

Evaluation of Self Healing Polymer and Rubber Composites: A Brief Review of Recent Achievements

Adolphe Edjenguele^{*}, Elodie Njeumen Nkayem, Njukeng Jetto Nkengafac

Rubber Technology Laboratory, Perennials and Industrials Crops Section, Ekona Agricultural Research Centre, Institute of Agricultural Research for Development, Buea, Cameroon

Email address:

adolphedjen@yahoo.fr (A. Edjenguele), njeumenelodie@gmail.com (E. N. Nkayem), njukengnkengafac@gmail.com (N. J. Nkengafac)

^{*}Corresponding author

To cite this article:

Adolphe Edjenguele, Elodie Njeumen Nkayem, Njukeng Jetto Nkengafac. Evaluation of Self Healing Polymer and Rubber Composites: A Brief Review of Recent Achievements. *American Journal of Polymer Science and Technology*. Vol. 7, No. 4, 2021, pp. 64-72.

doi: 10.11648/j.ajpst.20210704.13

Received: July 5, 2021; **Accepted:** November 10, 2021; **Published:** November 24, 2021

Abstract: Polymers contain extraordinary qualities, such as self-healing. Research and development of this form of polymer, which regenerates after injury, is an essential asset for artificial material lifetime and environmental sustainability. These polymers produced through polar interactions, hydrogen bonds, disulfide bonds, Diels Alders reactions and other types of interactions can totally recover their original qualities (high self healing effectiveness) at the molecular scale with repeatability without the need of chemicals. Self-healing capabilities may be introduced into a wide range of different materials, including concrete, ceramics, and metals, in addition to polymers and their composites. Despite extensive research in this field, mastering the self healing mechanism (intrinsic and extrinsic), characterization (spectroscopy and microscopy such as SEM, TEM to provide evidence of healing), and finding new sources of crosslinked fillers for polymers composites with high intrinsic self healing capabilities remain a significant difficulty. Microscope in the realm of creative product development, self-healing polymers and rubber composites have produced outstanding outcomes. Because of their exceptional excellent properties, such as strength/weight ratio, these materials have achieved great outcomes as well as corrosion resistance, fatigue resistance, specific heat resistance, specific modulus, high self healing capability. This article briefly reviews some important point of the mechanism, characterization, application and recent accomplishments of great self healing ability of rubber composites.

Keywords: Self Healing Efficiency, Mechanical Properties, Damage, Rubber Composites, Chemical Interactions, Characterizations

1. Introduction

Decades ago, rubber composites, polymers and polymer composites have drastically altered our everyday lives, and are extensively used in tremendous engineering fields in industries, such as aerospace, marine, automobiles, ground transportation, and sport equipment because of their advantages such as low cost, light weight, superior processability and chemical stability in all atmospheric conditions [1]. In recent years, the inefficient disposal and treatment of polymer waste has been regarded as one of the most serious environmental problems. For example, elastomers are at a disadvantage compared to thermoplastics because they are not easily reprocessed [2]. While polymeric

materials are important in our lives, they generate waste, so scientists have gone to great lengths to reduce polymeric waste as follows: Through the development of a new method for devulcanization of waste tyres [3, 4], use of waste tyres as fillers in other systems [5, 6], plastics are used in asphalt for road construction, and waste rubber materials are used to make tiles or reuse as filler in rubber composites. However, polymer and rubber waste remains an urgent problem to be solved. Furthermore, the longevity and dependability of polymeric materials in structural applications remain issues. [7]. Exposure to harsh environments can easily lead to degradation of polymer components. In contrast, due to mechanical stress or cyclic thermal fatigue, microcracks or hidden damage are among the fatal degradations produced during manufacturing or use. Its propagation and coalescence can lead to catastrophic

failure of the material, thus significantly shortening the service life of the structure [8].

A practical strategy to overcome all of the above limitations is to endow polymers or rubbers with self-healing capabilities, thus facilitating their reuse [2]. Self-healing materials have received a lot of interest recently because they have the potential to improve the dependability, durability, and longevity of materials [9–12], as well as their capacity to repair themselves autonomously and spontaneously after suffering from surface or interior damage. [13–18]. Polymers are of particular interest due to their extensive applications and the different type self healing mechanisms that can be used for polymers compared to other categories of materials. Traditional polymers, on the other hand, lack the capacity to heal; certain groups must be inserted into the polymeric substance to confer self-healing faculty [19]. As a result of these discoveries, ongoing efforts are being undertaken to emulate natural materials and include self-healing characteristics into polymers and polymeric compounds. This innovation ushered in a new age of smart materials. In general, research in this area is still in its infancy with an ever increasing number of researchers and organizations interested in it. New considerations and understanding regarding relevant mechanisms are constantly being developed. As a result, it is appropriate to look back at the efforts done thus far in various laboratories throughout the world.

The heal technique divides self-healing polymers and polymeric composites into two categories: i) extrinsic healing polymers and ii) intrinsic healing polymers that can mend cracks within the polymer itself. The healing agent is encased in an extrinsic self-healing matrix and is released in response to damage. [20–22]. White et al in 2001 reported a forestanding examples of external self-healing materials [20]. As indicated by Li in 2014 [23], the healing process can be carried out chemically or physically, depending on whether it is intrinsic or extrinsic healing. Physical healing is accomplished by molecular entanglement, whereas chemical healing is accomplished through the formation of chemical bonds, which may be further classified based on the type of bonds involved (covalent, hydrogen etc) [24].

