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Review Article

Self-Healing Carbon Fiber Composites with Thermoplastic Polymers

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Abstract

The utilization areas of composite materials are increasing day by day. However, these materials are difficult and expensive to manufacture. In addition, since they are thermoset structures, their recycling is very limited in case of damage. Self-healing materials are the ones that automatically and independently heal or repair the damage caused by any factors, without external intervention. Self-healing polymeric materials are in the range of smart materials. Research on self-healing polymers and polymer composites using this effect has increased rapidly in recent years due to the advantages such as cost reduction and less labour requirement that the current topic provides. In this review, first of all, brief information about self-healing mechanisms used in composites will be given in the light of the studies in literature, then the use of stitch method in composites and self-healing composites will be mentioned and finally, the test methods of self-healing composites will be addressed.

Keywords: 3-Dimensional reinforcement, carbon fibre reinforced polymers (CFRPs), self-healing, self-repairing, self-mendable, stitching process, filament

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1. Introduction

Recent studies show that fossil fuels are a significant contributor to the greenhouse effect, accounting for about a quarter of total carbon dioxide emissions [1]. The European Union aims to reduce greenhouse gas emission values below 60% by 2050 within the scope of the Kyoto Protocol [2]. There is a legal obligation in the automotive industry in this regard. Decreasing the CO2 emission level to 95 g/km in 2021 has become the most important issue for vehicle manufacturers today. The most common work done on this topic is to lightweight [3].

Due to its high strength, good fatigue resistance, lightweight and easy processability, composite materials have growing use in important sectors such as automotive, machinery, aviation, space, defence, white goods, and rail systems[4], [5]. This multi-phase system consists of matrix material including polymer, metal, inorganic non-metallic materials and reinforcing materials including fibres and particles, as shown in figure 1. The matrix material is a structure that binds the reinforcement materials together. It also ensures that the load on it is evenly distributed to the reinforcement materials [3].

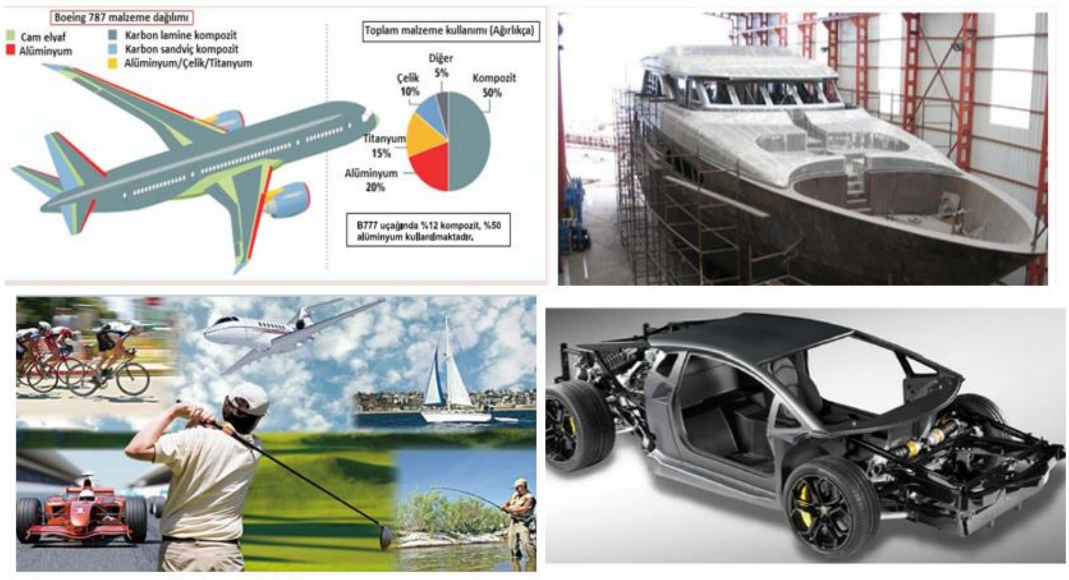

Figure 1. Utilization areas of composite materials [6]

Various fibres such as carbon fibres, glass fibres, aramid fibres, polyethylene fibres, cellulose-based fibres including banana, jute, sisal, flax and hemp, boron fibres, silicon carbide fibres, alumina fibres, etc. are often used to obtain fibre-reinforced composites with advanced or functional composites [7].

