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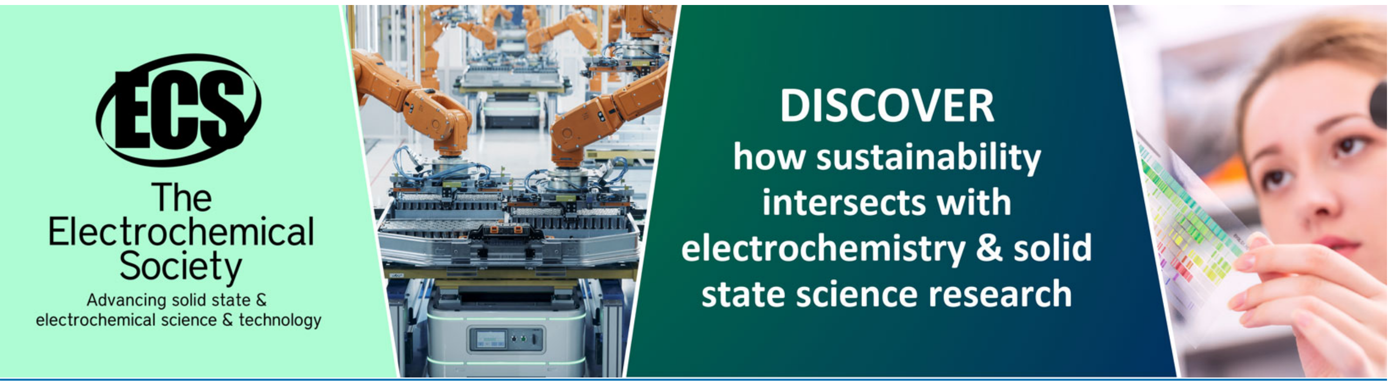

Montmorillonite (MMT) nanoclay in smart coatings for corrosion protection of metal alloy: a brief review

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Abstract. Montmorillonite (MMT) nanoclay is a natural raw material naturally occurring 2-dimensional lamellar silicate material. Many advantages of MMT clay are low cost, high dispersion properties, good mechanical properties, hydrophobic, good shield against corrosive media, non-toxic, easily accessible, and most importantly, it is natural. MMT was mainly used as an additive with other active smart materials to enhance the excellent properties for smart coatings. However, there is not much research done from the last 5 years regarding MMT in smart coating for corrosion protection. The discussion regarding MMT for corrosion protection is also contradict between each research. This paper provides a brief review on MMT clay in smart coatings and its advantages for corrosion protection for the last 5 years. There are also some drawbacks of MMT in smart coatings discussed at the end. Further research needs to be done as MMT has more potential that can be used in the real-world industries and to clarify the contradiction of statement existed in much research.

Keywords: Montmorillonite (MMT); nanoclay; smart coating; corrosion protection; metal alloy; additive

1. Introduction
As reported in 2017, the annually loss in economic section due to corrosion in metals of the Gross Domestic Product (GDP) turns out to be around at 3 to 4%, globally [1]. Due to corrosion, many industries such as aerospace and automotive, power and defense, electronic, biomedical, textile, and construction required corrosion protection to overcome this issue [2]. To achieve this, many industrialists and academicians have devoted themselves to coming up with various excellent corrosion protection strategies. Corrosion can be avoided to some extent or mitigate by using any corrosion resistant materials, proper material design, cathodic protection, corrosion inhibitor and coatings [2]. Among all these strategies, coatings are extremely famous and widely applied. However, they can only offer excellent protection if they are made with excellent materials and are very intact in application. Hence, active smart materials must be added as an additive into the coatings to trigger corrosion protection mechanism whenever necessary to the metal coated. One of the active smart materials many researchers recently used in smart coatings technology is Montmorillonite (MMT).

