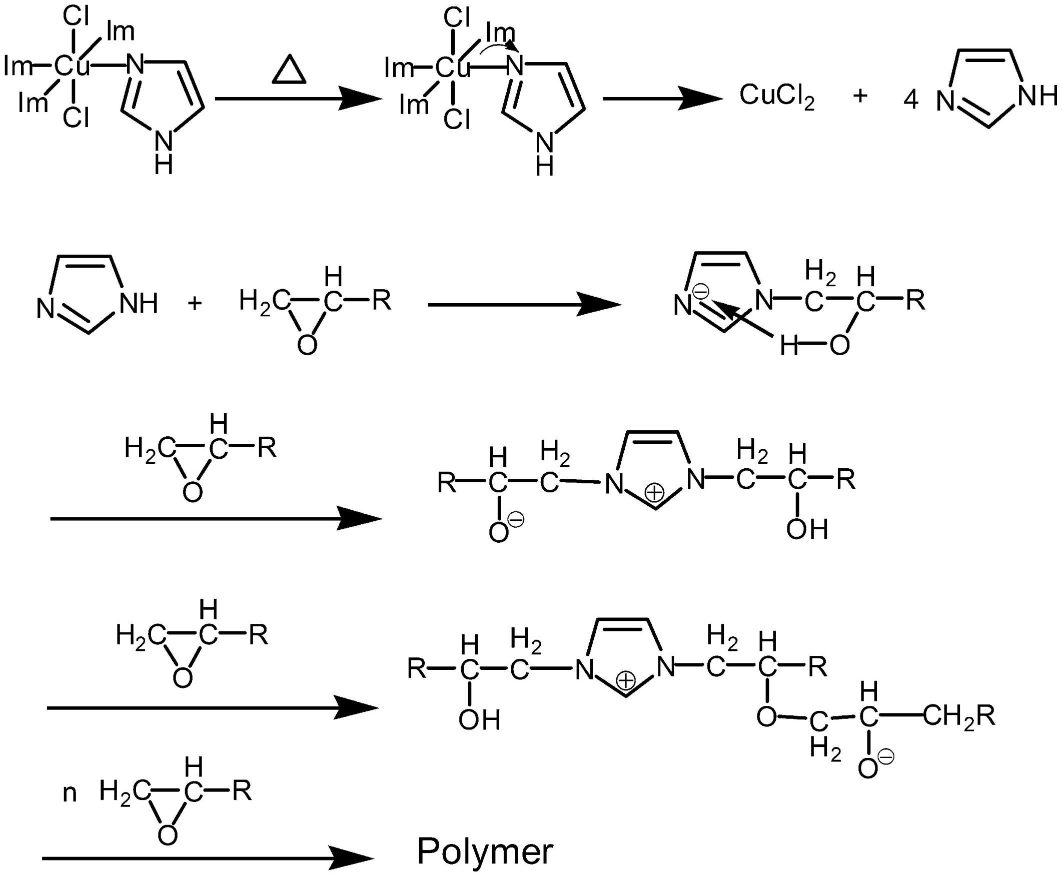


Fig. 23 Curing reaction between epoxide groups and dissociated imidazole

1.2.4 Click chemistry

Click chemistry is another attractive mechanism which throws into relief the potential of bioinspiration, since nature's most important metabolites are assembled from small molecules joined by heteroatom links[57]. As a matter of fact, polynucleotides, polypeptides and polysaccharides are fundamental for life growth and reproduction and are built by their monomeric counterparts. A crucial concept that led to this competitive chemistry is the thermodynamic driving force that pushes the reaction. Forming new carbon-carbon bonds via traditional carbonyl chemistry often requires an energy supplement or a finely tuned setup for byproducts removal, since their driving force is usually lower than 3 kcal mol^{-1}. Click-based reactions fulcrum is connecting minute molecules through heteroatom bonding to achieve a much more energetically favourable condition, typically greater than 20 kcal mol^{-1}. From this characteristic sundry criteria are attained: the reaction is modular, stereospecific, and then giving high yields, engendering few, easily removable byproducts. The authors specify that the latter must be inoffensive, and that the click process must be simple, insensitive to water and oxygen, without any malign solvent and based on readily available precursors. In the last two decades many research groups focused their attention on the copper(I)-catalyzed azide/alkyne cycloaddition (CuAAC) for self-healing purposes[58] (fig. 24).
This reaction satisfies the previously described parameters, and can be optimized by systematically screening various low-weight alkynes and azides. Kinetics can be tuned by selecting the appropriate copper ligands, which can also guarantee the long-term stability of the catalyst. Studies found $[Cu(PPh_3)_3]Br$ to be the best catalyst paired with alkyne 4 and azide 10, and fractured poly(isobutylene) (PIB) specimens recovered 91% of their tensile

modulus after 5 days at 25°C due to stress-induced self-healing. In this case, the incorporation method was a dual capsule system. Since diffusion of the reactants limits the healing potential, the authors used branched alkynes and azides with different rheologies and number of functional groups to provide a larger database for CuAAC. Autocatalytic effects were observed using star-shaped azides and alkyne telechelic PIBs, and decreasing the molecular weight accelerated the reaction rate thanks to the enhanced chain mobility. Other fascinating click reactions hinge upon thiol-ene chemistry[59], and have several advantages including a possible photoinduced polymerization[60]. Additionally, some copper salts are biotoxic, so this novel approach could lead to greener technologies.

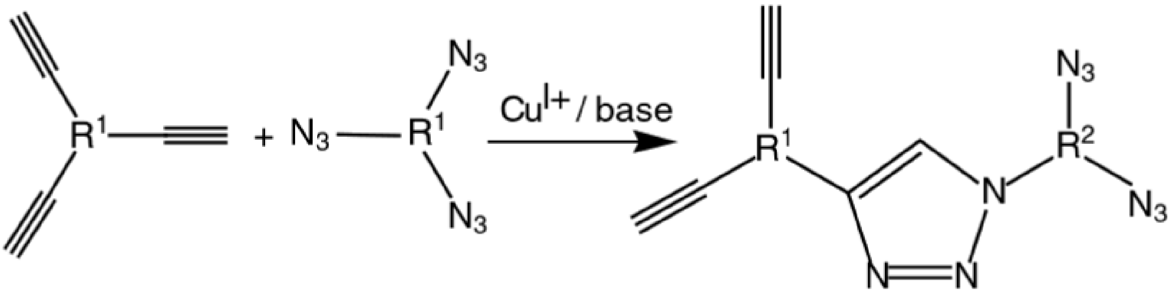


Fig. 24 Schematic CuAAC click reaction

2. Reversible covalent network formation

2.1 Diels-Alder and retro-Diels-Alder reactions

To achieve multiple healings different thermoreversible mechanisms have been examined in order to give birth to thermally remendable polymers. This tipology of self-healing materials thus requires an increment in temperature to activate their healing ability. One of the most studied chemistry are the Diels-Alder (DA) reactions, discovered by Otto Diels and Kurt Alder in 1927[61]. They are based on the formation of covalent bonds between a diene and a dienophile through a concerted [4+2]-cycloaddition[62]; the most interesting property of this chemical system is that it can also return to its original state through a retro-Diels-Alder (rDA) reaction, as illustrated in figure 25.

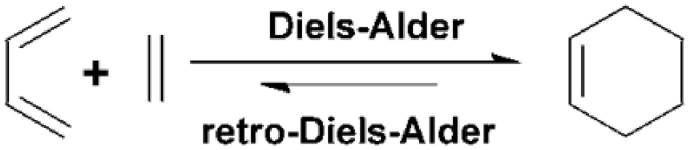


Fig. 25 Scheme of DA and rDA reactions

The most used electron donors are cyclopentadienes (CPD), furans, and their respective derivatives, while common electrophiles are maleimides. The latter provides a pathway for hetero-DA (HDA), that means the possibility to form carbon-heteroatom bonds. At molecular scale, the HOMO orbitals of the diene interact with the LUMO orbitals of the dienophile: by reducing the gap separating those energy levels the kinetic is faster, and occurrs at lower temperatures. Furthermore, the six π-electrons involved in this reaction permit the stabilization of the transition giving the DA adduct. Different strategies can be adotped to customize this peculiar chemistry in order to form a stable tridimensional network upon cooling. Murphy *et al.*[63] synthetized a remendable polymer by employing a DCPD-based ring monomer acting as both the diene and the dienophile. More specifically, heating it up to 120°C activates two DCPD moieties which undergo a DA reaction with the neighbouring monomer units. Further reaction of the obtained dimer enables trimer formation, allowing cross-linking which results in the formation of a tridimensional network (fig. 26).

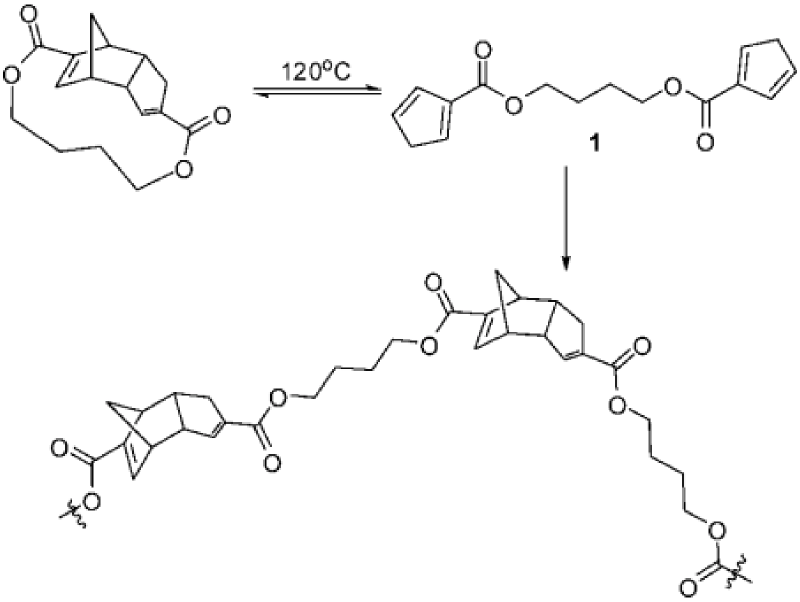


Fig. 26 Representation of cross-linking reaction

This approach simplifies the synthesis of the remendable polymer since it includes a single monomer and has no issues regarding the dispersion of a catalyst or a second component, thus preventing any unwanted phase separation that could take place. Due to the double nature of this molecule, also telechelic polymers possessing CPD moieties could be convenient in the design of thermoreversible networks. Other approaches involving HDA have been pondered[64]. Dithioesters have been chosen as electrophiles among other molecules because of their excellent reactivity with CPD, which ensues extremely rapid transitions. While furan-maleimide and CPD-based systems polymerize or cross-link in the bulk for hours or days, a functionalized PMMA can cross-link in minutes via a pyridinylthioformate tri-linker. However, due to the low decomposition temperature of the latter, few healing cycles are possible. Furthermore, the presence of trifluoroacetic acid as catalyst and the difficult synthesis of the various compounds hinder the process simplicity needed for a fruitful introduction on the market.