2. Self Healing Mechanism

2.1. Crack Formation

Composite materials are used in different types of applications, such as sporting goods, biomaterials, engineering sector and tire industry. However, different type of damage like thermal, mechanical, etc...and combination between them could occur. Stress that internally or externally occur, generate microcracking that is exhibited on a small size in several types of polymer materials, which propagates to minimize the degree of localised stress in the polymer, making it difficult to recognize and foretell the structural behavior of the polymer material. In this situation, the existence of these

microcracks present and spreading in the polymeric matrix would have a significant impact on the characteristics of the fibers and composite. [25]. The development of new surfaces in the material at low energy levels is observed and owing to cracks, whose growth and spread demand a high energy level. [26]. Several characteristics impact the formation of a crack, and research in this area has revealed that the parameter known as KI is the fundamental driver of fracture development. Elements like as the applied stress, the depth, and the sharp of the crack all impact the KI, and the combination of these effects also contributes to the crack's advancement via the KIQ component known as stress intensity threshold. [27]. The delay in crack growth is caused by an extrinsic process. This method takes into consideration processes including wedges, bridges, crack deviation, and shielding zones. Because crack propagation is slowed if energy is dissipated in the loaded material without breaking, these procedures use additives or modifiers or choose appropriate monomer and curing agent combinations to limit fracture propagation. [28].

2.2. Intrinsic and Extrinsic Self Healing

Supramolecular interactions, such as polar interactions and hydrogen bonding, aid in the recovery of inherent self-healing materials after injury. [29–33], disulfide bonds [34–36], other bonds from Diels–Alder [37] and transesterification reactions [38–40], metal–ligand and ionic interactions [41], shape memory [42], and combinations between them. [43, 44] So far, the shortcomings of these materials are twofold: they require external inputs (such as pressure or temperature) to initiate these interactions [9], and their mechanical characteristics are not perfect. However, these strategies have resulted in the development of very effective self-healing systems. [2]. It is important to note that not all self-healing polymers are appropriate for structural filler applications. The reason for this is because, even if fibers are utilized as reinforcing elements, the polymer matrix in the load-bearing structure must have appropriate strength and stiffness. Ionomers are important polymers in their own right. In comparison to other intrinsic self-healing polymers (usually gels or elastomers with insufficient mechanical strength and/or stiffness), ionomers have sufficient mechanical strength and stiffness, indicating that they are appropriate for supporting structures (tensile strength is in tens of MPa and the modulus is several) [45].

Extrinsic self-healing materials necessitate the incorporation of a healing agent into the current material. There are no self-healing qualities in this substance. External sources are used to perform the healing process in extrinsic materials. The healing ingredients in this substance are integrated into the material using an encapsulating procedure (GPa). [46].

2.3. Release of Healing Agents

During the production process, liquid active agents such as monomers, dyes, catalysts, and hardeners with

microcapsules, hollow fibers, or channels are implanted in the polymeric system. These reservoirs burst in the event of a fracture, reagents pour into the cracks by capillary force, solidify and heal the cracks in the presence of the predispersed catalyst. Crack propagation is the main driving force in this process. On the other hand, the stress from the crack which need to be released, is the main disadvantage of this process. This process is autonomous and it does not require manual or external intervention. The following section outlines the different possibilities for exploring this self-healing material design concept [47].

2.3.1. Encapsulation-based Healing in Composites

The microencapsulation technique encapsulates particles in various phases, such as solids, liquid droplets, or gases, in an inert shell, thereby safeguarding them from the external environment. [48, 49]

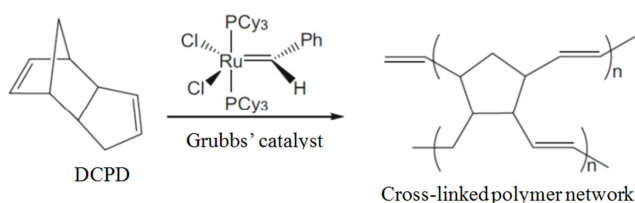


Figure 1. Ring-opening metathesis polymerization (ROMP) of dicyclopentadiene (DCPD) with Grubbs catalyst. Adapted from [20].

Microcapsules are the byproducts of the microencapsulation process. It is divided into two sections: the core and the shell. Microcapsules are round or irregular in form and range in size from nanometers to micrometers. Microcapsules are used as repair agents or catalysts in the construction of self-healing polymer composites. [50, 51] To accomplish the needed self-healing effect, a microencapsulated healing agent is utilized in the polyester matrix. [48, 52] The system consists of microencapsulated dicyclopentadiene embedded in an epoxy resin matrix containing Grubbs' catalyst (Figure 1). After cracks are formed,

dicyclopentadiene (DCPD) is released and the catalyst initiates ring-opening metathesis polymerization (ROMP) to form a strong, highly cross-linked network, which then causes crack to close (Figure 1). The self-healing effect is illustrated in Figure 2.

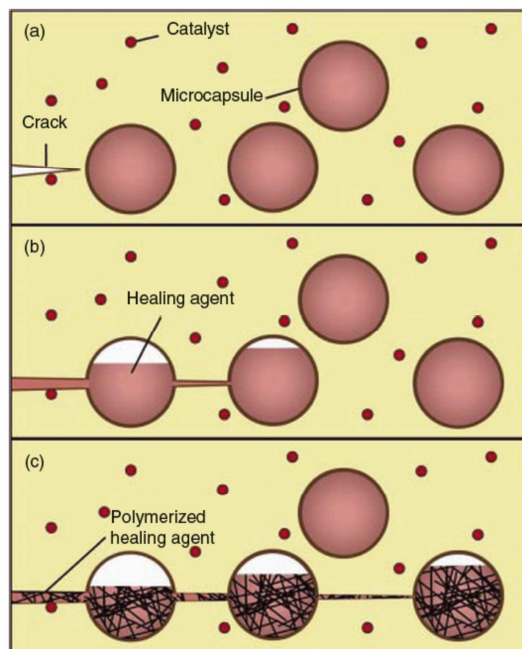


Figure 2. A microencapsulated healing agent is embedded in a structural composite matrix containing a catalyst capable of polymerizing the healing agent. Reproduced from [20]: (a) cracks form in the matrix wherever damage occurs; (b) the crack ruptures the microcapsules, releasing the healing agent into the crack plane through capillary action; (c) the healing agent contacts the catalyst, triggering polymerization that bonds the crack faces closed.

The important parameters that govern the microencapsulation-based self-healing technique used to create a self-healing material are summarized in table 1 below:

Table 1. The main aspects that impact the microencapsulation-based self-healing technique.