Montmorillonite (MMT) clay is one of the most commonly used material in various industries, highly known due to its excellent biocompatibility and biodegradability with good mechanical properties [3], anti-bacterial properties [4]–[6], anti-fungal properties [7]–[9], used in wound regeneration and healing [10]–[12] and bone regeneration [13]–[15]. MMT was also mainly used for food packaging due to its non-toxic properties [16], [17]. Nowadays, MMT is highly useful as one of the additives in smart coatings technology for metal alloy, MMT possesses a few advantages and properties famous for corrosion protection and resistance purposes. It is the most prominent layered silicate [18] and its nano-size particles with layered structure may be able to provide greater corrosion protection properties [19]–[21]. It also has a characteristics of massive reaction sites, wide variety resources and low in cost [22]–[24].

This paper focuses on the recent applications of MMT nanoclay in smart coatings technology for corrosion protection for the last 5 years. This work acknowledges how MMT was implemented in smart coating to avoid or mitigate corrosion. There are some contradictions of statements regarding the implementation of MMT for corrosion protection. The structures, properties, roles, advantages, and drawbacks of MMT related to smart coatings for metal alloy corrosion protection will be summarized and any future recommendation regarding MMT implementation in smart coatings research will be presented here.

2. MMT structures

MMT contains tetrahedral and octahedral with the ratio of 2:1. The tetrahedral sheet consists of silicon-oxygen tetrahedra connected to surrounding tetrahedra by sharing 3 corners resulting in a hexagonal-shaped network [25]. The other remaining tetrahedra are connected to the adjacent octahedral sheet to form a part. The octahedral sheet usually consists of aluminum or magnesium in sixfold coordination with oxygen from the tetrahedral sheet and hydroxyl. These two sheets become a layer. Several other layers may form together in a clay crystallite by interlayer cations, Van Der Waals force, electrostatic force, or hydrogen bonding [26]. Unlike other nanoclay particles, the MMT has an interlayer space between each triple-sheet layer, as shown in Figure 1. Chemically, the MMT is composed of isomorphic substitutions in the tetrahedral sheet of Si^{4+} by Al^{3+} and Al^{3+} by Mg^{2+} in the octahedral ones. Due to this arrangement, the montmorillonite possesses a negative residual charge compensated by cations in the interlayer space [25].

3. Applications of MMT in smart coatings for corrosion protection

In recent years, MMT-based nanoclay is widely used to modify polymer functions and performances [26], especially in smart coatings technology. A few research worth mentioning were done as an approach to increase the lifespan and effectiveness as well as the self-healing ability of the corrosion protection smart coatings by intercalated MMT with urushiol through in situ polymerization [20], tannic acid, and modified Cerium-MMT [28] and the mixture of benzimidazole, sodium, and zinc [29]. Below is more on the summary of the applications of MMT in multifunctional smart coatings for various industries for the last 5 years.

Sun et al. [30] developed functionalized MMT modified with cerium (M-Ce) ion-via intercalation that provide reaction for PFA (polymerization of 2-fluoroaniline), and their PFAM-Ce nanohybrid in the coating are used as an additives effective to protect from any corrosive media and UV, producing a high performance and multifunctional coatings against metal corrosion. The combined additives including MMT in epoxy resin produce good hydrophobic ability, excellent dispersion ability, and good UV shield and the coating in the end heals itself preventing further damage that might lead the substrate to corrode. Based on their results, the performance of the corrosion protection of this coating after UV radiation was measured using EIS and showed that UV radiation severely affected the corrosion resistance of pure epoxy resin coating more as compared to coating with MMT as an additive. MMT was also used in other approaches by Sun et al. for corrosion protection to obtain environmentally friendly and excellent anticorrosion coating [22], [24].

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In another approach, the cerium was added in between the layers space of MMT by ion exchange method in an article reported by Mo et al. [31]. The modified MMT was added to study the corrosion protection and water resistance improvement on the steel substrates. It was stated that as a nanoparticle clay, MMT did improved compactness of the structure inside the coating and also aid to forms an effect of a maze inside the coatings to extend the length of the diffusion path for corrosive agents due to its flake structure, to enhance the barrier properties [31]. Based on the results, the addition of MMT with cerium (Ce) and chitosan (CS) did enhance the water resistance properties of the coating as compared to other coatings they tested. Refer to Figure 2 for water resistance test results.