Diels and Alder were pioneers in what is now called dynamic covalent chemistry[65]. Most of the traditional methods to synthetise molecules through irreversible covalent bonding rest on the less energetic pathway to reach the desired product. This paradigm shifts when considering an equilibrium reaction: thermodynamic conditions can be controlled to enable the coexistence of different species, and stabilizing features can encourage a specific product to form. A sufficiently fast equilibration can overcome a bigger energy barrier and attain the wanted species. To shed light on this exotic mechanism, the underneath diagram wishes to represent two types of reaction (fig. 27). **A** gives **C** in a kinetically controlled reaction, since the considered transition state has more probability to be surmounted according to Arrhenius equation ($\Delta G_C^{\ddagger} < \Delta G_B^{\ddagger}$). In contrast, because $\Delta G_B < \Delta G_C$ the stability of **B** will dominate in a thermodinamically controlled reaction, and, in this occasion, **A** engenders **B** rather than **C**.

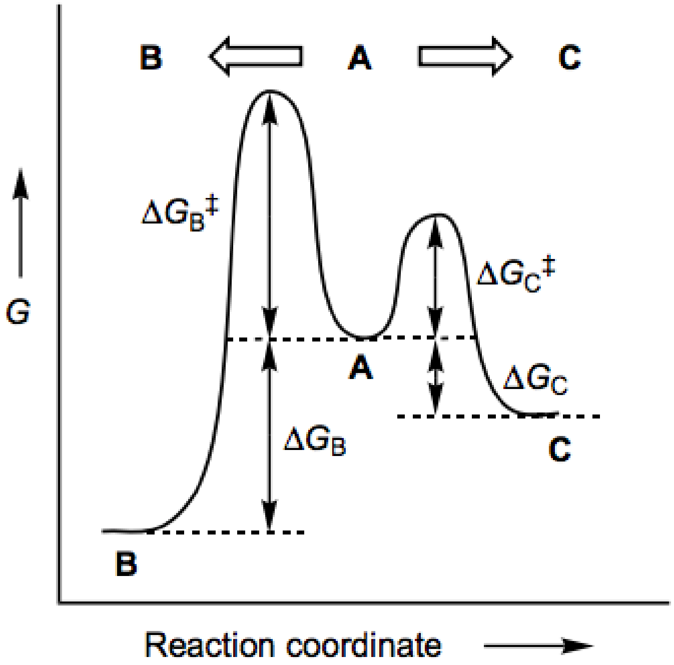


Fig. 27 Diagram illustrating the energy *niveau* depending on the reaction coordinate

Dynamic covalent chemistry can be useful in the design of novel remendable polymers by taking advantage of the reversibility of the reaction to construct different molecular architectures in order to tune the material's properties.

2.2 Alkoxyamines

A noteworthy healing mechanism stands on the dynamic NO-C bond of alkoxyamine[66](fig.28). This particular unit has been selected due to its thermodynamic stability and easily tunable temperature transition. At room temperature, this bond behaves as covalent, but through a radical exchange promoted by thermal energy it can homolytically cleave, leaving a styryl radical and a stable aminoxyl radical, such as 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO).
The concept of reversible terminator in free radical polymerization has been known for more than two decades, and has been exploited to obtain narrow polydispersity resins[67]. In 2007, a reversible sol-gel transition has been achieved by Higaki *et al.* from a linar poly(methacrylic ester) containing pendant alkoxyamine units, proving they can act as efficient cross-linkers. Heating the synthesized material induced the formation of carbon and nitroxide radicals, thus promoting their rearrangement, which originated a subsequent intermolecular bond, as depicted in figure 29. As previously discussed, dynamic covalent bond behaviour strictly depends on the equilibrium reaction: de-cross-linking is then achieved by adding an excess of alkoxyamine to disrupt the stoichiometric conditions. This self-healing strategy is surprisingly interesting due to the dynamic nature of these interactions, in some manner similar to those

present in supramolecular architectures, combined with the structural enhancement given by the strong covalent bonding.

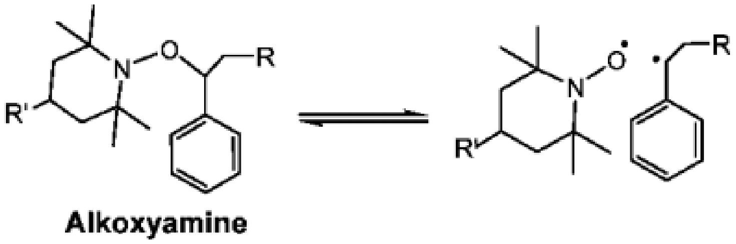


Fig. 28 Alkoxyamine dissociative equilibrium reaction

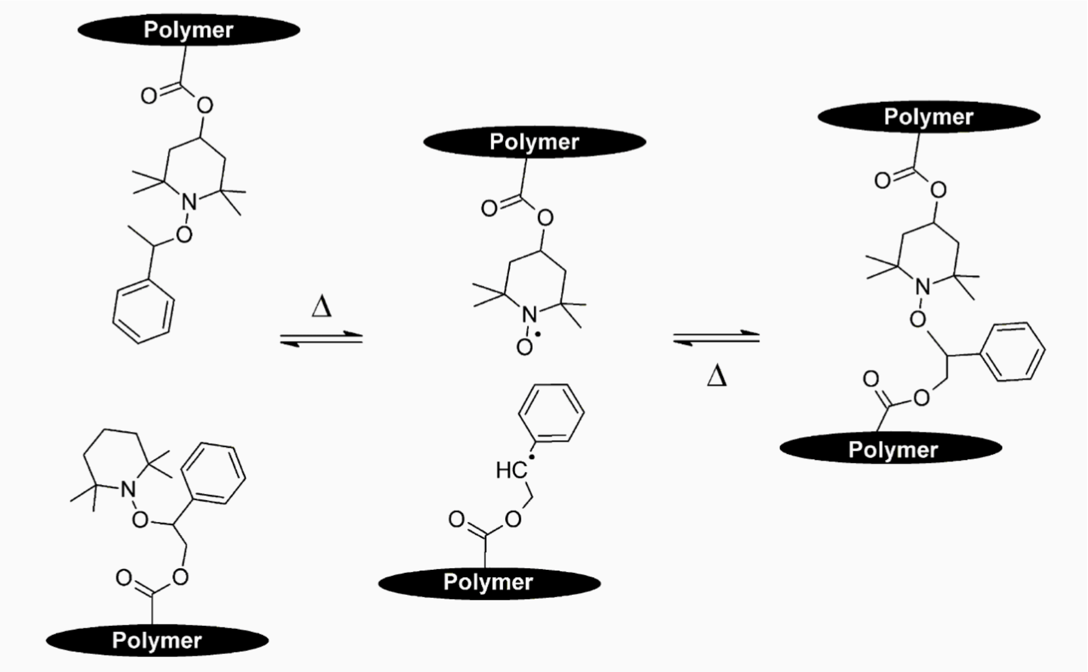


Fig. 29 Alkoxyamines radical exchange reaction promoting cross-linking

2.3 Disulfide bonds

Several other dynamic covalent bonds can be useful in self-healing chemistry, like the disulfide bridges[68]. Their self-healing property stems from the capability to cleave and create two thiol groups under reducing ambient coupled with the restoration of the link through oxidation. By functionalizing a rubbery epoxide, self-healing was achieved after 80 minutes at 60°C. In fact, the low T_g permitted the fast recovery of mechanical properties thanks to the polymer intrinsic chain mobility. The rapid recovery was confirmed by placing two pieces of epoxy into close contact: after 15 minutes they fused together and composed a monolithic structure.

2.4 Photoinduced healing

A different reversible covalent bonding concept was developed by Chung *et al.*[69]: in their work the recovery of mechanical properties was induced by UV irradiation (fig.30). Photoreactions are attractive for self-healing by virtue of being sensitively faster than most of reactions that occurr in thermally mendable polymers, while being environmentally friendly. The research team focused its efforts on 1,1,1-tris-(cinnamoyloxymethyl)ethane (TCE), which has the ability to convert its carbon-carbon double bonds into a cyclobutane cross-link via a [2+2] cycloaddition promoted by light.

