Behavior of microcapsules in FML under different pressure of manufacturing in autoclave

Monika Ostapiuk

Received: 23 June 2022 / Accepted: 20 October 2022 / Published online: 29 October 2022
© The Author(s) 2022

Abstract
Magnesium alloys are the lightest available structural metals. The low density and high strength-to-weight ratio make magnesium and its alloys an excellent option for use in the automotive and transport vehicles. In the case of magnesium and its alloys, the corrosion phenomenon is a serious problem especially when it is connected with epoxy-carbon composite (CFRP). Poor adhesion can easily cause delamination at the interface. So in this the work was analyzing the influence of pressure in laminate manufacturing in the autoclave process of a magnesium alloy/CFRP on the stability and distribution of microcapsules and observation about delamination. It was concluded that the PEO layer with sol–gel improves the adhesion between CFRP and the MCs. Different pressures in the autoclave process promote porosity if a pressure lower than 0.4 MPa is used.

Keywords FML · Microcapsules (MCs) · Microstructure · PEO layer

1 Introduction
One of the classes of hybrid composites is fiber metal laminates (FMLs) [1–4]. FMLs combine the advantages of metal and polymer composites. These laminates possess high-quality structure, as well as excellent properties of fatigue and impact resistance. FMLs with high temperature resistance are promising materials for use in the aerospace industry. They are especially propitious since the weight reduction of structures has always been one of the main objectives of the industry. Magnesium alloys are the lightest available structural metals. The low density and high strength-to-weight ratio make magnesium and its alloys an excellent option for use in the automotive and aerospace industries to reduce the weight and fuel consumption of transport vehicles [4].

Cortés and Cantwell [5] in their work mentioned the low density and improved electromagnetic shielding capability as advantages of magnesium alloys. Interestingly, in their work [5] they mentioned the better corrosion resistance, which is a rare opinion. As is well known, the problem of galvanic corrosion of FMLs is usually associated with the combination of aluminum alloys and composites with carbon fibers [5]. In the case of magnesium and its alloys, the corrosion phenomenon is a serious problem when analyzing other scientific works and common knowledge to date [6].

The authors [7, 8] discuss aspects related to corrosion in their research, especially referring to FMLs containing magnesium alloys and polymer composites based on carbon fibers. In this aspect, the surface preparation of magnesium alloys, where the metallic surface is modified, plays an important role. The modification concerns the bond strength, i.e., obtaining the most durable bond at the interface. In this case, the interface quality is a key aspect in carbon fiber-reinforced magnesium alloy laminates [7]. Poor adhesion can easily cause delamination at the interface, reducing the overall strength and stiffness of FMLs [8]. There are many methods of surface treatment, including mechanical [9, 10], chemical [11], electrochemical [12, 13], and plasma [14, 15] treatment. In this case, it is essential to optimize the surface treatment method for the specific metal and resin system.

The PEO (plasma electrolytic oxidation) method is gaining increasing interest as an environmentally friendly plasma-electrolytic technique due to the short process time. As a result, highly stable and relatively dense ceramic coatings are obtained with enhanced hardness, adhesion, corrosion resistance, and wear resistance compared to other surface preparation methods such as anodizing. However, the effectiveness of the PEO process depends on a number
of parameters; therefore, the most important factors such as electrolyte concentration, voltage, and processing time should be taken into account when creating the coating. The electrolyte concentration is an important parameter when deciding on the discharge characteristics and largely affects the quality of the PEO coating.

In the authors’ research [16, 17], PEO coatings exhibited high corrosion resistance and adhesion to metallic substrates. Nevertheless, when observing the behavior of ceramic coatings during production by the PEO method, two types of drawbacks can be noticed, namely, microcracks and interconnected porosities. The first of them are formed as a result of rapid cooling of the molten oxide by the surrounding cold electrolyte [18]. On the other hand, the interconnecting of porosity results from the release of dissolved oxygen in the molten oxide under the influence of high temperature and pressure conditions during the process of creating a ceramic layer of magnesium oxide [18].

These defects are paths for electrolytes to penetrate the coating and then initiate the corrosion process. The occurrence of these defects during the PEO process is inevitable, despite the execution of many works aimed at reducing these defects by optimizing the electrical and electrolytic parameters [11–23]. The PEO layer is distinguished by a dense inner layer in direct contact with the metal substrate as the leading layer in protection against corrosion, and a porous outer layer. The ceramic coating on magnesium alloys is the crystalline phase of MgO and phases related to the employed electrolyte such as Mg3SiO4 and Mg (PO4)2. Such a coating exhibits corrosion stability for a short time, but after some time it starts to corrode. To date, there have been few literature reports related to magnesium FML and the corrosion phenomena occurring in them. In addition, in spite of the benefits of the future use of magnesium in FMLs, there are several aspects that require further research before it can be concluded that the new range of magnesium-based FMLs is sufficiently understood.