Among all different types of composites, fibre-reinforced polymer composites are preferable in many areas since they have high specific strength, high specific modulus, good fatigue resistance, high damage tolerance and good damping characteristics. Fibre-reinforced polymer composites (FRPCs) are mostly formed by overlapping multiple FRPC or prepreg layers and curing them under heat and pressure [9]. With the help of their tailorable and adjustable properties, advanced composites can provide some important advantages including weight reduction, longer shell and usage life compared to conventional composites, (i.e. electrical or thermal)[8]. However, material and manufacturing costs are high to develop and produce in advanced composites. Besides, the matrix materials are still too weak to fulfil high-performance applications and also, reuse or recycling of both matrix and reinforcement can be difficult [8]. Another important point is that the long-term durability of FRPCs materials is still problematic. As shown in figure 2, stresses occurring during the production and use of composites, as well as deterioration, decay, and wearing due to environmental conditions (such as temperature, humidity, UV, scratches) lead to the straightforward emergence of the existing matrix crack or delamination in FRPCs while controlling and repairing these damages, which is difficult and costly[10]–[12]. The formation of these cracks leads to a decrease in the mechanical properties of the material and a shorter service life [13].

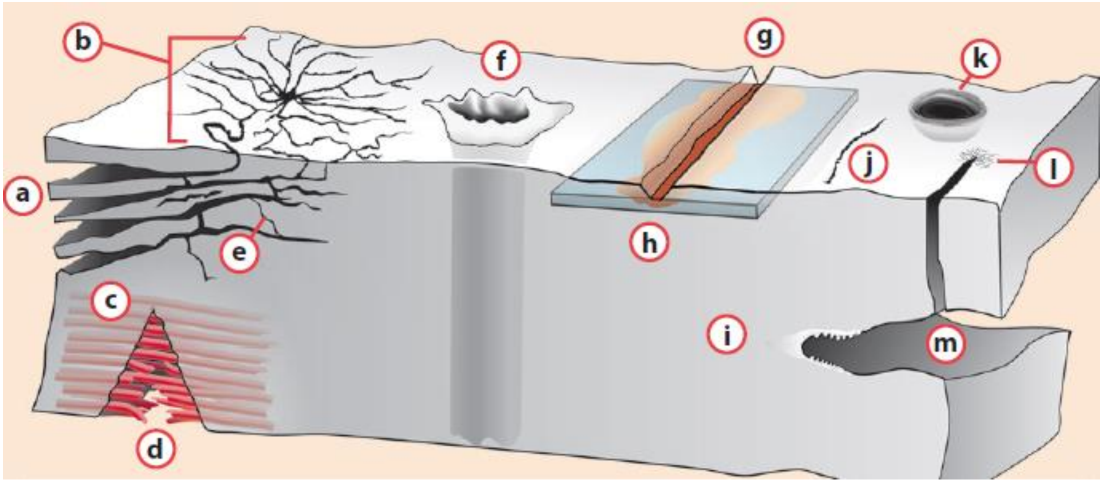

Figure 2. Damage modes in polymer composites [14]

In such cases, damaged parts are tried to be repaired with patch, welding, resin curing and bonding techniques [15]. However, these methods are not self-actualized. That is, they are not automatic and also expensive, technically difficult and time-consuming[16], [17]. This issue is an important research topic worldwide as the repair of the damage creates a serious financial problem. Developing countries are doing various studies on this subject. Among these studies, self-healing materials gain importance. Market analyses on this subject are shown in figure 3. It is estimated that the self-healing composites market will have grown 45.30% from 2021 to 2028 [18].