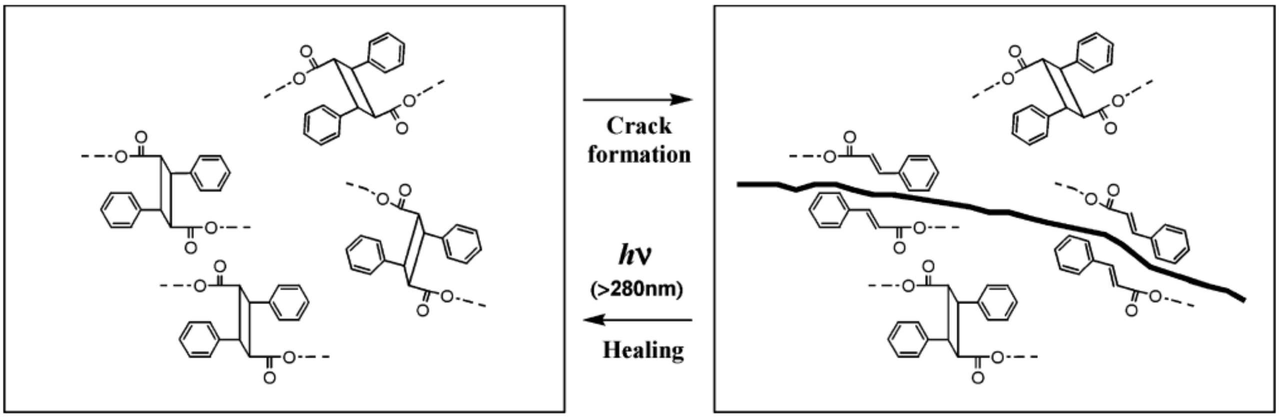
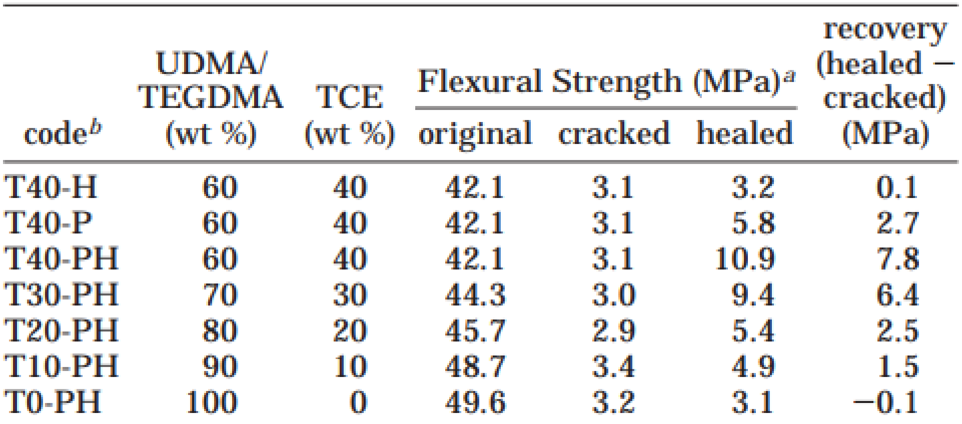


Fig. 30 Self-healing photoinduced mechanism of cinnamoyl moieties

Experimental results concerning specimens based on TCE, methacrylate monomers, and a visible-light photoinitiator (camphorquinone) were presented. In this proof of concept , 1,6-bis(2′-methacryloyloxyethoxycarbonylamino)-2,4,4-trimethylhexane (UDMA) and tri(ethylene glycol) dimethacrylate (TEGDMA) were used as monomers. Polymers were synthesized by light-induced radical polymerization, and have been irradiated (P stands for photoirradiation) for ten minutes with light of wavelength superior to 280 nanometres. Some of them were heat treated to 100°C for ten minutes, and the code representing those ones is H. Nonetheless, the flexural strength recovery wasn't too great, as reported in the table below (Tab.1), achieving at most 18,5% for T40-PH specimens.



code[b]	UDMA/ TEGDMA (wt %)	TCE (wt %)	Flexural Strength (MPa)[a]			recovery (healed − cracked) (MPa)
			original	cracked	healed	
T40-H	60	40	42.1	3.1	3.2	0.1
T40-P	60	40	42.1	3.1	5.8	2.7
T40-PH	60	40	42.1	3.1	10.9	7.8
T30-PH	70	30	44.3	3.0	9.4	6.4
T20-PH	80	20	45.7	2.9	5.4	2.5
T10-PH	90	10	48.7	3.4	4.9	1.5
T0-PH	100	0	49.6	3.2	3.1	−0.1

Tab. 1 Experimental results of Chung *et al.*

3. Stress-responsive systems

In recent years the intensive study of the mechanical degradation of polymers brought to life a groundbreaking, counterintuitive concept: mechanochemistry[70](fig.31). The widely accepted idea that mechanical action negatively affects polymers' mechanical properties perhaps led to a bias that the applied force always results in a mechanochemical chain degradation. But what if mechanical energy could selectively transform chemical species to enable a healing ability? Naturally, the building block of this chemistry is the mechanophore, a molecular group reacting in a predictable fashion when subjected to a mechanical perturbation. Recently, many research groups innovated this relatively young field, bringing to light the potentially productive chemistry obtainable through a proper mechanical force and molecular design.

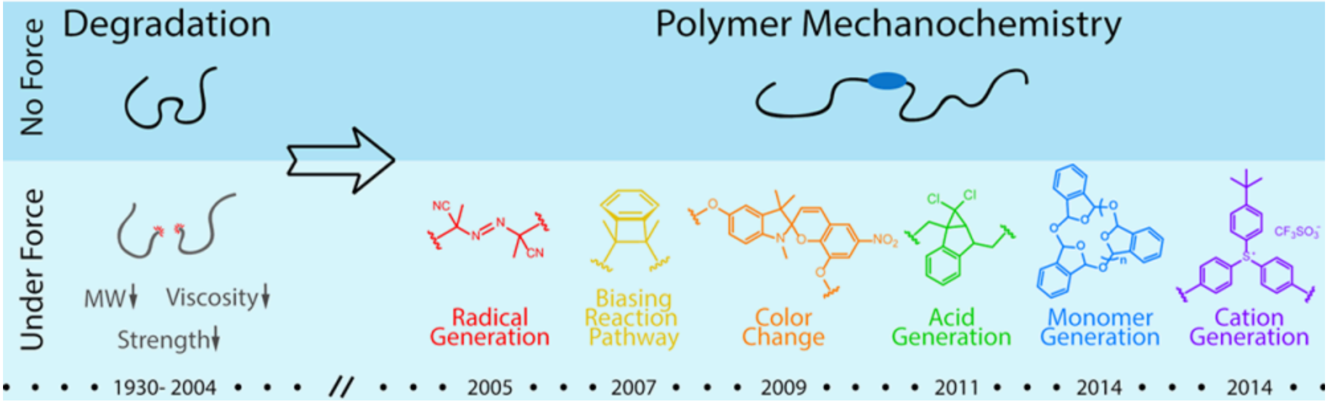


Fig. 31 Historical pathway of mechanochemistry

As a matter of fact, by introducing an azo linkage into a poly(ethylene glycol) backbone Berkowski *et al.*[71] proved that this labile linkage disrupted predominantly and in a specific manner via sonication, by analyzing the remaining chain fragments. The scission ensued the formation of relatively stable carbon radicals, which could recombine and restore the chain length. However, the reaction with oxygen or hydroxil radical probably hindered this radical recombination and produced cyanohydrin. Other systems have been examined to determine the possibility of generating reactive species. One of these has been explored by Kryger *et al.*[72] using a dicyanoacrylate-functionalized cyclobutane ring as mechanophore. Strained cyclic molecules such as cyclopropanes, cyclobutanes, and spiropyrans are commonly used mechanophores, while cyanoacrylates are known to be very reactive groups. To confirm the selective breakage a secondary amine has been chosen to provide a suitable active site; spectroscopy measurements clarified that the amine trapped the reactive cyanoacrylate. Potential self-healing can then be achieved by incorporating secondary amine groups in a polymer. Another approach to integrate self-healing abilities may rest on the activation of catalyst via mechanical stresses[73]. The biggest drawback of the majority of these systems, nonetheless, is the scarce mobility of the catalyst, which remains attached to the polymer backbone. For this reason, a new direction has been taken by Diesendruck *et al.*[74] by designing an elimination reaction, driven by aromatization, which gives off an acid catalyst. The low molecular weight of the latter allows its diffusion through the polymeric network, in this case constituted by poly(methy acrylate). To verify the mechanophore acid release, the authors performed Raman spectroscopy, differential scanning calorimetry (DSC), and further proved the expected mechanisms via methyl red as indicator. Other methods, based on the mechanical disruption of the equilibrium, have been investigated by several teams, demonstrating the wide range of possibilities of this novel approach[75,76].

4. Supramolecular networks

Since the advent of supramolecular chemistry, non-covalent bonding have been fundamental to understand and synthesize complex molecular architectures. The exceptional features displayed by such structures are inherent to the dynamism of their interactions, that may be exploited to achieve adaptive materials[77]. Supramolecular polymers are of interest in self-healing by reason of these characteristics, which can be designed to control their self-assembling. Depending on the nature of the monomers and on the typology of interactions, a wealth of novel functionalities can be implemented. Since non-covalent linkages are weaker than covalent bonds, they are more susceptible to rupture, and can elicit rapid healing under the appropriate conditions. Several concepts have helped polymer science to achieve it, such as hydrogen bonding, metal-ligand coordination, and ionic interactions[78] (fig. 32).

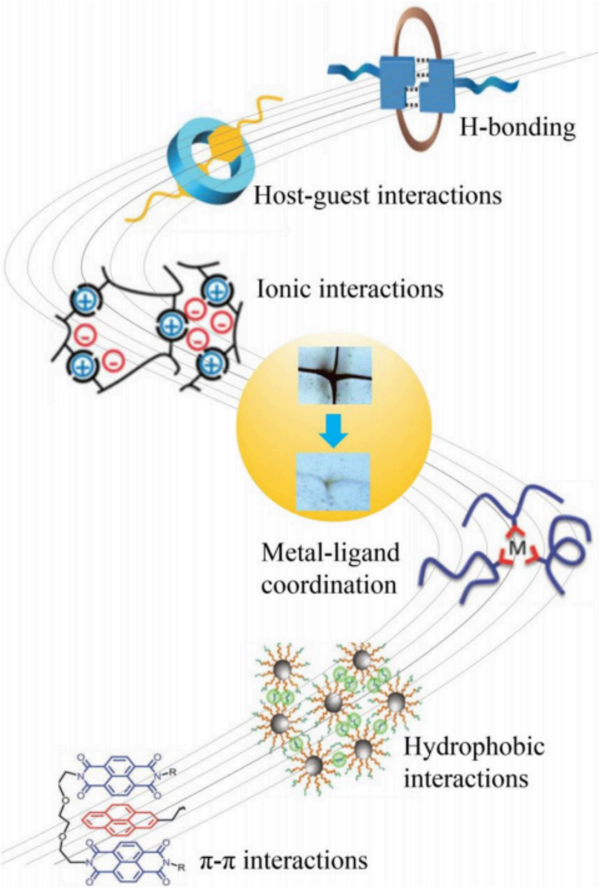


Fig. 32 Various supramolecular mechanisms to achieve self-healing polymers

4.1 Hydrogen bond

One of the most used methods to achieve supramolecular networks is via the H-bond. This linkage arises from the electronegativity of the atom bearing the hydrogen, called the hydrogen bond donor. Instead, the hydrogen bond acceptor is an atom possessing a lone pair of electrons, such as oxygen. Its dissociation energy is relatively low compared with covalent bond, ranging between 0,2 and 40 kcal mol $^{-1}$, and is sensitive to its surroundings[79]. To build a supramolecular polymer different chain units can be used (fig. 33). Furthermore, a linear polymer chain with a functional group attached to both chain ends can create several architectures, that relate to the specific association dynamics of the system.