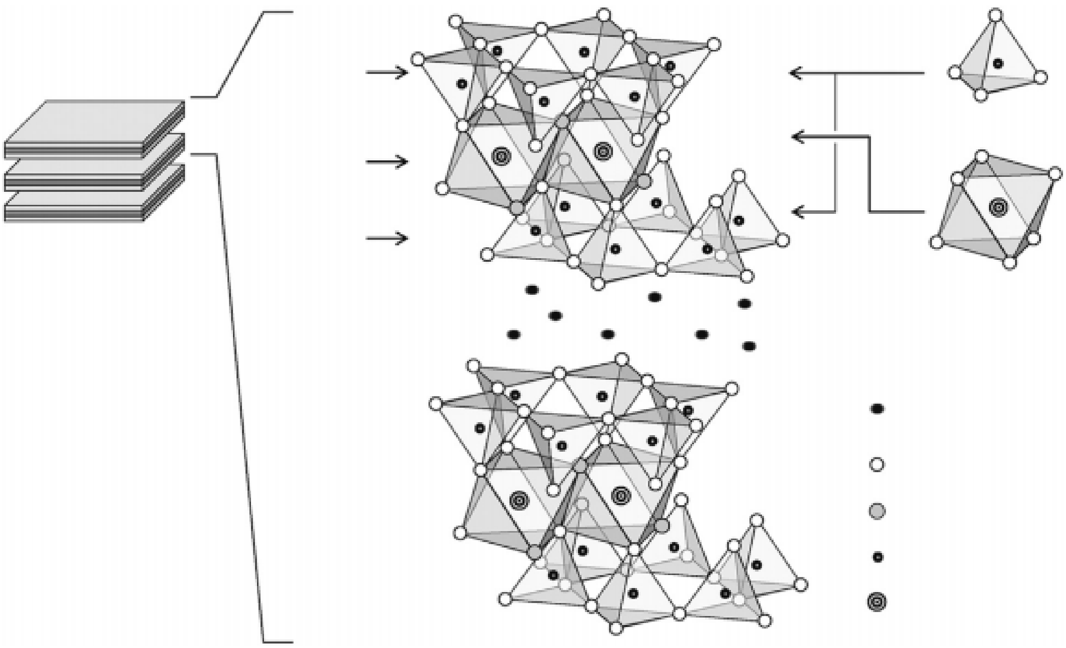

Figure 1. Molecular structure of montmorillonite (MMT) nanoclay [25][27].

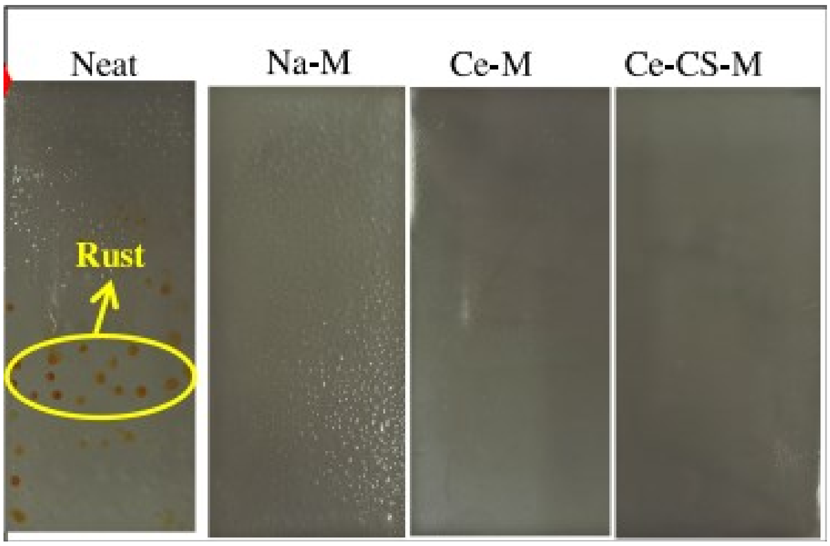

Figure 2. Images of surface morphology of coatings after the immersion for 8 days [31].

