Potential Opportunities of Self-Healing Polymers

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1. Theme Description

Polymers are widespread in different sectors, from packaging to construction. As shown in Figure 1, polymer production reached about 400 Mton in 2015[1] and is expected to grow with a CAGR of 3.9% in the period 2015-2020.[2]The production interests mainly the packaging (36%), building and construction (16%) and textiles (15%), while referring to the polymer type, the main ones are: PP (17%), LDPE (16%) and PPA fibers (15%).[3]The leading companies are Dow Chemical, BASF SE, Saudi Basic Industries Corporation, China Petrochemical Corporation, and Exxon Mobil.2 Whereas the main producing countries are China (29%), Europe (19%) and NAFTA (18%)[4].In this scenario among emerging polymers there are self-healing polymers that falls into the class of smart polymers[5]. It is considered that in 2025 these compounds could carry to4.1 billion of US$ with a CAGR of 27.2%.[6] Therefore in the following sections self-healing polymers and their characteristic are described.

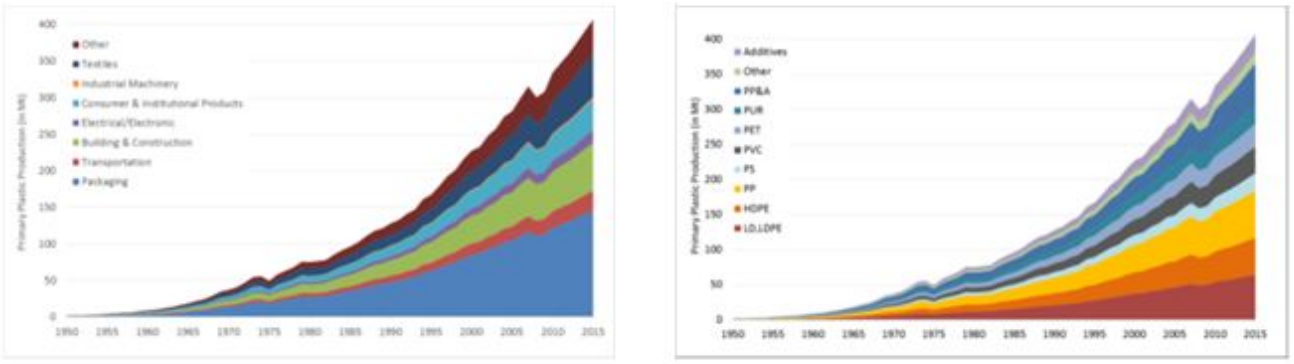


Figure 1 – World Plastic Production referring to Use Sector and Polymer Type from 1950 to 2015.3

2. Self-Healing Polymers

Self-healing polymers are materials that have "*the capability to repair themselves when they are damaged without the need for detection or repair by manual intervention of any kind.*"[7]When cracks begin these lead to the chain cleavage and/or slippage with the formation of reactive groups. These groups can form oxidative products or rearrange themselves to repair the leak.[8]According to the operation mechanism, self-healing can be divided into: extrinsic and intrinsic, automatic and non-automatic. In the first case the damage is repaired by means of an external agent put inside the matrix. The external agent can be liquid (confined into microcapsules, hollow fibers and microvascular networks) or solid (dispersed in a polymeric matrix). Whereas intrinsic ones can repair by themselves.[9] Referring to non-automatic materials, they need of an external stimulus such as light, heat, laser beam, chemical and mechanical to repair the crack. While for the automatic ones the repair is spontaneous.[10]

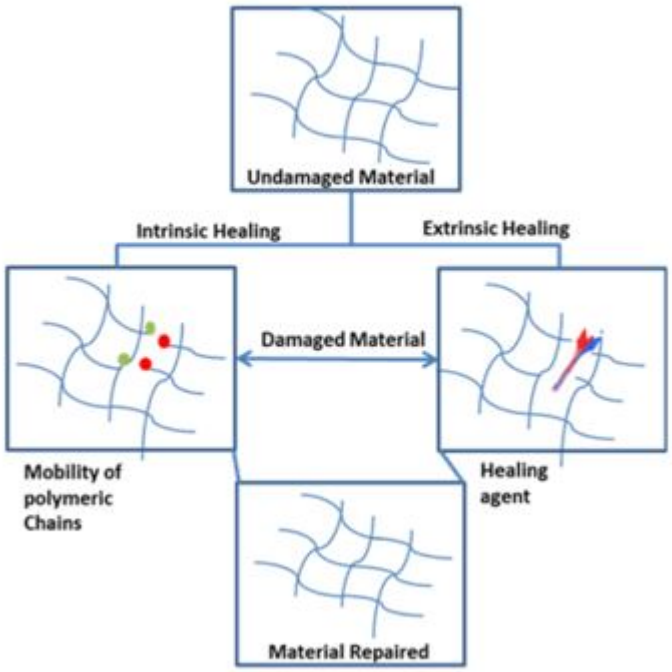


Figure 2 – Schematic representation of extrinsic/intrinsic self-healing polymers.[10]