Parameters	Influencing factors
Microcapsule	<ol style="list-style-type: none"> 1. The healing agent must be chemically inert to the polymer shell 2. Increased capsule shelf life 3. Compatibility with the dispersion polymer medium 4. Weakening of the shell wall to facilitate rupture 5. Proximity to the catalyst 6. High interfacial attraction between the polymer matrix and the capsule shell wall, promoting shell rupture
Monomer	<ol style="list-style-type: none"> 1. Low viscosity monomer that will flow to the crack due to capillary action 2. A low volatility monomer that will give enough time polymerization
Polymerization	<ol style="list-style-type: none"> 1. It should be quick 2. Stress relaxation and no cure induced shrinking 3. Polymerization at room temperature
Catalysts	<ol style="list-style-type: none"> 1. Dissolve in monomer 2. There is no agglomeration with the matrix polymer
Coatings	<ol style="list-style-type: none"> 1. Incorporation of microcapsules should have very little effect on matrix's physicomechanical characteristics 2. The thickness of the coating must be greater than the size of the microcapsule 3. No catalysts or microcapsules clustering in the matrix polymer
Healing	<ol style="list-style-type: none"> 1. It must be quicker 2. Multiple

2.3.2. Hollow Fiber and Vascular Systems

When the healing ingredients are in modest quantities, the self healing process can not be completed entirely unless it is done in phases and repeated. This phenomenon is a side effect of the microencapsulation method's self healing mechanism. As a result, an excess of self-healing agent is necessary to allow for repeated self healing in the polymer matrix. This type of self healing agent reservoir capsule, created by Dry, is capable of releasing excess self-healing agent in the polymer matrix. Dry and Coworker created bleed-able composites in order to overcome the failure of earlier approaches. They used biomimetic technique for the

bleed-able composite and proceeded by step with resin. Hollow fiber is prepared despite the uncured resin and hardener its containing and stacked to form a specific layer on the matrix. The hollow fiber in the fiberglass and composite board combination may store up to 97 percent of the original flexural strength. Figure 3 displays the dye leakage from the fractured hollow fiber to the crack plane. This self healing material design technique has several advantages, including a higher volume of healing agent to repair damage, various activation mechanisms, simple visual examination of damaged sections, and the ability to be combined and matched with standard reinforcing fibers. [53]

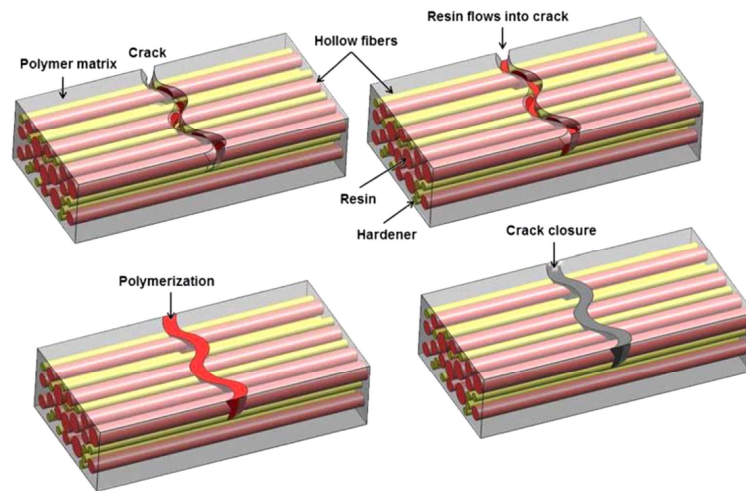


Figure 3. Self-healing concept using hollow fibers. Reproduced from [54].

To overcome the limits of microcapsule-based healing treatments, it has been recommended that an approach be established in the same manner as the biological vascular systems of plants and animals. This method is based on a centralized network for distributing healing chemicals to polymer systems on a continuous path. The polymeric

materials with microvascular networks were created by including chemical catalysts into the polymer utilized for the infiltration of organic ink scaffolds [54, 55]. After curing the polymer and removing the scaffolding, the healing agent is delivered to a microvascular channel. The notion of self-catering using the vascular network is shown in Figure 4.

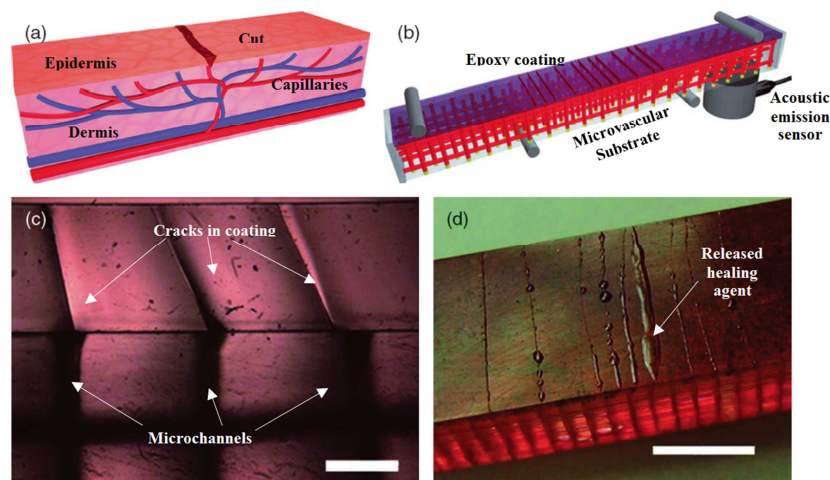


Figure 4. Self-healing of microvascular networks. Reproduced from [55]. (a) Pore diagram with notches in the dermis layer and capillaries in the epidermal layer of the skin; (b) schematic diagram of the self-healing structure composed of a microvascular substrate and a brittle epoxy coating containing embedded catalyst in a four point bending configuration monitored with an acoustic emission sensor; (c) A highly enlarged cross-sectional shot of the coating reveals that cracks begin at the bottom and progress towards the microchannel holes at the interface; (d) Self-healing optical picture (2.5 percent by weight) following breaks in the coating meaning that there is more repair fluid on the coated surface.