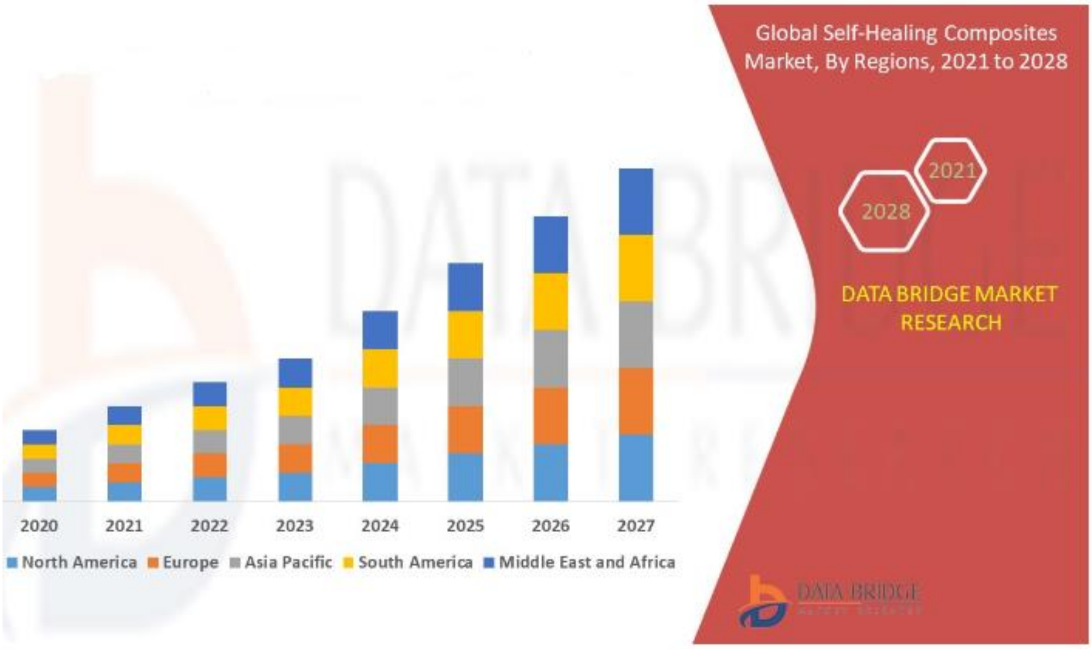

Figure 3. Global self-healing composites market [18].

Therefore, different approaches including self-healing processes were studied to improve the material properties and process.

2. Self-Healing Mechanisms in Composites

Self-healing can be defined as the ability of a material to heal the damage automatically and autonomously without the need for any external intervention [19]. In literature, several terms are used to describe such property in materials, such as self-repairing/healing/mendable, autonomic healing/repair. Self-healing materials range from polymers to metals and ceramics. Polymers are of great interest, especially in the field of self-healing composites due to their advantages including easy processability and low cost. As polymers can have very different improvement mechanisms compared to a wide range of application areas and other material classes, intensive studies are carried out in this field [20].

2.1. Extrinsic Self-Healing

For a long time, several studies have been carried out to eliminate the mechanical breakage and delamination problems of FRPCs and improve their service life; these efforts continue to improve the properties of existing composites or to heal the damaged composites [20]. If we look at the latter, studies are proceeding on two different methods: external and internal self-healing for the self-healing of composite materials [19], [21], [22]. Among them, the extrinsic self-healing method is divided into microcapsule [23]–[25] and microvascular method (Figure 4) [12], [26], [27]. Fluids are used as a healing agent in both methods. The main mechanism of these techniques can be expressed as follows [28]:

1-Breakdown of the capsule / vascular structure as a result of damage

2-Spreading of the self-healing liquid over the damaged area

3-Reaction of the healing agent in the damaged area.

In the self-healing mechanism of composites with microcapsules, the properties of shell and core materials are the most important parameters that determine the performance of this mechanism [29]–[32]. A wide variety of microcapsulation techniques is classified as in situ polymerization, interfacial polymerization, collecting emulsion polymerization, miniemulsion polymerization, solvent evaporation / solvent extraction and sol-gel polymerization based on the wall formation mechanism to encapsulate healing agents as mentioned in literature [33]. Among the microencapsulated healing agents, efficient healing systems are as follows: Single capsule system, Capsule/dispersed catalyst system, Phase-separated droplet/capsule system, double capsule system and all-in-one capsule system [34]. The main disadvantage of this method is that if the self-healing agent is released from the capsule/vascular system, the existing healing agent is depleted and in this way, a single local undesired healing occurs [35].

Figure 4. a) microencapsulation of healing agents and b) intrinsic self-healing mechanism [36]

2.2. Intrinsic Self-Healing

Unlike extrinsic self-healing mechanisms, intrinsic self-healing mechanism does not include a stored healing agent. However, this mechanism is based on the specific molecular structures of the materials and the performance of the polymers. Intrinsic healing mechanism is based on different approaches such as thermally reversible reactions (Diels–Alder (DA)) [21], [37], dynamic covalent bond reformation and reshuffling [38], ionomers [39], [40], dynamics of supramolecular chemistry or combinations [41], photochemical [42]–[44], dispersion of meltable thermoplastic materials [10], [45], [46], solvents and etc. [47]. A schematic representation of the Diels–Alder based shape memory assisted self-healing process is depicted in Fig. 5. [48].