Intrinsic Self-Healing Polymers

The cracks are repaired by local increase in the mobility of the polymeric chains. This is possible thanks to the reduction of the material viscosity and using an external/internal stimulus such as thermal energy, irradiation, pH changes, etc. (Figure 3).After cooling, the local properties are restored and the material can be used again. There are several parameters that can be modified to ensure good physical and mechanical properties: such as molecular weight, cluster distribution and size, crystallinity etc.[11]

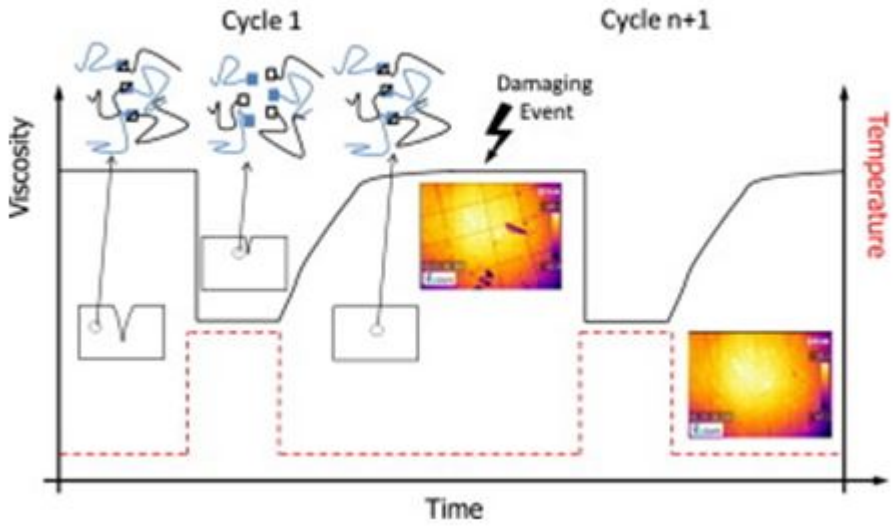


Figure 3 – Viscosity and temperature trends from the damage to repair process.[11]

On the basis of the healing mechanism these compounds can be divided into: polymers based on reversible covalent bonds, supramolecular polymers and shape memory polymers. The first category includes several bonds such as disulphide, imine, acyl hydrazones etc.[12]However, the most common are based on Diels-Alder/retro Diels-Alder reactions.[13] These are called [4+2] cycloaddition reactions because involve 4π electrons of the diene and 2π electrons of the dienophile. The most known and used system is the furan/maleimide due to low healing temperature near to 100 °C (for more details can be consulted A. Gandini).[14] In supramolecular polymers[15], monomers are held together by means of non-covalent interaction such as hydrogen bonding, π-π stacking interactions, metal ligand complexes and ionomers.9 Compared to covalent bonds, non-covalent ones are weaker but more reversible. The shape memory polymers[16], instead, are compounds that can be plastically deformed, but by means of external stimuli such as heat, light etc. can return to the original shape. The matrix is usually composed by two domains: one acts as netpoints defining the

original shape of polymer and the other one acts as molecular switches having memory of the original shape. A trade-off between mechanical strengths and healing capacity is represented by polymer blends[17] (for more detail can be consulted L. A. Utracki et al.).[18]

Extrinsic Self-Healing Polymers

Unlike intrinsic self-heling polymers, the extrinsic ones need of external agent, placed inside the material matrix, to repair the damage. The healing agent can be confined as liquid into capsules or networks such as capillaries and hollow fiber or blended as solid into the polymer. The healing agent is then released due to the rupture of these containers reaching the cracks by means of capillary forces. Microencapsulation and Microvascular network are the most common techniques for making extrinsic self-healing polymers. In the first case the healing agent can be encapsulated by means of the reactions of several mixtures (urea-formaldehyde, melamine-formaldehyde etc.) in an oil-water emulsion(in situ and interfacial techniques) or by the dispersion of the key component in a melted polymer. This compound is emulsified and solidified by changing the temperature or removing the solvent.[19] It is necessary that the healing agent has low viscosity, good wettability and minimum loses due to volatilisation or diffusion into the polymer matrix. Form the first system based on styrene/polysterene blends and phenolic based resin we move on dicyclopentadiene monomer (DCPD) with “Grubbs catalyst” up to the polydimethylsiloxane (PDMS).[20]Referring to vascular networks the most common technique is based on hollow glass tubes with different configuration: all tubes are filled with only one type of resin such as epoxy particles or cyanoacrylate or with two “adhesives” such as epoxy and its curing agent. Otherwise one of the compounds can be injected in the tubes and the other one in microcapsules.[21] However these techniques allow to create 1-2D networks. An emerging

method consists of making a scaffold that after solidification is removed from the polymer matrix. This allow to create a 3D structure. The healing agent is then injected in the network.[19]