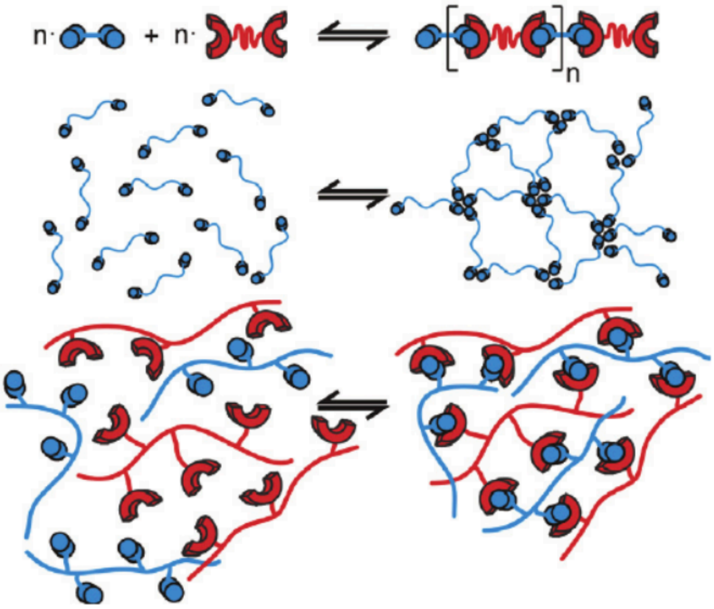


Fig. 33 Association modes of supramolecular networks

By controlling the number and the nature of hydrogen motifs as well as the matrix of the polymer, its properties can be tuned to achieve a healing ability combined with sufficient mechanical resistance. A vast variety of non-trivial effects can influence the aggregation behaviour of these materials and can lead to microphase separation[80], such as film and fibre formation[81], or crystallization[82] for example. These features can be useful if well controlled: Chen *et al.* obtained a thermoplastic elastomer composed of a soft polyacrylate amide (PA-amide) matrix and nanospherical polystyrene (PS) domains (fig. 34). The former acted as a molecular "velcro", controlled by the sticker-like response of the PA-amide brushes grafted onto the PS backbone. The latter, instead, contributed to the stiffness of the resulting polymer: by varying the styrene weight fraction from 3 to 7%, Young's modulus triplicated. Although the static properties (i.e. creep resistance) of non-covalently bonded materials are quite low, other applications are suitable, where the main load conditions are cyclic rather than static.
Self-assembly of supramolecular architectures can also result into other morphologies. Using poly(tetrahydrofuran) (THF) telechelic macromonomers Rowan *et al.* investigated the diverse connections of the binding motif. In this study, two materials have been synthesized, in which the end-chain group was either thymine or adenine; to prevent unwanted binding the adenine site was carefully protected. It has been claimed that the poly(THF) chains bearing the adenine group aggregated to form ordered structures, as mentioned before, even if the homodimerization constant of both nucleobases is relatively low. This feature is thought to arise from other factors, such as π-π stacking. These interactions are of attractive character, and originate from aromatic π orbitals. In fact, the reduced π surface of poly(THF) with thymine can be one of the reasons why fibres couldn't be observed. A paper focused on a self-healing elastomeric blend based on both hydrogen bonding and π-π stacking was published by Burattini *et al.*[83] to demonstrate the potential of these interactions. To enhance this

stacking behaviour a complementary motif has been developed by employing a polyimide containing π -electron-deficient naphtalene-diimide units and a π -electron-rich pyrenemethylurea end-capped polyamide. The functionalized structure of these two macromolecules leads to a singular chain conformation in which bis(diimide) chain folds accomodate the pyrenyl residues, as depicted in figure 35.

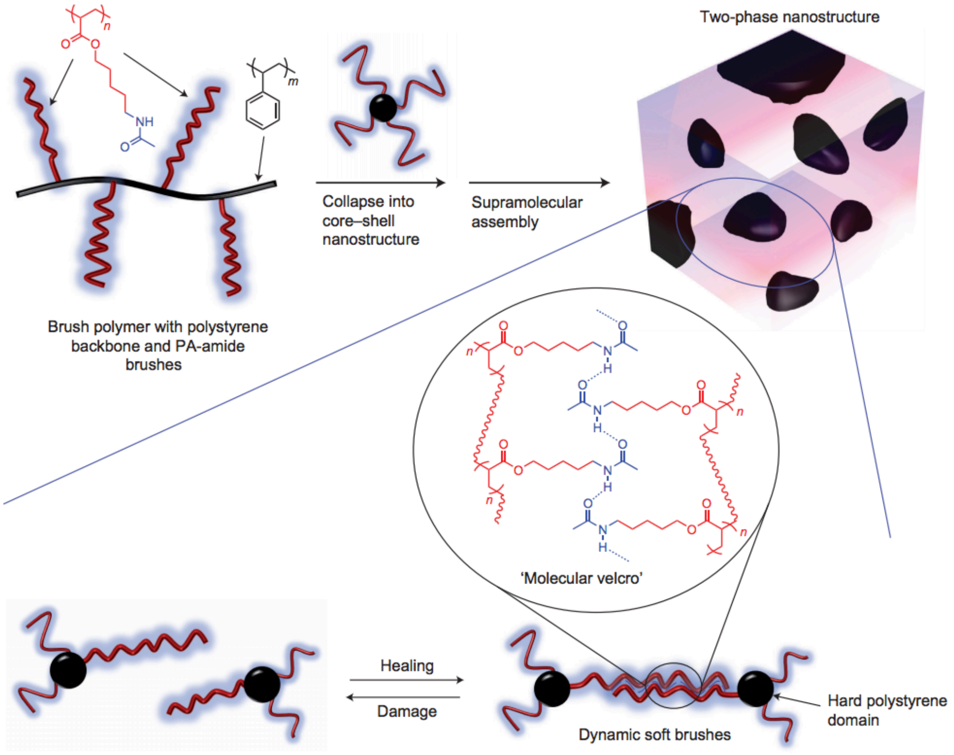


Fig. 34 Brush polymer supramolecular structure

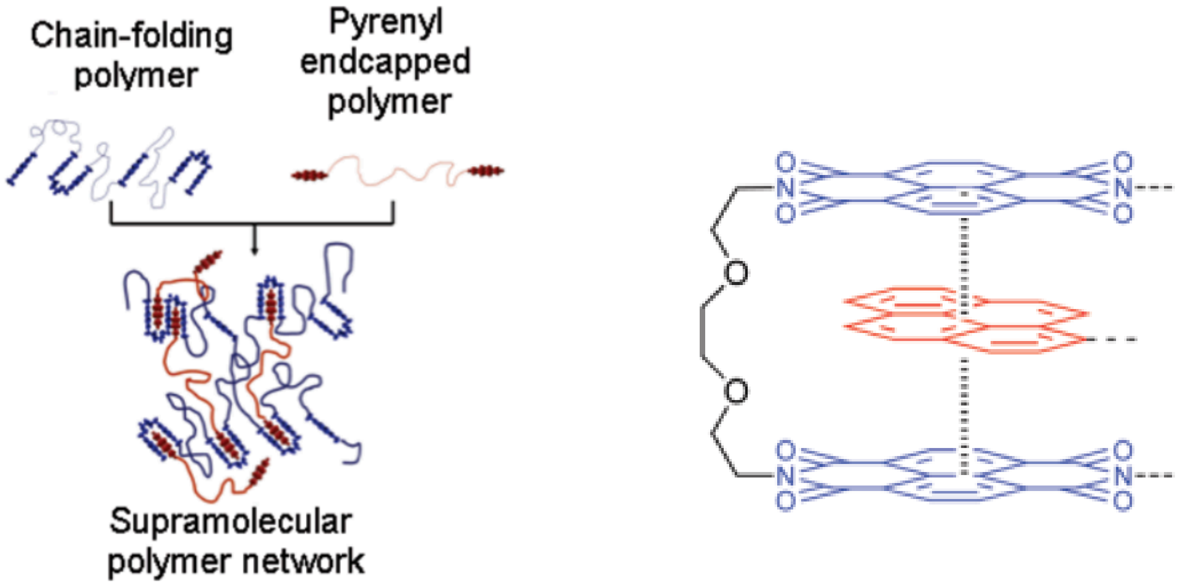


Fig. 35 On the left: Schematic structure of the elastomeric blend. On the right: Proposed stacking between π orbitals

Computational simulations using molecular dynamics allowed the team to explicit the complex interactions of the obtained blend. Not only π-π stacking, but also a less predictable hydrogen bonding was revealed between urea NH groups to a single diimide carbonyl moiety. This model was confirmed by both spectroscopic and X-ray scattering techniques. The obtained elastomer had good mechanical properties, possessing a tensile modulus of 0,3 MPa as well as an elongation at break of 170% and a modulus of toughness of 510 MPa. Healing was achieved by heating at 100°C for different periods, reaching the maximum recovery after 200 minutes approximately. The material regained 70% of its original modulus of toughness, and could sustain five healings, during which the recovered mechanical properties remained roughly constant.