Hence, the author has taken up the topic related to FMLs regarding the first step, which is the correct production of FMLs based on magnesium and carbon fibers. During their production, phenomena occur that influence the stress cycle in the metal layer as a consequence of the difference in stiffness between the metal and fiber layers, which may be advantageous for magnesium owing to its low stiffness. To this must be added the residual stresses caused by the hardening process. The required higher curing temperatures increase the residual stresses, resulting in a significant reduction in the laminate service life. This becomes more important when the full range of operating temperatures of an airplane are considered. The residual stresses during curing at about 185 °C are considered very high. Gonzalez-Canche et al. [24] found that the adhesion of various materials allows an increase in plastic deformation as a result of partial inhibition of localized deformation, delaying the beginning of laminate cracking. The use of epoxy resin is suitable to increase the residual strength, fatigue limit, and damage tolerance; it has additionally been observed that the high temperature to which the material is exposed during the curing cycle did not affect these mechanical properties [24].

Moreover, the formation of voids at the interface has a negative impact on the structural strength of FMLs as it causes a poor bond between the metal and the composite material [24]. Abouhamzeh et al. [25] proposed a modeling procedure suitable for this type of material, while Jakubczak et al. [26] investigated the effect of thermal aging on ILSS (interlaminar shear strength) for CARALL with different aluminum surface preparation methods and fiber combinations. They found that the addition of a thin glass layer at the interface between the sheets and the carbon composite, suitable to aver galvanic corrosion, did not affect either the ILSS or thermal fatigue of the laminates [27].

Kozioł et al. [28] assessed the effect of carbon nanotubes and addition of graphene to the resin of a composite material and found improvement in the shear strength. Currently, self-healing layers are of wide interest in research centers.

It is especially related to the cracking processes in various strength and stress ranges occurring in FMLs. In the area of contact of the Mg/PEO/CFRP layers, the authors of [29] introduced an inter-layer self-healing agent to increase durability by repairing interlayer cracks. Various self-healing agents are widely proposed. In this case, microcapsules with self-healing properties are beneficial because of their simplicity, preparation, and application [29]. In this healing system, first proposed by Ullah et al. [30], the healing substance is stored in capsules and dispersed throughout the matrix. As the interlayer fracture grows, it rips the capsules apart, releases the healing cores into the fracture zone, and the delamination layers are then repaired. According to the authors, the presence of microcapsules in FML may act as reinforcement with the advantage of crack self-healing.

This is mainly because the materials contained in the microcapsules can provide immediate feedback to external signals [31–33]; complete self-healing automatically and significantly extends the service life of laminates [34–36].

Self-healing materials in the form of microcapsules [36] have attracted increasingly greater attention and have been widely researched, especially since the first generation healing system described by White et al. [31]. Moreover, for the use of microcapsules in the coating industry, the simplicity of its preparation process and mass production is also important [37].

The aim of the work was to analyze the influence of pressure in laminate manufacturing in the autoclave process of a magnesium alloy/epoxy-carbon composite (CFRP) on the stability and distribution of microcapsules. In addition, the
quality of the polymer composite and the metal-composite interface were assessed.

2 Materials and methods

2.1 Materials

2.1.1 Microcapsules (MCs)

The emulsion stabilizer, gum arabic (GA), was obtained from LabChem. The active H source compounds, namely, poly(ethyleneimine) (PEI) aqueous solution (Mw 60,000, 50 wt% in H2O) and triethoxy(octyl)silane (n-OTES), were supplied from Sigma-Aldrich.

Isophorone diisocyanate (IPDI, with 98% purity), with the commercial name of Desmodur® I, was obtained from Covestro. The isocyanate was encapsulated. A polyisocyanate with the commercial name Desmodur® RC for the shell precursor was kindly supplied by CIPADE JSC.

The MCs were produced by an oil-in-water (O/W) microemulsion system in combination with interfacial polymerization processing. The W phase was composed of water and 4.7% of the emulsion stabilizer, gum arabic (GA). The O/W microemulsion was prepared by vigorous stirring of the two immiscible water and oil phases. MCs containing 4.85 wt% of the entire emulsion system were processed by means of an Ultra-Turrax Crushing Disperser (IKA T25 digital ULTRA TURRAX, Germany) at the speed of 1200 rpm for 10 min at room temperature (RT). Desmodur RC is a mixture of an isocyanate prepolymer in ethyl acetate with content of 25 wt%. The oil phase consists of two isocyanates. The first one was IPDI (51.2 wt% of the O phase), to be encapsulated, and the second one Desmodur RC (48.8 wt% of the O phase), to form the shell of the MCs.