3. Characterization and Self Healing Efficiency of Rubber Composites

3.1. Characterization Techniques

Given the importance of the mechanical properties of composite materials, the self-healing capacity of this type of material is known in general by evaluating its mechanical properties and the recovery of the functional properties of the material after mechanical damage [56]. The type of polymer, the application areas, and the procedures to be employed are all fundamentally related. Knowledge about the mechanism of self healing at the molecular level is not widely available, owing to the restricted methodologies and equipment available, which prevents mastery or the creation of novel self healing systems [57].

The following are the most important methodologies used to characterize self healing systems: atomic force microscopy (AFM), Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and X-ray computed tomography in a three-dimensional representation.

3.1.1. Scanning Electron Microscopy and Transmission Electron Microscopy

In the study of materials, particle size or structure is of important relevance. SEM and TEM microscopy are utilized to differentiate and confirm these factors, which are also involved in the self healing mechanism. The surface of the material will be imaged in high resolution by SEM. [58]. It interacts with atoms using an electron beam to provide surface structure information [59]. When this microscopic technology (SEM) is involved in the self healing process, it is often utilized to analyze and to see the various capsules ranging in size from micrometers to less than 100 nanometers. [60]. In contrast to SEM, which is far more extensively utilized in this domain, TEM is involved when there is nanoinclusion in the self healing system. Several scientists studied various characteristics using SEM as it was the case of Haiyan's team when they characterized microcapsules containing epoxy/hardener [61], and Jin et al. when characterizing the fracture surfaces of hollow composites of resin microcapsules and microcapsules. [62]

3.1.2. Fourier Transform Infrared Spectroscopy

FTIR is a well utilized analytical method that will be employed here to monitor the self-healing process and describe the different types of bonds involved between the capsule and the polymer. [63, 64] FTIR will be utilized to investigate the properties of Diels Alder cycloaddition bonds [65], gels [66], and certain self mending nanocomposites such as polyurethane/graphene. [67] Cao et al. praised the usage of this technology in their published work, proposing a transparent self healing process in which the mechanical characteristics of the material involved, which had been decreased owing to damage, were regained by self healing and without external input. [68]

3.1.3. Atomic Force Microscopy

When using the AFM technique to evaluate the self-healing characteristics of a polymeric system, the mobility of the atoms in the polymeric system and the rising temperature as a function of time are important factors to consider. Thermal analysis combined with AFM produce good findings for controlling and understanding self-healing capsules. Brancart's team also utilized AFM to investigate the behavior of coatings in the polymer matrix. [69, 70] Faghehnejad et al. used AFM in their research to better understand the rebuilding of numerous hydrogen bonds in polymers that are subjected to several stimuli and self-curing. [71]

3.1.4. X-ray Computed Tomography

In a three-dimensional picture, X-ray computed tomography is utilized to offer additional information about the damage and healing process. Furthermore, this method may be used to observe the release of healing components encased in microcapsules or fibers [72]. The identification of fracture openings in fiber-polymer composites is another another use of X-ray computed tomography. [73].

3.1.5. Other Techniques of Characterization

Because the process happens within the polymeric matrix and in a molecular level, spectroscopy is ideal for researching self healing characteristic. Nuclear magnetic resonance (NMR) spectroscopy, scattering techniques, infrared and Raman spectroscopy are all used to monitor self-healing chemistry utilizing vibrational spectroscopy. [74] NMR, which is an intriguing technique for self-healing polymers, can study atomic level alteration and molecular structure of polymers. Scattering methods such as neutron scattering and X-ray may, on the other hand, can also be used to more precisely monitor the molecular structure of materials as a function of temperature and time. [75]

Other important techniques for studying polymer with self-healing ability are infrared spectroscopy and Raman spectroscopy mentioned above. The purpose of using these methods is also to distinguish the chemicals present and to monitor reversible chemical reactions [76, 77]. Furthermore, this method is adopted to control encapsulation monomers in polymerization process when self healing agents are within the polymer. [78, 79]

3.2. Some Studies on Self Healing Efficiency of Rubber Composites

Due to the polymer's outstanding self-healing capacity, mechanical characteristics may be regained after damage. Healing efficiency is defined using the equation:

$$R(Q) = \frac{Q_{\text{healed}}}{Q_{\text{initial}}}$$

In this equation, Q_{healed} denotes the characteristics of the sample after healing, and Q_{initial} denotes the qualities of the material before to damage [20]. $R(Q)=1$ for the perfect healing

material, however the level of efficiency in the experiment is radically different. Engineers can obtain 100% breaking strength healing efficiency using hollow fiber reinforced epoxy composites, according to certain research [80].

Furthermore, healing efficiency can be expressed as fracture stress or material strength $R(s)$ [81], fracture toughness $R(K)$ [29, 82], or elongation or ductility [83, 17]. Many studies have been undertaken to assess the influence of various factors on polymer efficiency; as a result, it has been discovered that characteristics such as polymer type, healing agent viscosity, capsule shape, and crack size have a direct effect on self-healing efficiency [84, 85]. By expanding the size of the capsule, for example, the healing agent can be released more rapidly and readily, enhancing healing efficiency.

Following the aforementioned approach, Chuanhui et al. in 2016 studied the design of self-healing supramolecular natural rubber by introducing ionic crosslinking into natural rubber through controlled vulcanization, to prove that zinc dimethacrylate (ZDMA) polymerizes in natural rubber to produce a large amount of ionic crosslinking. For rubber (NR), the stress-strain experiment showed that after healing for 30 s at room temperature, the elongation at break and tensile strength of the sample can recover more than 50%, and after curing for 5 minutes, the sample recovers more than 95% of the original stress-strain curve. This strengthens the idea of crosslinking as a filler in rubber composites for better self-healing effect [86]. This trend was recently confirmed in 2020 by Santana et al. who designed a self-healing rubber composite material and reported that one strategy to improve the mechanical properties of self-healing elastomers was to add fillers. Therefore, they developed epoxidized natural rubber (ENR), which was reinforced with in-house synthesized thermally reduced graphene oxide (TRGO), which has the ability to self-heal. The results of these studies paved the way for the development of other elastic materials, which contain nanofillers as good alternative to overcome the balance between mechanical / structural performance and healing ability [2]. Other research reports indicated that rubber composites containing chitin nanocrystals [33], graphene oxide [87], bentonite [39], carboxymethyl chitosan [88] and other fillers showed good self-healing efficacy.