4.2 Metallopolymers

Metal-ligand coordination is an attractive feature for self-healing polymers. Compared with H-bond, these interactions can reach up to 95% of the binding strength of a covalent C-C bond, and can display interesting attributes, such as optical and magnetic properties[84]. Already in 2001 Vaccaro and Waite reported the natural recover of mussel byssal threads[85]. They observed how several metals, among which iron, zinc and copper, could influence the mechanical properties of this biological material. In fact, the latter contains a catechol-like aminoacid, dihydroxy-phenylalanine (dopa), which possess chelating properties; for this reason, other researchers further investigated the metal-ligand interaction of this organic moiety. Holten-Andersen *et al.*[86] synthesized a polyethylene glycol decorated with dopa to introduce catechol-Fe^{3+} complexes in the polymer structure. These possess a high stability, and can be tuned by varying the pH conditions, as shown below (fig. 36). Spectral and rheological measurements indicated that *bis*- and *tris*-catechol-Fe^{3+} appeared in the structure when raising the pH , and the elastic response increased accordingly to the formation of these metal-ligand cross-links. For this reason, it was proposed that byssal gland cells maintain the mono-complex thanks to a low pH, and the consequent raise in the pH due to seawater contact automatically induces a cross-linking reaction.

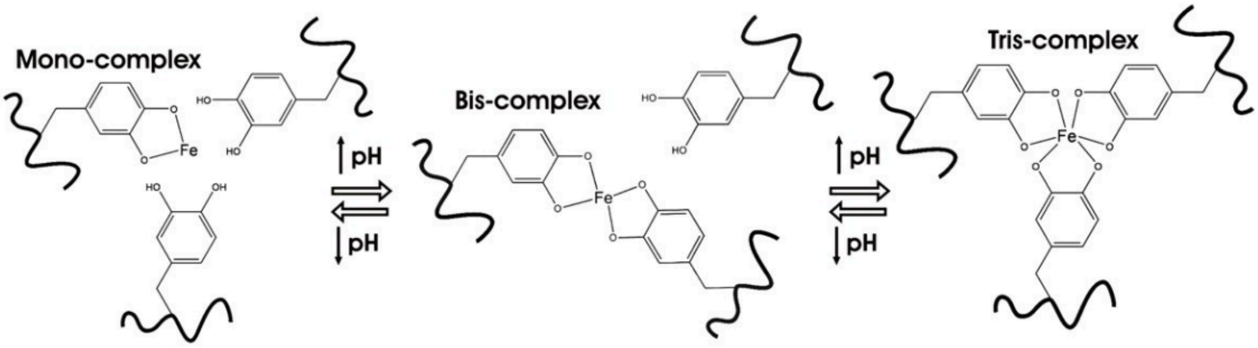


Fig. 36 Catechol-Fe^{3+} complexes behaviour at various pH

Several other ligands can be employed to build supramolecular structures, such as histidine[87], and pyridinyl[88] moieties. Burnworth *et al.* used the latter to construct a linear metallopolymer showing self-healing abilities under UV irradiation. The elastomeric material was composed by a poly(ethylene-*co*-butylene) hydrophobic core capped by 1,6-bis(1'-methylbenzimidazolyl)pyridine (Mebip) at both ends, which acted as a chelating agent on La^{3+}

or Zn^{2+}. The metallic component was incorporated through bistriflimide (Ntf_2^-), a weakly coordinating counterion which is thermally stable. After solvent evaporation and compression moulding, the obtained films were investigated by means of transmission electron microscopy and small-angle X-ray scattering (SAXS). It was deduced that the material formed a lamellar nanostructure by phase separation between the soft copolymer matrix and the strong metal-ligand cross-links. Healing experiments were conducted by irradiating the films with UV light with a wavelength corresponding to the absorption band of the polymer. Two consecutive exposures of 30 seconds were sufficient to heal a scratch completely by disrupting the coordination sites through thermal energy. The complexes reformed upon cooling, immobilizing the soft phase and regaining the material mechanical strength.

4.3 Ionomers

Other types of non-covalent bonding can allow healing abilities, such as ionic interactions. When polymers bear up to 20 mol.% of ionic species, they cannot be considered polyelectrolytes, and possess different features compared with neutral macromolecules[89]. As such, ionomers represent a particular set of materials, combining ionic and neutral regions in the same chain. A concept, based on thermal expansion studies and differential scanning calorimetry (DSC) of a methacrylate-based ionomer, paved the way for the understanding of structure-property relationships[90] . This thesis demonstrated the importance of microphase separation, since these experiments showed an order-disorder transition which has been related to ionic cluster relaxation. These aggregates are formed by the overlap of several subunits, known as multiplets (fig. 37). In these regions, the ionic binding exerts a constraint over the polymeric backbone, and serves as cross-linking function.

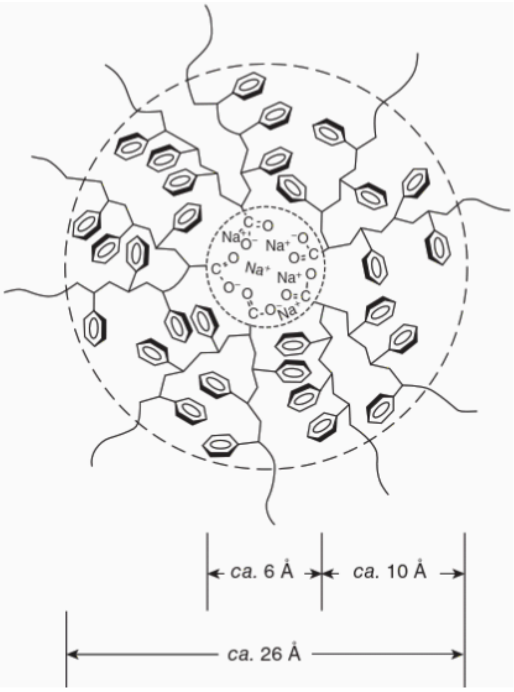


Fig. 37 Schematic representation of a poly(styrene-*co*-sodium-methacrylate) multiplet

This peculiar nanostructure rewards ionomers with some mechanical properties over their neutral counterpart, as illustrated in rheological measures[91]. It is true that an increased temperature perturbates the aggregational order of multiplets, but flow can be achieved even without completely suppressing ionic interactions, which, on average, sensitively raise the melt viscosity. By changing the nature of the ionic groups, their position and number along the chain, its flexibility, the coordination strength of the counter-ions and the dielectric constant of both the polar and non-polar groups ionomers can be tailored to fulfill specific purposes. One of these can be the self-sealing capability after a ballistic impact[92]. It is proposed a two-stage mechanism during which the ionomer reacts to seal and consequently heal the damage. Different poly(ethylene-co-methacrylic acid) (EMAA) random copolymers were subjected to a penetrating ballistic impact, and diverse test were used to investigate the effective sealing strength. The thermal energy dissipated upon impact locally melts the EMAA, which elastically responds to close the fracture. Then, the molten interfaces merge together via molecular interdiffusion, which allows mechanical properties to recover. However, it was found that it is not merely the ionic content that contributes to this healing behaviour. Instead, polymers having a sufficient acid content displayed thermomechanical recovery, proving that ionic content is not necessary to ensure elastic retraction.

IV. Characterization of self-healing performances

Self-healing polymers are now a growing sector in polymer science, due to the numerous possibilities to overcome the natural degradation of these materials. As a matter of fact, bioinspiration has a key role in the developement of this visionary paradigm: the relationship correlating structure with functionality seems to be a fundamental constant in all hierarchical levels of living beings. From the molecular to macroscopic dimensions, life can provide an exceptional source of information that can be acquired by a detailed analysis. It has been described how the complex world of healing can endow polymers with great potential to excel. However, this paradigm shift in the damage field must be accompanied by a similar translation of the traditional, static characterization methods into more dynamical ones to monitor the recovery of properties.

1. Visualization techniques

Various procedures can be implemented to assess the quality of the healing. One of the most used technology is microscopy, which is based on the interaction between mechanical or electromagnetic waves and the material to analyze. Optical microscopes use visible light to extrapolate information about its microstructure, and are limited by the diffraction limit d

$$d = \frac{\lambda}{2\,NA}$$

where λ is the wavelength, roughly ranging from 400 to 700 nm, and NA is the numerical aperture of the optical system. This means that the minimum resolvable distance for these apparatus lays between 0,3 and 0,4 microns, but thanks to high refractive index oils the resolution can be improved to approximately 0,2 μm. Although this method is qualitative more than quantitative, several softwares can be implemented to generate important statistical informations such as the size distribution of microcapsules[41].

To avoid diffraction-limiting measures, scanning electron microscope (SEM) is often employed, as it presents several advantages, such as a larger depth of focus and a higher resolving power, which allow to render features of the order of the nanometre by using field emission effects. Electron-matter interactions have been extensively studied, and SEM can also infer compositional features through the analysis of backscattered electrons . However, the electron beam penetration depth restricts its usage to near-surface analysis, hindering the evaluation of subsurface mechanisms. In addition, to extend the mean free path of the propulsed electrons, vacuum is needed to gather valuable data. This condition reduces the possibilities to monitor healing via liquid and volatile substances, frequently utilized in extrinsic self-healing. The environmental SEM (ESEM) overcame this physical constraint by separating the high vacuum region near the emitting tip from the high pressure chamber where the sample is placed[93]. Liquid healing agents can be then monitored as they fill the crack plane; additionally, ESEM can show how moisture can influence the healing behaviour. Miccichè *et al.*[94] proved the effectiveness of this technique by allowing a multi-layered coating to absorb the ambient humidity. The coating was composed by a polysiloxane topcoat over a thin montmorillonite film, and the latter acted as the healant. Montmorillonite is a phyllosilicate with a lamellar structure, and expands in contact with moisture due to the increase in size of the solvation shell of interlamellar cations. The coating was scratched, and the ESEM provided a clear picture of the filling compound (fig. 38); an energy-dispersive X-ray spectroscopy (EDX) confirmed that it was montmorillonite.