When the stable O/W microemulsion system was processed, the active H sources, namely, the n-OTES (triethoxy(octyl)silane) and an aqueous solution of PEI (polyethyleneimine), were added dropwise to the emulsion system during mechanical stirring at 500 rpm, at 50 °C. These active H sources are designed to support the process of creating shells. The synthesis was maintained under the referred conditions for 3 h 30 min. During that time, every sample was observed under a light microscope in order to assess the shell formation and the maturation of the MCs. Distilled water was used to wash the MCs in order to avoid their aggregation. The MCs were dried at atmospheric pressure for 96 h at ambient temperature.

2.2.2 FML manufacturing

The FMLs consist of AZ31 Mg alloy and unidirectional carbon fiber/epoxy prepreg tape (0.131 mm for one layer, AS7J Hexcel, USA). The magnesium sheets with the PEO layer were coated with a sol–gel layer. The commercial EC2333 (3 M Scotch Weld™, USA) primer based on resin and inorganic–organic silanes (sol–gel based on toluene, glycidyl 3-(trimethoxysilyl)propyl ether) was used. The employed primer was applied by means of an atomizer on the Mg/PEO surface after being mixed with selected amounts of MCs. The self-healing layer was between the AZ31/PEO and CFRP layers (Fig. 1).

Afterwards, the samples were dried for 72 h at RT. The FMLs were manufactured in an autoclave chamber the under pressure of −0.08 MPa, curing temperature 135 °C, curing time 2 h, and heating/cooling 0.033 K/s. The laminates were

Table 1 Composition of AZ31 magnesium alloy substrate

| Elements | Mg | Ca | Na | Fe | Si | Mn | Zn | Al |
|----------|----|----|----|----|----|----|----|----|
| Composition (wt%) | Rest | <0.001 | 0.001 | 0.24 | 0.004 | 0.307 | 0.914 | 3.109 |
cured by applying three different autoclave pressures (0.1, 0.2, and 0.4 MPa). A full vacuum of $-0.02$ MPa was applied throughout the cure cycle.

Figure 2 shows a diagram of the FML hardening process. The samples that were used for the SFE analysis and surface topography were 50 mm $\times$ 50 mm $\times$ 0.5 mm (5 pieces for each measurement). On the other hand, the samples for the microstructure investigations had the dimensions 20 mm $\times$ 10 mm $\times$ 1.5 mm (5 pieces for each laminate configuration). The dimensions of the samples were adjusted to the autoclave process (vacuum bag) so that no cutting process was performed. Any influence of the edge degradation process is thus eliminated. Samples using different pressures for the AZ31 layers with PEO and CFRP polymer composite, and separate samples with the mixture of MCs with sol–gel were prepared and analyzed.

2.2.3 Microstructure observation

A high-resolution Nova Nano SEM 450 scanning electron microscope (FEI, The Netherlands) was used for the morphological and microstructural analyses. They were carried out employing secondary electron (SE) imaging under 5.0 and 30.00 kV accelerating voltage conditions.

The samples were previously coated by gold sputtering utilizing a Quorum Technologies sputter coater model Q150T ES (QUORUM, UK).

Panoramic microstructure micrographs (a sequence of several photos from the whole surface area of the specimen) were taken by means of a NIKON MA 200 (OLYMPUS, Germany) light microscope using Nomarski contrast.

2.2.4 Fourier transform infrared spectroscopy (FTIR)

An FTIR apparatus spectrometer (PerkinElmer, Spectrum Two), equipped with a UATR Two accessory with a resolution of 4 cm$^{-1}$ and data collection of 8 scans, was used. It was necessary to verify the chemical composition of the obtained MCs. Characteristic groups were identified—the presence of encapsulated isocyanate and confirmation of the chemical structure of the MC shell. Therefore, in addition to the spectra of the MCs, those of the isocyanate compounds that were employed in the MC synthesis were also obtained.

2.2.5 Surface roughness

A Dektak 150 surface profilometer (Veeco, USA) was utilized to determine the basic geometrical parameters of the surface layer of the investigated materials and the surface topography.

Surface profilograms of the samples were made and the stereometric parameters, arithmetic means, were determined.

2.2.6 Wetting angle

The physico-chemical/adhesive properties of the surface layer were determined by a wettability test using contact angle measurements. Direct measurement of the angle with a drop of liquid (distilled water, diiodomethane) on the surface was made. Determination of the surface free energy (SFE)
value was performed by the Owens–Wendt method, calculating SFE based on measurements of the contact angle of the examined surfaces.

3 Results and discussion

3.1 Surface topography

Characteristic 2D and 3D roughness profiles of the surface layers obtained from the studied base materials are shown in Fig. 3.