Although crosslinked fillers can enhance the self healing effect, certain types of H-bonding and types of chemical reactions also play a key role in the self-healing effect. Therefore in 2019, Mohammad et al. designed a dual hybrid network of natural rubber- SiO_2 elastomer with tailored mechanical and self-healing properties. Using broadband dielectric spectroscopy, the intrinsic self-healing ability of the composite at the molecular level was studied, and the mechanism of the healing process was revealed. The synergy between the molecular interdiffusion of the cross-linked NR chain and the electrostatic and H-bonding interaction gave the NR- SiO_2 composite prepared by liquid mixing, excellent self-healing properties and improved mechanical properties. They also concluded that the supramolecular reversible ion and H-bonding network between NR and SiO_2 promotes the

self-healing ability [89]. In the same way in 2019, Santana et al. studied the use of Diels Alder reaction to obtain fully reversible cross-linked NR with self-healing ability. Observations of the macroscopic damage healing mechanism indicate that the repair process seems to start from a lower plane until the damaged surface is completely sealed. The strategy they put forward in the study of reversibly cross-linked natural rubber opened the way for a simple way to recycle elastomer products (especially tires) and extend their service life by repairing local damage [37].

4. Conclusion

The numerous advancements made in the field of self-healing polymers and rubber composites are irrefutable. More researches are needed in this sector to produce novel composites for breakthrough self-healing systems. In light of technical improvements, what is now being done is far from sufficient. Preparing polymers and rubber composites with the option of including novel self-healing agents is a task that necessitates a bit more interdisciplinarity, which is not yet at a commendable level. According to scientists, certain types of fillers used in polymer or rubber composites improve the mechanical properties and self-healing efficiency of composites. Improved self-healing mechanisms and characterization techniques are also important to better understand these materials. Polymer materials with self-healing properties are still being discovered and are not generally available. Until far, only a few polymer materials with self-healing capabilities have been discovered in highly particular applications such as tire industries. Therefore, because of the use of a healing agent that is conducive to industrialization, the external self-healing technology may now be easier to use on a large scale. Furthermore, the lengthy lifespan of components made up from these smart materials would aid in waste reduction. It is undeniable that creating a sustainable environment for our society is critical to ensuring a brighter future.

References

- [1] Yuan, Y. C., Yin, T., Rong, M. Z. and Zhang, M. Q., (2008). Self healing in polymers and polymer composites. Concepts, realization and outlook: A review. *Express Polymer Letters*, 2 (4): 238-250.
- [2] Utrera-Barrios, S., Hernández Santana, M., Verdejo, R. and López-Manchado, M. A., (2020). Design of rubber composites with autonomous self-healing capability. *ACS omega*, 5 (4): 1902-1910.
- [3] Ghorai, S., Bhunia, S., Roy, M., & De, D. (2016). Mechanochemical devulcanization of natural rubber vulcanizate by dual function disulfide chemicals. *Polymer Degradation and Stability*, 129, 34-46.
- [4] Aoudia, K., Azem, S., Hocine, N. A., Gratton, M., Pettarin, V., & Seghar, S. (2017). Recycling of waste tire rubber: Microwave devulcanization and incorporation in a thermoset resin. *Waste management*, 60, 471-481.