Mohammadi et al. [32] studied intercalation between sodium and MMT and cerium (Epoxy-MMT(Ce)) for corrosion resistance of mild steel. They found out that there had been an improvement in the anti-corrosion behavior with the presence of cerium and MMT extract, and Figure 3 had shown the comparison of the coating surface between these 2 types of coatings. Additionally, coating blistering and delamination can be mitigated by using active smart material such as MMT in the container as an inhibitive. The MMT also demonstrated particles flaky in shape with the particles stick together and connected to each other in a micrograph image analyzed. However, the result shows that the morphology of the sample altered after the ion exchange of Ce^{3+} with the Na^{+} cations, and due to the obvious conglomeration of cerium and MMT, they became irregular in shape, as shown in Figure 4 (a) and (c). Figure 4 (b) and (d) are the enlarged images of Figure 4 (a) and (c), respectively.

According to Figure 5, the $|Z|_{10\ mHz}$ value shows the anti-corrosion behavior of the protective coating tested. The $|Z|_{10\ mHz}$ value of pure epoxy coating is lower than the value of Epoxy-MMT(Ce) coating. This means that the MMT(Ce) can act better as a resistance barrier against the corrosive ions in the epoxy coating. Also as seen in Figure 5, from 20 to 40 days, the value of $|Z|_{10\ mHz}$ of Epoxy-MMT(Ce) increased with time. This could be due to the Ce^{3+} cations released from MMT(Ce) particles into the epoxy coating and moved to the metal piece through diffusion path at certain period which in this case is 20 to 40 days. The $|Z|_{10\ mHz}$ value could also be increased by thin layer of film formatted at the metal piece interface after 20 days exposure.

Another parameter used to study the corrosion properties of the coating is $-\Theta_{100\ kHz}$. Phase plots in Figure 5 show that the phase angle, $-\Theta_{100\ kHz}$ of the Epoxy-MMT(Ce) sample is almost 90° after all immersion times. However, the corresponding values for the pure epoxy coating decreased to 70° after 40 days of immersion. These results confirm the better corrosion protection performance of the Epoxy-MMT(Ce) coating sample. Also, the obtained $-\Theta_{100\ kHz}$ values indicate the better adhesion of the Epoxy-MMT(Ce) to the metallic substrate due to presence of the Ce3+ cations. Then, the $\log f_b$ value of pure epoxy coating increased from 2.5Hz to 4.4Hz from 20 to 60 days of immersion time.

Another research on smart coating was done with epoxy resin and MMT by Kumar et al [19]. They added MMT as an additive into the epoxy resin coating to study the coating's properties applied to copper alloy. The surface images in Figure 6 obtained showed that the coating provided better corrosion protection than other compositions of epoxy resin coatings due to the layered structure of MMT assisting to block the NaCl molecules more effectively, and thus prevent corrosion from happening. The MMT clay was analyzed by FESEM and EDX, which confirmed that MMT had a layered structure and was the size of nanoparticles, as shown in Figure 7. Figure 8 shows the EIS results to evaluate the performance of the corrosion protection of the coating, which displays the corrosion resistances of bare copper alloy and coated copper alloy in 0.5 M NaCl. It was seen in Figure 8 (a) that the size of Nyquist plot was enlarged for epoxy resin coating and epoxy nanoclay coating (EPMC) coated copper alloy in comparison to bare copper alloy. The largest size of Nyquist plot was observed for EPMC (5 % MMT clay) coated copper alloy. This result shows the EPMC coating with 5% MMT nanoclay did provide an excellent corrosion protection and resistance to the copper alloy.