The intrinsic mechanism is less complicated than the extrinsic self-healing mechanism, since the intrinsic mechanism may perform more than one healing process while there is no need to have the stored healing agent for this repair. Besides, the need for external stimuli (such as heat, light, UV) is a disadvantage [49] and internal self-healing is often limited to repairing a small damaged area [50].

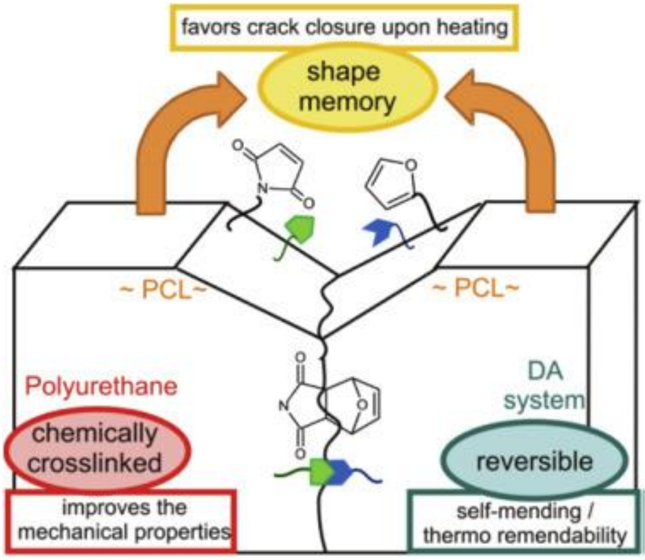

Figure 5. Schematic representation of the Diels - Alder based shape memory self-healing process based on PCL and furan-maleimide chemistry [51]

Among the intrinsic self-healing mechanisms, the use of thermoplastic or thermoset solid state elements, such as fibres or filaments, as the curing agent in the polymer matrix is one of the effective methods for healing the matrix cracking, preventing delamination and repairing defective parts in polymer composites [52], [53].

Since, in general, the damage to composite materials occurs between the composite layers (delamination), the intrinsic mechanism may be the most appropriate method for self-healing of the composites [54]. The thermoplastic healing agent is added as short/long-staple fibres, filaments or particles to the epoxy composite material and when the damage occurs, the healing is occurred by applying heat and/or pressure to the composite. However, not every thermoplastic polymer can be used as a curing/repairing agent; the following specific features are required [55]–[57]:

1. The healing agent must have a reactive functional structure to react with amine groups in the epoxy.
2. Once the healing agents have entered the damaged area, they must be capable of binding to form a strong bond with the damaged surfaces.
3. The healing agent should have a low viscosity and melting point to facilitate penetration into the damaged area.
4. The healing agents should remain inactive until they are heat activated.
5. The size and distribution of the healing agents should be sufficient to react with all fracture surfaces.
6. The healing agents must be semi-crystalline. This is because they exhibit a sufficiently low viscosity above their melting point and also, have high mechanical properties in the crystalline structure

So far thermoplastic polymers such as poly (ethylene-co-methacrylic acid) (EMAA) [58]–[60]; poly (ethylene-co-glycidyl)-methacrylate (PEGMA), ethylene vinyl acetate (EVA), acrylonitrile-butadiene-styrene (ABS) [56], [61], [62], poly(vinyl-butyral) (PVB) and styrene-ethylene-butadiene copolymer (SEBS) [62] have been studied as the intrinsic self-healing agents. These thermoplastic polymers are used as particles in resin to form composite materials. However, several studies have indicated that using the repair agent in filament form gives better results [53], [58], [59], [63].

Moreover, among the other healing agents, EMAA has been found to be the most effective and durable curing agent, since the acid group in its structure reacts strongly with hydroxyl groups in the epoxy [64].

3. Self-Healing Composites by Stitching

3.1. Stitching Process in Composites

Carbon fiber reinforced composite (CFRC) materials are used in many different industries to provide high mechanical properties and significant weight savings due to their high in-plane specific strength and stiffness. However, carbon fiber is relatively expensive compared to other reinforcement materials. In addition, composite materials have low fracture toughness and low damage tolerance due to their high sensitivity to out-of-plane fracture. For this reason, researchers are working on different methods to increase translaminar strength and reduce delamination formation. In composites, the use of fabrics produced by weaving, knitting or braiding with different weave types, or stitching composites with special threads and filaments and then laminating them can increase the strength of the structure and prevent crack propagation [65] [66].

The type and structure of the seam applied to composite materials is one of the most important parameters affecting the performance of the composite. As seen in Figure 6, 4 different stitching types are applied: Lock stitch, Modified Lock stitch, Chain stitch and Dual lock stitch. While lock stitches are used in the fabric industry, other stitch types are frequently used in the composite industry. [67].