Based on the analyses of the surface topography and the obtained 3D images of the surface of the investigated materials, it can be concluded that AZ31 with PEO with the sol–gel layer is characterized by the highest homogeneity. The surface topography indicates a geometric layer structure with the lowest variability and the most balanced individual topographic features of the surface. It is characterized by micro-inequalities with a high degree of uniformity of their distribution on the surface. Taking into account the aspect of classification, this surface, depending on the geometrical features, may be classified as a surface characterized by the presence of significant micro-roughness, which may contribute to obtaining a proper bond. In other cases, both for the AZ31 alloy subjected to the PEO treatment process and for the alloy without treatment, the surface is characterized by greater heterogeneity. Larger fluctuations in the height characteristics of the surface profile and the presence of areas of significant geometrical differentiation can be observed. These surfaces are characterized by the presence of significant single roughness peaks.

The selected stereometric parameters characterizing the surface topography of the layers produced on the magnesium alloy are presented in Table 2.

The obtained characteristic stereometric parameters of the surface topography of the examined layers on the magnesium alloy showed the dependence of the geometric structure of the surface on the method of layer production. The lowest roughness parameters (Ra and Rq) were recorded for the AZ31 magnesium alloy with the PEO layer with sol–gel. Moreover, for this layer, the smallest values for the depth of the smallest recess (Rv) and the height of the highest elevation of the profile (Rp) were recorded, resulting in the lowest values of the overall height of the profile. The AZ31 magnesium alloy subjected to the PEO process is characterized by intermediate values of roughness parameters characterizing the geometric structure of the surface layer of the modified surface. The surface of the base material, magnesium, has the highest values of roughness parameters.

All the Ra, Rq, and Rz parameters, as well as the values of the lowest recesses and the highest profile elevations, are significantly higher compared to the surface subjected to the PEO process and PEO with sol–gel.

To sum up, on the basis of the obtained results of roughness parameter measurements, the degree of geometric homogeneity of the surface can be arranged in the following order: magnesium alloy PEO with sol–gel, AZ31 with PEO, and AZ31. Therefore, it can be predicted that, among all the analyzed surface modifications, the preparation process by PEO with sol–gel will allow a high-strength adhesive bond to be achieved on the metal-MC-composite interface, with the participation of mechanical adhesion through a large amount of tacking.

3.2 Physico-chemical properties of surface

The physico-chemical properties of the surface in terms of assessing the ability to create an adhesive bond of high strength and durability were analyzed by means of wettability expressed by the value of the contact angle $\Theta$ and the surface free energy. The values of the contact angle and the surface free energy as well as its individual components for the surface layers of the studied materials are presented in Table 3.

The obtained contact angle results classify the near surface of the alloy as slightly hydrophobic and the PEO and PEO/sol–gel layers as hydrophilic as the contact angles were 102.4°, 82.9°, and 73°, respectively. By analyzing the contact angle, it can be concluded that the use of sol–gel on the magnesium alloy after PEO treatment resulted in an increase in wettability.

The determined values of the surface free energy, as well as its components, polarity, and dispersion, indicate that the SFE values significantly depend on the method of metal surface preparation. The surface of the AZ31 magnesium alloy treated with PEO with sol–gel exhibited the highest values of surface free energy. On the other hand, the lowest SFE values were recorded for the magnesium AZ31 not subjected to any surface preparation process. For the AZ31 magnesium alloy treated with PEO, an increase in SFE by about 1 mJ/m² was also noted as compared to the unmodified magnesium alloy surface. On the other hand, for the magnesium alloy treated with PEO and sol–gel, the SFE value increased to 49.5 mJ/m², which is the highest value among all the examined surfaces.

Summing up, the conducted tests of the physicochemical properties of the modified surfaces, expressed by the contact angle and SFE, again allow it to be assumed that the magnesium surface subjected to the PEO process with sol–gel is characterized by the greatest ability to create an appropriate adhesive bond. In addition, as a result of the PEO treatment with sol–gel, the surface is characterized by a significant proportion of the polar component of SFE, which indicates the possibility of
forming strong chemical bonds. The combination of the above features makes it possible to create an adhesive bond of high strength and durability on the metal-MC-composite interface.

### 3.3 Microcapsules

In Fig. 4a and b, the morphology and size distribution of the MCs are presented.
The spherical shape of the microcapsules was obtained by core–shell morphology and the average size of a single MC was 20 µm. In Fig. 4b, one can also notice inhomogeneities and wrinkles in the MC coating. Heterogeneous reaction kinetics and shear forces caused by the internal fluid [38, 39] gave rise to this phenomenon. Moreover, it is also related to the contraction of the core [40], in addition to the rapid formation of the rigid shell as a result of the reaction between the active sources of hydrogen and highly reactive isocyanate compounds.

The FTIR spectra of the MCs are shown in Fig. 5 with the isocyanate used in the MCs. The presence of liquid and unreacted isocyanate, which should be trapped in the MCs, corresponds to the peak at about 2250 cm\(^{-1}\), which relates to NH\(_2\) stretching vibrations. The peak at 1580 cm\(^{-1}\) is typical for secondary amides due to in-plane NH bending.