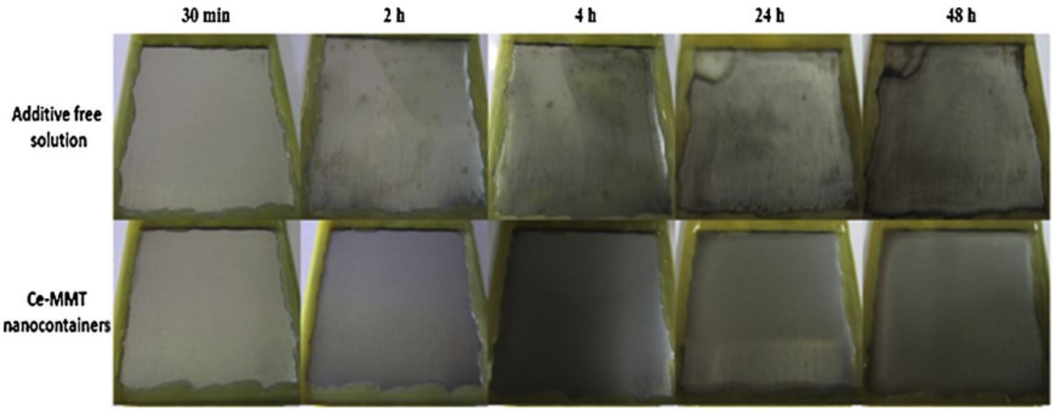

Figure 3. Visual image comparison between additive-free and MMT as one of the additive nanocontainers [32].

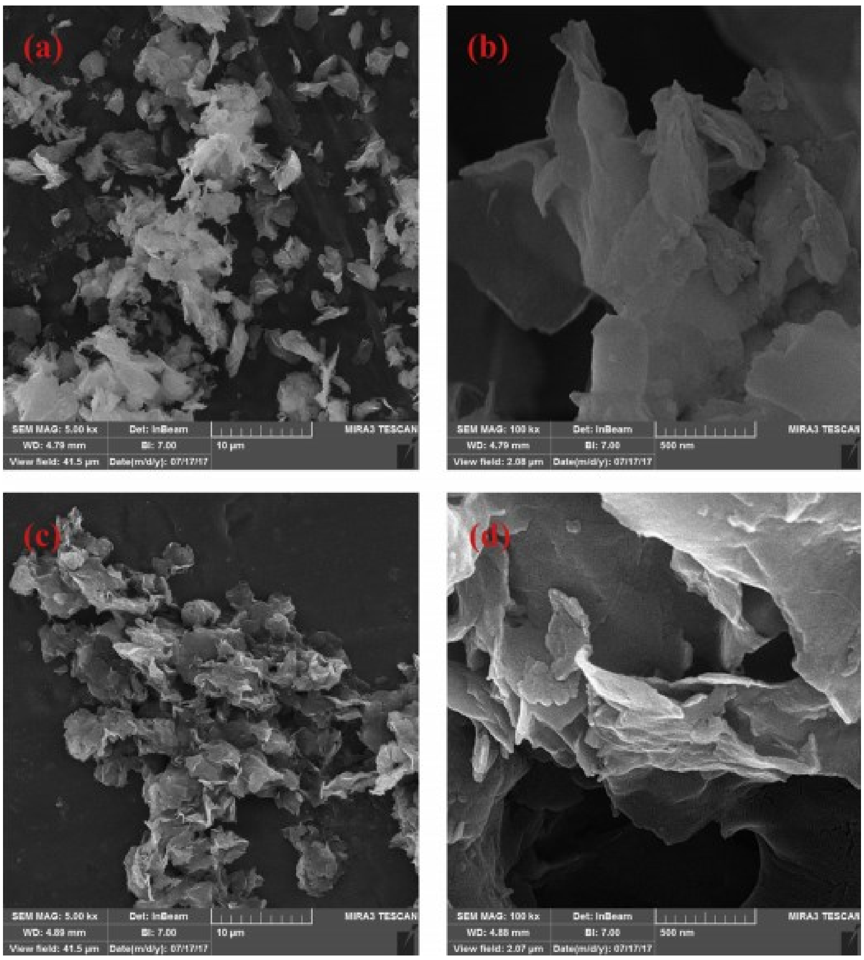

Figure 4. The comparison between (a) MMT nanoclay and (c) MMT with Cerium, (b) and (d) are the enlarge images of (a) and (c), respectively [32].

Ashassi-Sorkhabi et al. [33] developed a synergy effect originating from the presence of amino acid and MMT nanoclay simultaneously for the hybrid smart coating on AZ91 Magnesium alloy. MMT was added to enhance the coating's resistance from corrosion due to its nanoparticle size. Porosity and cracks also became lower in results. The article had shown a result that the presence of the MMT nanoparticles in the contents higher than the optimum leads to the formation of a defective sol-gel network in the nanoparticle. This means that MMT increases the hydrophobic properties and restricts their solubility in water solution, hence further providing corrosion protection.