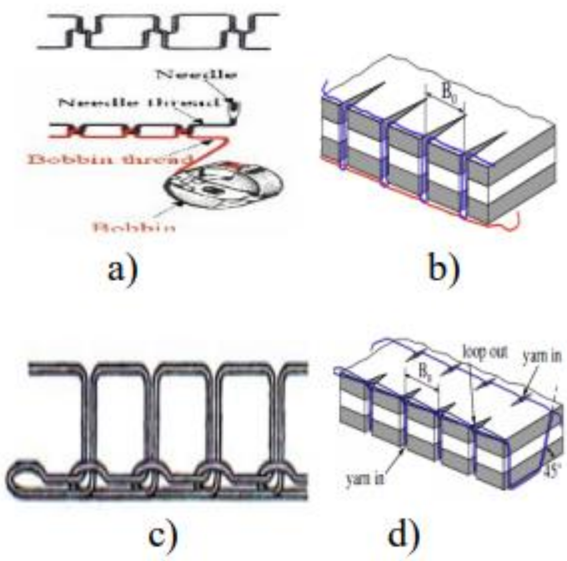

Figure 6. Stitching Types (a) Lock stitch; (b) Modified Lock stitch; (c) Chain stitch and (d) Dual lock stitch [68]

Stitching the composites is advantageous over other textile processes as it allows the stitching of both dry fabric and uncured prepreg layers [69]. Constructing structural parts such as fittings from composite materials requires more mechanical strength. Delamination damage caused by impact occurs at joints or load application centres of structural parts made of composite materials. In the future, a technology that allows a specific and local effect on the three-dimensional properties of the material will be required to form increasingly complex composite structures [70].

Through-the-thickness stitching is the most effective method for joining composite structures such as stiffeners, lap joints and wing/spar joints is shown in Figure 7. This method increases high in-plane strength, interlaminar fracture toughness, impact damage tolerance [71], low cost, high in-plane strength, interlaminar fracture toughness and tensile strength in composite materials [72]–[74]. It also has a higher resistance to delamination cracking under low energy, high energy, dynamic loading and ballistic effects [75], [76].

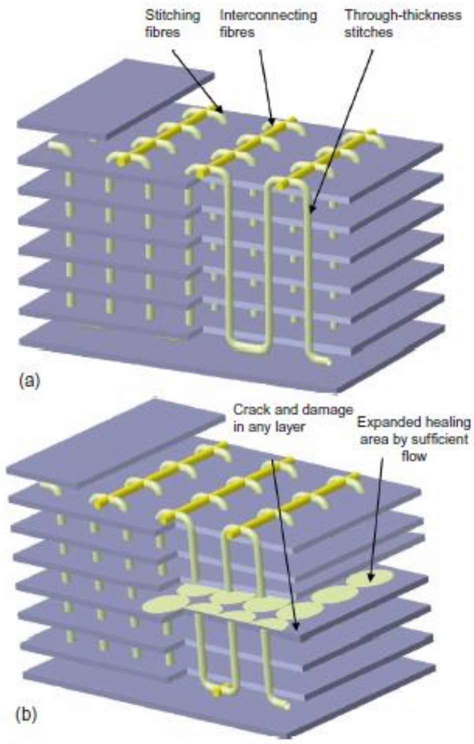

Figure 7. Architecture of the EMAA stitches in the carbon fibre–epoxy composite (a) before (b) after [77]

Stitched FRPC materials have an advantages as well as disadvantages [78]. Especially when the stitching needle passes through the prepreg tape or fabric, a gap is formed in the area and the fibres are separated from each other. Also needles do not easily pass through in the prepreg or tape and therefore the formation of resin-rich regions, porosity, voids, slippage of in-plane and out-of-plane fibres, fracture of fibres and crack formation between the resin occur [79].

In general the damage to composite materials, can be controlled depending on the stitching yarn type and density of stitching, filament structure and diameter, needle size and diameter, the orientation of the stitch rows [80] and processing technique [81].

3.2. Self-Healing Performance by Stitching

The self-healing thermoplastic polymers in the review will be summarized separately as particles and filament forms. While different thermoplastic polymers are used in granular form, only EMMA thermoplastic polymer is used in filament form. EMMA is preferred because its molecular structure plays a better role in the improvement of the delamination regions formed between the layers and the filament form of EMMA,which makes it more suitable for the stitching method and more effective in recovery [56], [60], [82].