Comparing the wavenumber used in the synthesis, the one in the MC spectrum, and the shape of the NCO peak, this confirms that indeed the encapsulated isocyanate is IPDI. This indicates the efficient encapsulation of a large amount of IPDI, as was expected.

### 3.4 PEO layer on AZ31

As for the composition of PUa in the MC coating, this is confirmed by the presence of the band between 3000 and 300 cm\(^{-1}\), which relates to NH\(_2\) stretching vibrations. The peak at 1580 cm\(^{-1}\) is typical for secondary amides due to in-plane NH bending.

Table 2  Selected stereometric parameters of layer surfaces

| Material          | Ra (µm) | Rq (µm) | Rv (µm) | Rp (µm) | Rt (µm) |
|-------------------|---------|---------|---------|---------|---------|
| AZ31              | 3.687   | 4.86    | −36.57  | 45.79   | 82.37   |
| AZ31/PEO          | 1.973   | 2.51    | −36.03  | 39.41   | 75.44   |
| AZ31/PEO/sol–gel  | 1.66    | 2.13    | −35.07  | 37.94   | 73.02   |

As for the composition of PUa in the MC coating, this is confirmed by the presence of the band between 3000 and 300 cm\(^{-1}\), which relates to NH\(_2\) stretching vibrations. The peak at 1580 cm\(^{-1}\) is typical for secondary amides due to in-plane NH bending.

Comparing the wavenumber used in the synthesis, the one in the MC spectrum, and the shape of the NCO peak, this confirms that indeed the encapsulated isocyanate is IPDI. This indicates the efficient encapsulation of a large amount of IPDI, as was expected.

### 3.4 PEO layer on AZ31

In Fig. 6a, the cross-section of the oxide layer after PEO treatment is shown. The outer one is about 8–12 µm thick and porous in nature. In fact, these pores are discharge channels that were produced by the plasma process, and

The spherical shape of the microcapsules was obtained by core–shell morphology and the average size of a single MC was 20 µm. In Fig. 4b, one can also notice inhomogeneities and wrinkles in the MC coating. Heterogeneous reaction kinetics and shear forces caused by the internal fluid [38, 39] gave rise to this phenomenon. Moreover, it is also related to the contraction of the core [40], in addition to the rapid formation of the rigid shell as a result of the reaction between the active sources of hydrogen and highly reactive isocyanate compounds.

The FTIR spectra of the MCs are shown in Fig. 5 with the isocyanate used in the MCs. The presence of liquid and unreacted isocyanate, which should be trapped in the MCs, corresponds to the peak at about 2250 cm\(^{-1}\). This is confirmed by the N=C=O bonds related to stretching vibrations. This makes it possible to identify the MCs.

In the MC spectrum at ca. 1710 cm\(^{-1}\), the presence of carbonyl peaks can be identified as the C=O of the urethane. The peak at ca. 1698 cm\(^{-1}\), from urea C=O, is also present in the MC spectrum due to the interfacial reactions between the NCO groups and the OH and NH groups from the active H sources used, confirming the composition of PU and PUa in the MCs.
3.5 Microstructure observation of FML

Figure 8 presents the laminate microstructure after manufacturing in the autoclave under different pressures. In FMLs, the pressure acting on the surface is a factor that directly influences the durability of the metal-composite bond. As a result, a homogeneous structure of the polymer composite was obtained. This article presents studies investigating how a change in pressure affects MCs and what the quality is of the composite and metal-composite interface (Fig. 7).

The characteristic structures of FMLs obtained at different pressures are shown in Figs. 8 and 9. Figure 8 presents a laminate with a visible interface between the PEO layer and the CFRP composite.

FMLs are characterized by good adhesion of the layers to each other. A separation line is clearly visible between PEO, AZ31, and the polymer composite. The fibers are evenly distributed throughout the volume of the laminate.

It can be seen in the case of pressures of 0.1 and 0.2 MPa that there were porosities in the entire area in the polymer...
composite. Nonetheless, in the case of the value of 0.4 MPa, dedicated to this type of prepreg, porosity does not occur. Moreover, in Fig. 8 the delamination between the CFRP composite and the PEO layer is the leading one. This is most likely a result of the lack of sol–gel that would improve the wettability of the surface, and thus the quality of the bond at the interface. Figures 9 and 10 show the microstructures of FMLs.