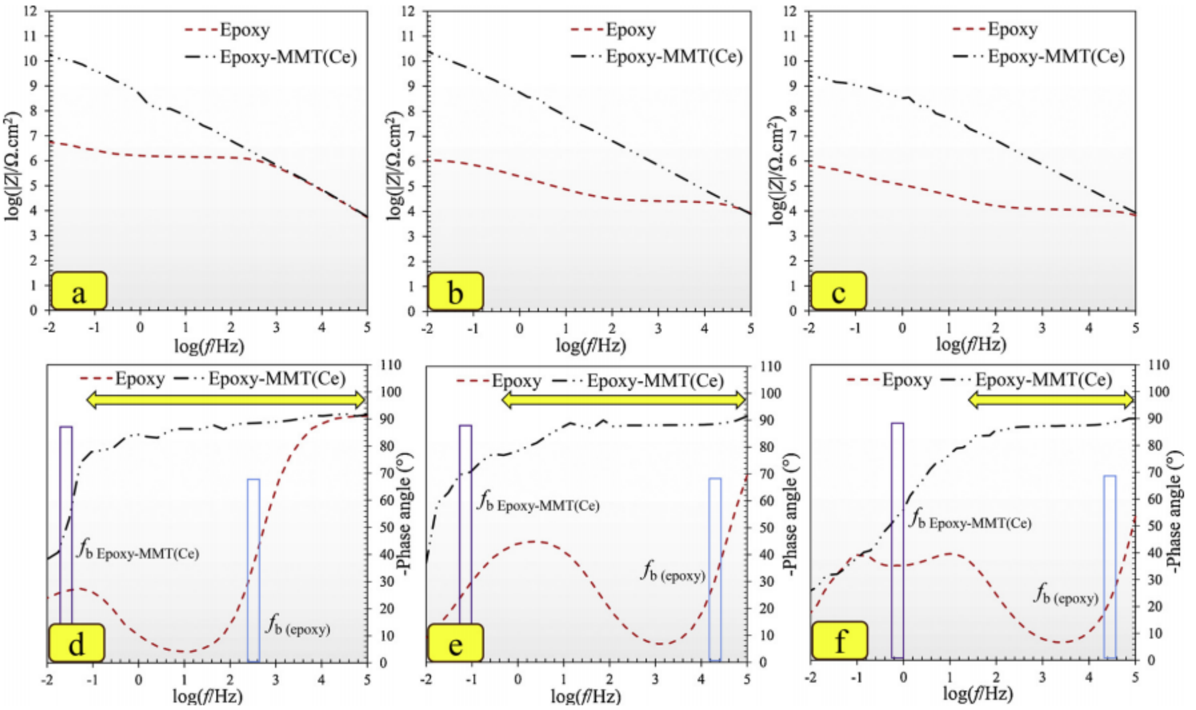

Figure 5. Bode and phase plots of pure epoxy coating and coating with MMT as additive samples after (a, d) 20 (b, e) 40, and (c, f) 60 days of immersion in the saline solution of 3.5 wt.% NaCl. [32].

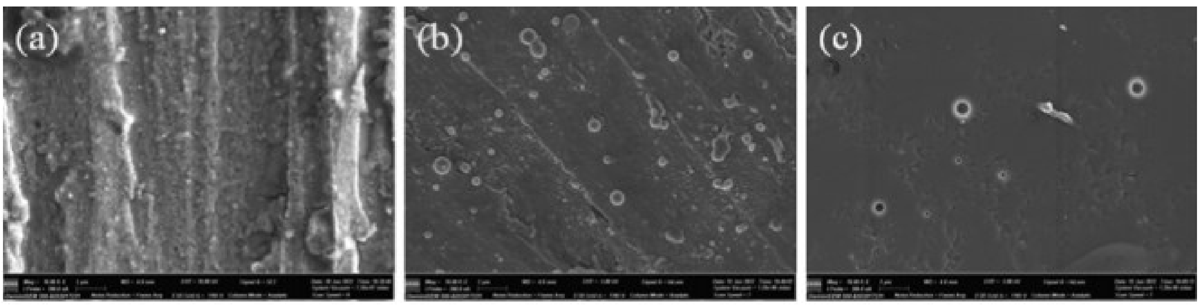

Figure 6. FESEM images (10 K) of (a) pristine Cu, (b) EP-coated Cu, and (c) EPMC (5 % MMT) coated Cu after corrosion in 0.5 M NaCl [19].