On the other hand, the use of other thermoplastic polymers other than EMMA in the form of particles for self-healing purposes can be summarized as follows: Pingkarawat et. al. [56] investigated the effect of different types of healing agents (EMMA, EVA and PEGMA) on the compression, heal and tensile properties of composite materials by using different concentrations (5%, 10%, 15%). Varley et al. [62] investigated the healing mechanisms of self-healing materials using different thermoplastic polymers to investigate the healing efficiency and mechanical properties of composite materials. In this study, thermoplastic healing agents such as EMMA, EVA, SEBS, PEGMA, PVB and ABS were selected because of their chemical structures. Pingkarawat et al. [61] selected EMMA, EVA, PEGMA and ABS thermoplastic polymers as repairing agents and examined the effect of interlayered damage on composite materials and their mechanical properties. The initial healing process was PVB> EVA> SEBS ~ ABS ~ EMMA> PEGMA. However, the successive recovery ability was listed as EVA> EMAA> PEGMA> PVB> SEBS ~ ABS. Thus, it was concluded that EMMA, EVA and PEGMA are reproducible healing agents.

The molecular structures of ABS, EVA and EMMA are shown in Figure 8 [83]. Acrylonitrile–butadiene–styrene is an opaque, amorphous polymer. It is composed of the polymerization of styrene, acrylonitrile and butadiene elements as shown in Figure 7 [83]. ABS includes unsaturated hydrocarbon, nitrile, maleic anhydride and cyanide functional groups which react with epoxy groups. However, due to its high melting temperature, high viscosity, low glass transition temperature and poor adhesion, its self-healing efficiency is low [62].

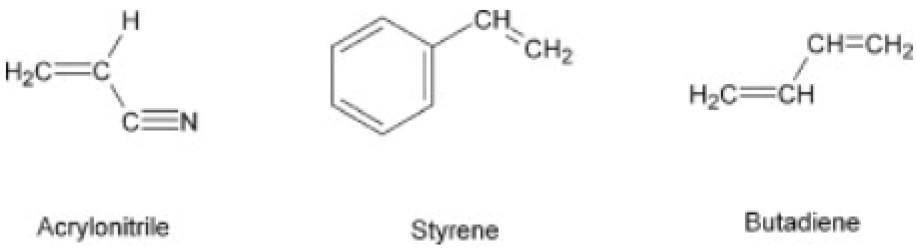

Figure 8. Chemical structure of ABS raw materials [83]

EVA is a random copolymer and it is made of with varying amounts vinyl acetate (VA) and ethylene. The end property depends on vinyl acetate (VA) content. The elastomeric grade of EVA consists of VA content varying from 40–60 wt %, which is used in adhesives. In EVA, as the VA content increases, its crystallinity decreases, so Tm lowers [84]. The increase in VA proportion in EVA causes the growth of oxygen and O/C contribution. Corona discharges cause the emergence of new C=O groups and the creation of RCOO− groups. EVA does not fully react with epoxy, but when RCOO− groups are formed in its structure, the reaction takes place [85]. Compared to other thermoplastics, it has a much lower viscosity in the presence of heat and exhibits a fluid-like behaviour, so that it can easily penetrates into cracks and heal by reacting with the damaged surface [56], [62].
EMAA is used as the most effective repair agent due to its low melting point, toughness and high melt flow index [52]. It is used in the form of particles, films, fibres or filaments dispersed in the epoxy matrix and composite materials. In

general, the repair mechanism takes place in the presence of heat (about 150 ° C) between the hydroxyl group in the epoxy and the acid groups in the EMMA structure. It produces water vapour in the matrix in the presence of heat. Molten EMMA is spread to the damaged area under the influence of water vapour and is healed by reacting with the damaged structure [85]. EMAA does not run out during the reaction and a reproducible process occurs.