- [5] Ramarad, S., Khalid, M., Ratnam, C. T., Chuah, A. L., & Rashmi, W. (2015). Waste tire rubber in polymer blends: A review on the evolution, properties and future. *Progress in Materials Science*, 72, 100-140.
- [6] Sienkiewicz, M., Janik, H., Borzędowska-Labuda, K., & Kucińska-Lipka, J. (2017). Environmentally friendly polymer-rubber composites obtained from waste tyres: A review. *Journal of cleaner production*, 147, 560-571.
- [7] Cardon, A. H., & Verchery, G. (1990). Durability of polymer based composite systems for structural applications.
- [8] Zhang, M. Q., & Rong, M. Z. (2011). *Self-healing polymers and polymer composites*. John Wiley & Sons.
- [9] Hager, M. D., Greil, P., Leyens, C., van der Zwaag, S., & Schubert, U. S. (2010). Self-healing materials. *Advanced Materials*, 22 (47), 5424-5430.
- [10] Wu, D. Y., Meure, S., & Solomon, D. (2008). Self-healing polymeric materials: A review of recent developments. *Progress in polymer science*, 33 (5), 479-522.
- [11] Guimard, N. K., Oehlenschlaeger, K. K., Zhou, J., Hilf, S., Schmidt, F. G., & Barner-Kowollik, C. (2012). Current trends in the field of self-healing materials. *Macromolecular Chemistry and Physics*, 213 (2), 131-143.
- [12] Billiet, S., Hillewaere, X. K., Teixeira, R. F., & Du Prez, F. E. (2013). Chemistry of crosslinking processes for self-healing polymers. *Macromolecular rapid communications*, 34 (4), 290-309.
- [13] van Gemert, G. M., Peeters, J. W., Söntjens, S. H., Janssen, H. M., & Bosman, A. W. (2012). Self-healing supramolecular polymers in action. *Macromolecular Chemistry and Physics*, 213 (2), 234-242.
- [14] Cordier, P., Tournilhac, F., Soulié-Ziakovic, C., & Leibler, L. (2008). Self-healing and thermoreversible rubber from supramolecular assembly. *Nature*, 451 (7181), 977-980.
- [15] Montarnal, D., Cordier, P., Soulié-Ziakovic, C., Tournilhac, F., & Leibler, L. (2008). Synthesis of self-healing supramolecular rubbers from fatty acid derivatives, diethylene triamine, and urea. *Journal of Polymer Science Part A: Polymer Chemistry*, 46 (24), 7925-7936.
- [16] Sottos, N. R., & Moore, J. S. (2011). Spot-on healing. *Nature*, 472 (7343), 299-300.
- [17] Chen, Y., Kushner, A. M., Williams, G. A., & Guan, Z. (2012). Multiphase design of autonomic self-healing thermoplastic elastomers. *Nature chemistry*, 4 (6), 467-472.
- [18] Wool, R. P. (2008). Self-healing materials: a review. *Soft Matter*, 4 (3), 400-418.
- [19] Kuhl, N., Bode, S., Hager, M. D., & Schubert, U. S. (2015). Self-healing polymers based on reversible covalent bonds. *Self-Healing Materials*, 1-58.
- [20] White, S. R., Sottos, N. R., Geubelle, P. H., Moore, J. S., Kessler, M. R., Sriram, S. R., & Viswanathan, S. (2001). Autonomic healing of polymer composites. *Nature*, 409 (6822), 794-797.
- [21] Blaiszik, B. J., Sottos, N. R., & White, S. R. (2008). Nanocapsules for self-healing materials. *Composites Science and Technology*, 68 (3-4), 978-986.
- [22] Bekas, D. G., Baltzis, D., & Paipetis, A. S. (2017). Nano-reinforced polymeric healing agents for vascular self-repairing composites. *Materials & Design*, 116, 538-544.
- [23] Li, G. (2014). *Self-healing composites: shape memory polymer based structures*. John Wiley & Sons.
- [24] Li, G., & Meng, H. (2015). Overview of crack self-healing. In *Recent advances in smart self-healing polymers and composites* (pp. 1-19). Woodhead Publishing.
- [25] Brochu, A. B., Craig, S. L., & Reichert, W. M. (2011). Self-healing biomaterials. *Journal of Biomedical Materials Research Part A*, 96 (2), 492-506.
- [26] Kinloch, A. J. (1985). Mechanics and mechanisms of fracture of thermosetting epoxy polymers. *Epoxy resins and composites I*, 45-67.
- [27] Vasudeven, A. K., Sadananda, K., & Louat, N. (1994). A review of crack closure, fatigue crack threshold and related phenomena. *Materials Science and Engineering: A*, 188 (1-2), 1-22.
- [28] Ritchie, R. O. (1999). Mechanisms of fatigue-crack propagation in ductile and brittle solids. *International journal of Fracture*, 100 (1), 55-83.
- [29] Zhang, H., Xia, H., & Zhao, Y. (2012). Poly (vinyl alcohol) hydrogel can autonomously self-heal. *ACS Macro Letters*, 1 (11), 1233-1236.
- [30] Rahman, M. A., Sartore, L., Bignotti, F., & Di Landro, L. (2013). Autonomic self-healing in epoxidized natural rubber. *ACS applied materials & interfaces*, 5 (4), 1494-1502.
- [31] Cao, L., Yuan, D., Xu, C., & Chen, Y. (2017). Biobased, self-healable, high strength rubber with tunicate cellulose nanocrystals. *Nanoscale*, 9 (40), 15696-15706.
- [32] Guadagno, L., Vertuccio, L., Naddeo, C., Calabrese, E., Barra, G., Raimondo, M., & Rana, S. (2019). Self-healing epoxy nanocomposites via reversible hydrogen bonding. *Composites Part B: Engineering*, 157, 1-13.
- [33] Nie, J., Mou, W., Ding, J., & Chen, Y. (2019). Bio-based epoxidized natural rubber/chitin nanocrystals composites: Self-healing and enhanced mechanical properties. *Composites Part B: Engineering*, 172, 152-160.
- [34] Hernandez, M., Grande, A. M., Dierkes, W., Bijleveld, J., Van Der Zwaag, S., & García, S. J. (2016). Turning vulcanized natural rubber into a self-healing polymer: Effect of the disulfide/polysulfide ratio. *ACS sustainable chemistry & engineering*, 4 (10), 5776-5784.
- [35] Yang, Y., Lu, X., & Wang, W. (2017). A tough polyurethane elastomer with self-healing ability. *Materials & Design*, 127, 30-36.
- [36] Santana, M. H., Huete, M., Lameda, P., Araujo, J., Verdejo, R., & López-Manchado, M. A. (2018). Design of a new generation of sustainable SBR compounds with good trade-off between mechanical properties and self-healing ability. *European Polymer Journal*, 106, 273-283.
- [37] Tanasi, P., Santana, M. H., Carretero-González, J., Verdejo, R., & López-Manchado, M. A. (2019). Thermo-reversible crosslinked natural rubber: A Diels-Alder route for reuse and self-healing properties in elastomers. *Polymer*, 175, 15-24.
- [38] Qiu, M., Wu, S., Tang, Z., & Guo, B. (2018). Exchangeable interfacial crosslinks towards mechanically robust elastomer/carbon nanotubes vitrimers. *Composites Science and Technology*, 165, 24-30.