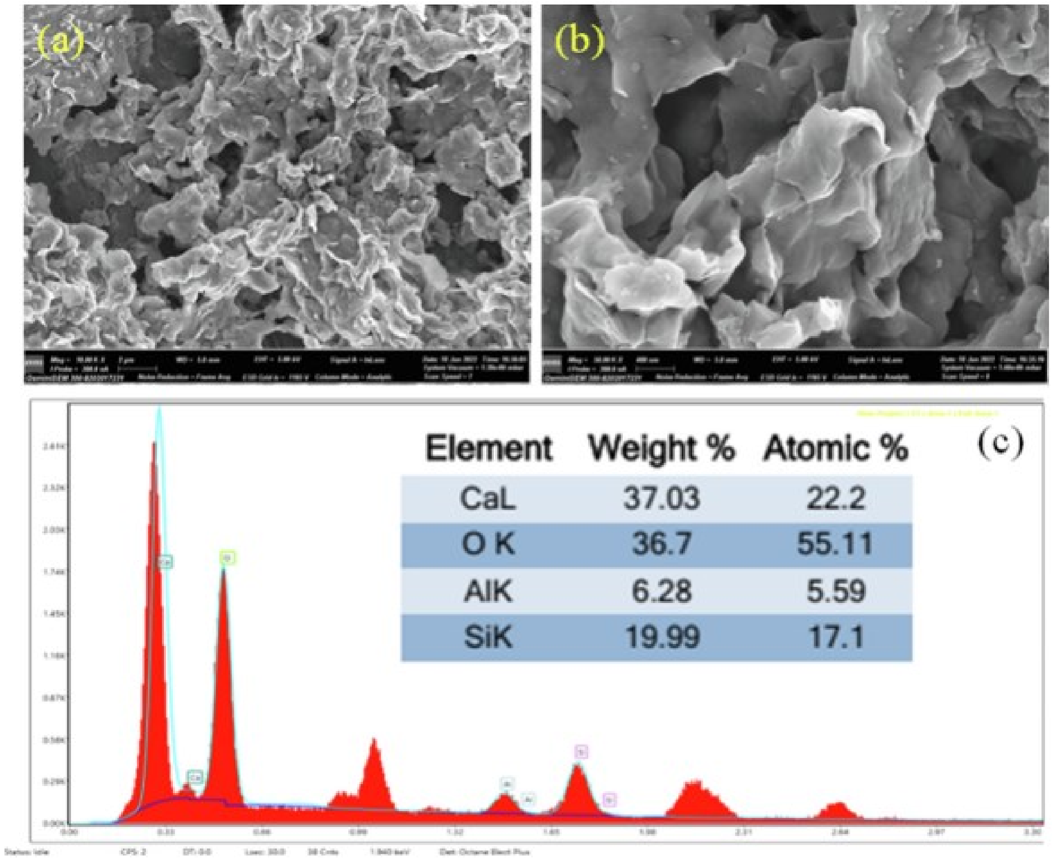

Figure 7. Microstructure of MMT nanoclay powder by FESEM at (a) 10K and (b) 50K magnifications, and (c) EDX spectrum of MMT nanoclay [19].