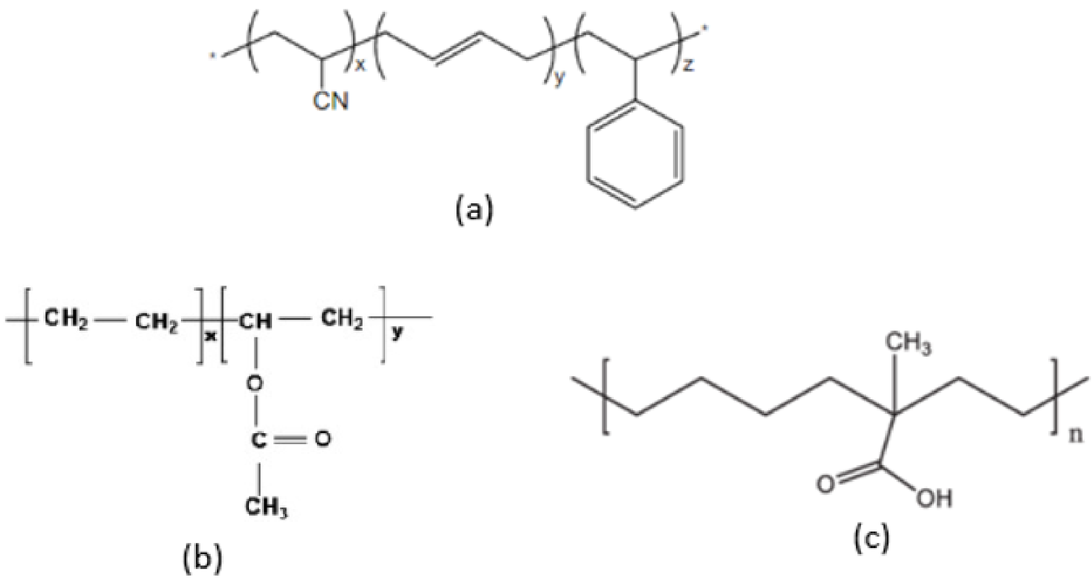

Figure 9. Chemical structure of the thermoplastic healing agents used in this work showing the range of functional group and polymer architectures. (a) acrylonitrile butadiene styrene (ABS) [86], (b) ethylene vinyl acetate (EVA) [87], (c) Poly(ethylene-co-methacrylic acid (EMAA) [88]

As shown in the studies mentioned below, self-healing composite material development studies were examined with the stitching method. The effect of stitch density on inter-layer fracture toughness and self-healing properties of carbon-epoxy composite materials was investigated [59]. By using the EMAA filament, the stitching increased the interlaminar fracture toughness during delamination by forming a large diameter crack bridging traction zone, as shown in Figure 10.

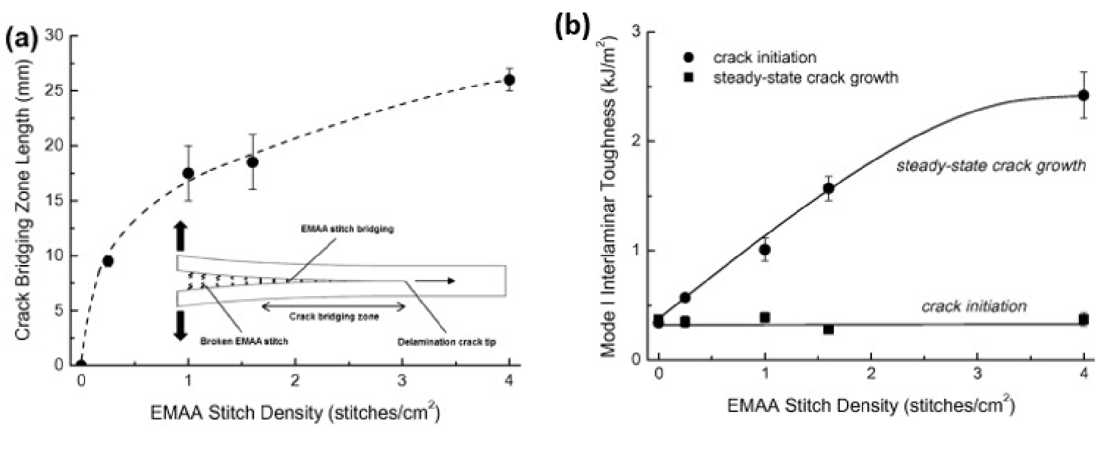

Figure 10. Effect of EMAA stitch density on the (a) length of the crack bridging zone and (b) number of stitches within the interlaminar fracture toughness [89]

Pingkarawat et al. [90] investigated the effect of stitching with EMMA filaments in carbon-epoxy laminate on self-healing and delamination toughness. According to the results, fracture toughness was completely recovered by stitching EMMA filaments. When the stitch density reached 4 stitches/cm^2, resistance to fatigue and fracture toughness increased due to the rise in the crack bridging zone. In another study [91], EMAA filaments with a diameter of 1.5 mm were stitched with carbon prepregs to form self-healing composite materials as shown in Figure 11.