- [39] Xu, C., Cui, R., Fu, L., & Lin, B. (2018). Recyclable and heat-healable epoxidized natural rubber/bentonite composites. *Composites Science and Technology*, 167, 421-430.
- [40] Cao, L., Fan, J., Huang, J., & Chen, Y. (2019). A robust and stretchable cross-linked rubber network with recyclable and self-healable capabilities based on dynamic covalent bonds. *Journal of Materials Chemistry A*, 7 (9), 4922-4933.
- [41] Zhang, Z. F., Liu, X. T., Yang, K., & Zhao, S. G. (2019). Design of Coordination-Crosslinked Nitrile Rubber with Self-Healing and Reprocessing Ability. *Macromolecular Research*, 27 (8), 803-810.
- [42] Huang, J., Cao, L., Yuan, D., & Chen, Y. (2018). Design of novel self-healing thermoplastic vulcanizates utilizing thermal/magnetic/light-triggered shape memory effects. *ACS applied materials & interfaces*, 10 (48), 40996-41002.
- [43] Liu, J., Liu, J., Wang, S., Huang, J., Wu, S., Tang, Z.,... & Zhang, L. (2017). An advanced elastomer with an unprecedented combination of excellent mechanical properties and high self-healing capability. *Journal of Materials Chemistry A*, 5 (48), 25660-25671.
- [44] Lee, S. H., Shin, S. R., & Lee, D. S. (2019). Self-healing of cross-linked PU via dual-dynamic covalent bonds of a Schiff base from cystine and vanillin. *Materials & Design*, 172, 107774.
- [45] Francesconi, A., Giacomuzzo, C., Grande, A. M., Mudric, T., Zaccariotto, M., Etemadi, E.,... & Galvanetto, U. (2013). Comparison of self-healing ionomer to aluminium-alloy bumpers for protecting spacecraft equipment from space debris impacts. *Advances in Space Research*, 51 (5), 930-940.
- [46] Ramesh, M., Ramnath, R. A., Khan, A., Khan, A. A. P., & Asiri, A. M. (2020). Electrically conductive self-healing materials: preparation, properties, and applications. In *Self-Healing Composite Materials* (pp. 1-13). Woodhead Publishing.
- [47] Ghosh, S. K. (Ed.). (2009). *Self-healing materials: fundamentals, design strategies, and applications* (pp. 138-217). Weinheim: Wiley-vch.
- [48] Ghosh, S. K. (2006). Functional coating by polymer microencapsulation. *Wiley-VCH Verlag GmbH & CoKGaA: Weinheim*.
- [49] Seiller, M., Martini, M. C., & Benita, S. (1996). Microencapsulation: Methods and industrial applications. In *Drugs and the pharmaceutical sciences* (p. 587). Marcel Dekker New York.
- [50] Thies C. (2004). Microencapsulation. *Encyclopedia of polymer science and engineering*, vol. 9. New York: John Wiley & Sons, Inc. 724, 5.
- [51] Benita, S. (Ed.). (2005). *Microencapsulation: methods and industrial applications*. Crc Press.
- [52] Dry, C. (1996). Procedures developed for self-repair of polymer matrix composite materials. *Composite structures*, 35 (3), 263-269.
- [53] Williams, H. R., Trask, R. S., & Bond, I. P. (2007). Self-healing composite sandwich structures. *Smart Materials and Structures*, 16 (4), 1198.
- [54] Jones, A. S., Rule, J. D., Moore, J. S., Sottos, N. R., & White, S. R. (2007). Life extension of self-healing polymers with rapidly growing fatigue cracks. *Journal of the Royal Society Interface*, 4 (13), 395-403.
- [55] Toohey, K. S., Sottos, N. R., Lewis, J. A., Moore, J. S., & White, S. R. (2007). Self-healing materials with microvascular networks. *Nature materials*, 6 (8), 581-585.
- [56] Qazi, T. H., Rai, R., Dippold, D., Roether, J. E., Schubert, D. W., Rosellini, E.,... & Boccaccini, A. R. (2014). Development and characterization of novel electrically conductive PANI-PGS composites for cardiac tissue engineering applications. *Acta biomaterialia*, 10 (6), 2434-2445.
- [57] Wang, L., Jiang, J., Hua, W., Darabi, A., Song, X., Song, C.,... & Qiu, X. (2016). Mussel-inspired conductive cryogel as cardiac tissue patch to repair myocardial infarction by migration of conductive nanoparticles. *Advanced Functional Materials*, 26 (24), 4293-4305.
- [58] Egerton, R. F. (2005). *Physical principles of electron microscopy* (Vol. 56). New York: Springer. [17] Sun, D.,
- [59] Sun, G., Zhu, X., Guarin, A., Li, B., Dai, Z., & Ling, J. (2018). A comprehensive review on self-healing of asphalt materials: Mechanism, model, characterization and enhancement. *Advances in colloid and interface science*, 256, 65-93.
- [60] Bekas, D. G., Tsirka, K., Baltzis, D., & Paipetis, A. S. (2016). Self-healing materials: A review of advances in materials, evaluation, characterization and monitoring techniques. *Composites Part B: Engineering*, 87, 92-119.
- [61] Haiyan, L., Rongguo, W., & Wenbo, L. (2012). Preparation and self-healing performance of epoxy composites with microcapsules and tungsten (VI) chloride catalyst. *Journal of reinforced plastics and composites*, 31 (13), 924-932.
- [62] Jin, H., Mangun, C. L., Stradley, D. S., Moore, J. S., Sottos, N. R., & White, S. R. (2012). Self-healing thermoset using encapsulated epoxy-amine healing chemistry. *Polymer*, 53 (2), 581-587.
- [63] Yuan, L., Huang, S., Gu, A., Liang, G., Chen, F., Hu, Y., & Nutt, S. (2013). A cyanate ester/microcapsule system with low cure temperature and self-healing capacity. *Composites science and technology*, 87, 111-117.
- [64] Wang, H. P., Hu, S. Q., Cai, S. J., & Yu, F. (2014). Preparation and properties of bisphenol A epoxy resin microcapsules coated with melamine-formaldehyde resin. *Polymer bulletin*, 71 (9), 2407-2419.
- [65] Toncelli, C., De Reus, D. C., Picchioni, F., & Broekhuis, A. A. (2012). Properties of reversible Diels-Alder furan/maleimide polymer networks as function of crosslink density. *Macromolecular Chemistry and Physics*, 213 (2), 157-165.
- [66] Sharma, M., Mondal, D., Mukesh, C., & Prasad, K. (2013). Self-healing guar gum and guar gum-multiwalled carbon nanotubes nanocomposite gels prepared in an ionic liquid. *Carbohydrate polymers*, 98 (1), 1025-1030.
- [67] Kim, J. T., Kim, B. K., Kim, E. Y., Kwon, S. H., & Jeong, H. M. (2013). Synthesis and properties of near IR induced self-healable polyurethane/graphene nanocomposites. *European polymer journal*, 49 (12), 3889-3896.
- [68] Cao, Y., Morrissey, T. G., Acome, E., Allec, S. I., Wong, B. M., Keplinger, C., & Wang, C. (2017). A transparent, self-healing, highly stretchable ionic conductor. *Advanced Materials*, 29 (10), 1605099.
- [69] Deville, S., Chevalier, J., Fantozzi, G., Torrecillas, R., Bartolomé, J. F., & Moya, J. S. (2018). Atomic force microscopy study of the surface degradation mechanisms of zirconia based ceramics. *arXiv preprint arXiv: 1804.00002*.