With the increase in the applied pressure, an increment in the homogeneity of the FML structure can be observed, similar to Fig. 8, and no damage to the MCs (Fig. 9). Numerous porosities are visible in the structure of the fiber composite in the case of the low pressure of 0.1 MPa. On the other hand, the increase in pressure to the value of 0.2 MPa resulted in a reduction in porosity in the polymer composite layer. At the applied pressure of 0.4 MPa, no porosity or delaminations were observed in the structure of the laminates at the interface of individual phases, nor in the self-healing MC layer (Fig. 9c). The distribution of MCs for the pressures of 0.1 and 0.2 MPa is random, and the capsules are
located in areas with high porosity. Figure 9e and f present FMLs manufactured at the pressure of 0.4 MPa. The MCs are evenly distributed over the sol–gel layer and the interface is correct. MC cracking is not observed at the highest pressure of 0.4 MPa, which has a beneficial effect on the structure and application as a self-healing layer.

The use of appropriate pressure and vacuum is an important issue in curing laminates in an autoclave. The excess epoxy resin and volatile reaction products in FMLs are drained only through the edges (side surfaces) of the laminate. Therefore, the value of vacuum in the vacuum bag that is placed in the autoclave is important. Employing too high pressure and vacuum may cause excessive removal of the matrix from the composite interlayers, leading to its uneven distribution in the volume of the material. Too low pressure can lead to porosity in the area of the composite. In these studies, the vacuum value in the vacuum autoclave package for the FML was set at −0.08 MPa throughout the curing process. It results from the recommendations of the prepreg manufacturer and the experience that the author has in manufacturing FMLs.

Figure 10 shows the FML microstructure with MCs at the pressure of 0.4 MPa, dedicated to this type of prepreg. The microstructure shows the individual layers and the MCs placed most likely in a cluster. This can be of great importance in the case of the self-healing layer because when porosity or other damage to the laminate occurs, the capsules should fulfill their role by bursting and releasing their contents.

By analyzing the structure of the examined FMLs in terms of the interface, it can be concluded that the structure of metal-fiber laminates consists of the following interfaces between individual components:

- composite matrix and reinforcing fiber—epoxy-carbon fiber interface
- metal and the layer produced in the surface preparation process—magnesium alloy-PEO coating interface
- layer created in the metal surface preparation process and the matrix of the composite—sol–gel with MCs-CFRP interface
- microcapsules and primer—MCs-resin interface (Fig. 10)

The individual interface surfaces may have a decisive influence on obtaining the final metal-composite bonding with high strength and durability. The MCs used in the FML can act as a self-healing layer because they did not undergo damage. As shown in the article by the authors of [40], MCs fulfill their function in the FML, demonstrating the self-healing phenomenon between the AZ31/PEO layer and CFRP during three-point bending tests.

By analyzing the microstructures of FML, and the polymer layers in particular, it can be noticed that they are characterized by high homogeneity. The distribution of the carbon fibers in the polymer composite is uniform. The laminate interface confirms that the correct structure was obtained, in which no excessive amount of epoxy resin was noticed, and the MCs are evenly distributed, especially visible in Fig. 10. There is proper bonding at the interface between the carbon fibers and the matrix. In the case of the pressure of 0.4 MPa and vacuum of −0.08 MPa, no delamination, porosity, or microcracks are observed. No direct adhesion of the reinforcing fibers to the oxide layer after the PEO process was noticed either. This can significantly affect the correct bond of the metal with the composite [41].

4 Conclusions

In the article, the behavior of CFRP and MCs as a self-healing layer produced in an autoclave employing various pressures is presented. The structure with a PEO layer on a magnesium alloy is analyzed, indicating the surface parameters in terms of the CFRP resin to the metal. It was concluded that the PEO layer with sol–gel improves the adhesion between CFRP and the MCs. Different pressures in the autoclave process promote porosity if a pressure lower than 0.4 MPa is used. Porosities are then found in the entire volume of the polymer composite, which may reduce the properties of the FML. The use of 0.4-MPa pressure does not damage the MCs, which is an expected phenomenon in terms of obtaining a high-quality FML laminate, without the effect of damaging the MCs. After the hardening process, the MCs are evenly distributed in the epoxy layer, and also in the pores formed in the process carried out at lower pressure. As a result, the MCs will fulfill their role as a self-healing layer on the Mg/PEO and CFRP interface.

Author contribution Author contributed to the study conception and design. Material preparation, data collection, and analysis were performed by Monika Ostapiuk. The first draft of the manuscript was
written by Monika Ostapiuk and commented on previous versions of the manuscript. Author read and approved the final manuscript.

**Funding**  This work was supported by the Polish National Agency for Academic Exchange called the Bekker program (Grant number PPN/BEK/2018/1/00213).