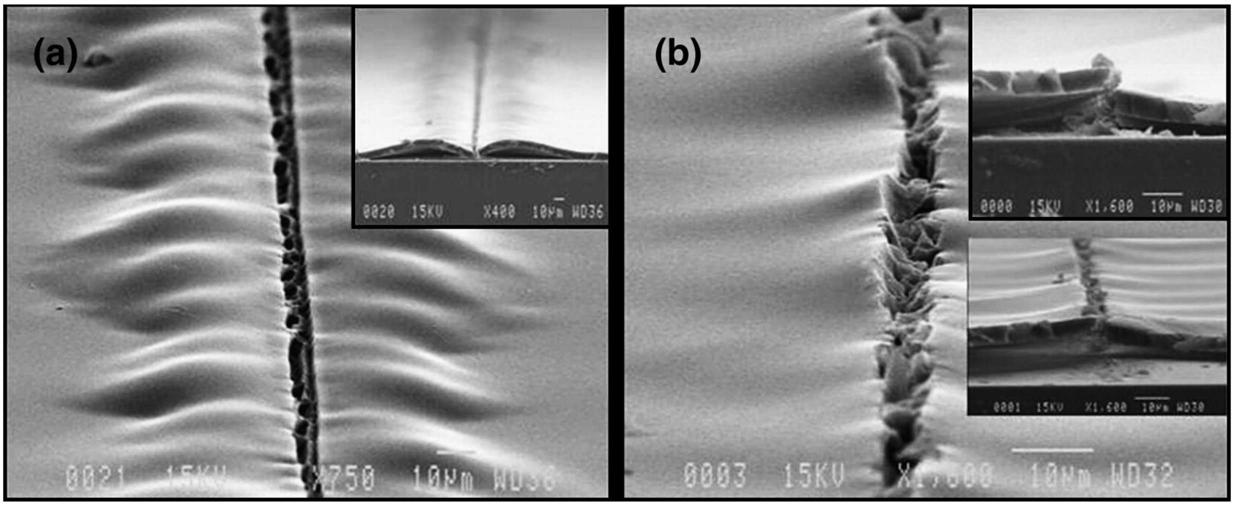


Fig. 38 ESEM images of a scratch before(a) and after 21 hours of healing (b)

As previously mentioned, inferring a quantitative performance from images can be challenging. In the discussed study, another visualization technique has been used, the confocal microscopy, or scanning laser confocal microscopy (SLCM). This method acquires topological informations of surfaces through an optical sectioning. The scratches produced a variation of roughness, which could be measured by the line profiles obtained by slicing the three-dimensional confocal image (fig. 39). The dash line was chosen to quantify the damaged area, and the dashed region identifies the induced defect volume. After two hours at 50°C under moist conditions, the crater width was significantly reduced. Keeping the coating with these conditions provoked a further expansion of the clay layer, which created higher peaks. These techniques are extremely valuable to characterize surface healing, which is critical in different applications due to the adverse effects of surface defects. These can act as stress concentrators or incubate corrosive products which may lead to environmental stress cracking, and it is well known that surface quality sensitively impacts fatigue resistance. Furthermore, they can be esthetically unpleasant, reducing surface gloss.

SLCM has also the potential to induce fluorescence[95]. By introducing fluorophores into a supramolecular structure, not only surface information, but also depth-dependent data can be collected. The emission intensity of the fluorophore is attenuated by the overlaying polymer, and can then provide a clearer picture of the healing in the bulk.

Another important technology that permits a three-dimensional visualization of healing is computed X-ray microtomography[96] (μ-CT). By reason of the high penetration ability of X-rays, the internal structure can be examined thanks to the constrast stemming from the different densities of the various phases. This technique in particular can help visualizing the rupture of embedded microcapsules containing a liquid. Process imaging can further improve the investigation (fig. 40).

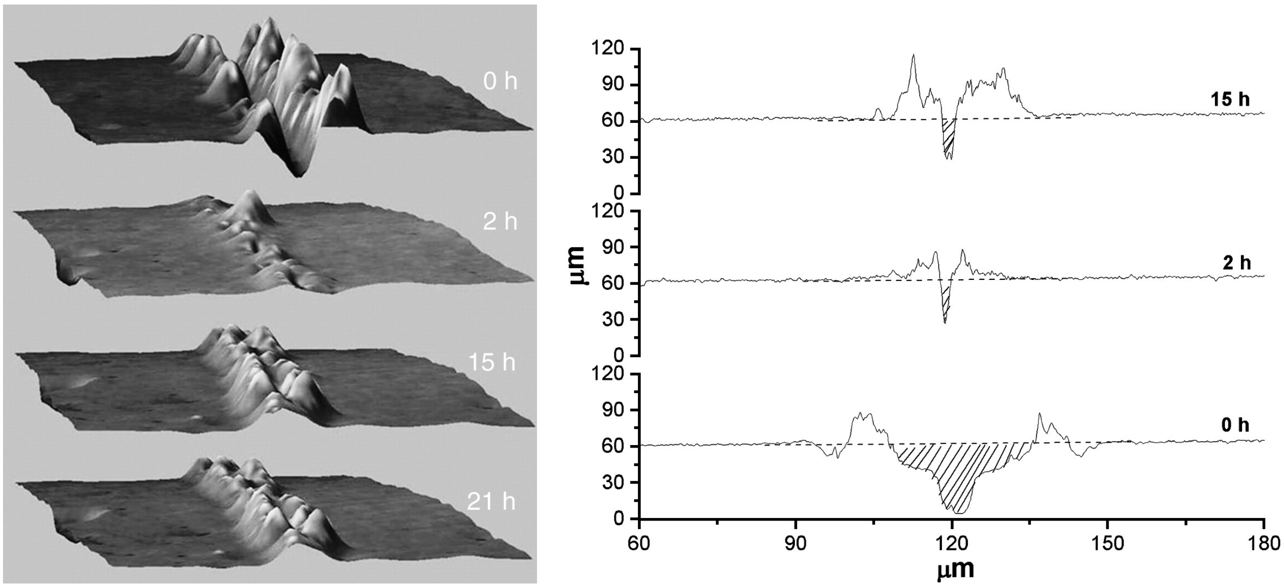


Fig. 39 On the left: Healing monitored by confocal microscopy. On the right: Surface roughness profile over time.

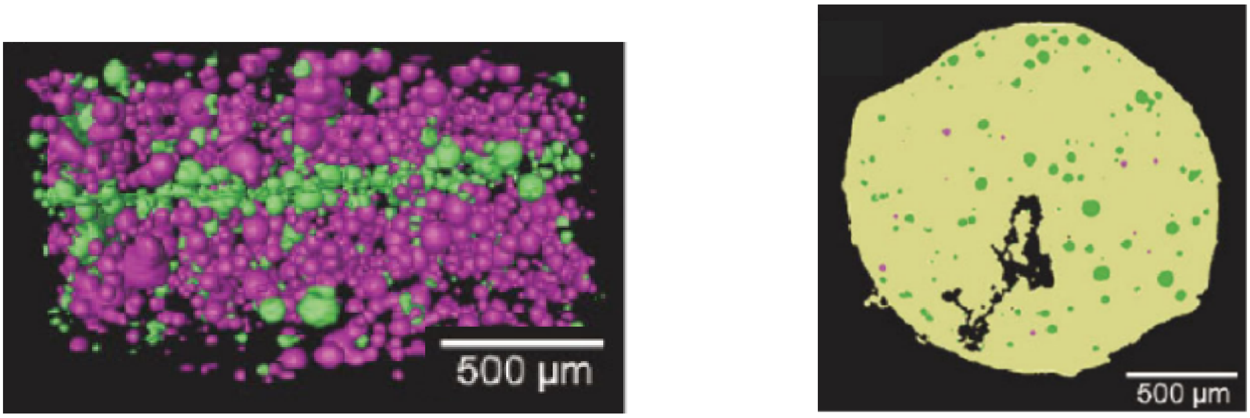


Fig. 40 The image on the left represents the ruptured capsules in green and the full capsules in purple. The image on the right shows a bidimensional slice of the reconstructed data near the crack plane. The darker region was unaffected by healing.

2. Mechanical recovery

As already discussed in the second chapter, the recovery of the mechanical properties can be calculated as a percentage of the virgin material property. Diverses methods are used, depending on the property to quantify (yield strength, strain at break, shear strength, etc.) . One of the most used technique employes an universal testing machine to infer several parameters, such as the fracture load[28,40]. The tapered double cantilever beam (TDCB) specimen (fig. 41) is one of the most used because of its insensitivity to crack length. This geometry reduces the bias caused by the dimension of the crack, which can strongly influence the healing efficiency. Moreover, multiple healing cycles can be conducted and the realignment of partial fractured specimens can be done with relative ease compared with other tests. It was showed that this method can also be applied to evaluate the fatigue healing efficiency[97]. Other typical measurements test the compressive strength of the specimen, which can be then healed to recover their initial shape (fig. 42).

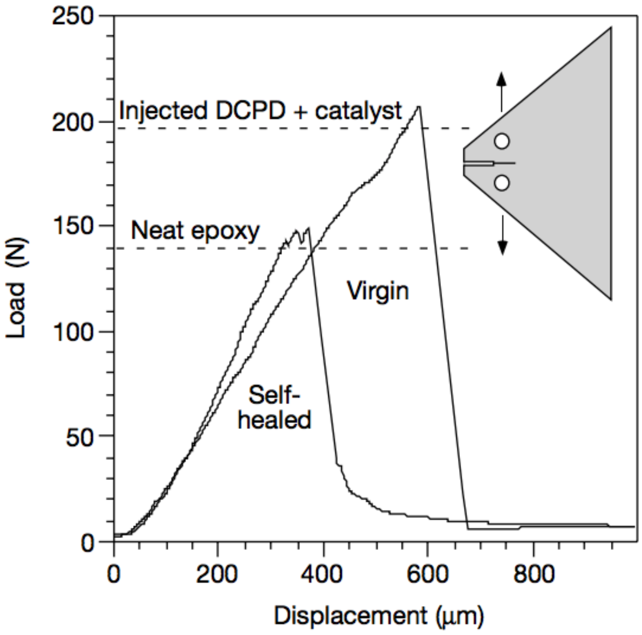


Fig. 41 Typical load-displacement curve for a TDCB test

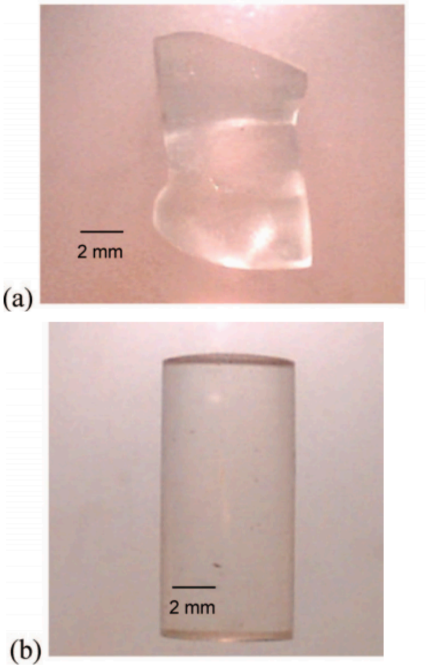


Fig. 42 DCPD-based specimen before (a) and after healing (b)

The adhesive capability of healed samples can also be tested by a lap shear test. In this case, the two surfaces can be accomodated in a predictable fashion which minimizes topological defects due to a misalignment. The ultimate shear strength or the displacement at break can both be essential parameters to value the healing capability of the system. As in the TDCB test, multiple healing can be evaluated on the same sample without changin the setting of the experiment.