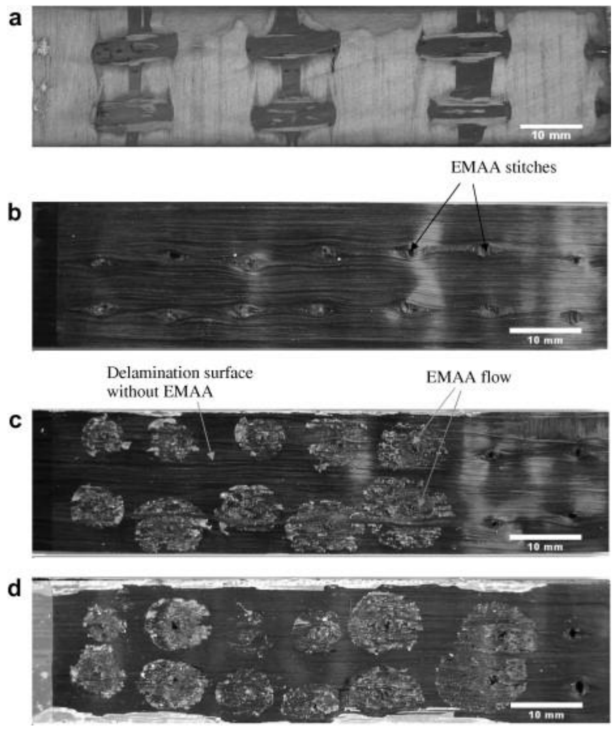

Figure 11. (a) The top surface interconnected EMAA fibres, (b) the fracture surfaces before healing, (c) after first healing and (d) after second healing [92].

In another study, self-healing efficiency, delamination toughness and mechanical properties of composite materials stitched using four different EMMA filament diameters were investigated [58]. As the diameter of the filament increases, the thickness (mm) of the composite material increases while the carbon density in it decreases and thus its mechanical properties decrease. Yang et al. arc. [93] developed a 3-dimensional composite T-joint, through-thickness direction stitching with EMMA filaments.

4. Testing of Self-Healing Composites

Various characterization techniques are used in the evaluation of self-healing properties and performance. The most commonly used thermal characterization techniques can be summarized as follows:

1. Dynamic Mechanical Analysis (DMA) is used to determine self-healing materials, glass transition temperature and viscoelastic properties [94]
2. Differential Scanning Calorimeters (DSC) is used to measure the melting and glass transition temperature besides examining the thermal properties and curing behaviour of the matrix and self-healing agents [94]

3. Thermal Gravimetric Analysis (TGA) is widely used to determine the composition and thermal stability of the matrix and self-healing agents [94].
4. The fibre content of the laminates is measured by using the resin combustion test according to ASTM D2548-11 specifications [95].

The main mechanical characterization techniques;
1. Tensile testing determines the semi-static mechanical properties of a material according to ASTM D3039 specifications. It provides the ability to understand tensile strength and stress-strain behaviour such as stress, elongation or Young's modulus as a function of temperature, time and stress ratio [96].
1. Mode I and Mode II interlaminar fracture toughness and self-healing efficiency are achieved using a double cantilever beam (DCB) and End-Notched Flexure (ENF) test in accordance with ASTM D5528-01 and ASTM D7905 / D7905M specifications respectively [97] [98].
2. The three-point bending test is performed in accordance with ASTM D7264/D7264M-07 specifications to find the flexural strength properties and flexural modulus of flexure of hybrid composites [99].

Besides, the molecular structure of the self-healing composite materials is examined using Fourier transform infrared spectroscopy (FT-IR) and Scanning Electron Microscopy (SEM) is investigated before and after the formation of microbubbles formed in the material, pore structure [91].

5. Conclusion

In this article, the effects of the use of thermoplastic polymers in the form of stitches in composite materials on self-healing efficiency and other properties are presented. As a result of stitching composites with thermoplastic filaments, it has been proven that mechanical properties and repair efficiency are greatly affected. The parameters such as type and diameter of the needle and filament, seam density, laminate thickness and fabric/prepreg structure affect the properties of the self-repairing composite material to be created. Also, due to the stitching process, filament breakage, misalignment and too tight / loose s stitching, many different damages on composite materials, such as resin-intensive zone formation, seam distortions, microcracking, excessive looseness or tightness can be caused. Therefore, more studies are needed in this area. In particular, optimization of stitch parameters to increase interlaminar delamination resistance has not yet been studied with a strong theoretical approach and studies are ongoing in this respect.

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