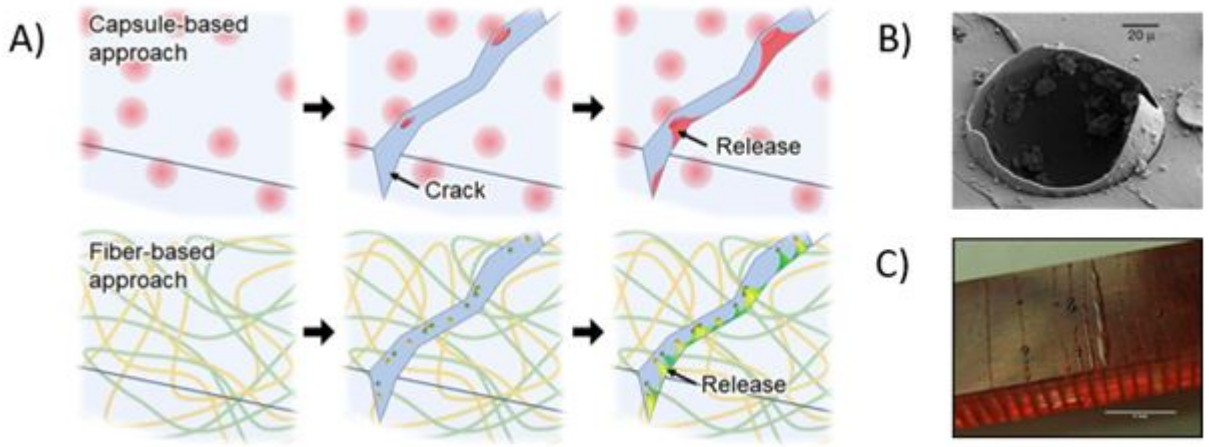


Figure 4—A) Operatingmechanism of capsuled and vascular networks,[22]B)SEM of the rupture of anurea-formaldehyde microcapsule in a thermosetting matrix[23], C)Optical Image showing the released of healing agent.[24]

Healing Efficiency

The main techniques used to evaluate the healing efficiency are Undamaged Tapered Double Cantilever Beam (TDCB) and Tear Test. In the first case the crack is generated in the center of the sample and is propagate until failure. Then the coupon is repaired by means of healing properties of the material and loaded again. Whereas Tear Test is used for elastomeric material such as PDMS. The rectangular sample has an axial cut and two legs that are loaded until the cracks propagates to the rest of the material. The healing efficiency is worked out comparing the property of virgin sample.[25]

$$1.\ \eta = \frac{K_{IC}^{Healed}}{K_{IC}^{Virgin}} = \frac{P_C^{Healed}}{P_C^{Virgin}} (TDCB)$$

$$2.\ \eta = \frac{T_{Healed}}{T_{Virgin}} = \frac{F_{Healed}^{Avg}}{F_{Virgin}^{Avg}} (Tear\ Test)$$

Where K_{IC} fracture toughness, P_C critical fracture load, T tear strength and F^{Avg} is the mean tearing force.

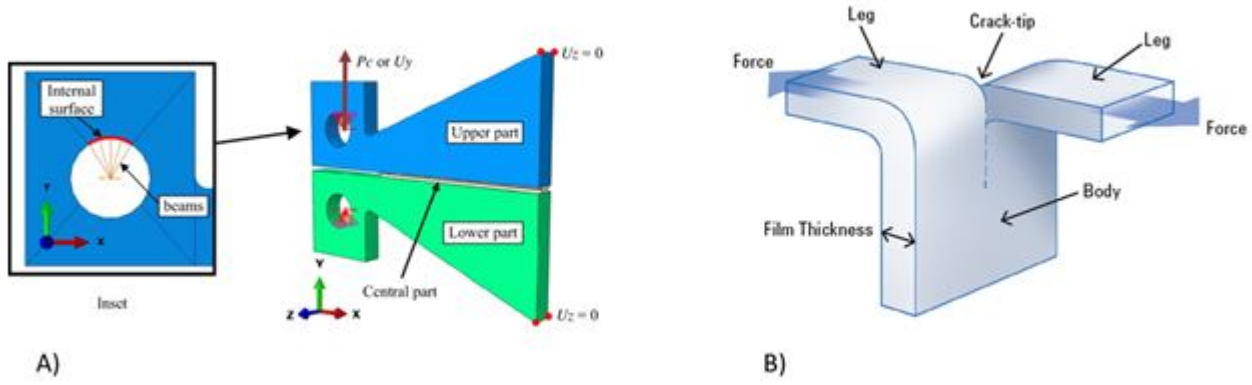


Figure 5 – A) TDCB sample[26], B) Tear Test.[27]