Defects in a material contribute to a variation of not only mechanical, but also electrical and thermal properties. Current-voltage measurements can be conducted on pristine samples, and the observation of current drops or rise can be an evaluation parameter to estimate the impact of damage. Using this technique Caruso *et al.*[44] demonstrated its feasibility.

3. Functional characterization

Thermal analysis are one of the most important techniques used to characterize the healing behaviour, since many mechanisms involve an increase in temperature to activate. Especially in extrinsic healing, the dispersed phase must sustain the curing temperature of the resin, and thermogravimetric analysis (TGA) is crucial to determine the thermal stability of the embedded agent. Another typical techniques employed to determine the characteristic temperatures of polymers is differential scanning calorimetry (DSC), from which the glass transition temperature, as well as other phase transition temperatures can be determined.

Rheological measurements are also fundamental not just in the evaluation of viscoelastic changes, as occurr in ionomers[91], but can also provide a wider view of the specific self-healing mechanism. Supramolecular architectures and dynamic covalent bonds yield a complex rheological behaviour which reflect their molecular structure. To understand the viscous and elastic responses of melt dynamics the dynamic mechanical analysis (DMA) has been largely used (fig. 43).

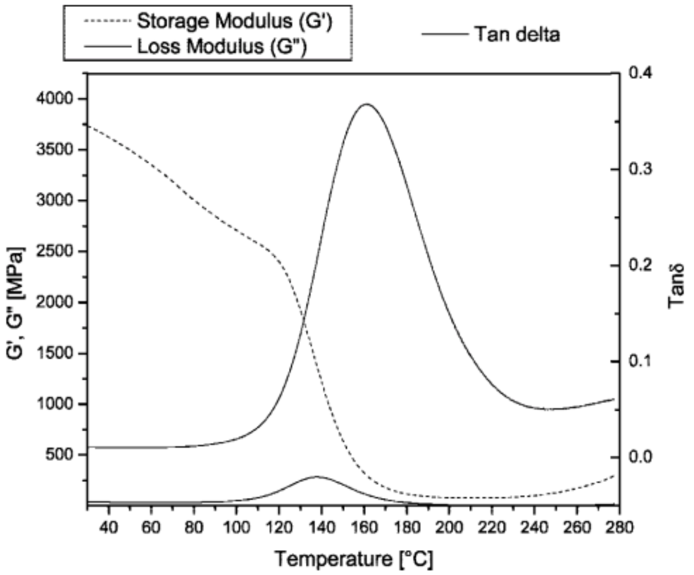


Fig. 43 Example of DMA of a DCPD-base polymer

Self-healing polymers have a great potential in the fabrication of innovative coatings, hence the esthetic performance must be assessed. A crockmeter can be employed to measure variations on the surface gloss: a controlled transverse load scratches the surface[100]. The coating can then be healed and its reflecting light intensity would correspond to the repairing that occurred. A more detailed quantification of gloss recovery can also be achieved through attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR) and internal reflection infrared imaging (IRIR)[101]. These two techniques allow to monitor the healing with high spatial resolution and can provide some informations on the chemical species supporting it. Several other spectroscopic measurements are helpful in determining the reaction kinetics, such as the nuclear magnetic resonance microscopy (NMR), which can precisely discriminate between various chemical species. In that way, a deep understanding of the reactions that establish the healing function can be reached[71].

Electrochemical impedance spectroscopy (EIS) is one of the most used procedures in corrosion science to identify degradation. This measurement is done by using a small, alternating electric field which induces several dielectric mechanisms depending on the impedance character of the analyzed material, which is immerged into an electrolyte. This technique can be useful to optimize the corrosion resistance of self-healing polymers with embedded microcapsules[102].

V. Applications

The damage management character of self-healing materials reflects one of the many features that distinguish complex biological organisms. This peculiarity has found some important interest in the aerospace sector, as demonstrated by one of the first papers on autonomic healing[40], which was sponsored by Air Force Office of Scientific Research (AFOSR) Aerospace and Materials Science Directorate. But other specific purposes can be improved through the implementation of a healing property. For instance, self-sealing tires[103], protective coatings[104] and other applications are of commercial interest.

1. Fibre-reinforced composites

Since the advent of epoxy composites, which possess high specific strength, a thoroughly research was performed to reduce several critical aspects regarding composites. Specifically, these components suffer from fatigue and impact degradation. A central parameter in composites is notoriously the interface bonding between fibres and the matrix. Delamination is a common cause of mechanical failure in such structures, and healing of interfacial cracks can significantly enhance their service life. A thermoremendable composite have been developed to overcome this issue[105]. By exploiting the DA/rDA reactions between furan and maleimide moieties, the surface of glass fibres have been functionalized with maleimide and introduced in a thermosetting network involving furan. By heating for one hour at 90°C a healing functionality could be appreciated, demonstrating the validity of the process, which can be easily scalable. However, the scarce healing efficiency of 41% should be improved by increasing the density of maleimide groups on the fibres sizing and by further investigating the role of the T_g on the mobility required to attain a superior bonding.

Another approach has been taken by Merle *et al.*[106], focusing on the vast temperature range typical of aeronautic and aerospace operations. In fact, in space ambient the temperature may vary between -150°C and 150°C, depending on the orientation of the component with respect to the sunlight. This practical constraint propulsed the research toward chemical systems which can be activated also at low temperatures. Two types of capsules have been integrated: one with 5-ethylidene-2-norbornene (ENB), and another with a mixture of liquids in which was dispersed or dissolved a catalyst. Additionally, another catalyst was embedded in the matrix. The choice of ENB over the common DCPD lays on its lower melting point, which guarantees its flowability at lower temperature. Obviously, this strategy is expensive and complicated due to the harsh work conditions of the space environment.

Impact damages are frequent in aircraft vehicles, and can lead to almost undetectable voids which can propagate and reduce the reliability of the composite. In order to produce a self-healing composite, Sundaresan *et al.*[107] decided to combine the interesting properties of an ionomer with the excellent conductivity and mechanical strength of carbon fibres. The proposed ionomer is Surlyn 8940, which had already been tested by Kalista *el al.*[92]. The manufacture of a sandwich composite was obtained by melt-pressing; afterwards, it was subjected to a medium-velocity impact. The innovation of this approach consists in heating the carbon fibres via Joule effect to induce the melting of the Surlyn matrix. This physical approach can be helpful for the realization of healing, but supplementary studies should be conducted to prove its practical feasibility.

2. Self-sealing foams for pneumatic structures

Dutchman's pipe (*Aristolochia macrophylla*) is a type of vine commonly found in eastern United States, and has attracted several researchers by reason of a peculiar property[108]. In fact, the mechanical characteristics of its twigs has been studied, and it has been found a unique mechanism that efficiently seals the fissures caused by growth processes. This rapid repair is mainly accomplished by some turgescent cells, which have an internal overpressure. This plant inspired the synthesis of novel layers for pneumatic structures design. Polyurethane (PU) foam coatings have been cured under pressurized atmospheres to mimic the turgor of these parenchyma cells. To enhance the sealing effect, the foam was placed in the internal side of the structure in order to take advantage of the compressive strains provoked by the curvature. The system was constituted by the foam and a fibre-reinforced PVC membrane, as depicted in figure 44. The healing efficiency was assessed using the mass flow rate of air through a PU-coated membrane ($\dot{m}_{coat}$) and a non-coated one ($\dot{m}_{ref}$):

$$R_{flow} = 1 - \frac{\dot{m}_{coat}}{\dot{m}_{ref}}$$

The R_{flow} value of a PU foam cured with an applied overpressure of 1 bar achieved an excellent sealing efficiency of 0,999. A bioinspired chemical transfer has also been proposed, using polybutylacrylate grafted onto branched polyether cores (hyperPBA). This tailored system has a core-shell topology which acts as vescicle-like agent which diffuses near the damage to seal it. The PU foam modified with this peculiar chemistry showed good efficacy, with $R_{flow} = 0{,}992$. A supplementary latex layer has further improved the sealing capability, raising the efficiency to 0,999.

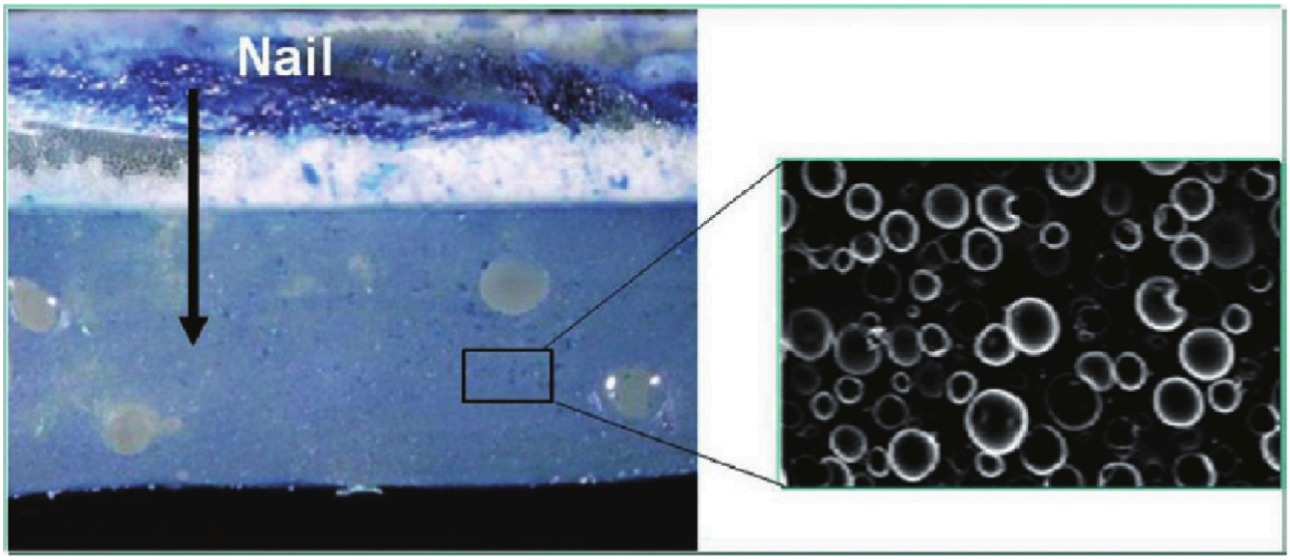


Fig. 44 On the left: PU-coated PVC membrane with an arrow representing the direction of the puncturing nail. On the right: SEM magnification of the PU coating.