**Data availability**  Not applicable.

**Code availability**  Not applicable.

**Declarations**

**Ethics approval**  Not applicable.

**Consent to participate**  Not applicable.

**Consent for publication**  Not applicable.

**Competing interests**  The author declares no competing interests.

**Open Access**  This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/.

**References**

1. Ji C, Wang B, Hu J and Zhang C et al (2020) Effect of different preparation methods on mechanical behaviors of carbon fibre-reinforced PEEK-titanium hybrid laminates. Polym Test 85:4–5. 1 0.1016/j. polym test. 106462
2. Che L, Fang G, Wu Z et al (2020) Investigation of curing deformation behavior of cured fibre metal laminates. Comp Struct 232. https://doi.org/10.1016/j.comstruct.2019.111570
3. Gonzalez-Canche NG, Flores-Johnson EA, Carrillo JG (2017) Mechanical characterization of fiber metal laminate based on aramid fiber reinforced polypropylene. Comp Struct 172:259–266. https://doi.org/10.1016/j.comstruct.2017.02.100
4. Hu Y, Zhou J, Ji F et al (2020) Optimization of preparation technology on fiber metal laminates (FML) for high temperature applications. Int J of Light Mat and Man 3(4):317–333. https://doi.org/10.1016/j.jlmm.2020.05.001
5. Cortes P, Cantwell WJ (2005) The fracture properties of a fibre–metal laminate based on magnesium alloy. Comp Part B Eng 37(2–3):163–170. https://doi.org/10.1016/j.compositesb.2005.06.002
6. Vlot A (2001) Fibre metal laminates; an introduction. Dordrecht: Kluwer Academic Publishers
7. Supplitt R, Koch T, Schulbert U (2007) Evaluation of the anti-corrosive effect of acid pickling and sol–gel coating on magnesium AZ31 alloy. Corr Sci 49:3015–3023. https://doi.org/10.1016/j.corsci.2007.02.006
8. Kleinendorst RGI (1990) Corrosion properties of carbon ARALL. Master thesis, Delft University of Technology
9. Kim YW (2010) Surface modification of Ti dental implants by grit-blasting and micro-arc oxidation mater manu process 25(5):307–310
10. Lakstein D, Kopelowitch V, Barkay Z et al (2009) Enhanced osseointegration of grit-blasted, NaOH-treated and electrochemically hydroxyapatite-coated Ti6Al4V implants in rabbits. Acta Biomat 5(6):2258–2269. https://doi.org/10.1016/j.actbio.2009.01.103
11. Man HC, Zhao NQ, Cui ZD (2005) Surface morphology of a laser surface nitrided and etched Ti6Al4V alloy. Surf Coating Technol 192:341–346. https://doi.org/10.1016/j.surfcoat.2004.07.076
12. Chen P, Chen K, Yang J (2015) Surface modifications of Ti alloy with tunable hierarchical structures and chemistry for improved metal polymer interface used in deepwater composite rise. App Surf Sci 328:614–622. https://doi.org/10.1016/j.apsusc.2014.12.008
13. Liu Z, Liu H, Zhong X et al (2014) Characterization of anodic oxide growth on commercially pure titanium in NaTESi electrolyte. Surf Coating Technol 258:1025–1031. https://doi.org/10.1016/j.surfcoat.2014.07.036
14. Lin Y, Li H, Wang Q et al (2020) Effect of plasma surface treatment of aluminium alloy sheet on the properties of Al/GP/P laminate. Appl Surf Sci 507:154–162. https://doi.org/10.1016/j.apusc.2019.145062
15. Akram M, Jansen KMB, Ernst LJ et al (2016) Atmospheric plasma modification of polyimide sheet for joining to titanium with high temperature adhesive. Int J Adh Adhes 65:63–69. https://doi.org/10.1016/j.ijadhadh.2015.11.005
16. Pan YC, Wu GQ, Huang Z et al (2017) Corrosion behaviour of carbon fibre reinforced polymer/magnesium alloy hybrid laminates. Corr Sci 115:152–158. https://doi.org/10.1016/j.corsci.2016.11.022
17. Pärnnäen T, Alderliesten RC, Rans C et al (2012) Applicability of AZ31B–H24 magnesium in fibre metal laminates—an experimental impact research. Comp: Part A 43:1578–86. https://doi.org/10.1016/j.compositesa.2012.04.008
18. Sun S, Pan Y, Wu G et al (2018) Effect of electrolyte composition ratio of micro-arc oxidation oninterlaminar strength of CFRP/Mg laminates, Int J of Adh Adhesives 87: https://doi.org/10.1016/j.ijadhadh.2018.09.013
19. Ning H, Weng S, Hu Y et al (2017) Mode-II interlaminar fracture toughness of GFRP/Al laminates improved by surface modified VGCF interleaves. Comp: Part B 114:365–72. https://doi.org/10.1016/j.compositesb.2017.02.022
20. Liu Z, Sun R, Mao Z, Wang PC (2012) Effects of phosphate pretreatment and hot humid environmental exposure on static strength of adhesive-bonded magnesium AZ31 sheets. Surf Coat Techn 206:3517–3525. https://doi.org/10.1016/j.surfcoat.2012.02.031
21. Gao HT, Zhang M, Yang X et al (2014) Effect of Na2SiO3 solution concentration of micro-arc oxidation process on lap-shear strength of adhesive-bonded magnesium alloys. Appl Surf Sci 314:447–52. https://doi.org/10.1016/j.apsusc.2014.06.117
22. Alfano M, Lubineau G, Furgiuele FA et al (2021) Study on the role of laser surface irradiation on damage and decohesion of Al/epoxy joints. Int J Adhes Adhes 39:33–41. https://doi.org/10.1016/j.ijadhadh.2012.03.002
23. Mingo B, Arrabal R, Mohedano M et al (2018) Influence of sealing post-treatments on the corrosion resistance of PEO coated AZ91 magnesium alloy. Appl Surf Sci 433:653–667. https://doi.org/10.1016/j.apsusc.2017.10.083
24. Gonzalez-Canche NG, Flores-Johnson EA, Carrillo JG (2017) Mechanical characterization of fiber metal laminate based on aramid fiber reinforced polypropylene. Compos Struct 172:259–266. https://doi.org/10.1016/j.comstruct.2017.02.100
25. Abouhamze M, Sinke J, Jansen KMB et al (2015) A new procedure for thermo-viscoelastic modelling of composites with general
orthotropy and geometry. Comp Struct 133:871–877. https://doi.org/10.1016/j.composites.2015.08.050