3. Last Advancement in Self-Healing Polymers

Among intrinsic self-healing polymer an emerging technique is represented by the injection of a thermoplastic particles (250-425 µm) of polyethylene-co-methacrylicacid (EMAA), into diglycidyl ether of bisphenol A (DGEBA) epoxy resin polymerized with triethyltetramine (TETA). The TDCB test

performed at 150°C for 30 minutes showed a healing efficiency of about 85%. This was achieved by the formation of bubble that expanding forcing the healing agent into cracks.[28]

Keller at al. in their first work tested a matrix of Sylgard 184 PDMS provided by Dow Corning in which the healing agent was confined into two different urea-formaldehyde capsules: one containing a vinyl terminated poly-dimethyl siloxane (PDMS) resin and platinum catalyst and the other containing a PDMS copolymer diluted with a 20 wt% of heptane to reduce the resin viscosity. Therefore, polymer and healing agent have the same nature. Tear tests showed a healing efficiency ranging between 70-100%.[29]In a subsequent work the same polymer and the elastomer RTV 630 provided by GE Silicones were tested under torsional fatigue. The experiments involved four samples for each compound with different amount of substance in both capsules. The results showed that torsional stiffness was recovered after 5hours while the fatigue crack was reduced by 24%.[30]

Toohey et al. instead tried to mimic human skin creating a 3D microvascular network covered by an epoxy substrate. The coating contained "Grubbs" catalysts while the structure was filled with DCPD healing agent. Furthermore, an acoustic emission sensor was used to detect the crack events. The concentration of catalyst was increased up to 10 % w/w showing a maximum number of cycle equal to seven.[31] Therefore, to obtain a greater number of cycles this structure was modified by introducing a multiple isolated network structure where different healing agents can be confined. In this way a two part (epoxy resin-amine harder)altering structure was obtained and the number of cycle was increased up to 16.[32]

An exhaustive description of the last advancement in self-healing polymers can be found in Zhag et. al [33] and Mauldin et. al[20].

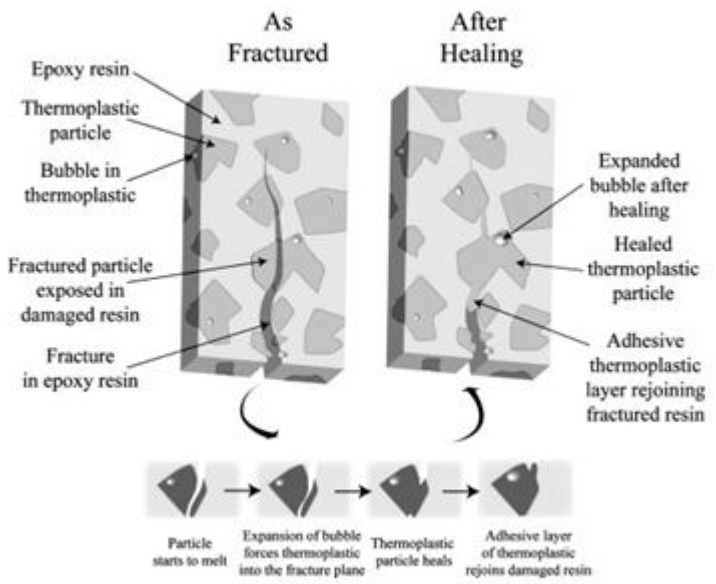


Figure 6—Operation of EMAA particles.[34]

4. Conclusions

Self-healing polymers are promising smart materials that try to mimic the nature (i.e. healing a skin wound, broken bone etc.) repairing themselves without an external intervention of any kind (i.e welding, fusion etc.)10. These compounds can be applied in several sectors from packaging up to aerospace[35], from coating to corrosion prevention22and it is estimated that in 2025 could have a market size of 4.1 billion of US$ with a CAGR of 27.2%.6Nowadays,they are divided into extrinsic and intrinsic, automatic and non-automatic polymer depending on the mechanism of action. Some emerging material are listed from EMAA particles up to 3D microvascular network. However, these works are concerning the laboratory scale and only few products are available. Therefore, more efforts are necessary for the commercialization.

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