3. Anticorrosive coatings

Protective polymeric coatings are an essential component in a wide variety of fields. From automotive to marine structures, they prevent corrosion and provide an accrued life service.
Since they are in contact with the ambient, they must possess a high stability to the present reactive species. Cho *et al.*[104] developed a coating based on two encapsulation approaches. The first considers the encapsulation of the catalyst (dimethyldineodecanoatetin, or DMDNT) and the phase-separation of two healing agents, HOPDMS and PDES (see chapter III, 1.2). The second is a dual capsule system, where both the catalyst and the reactive healants were encapsulated in a PUF shell. Despite the poor mechanical properties of the polymeric network resulting from healing, the reaction is unaffected by oxygen and water, thus guaranteeing a good protection also in a wet environment. To achieve a healing ability at room temperature, the catalyst has been changed to TKAS, and corrosion testing demonstrated its utility. Compared to DMDNT, it also doesn't require moisture for activation. To quantify the healing efficiency, four samples were prepared on a primed steel substrate (fig. 45). The first is the control specimen (a), and it consists of the neat epoxy matrix used for the coating, while the second (b) is the same resin supplemented with the two siloxanes and TKAS. The third (c) is a bi-layered commercial marine coating, and the last (d) is constituted by this last-mentioned thermoset and the self-healing system. The damage has been done with a razor blade by hand writing on the 100 microns coating. The test was conducted in 5 wt% NaCl aqueous for 120 h, while healing was performed at 20°C for 24 h. Striking differences between these materials undoubtedly supports the usefulness of the encapsulated healants.

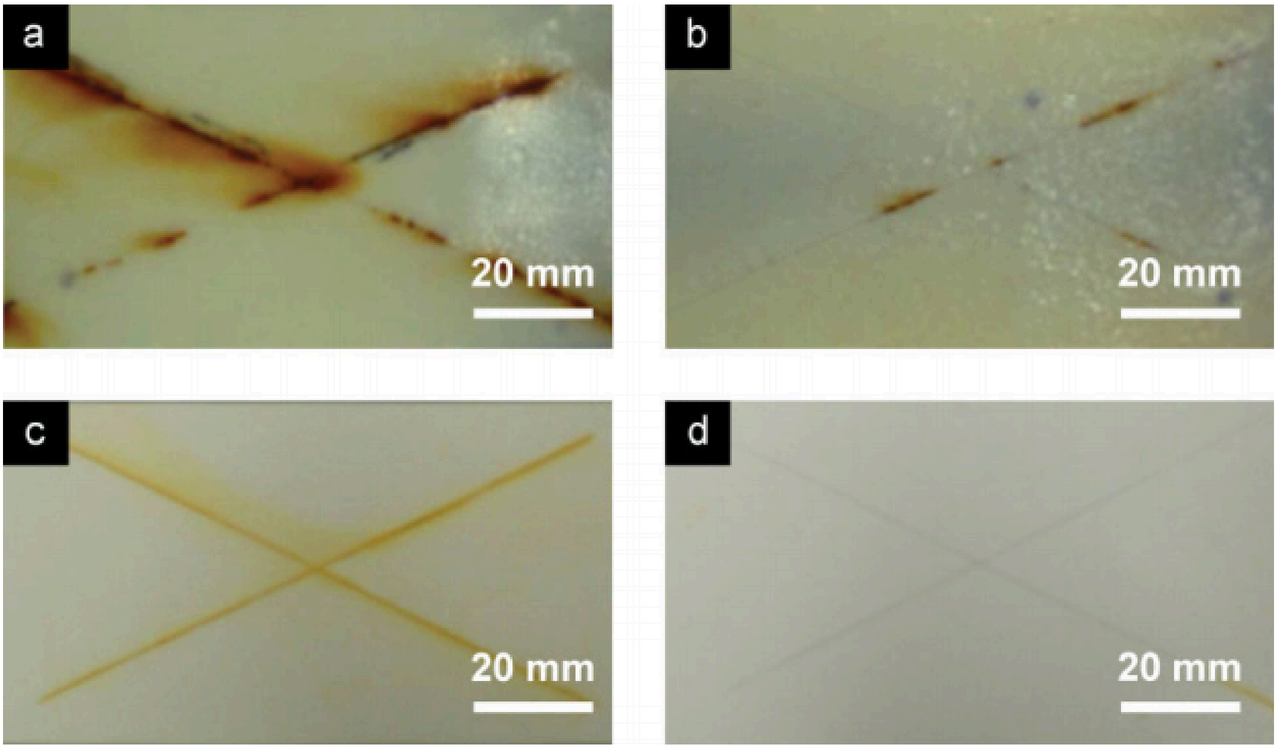


Fig. 45 Optical images of different specimens after corrosion testing

4. Other applications

In these last years, supramolecular chemistry has permitted to explore a wealth of astonishing features generated by the complex bonding behaviour possessed by these architectures. Self-healing is one of these characteristics, and can be combined to several others. For example, Martínez-Calvo *et al.*[109] synthesized supramolecolar gels using metal-ligand coordination in a host-guest approach. The ligand was composed by a pyridine-2,6-dicarboxylic acid together with picolinic acid, whereas the host consisted in a lanthanide ion, such as Eu(III) and Tb(III). When methanol was added, the polymer gelled thanks to the formation of dynamic cross-links. These ions possess some interesting photophysical properties, and even if their coordination properties are similar, their different electronic structure shapes the simmetry of the ligand electric field. In fact, under UV light these metallogels revealed completely different emission patterns, as showed by figure 46. Thanks to the high coordination number of lanthanides, a tridimensional network was formed and, thanks to its supramolecular character, had self-healing abilities. These combination of features may be useful in the production of electroluminescent devices with long lasting functionality.

Fig. 46 Luminescence due to Tb (green), Eu (red) and a mixture of both (orange)

Self-healing may also improve the durability of silicon microparticle anodes for electrical energy storage[110]. During the charge and discharge of Li-ion batteries, the anodes are subjected to important volumetric changes. This fatigue stress may cause cracks both in the silicon and in the conductive binder, hence, the long-term capacity is greatly reduced. Replacing the traditional binder with a more stretchable, self-healing one can effectively increase its service life while maintaining an acceptable capacity.

Dynamical bonds are extremely sensitive to their environment, and a stimuli-responsive character can be implemented in healing polymers. Tee *et al.*[111] developed a conductive organometallic supramolecular film which can act as an artificial skin for soft robotics applications. Another electronic application in which self-healing is desirable is in supercapacitors production[112]. Due to the increased flexibility of components and the continous miniaturization in electronics, the interplay between the electric flow and the mechanical deformation becomes more and more keen. These extensive cycling stresses can crack the material and cause a disfunction in the device. These issues can be overcome by implementing a self-healing ability to the polymeric substrate.

Conclusion

Self-healing is an important step in the paradigm shift of damage management. Time flow is unavoidable, and damages always occurr, potentially causing failures. Improving the performance of new polymeric materials is crucial in view of a greener future, where less material is required and quality is foremost. New, exceptional techniques provide profound and enriching insights into the nanometrical events that populate these extraordinary materials.

Biomimicry has been an important actor in the blooming of these polymers, showing that natural world is full of fine-tuned systems where everything is utterly optimized and balanced with its environment. Clarifying the structure-function relationship yields configurable, exotic behaviours which can be exploited to ameliorate the performance of devices and structures. Diverse physical models have been conceived during years, and computational methods have helped acknowledging the hierarchical dynamics of polymers, from the chemical structure to its viscoelastic behaviour. Nowadays, self-healing is no more confined to a purely mechanical function. The strength recovery is still investigated for structural purposes, but the ambition of scientists broadened its potential in many other sectors. Long-lasting, safer and more reliable polymeric products: this is the challenge of self-healing. The variety of interactions to obtain self-healing is constantly growing and widens the set of possibilities to functionalize existing materials and to design novel ones. The potential is high, and manifold fields of industry, from soft robotics to aerospace, could capitalize on these discoveries.

Nonetheless, there are still unsolved problems that need to be addressed. One of the most obvious yet overlooked requirement is the contact between the fractured surfaces. Many experiments used to assess healing efficiencies involve the manually approach of the two interfaces to bound. In realistic engineering systems, this fundamental step is not so easy to complete, especially when the structure is subjected to tensile stresses which enlarge the gap. Besides this difficulty, other drawbacks exist: healing of macro-cracks is still a challenging issue, as well as the cost-effectiveness of several technologies, especially where a catalyst is required. Supramolecular systems possess the right features for self-healing, but the dynamism and the strength of the associations must be tuned to acquire structural properties without penalizing healing kinetics. Another critical aspect is the low-temperature condition, which greatly affects the chain mobility.

Despite these issues, mainly surging from the infancy of self-healing, cooperative efforts of biologists, chemists, physicists and materials scientists shed light on self-healing mechanisms and implementation. Indeed, this vast field drives more and more attention from researchers worldwide, and its marked interdisciplinary nature allows to collect a variety of different backgrounds which can generate excellent findings which will build a path for a novel class of materials. Future outlooks aim at adaptive materials, that can react with their ambient to delay degradation: sunlight can provide both thermal and photonic energy to trigger healing, electronic devices generate heat that can be exploited to enhance interdiffusion kinetics, and so on.

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