- [70] Brancart, J., Scheltjens, G., Muselle, T., Van Mele, B., Terryn, H., & Van Assche, G. (2014). Atomic force microscopy-based study of self-healing coatings based on reversible polymer network systems. *Journal of intelligent material systems and structures*, 25 (1), 40-46.
- [71] Faghihnejad, A., Feldman, K. E., Yu, J., Tirrell, M. V., Israelachvili, J. N., Hawker, C. J.,... & Zeng, H. (2014). Adhesion and surface interactions of a self-healing polymer with multiple hydrogen-bonding groups. *Advanced Functional Materials*, 24 (16), 2322-2333.
- [72] Mookhoek, S. D., Mayo, S. C., Hughes, A. E., Furman, S. A., Fischer, H. R., & Van der Zwaag, S. (2010). Applying SEM-based X-ray microtomography to observe self-healing in solvent encapsulated thermoplastic materials. *Advanced engineering materials*, 12 (3), 228-234.
- [73] Prajer, M., Wu, X., Garcia, S. J., & Van der Zwaag, S. (2015). Direct and indirect observation of multiple local healing events in successively loaded fibre reinforced polymer model composites using healing agent-filled compartmented fibres. *Composites Science and Technology*, 106, 127-133.
- [74] Zedler, L., Hager, M. D., Schubert, U. S., Harrington, M. J., Schmitt, M., Popp, J., & Dietzek, B. (2014). Monitoring the chemistry of self-healing by vibrational spectroscopy—current state and perspectives. *Materials Today*, 17 (2), 57-69.
- [75] Chen, X., Wudl, F., Mal, A. K., Shen, H., & Nutt, S. R. (2003). New thermally remendable highly cross-linked polymeric materials. *Macromolecules*, 36 (6), 1802-1807.
- [76] Varley, R. J., & van der Zwaag, S. (2010). Autonomous damage initiated healing in a thermo-responsive ionomer. *Polymer International*, 59 (8), 1031-1038.
- [77] Holten-Andersen, N., Harrington, M. J., Birkedal, H., Lee, B. P., Messersmith, P. B., Lee, K. Y. C., & Waite, J. H. (2011). pH-induced metal-ligand cross-links inspired by mussel yield self-healing polymer networks with near-covalent elastic moduli. *Proceedings of the National Academy of Sciences*, 108 (7), 2651-2655.
- [78] Sandmann, B., Happ, B., Hager, M. D., Vitz, J., Rettler, E., Burtcher, P.,... & Schubert, U. S. (2014). Efficient Cu (I) acetate-catalyzed cycloaddition of multifunctional alkynes and azides: From solution to bulk polymerization. *Journal of Polymer Science Part A: Polymer Chemistry*, 52 (2), 239-247.
- [79] Vasiliu, S., Kampe, B., Theil, F., Dietzek, B., Döhler, D., Michael, P.,... & Popp, J. (2014). Insights into the mechanism of polymer coating self-healing using Raman spectroscopy. *Applied spectroscopy*, 68 (5), 541-548.
- [80] Zhu, D. Y., Cao, G. S., Qiu, W. L., Rong, M. Z., & Zhang, M. Q. (2015). Self-healing polyvinyl chloride (PVC) based on microencapsulated nucleophilic thiol-click chemistry. *Polymer*, 69, 1-9.
- [81] Trask, R. S., Williams, G. J., & Bond, I. P. (2007). Bioinspired self-healing of advanced composite structures using hollow glass fibres. *Journal of the royal society Interface*, 4 (13), 363-371.
- [82] Brown, E. N., Sottos, N. R., & White, S. R. (2002). Fracture testing of a self-healing polymer composite. *Experimental mechanics*, 42 (4), 372-379.
- [83] Hamilton, A. R., Sottos, N. R., & White, S. R. (2010). Self-healing of internal damage in synthetic vascular materials. *Advanced Materials*, 22 (45), 5159-5163.
- [84] Tuncaboylu, D. C., Sari, M., Oppermann, W., & Okay, O. (2011). Tough and self-healing hydrogels formed via hydrophobic interactions. *Macromolecules*, 44 (12), 4997-5005.
- [85] Lv, Z., Li, S., & Chen, H. (2017). Analytical model for effects of capsule shape on the healing efficiency in self-healing materials. *Plos one*, 12 (11), e0187299.
- [86] Xu, C., Cao, L., Lin, B., Liang, X., & Chen, Y. (2016). Design of self-healing supramolecular rubbers by introducing ionic cross-links into natural rubber via a controlled vulcanization. *ACS applied materials & interfaces*, 8 (27), 17728-17737.
- [87] Wang, C., Liu, N., Allen, R., Tok, J. B. H., Wu, Y., Zhang, F.,... & Bao, Z. (2013). A rapid and efficient self-healing thermo-reversible elastomer crosslinked with graphene oxide. *Advanced materials*, 25 (40), 5785-5790.
- [88] Xu, C., Nie, J., Wu, W., Zheng, Z., & Chen, Y. (2019). Self-healable, recyclable, and strengthened epoxidized natural rubber/carboxymethyl chitosan biobased composites with hydrogen bonding supramolecular hybrid networks. *ACS Sustainable Chemistry & Engineering*, 7 (18), 15778-15789.
- [89] Sattar, M. A., Gangadharan, S., & Patnaik, A. (2019). Design of dual hybrid network natural rubber-SiO₂ elastomers with tailored mechanical and self-healing properties. *ACS omega*, 4 (6), 10939-10949.