26. Jakubczak P, Bienias J, Surowska B (2018) Interlaminar shear strength of fibre metal laminates after thermal cycles. Comp Struct 206:876–887. https://doi.org/10.1016/j.composites.2018.09.00

27. Bellini C, Di Cocco V, Iacoviello F et al (2019) Performance evaluation of CFRP/Al fibre metal laminates with different structural characteristics. Comp Struct 225: https://doi.org/10.1016/j.composites.2019.111117

28. Koziol M, Jesionek M (2017) Szperlich P (2017) Addition of a small amount of multiwalled carbon nanotubes and flaked graphene to epoxy resin. J Reinf Plast Comp 36:640–654. https://doi.org/10.1177/0731684416689144

29. White SR, Sottos NR, Geubelle PH et al (2001) Autonomic healing of polymer composites Nat 409:794–797. https://doi.org/10.1038/35057232

30. Ullah H, Azizli K, Man ZB et al (2016) Synthesis and characterization of urea-formaldehyde microcapsules containing functionalized polydimethylsiloxanes. Procedia Eng 148:168–175. https://doi.org/10.1016/j.proeng.2016.06.519

31. White SR, Sottos NR, Geubelle PH et al (2001) Aut healing of Pol Comp 409:794–797. https://doi.org/10.1038/35057232

32. Dokht M, Karim S, Karim SN et al (2020) The inter laminar resistance of carbon fiber-Al laminate reinforced with hollow and core-shell microcapsules. Theor Appl Fract Mech. https://doi.org/10.1016/j.tafmec.2020.102778

33. Wilson GO, Moore JS, White SR et al (2008) Autonomic healing of epoxy vinyl esters via ring opening metathesis polymerization. Adv Funct Mater 18:44–52. https://doi.org/10.1002/adfm.200700419

34. Jin H, Mangun CL, Stradley D et al (2012) Self-healing thermoset using encapsulated epoxy-amine healing chemistry. Polym 53:581–587. https://doi.org/10.1016/j.polymer.2011.12.005

35. Zhu DY, Wetzel B, Noll, et al (2013) Thermo-molded self-healing thermoplastics containing multilayer microreactors. J Mater Chem A 1:7191–7198

36. Jin H, Mangun CL, Griffin AS et al (2014) Thermally stable autonomic healing in epoxy using a dual-microcapsule system. Adv Mater 26:282–287. https://doi.org/10.1002/adma.201303179

37. Teixeira RFA, van den Berg O, Nguyen LTT et al (2014) Microencapsulation of active ingredients using PDMS as shell material. Macrom 47:8231–8237. https://doi.org/10.1016/j.ma501897j

38. Han N, Takafuli M, Ichra H (2017) One-pot preparation of polymer microspheres having wrinkled hard surfaces through self-assembly of silica nanoparticles. Chem Commun 53:9147–9150

39. Yang J, Keller MW, Moore JS et al (2008) Microencapsulation of isocyanates for self-healing polymers. Macrom 41:9650–9655. https://doi.org/10.1021/ma801718v

40. Kardar P (2015) Preparation of polyurethane microcapsules with different polyols component for encapsulation of isophorone diisocyanate healing agent. Prog Or Coat 89:271–276. https://doi.org/10.1016/j.porgcoat.2015.09.00

41. Ostapiuk M, Loureiro MV, Bienias J et al (2021) Interlaminar shear strength study of Mg and carbon fiber-based hybrid laminates with self-healing microcapsules, Comp Struct 55. https://doi.org/10.1016/j.composites.2020.113042

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.