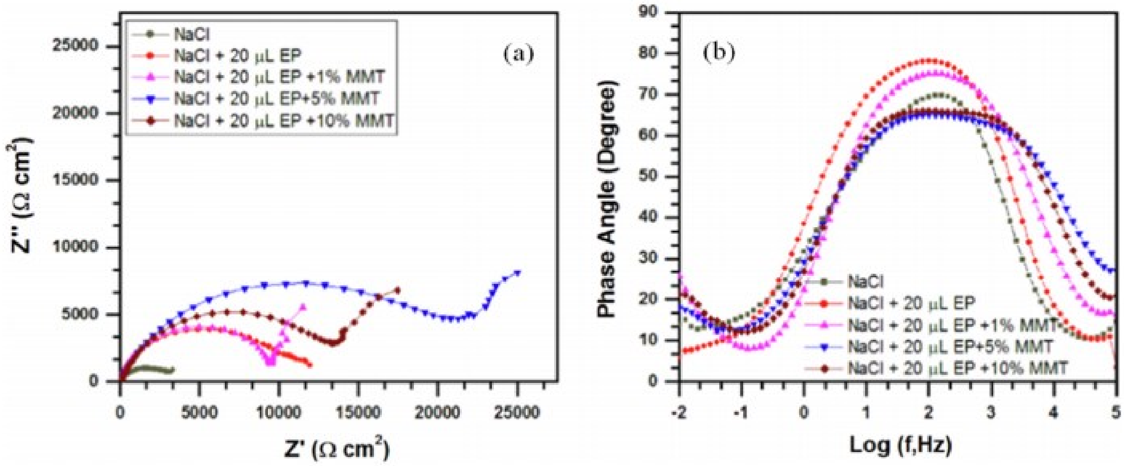

Figure 8. (a) Nyquist and (b) Bode phase angle plots for bare Cu, EP and EPMC coated Cu immersed in 0.5 M NaCl at room temperature [19].

Table 1. Summary of literature of MMT implementation in smart coating for corrosion protection for the last 5 years.

Type of Additive	Substrate	Coating's Properties	Effect on corrosion protection	References
2-fluoroaniline polymerization, MMT, Cerium (PFAM-Ce)	Carbon steel	UV-absorber, anti-oxidizer, anti-corrosion, good dispersibility, hydrophobicity	Impedance value higher than other coating samples at above 10^{11} $\Omega\cdot cm^2$, showed that the film coating prevented further corrosion of carbon steel	[30]
Cerium, Sodium, MMT,	Q235 steel	Water resistance, dispersion stability, protect from corrosion	Coating with MMT & Cerium has highest impedance value in EIS measurement	[31]
Cerium, MMT	CK10 mild steel	Anti-corrosion	The phase angle reduced to 70º after 40 days of immersion and confirms better corrosion protection than pure epoxy coating	[32]
MMT	Copper alloy	Anti-corrosion	The largest size of Nyquist plot was observed for EPMC (5 % MMT clay) coated copper alloy	[19]
MMT	AZ91	Hydrophobic, anti-corrosion	Porosity and cracks also became lower in results.	[33]

4. The drawbacks of MMT

Although many had claimed great advantages of MMT in their coating's application, there are some drawbacks also mentioned that contradict the statement in these previous articles. Li et al. [34] mentioned that MMT plays a role of a physical barrier and a container. However, the modified MMT had shown a more disordered structure and fewer stacked layers. Their results showed the combination of tannic acid, cerium, and MMT did improved the long-term performance of the corrosion protection of the coating, and it was attributed to the addition of tannic acid and cerium that enhanced the physical barrier properties, instead of MMT. Sun et al. [35] mentioned that when MMT is incorporated with polymer, they tend to get agglomerate and this is bad for corrosion protection. Hence, they added cerium to counter the drawbacks of the MMT, since MMT has good dispersion and mechanical properties that can further improve the coating layers. Despite these drawbacks mentioned, MMT was still widely used as one of the smart materials in smart coating because the advantages of MMT surpass its limitation.

5. Conclusions

This paper summarizes all the properties and applications of MMT nanoclay in smart coatings technology for corrosion protection. The mechanical properties of MMT in smart coatings are excellent and most coatings can even self-heal without affecting the coating's mechanical properties due to the MMT addition. These advantages made MMT one of the excellent smart materials for corrosion protection. However, there are claims stating that MMT nanoclay is an independent platelet hence it will not interfere with the self-healing mechanism. MMT also claimed to tend to agglomerate in polymer and need to be dependent on other additives to make the polymer coating work. With these many claims and statements, further research on the implementation of MMT in smart coating needs to be done to gain more knowledge on the potential and drawbacks of the MMT nanoclay so the industry would be able to implement them in the real-world industry.

Declaration of competing interest
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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