Chapter 14
Tensile and Corrosion Resistance Studies of MXenes/Nanocomposites: A Review

Mohd Shahneel Saharudin, Nur Ahza Che Nasir, and Syafawati Hasbi

Abstract MXenes are a relatively new and interesting class of two-dimensional materials with diverse compositions and outstanding characteristics such as dispersibility and metallic conductivity. MXenes appear to be promising fillers for polymer nanocomposites, and data from several studies suggest that this promising material could significantly improve the tensile strength and modulus by 314% and 89%, respectively, when incorporated into a polymer matrix. Corrosion, on the other hand, is a significant issue in numerous industries worldwide, including automotive, defence, aerospace and biomedical. There is a growing body of the literature that recognises MXenes as high-performance corrosion inhibitors. In this review, recent research on the corrosion resistance properties of MXenes-reinforced polymeric composites is also discussed.

Keywords MXenes · Tensile properties · Corrosion inhibitors · Nanocomposites · Coatings

14.1 Introduction

Because of their distinct characteristics, such as low cost, low density and ease of processing, polymeric materials have been used in numerous applications [1]. On the other hand, polymeric materials have limited applicability due to their weak mechanical and tribological properties [2–4]. Many of these polymeric coatings are used owing to their high corrosion resistance properties. Even though, under

---

M. S. Saharudin (✉) · N. A. Che Nasir
Universiti Kuala Lumpur Malaysia Italy Design Institute, 119 Jalan 7/91, 56100 Kuala Lumpur, Cheras, Malaysia
e-mail: mshahneel@unikl.edu.my

N. A. Che Nasir
e-mail: ahza.nasir@s.unikl.edu.my

S. Hasbi
Department of Mechanical Engineering, National Defense University of Malaysia, 57000 Kuala Lumpur, Malaysia
e-mail: syafawati@upnm.edu.my

A. Ismail et al. (eds.), *Design in Maritime Engineering*, Advanced Structured Materials 167, https://doi.org/10.1007/978-3-030-89988-2_14

tribological conditions, they have low wear resistance there are several methods of enhancing polymeric composite mechanical and tribological performance [5].

Corrosion has always been a major concern in the oil and gas industries, with consequences comparable to natural disasters. Corrosion occurs typically in oil and gas pipelines. These pipelines are constantly threatened by corrosion from the time they are commissioned until they are withdrawn. According to a new report, the entire annual cost of corrosion is estimated to be $1.372 billion [6]. Corrosion is a severe problem because it wastes thousands of tonnes of iron each year and costs much money to fix or replace. Corrosion inhibitors are one of the effective methods used in the petroleum industry to reduce corrosion. The inhibitors must be added above a specified minimum concentration to achieve optimal inhibition. There are several strategies for fighting corrosion, such as cathodic protection, organic coatings and the use of high-quality corrosion-resistant alloys [7]. Film-forming inhibitors are still known to be the unrivalled means of defence for mild steel in an acidic environment [6]. In industries, film-forming inhibitors are used to establish a molecular layer on the steel surface and an aliphatic tail as a second layer in the hydrocarbon to prevent water from reaching the steel surface and corroding it.

This review paper assesses the most recent publications of MXenes as corrosion inhibitors. The review is expected to lay the groundwork for more study into MXenes as corrosion inhibitors in the future. MXenes, which were discovered in 2011, are one of the fastest-growing 2D materials that have received a lot of scientific attention. MXenes are a novel type of hydrophilic and conductive two-dimensional (2D) nanomaterial. They are 2D sheets of transition metal carbides, nitrides, or carbonitrides derived from the layered ternary $Mn_{+1}AXn$, or MAX, phases which only can be selectively etched to form MXenes. This terminology refers to their dual role as MAX phases and 2D. M-X bonds are supposedly stronger than M-A bonds. A mix of functional groups, good mechanical properties, self-lubricating and high thermal conductivity result in MXenes being formed by the selective etching of the A elements. Figure 14.1 shows the total journal articles published from 2010 to 2020. It can be seen that the research of MXenes only started in 2012 where ten research articles were initially published. The interest in the MXenes' research increased every year. In 2020, around 1585 articles were published, an increase of 60% compared to 2019. The number is expected to rise in 2021 because of the quickly growing interest in this family of materials.

14.2 Synthesis of MXenes

Wet chemical acidic etching of MAX phases yields MXenes in either the colloidal suspension of a few flakes or ML stacks of MXene sheets. Following etching, the post-processing techniques used can have an impact on how each of these forms is formed with the intended quality. As previously reported, Ti_3C_2 nanosheets were created by etching the Ti_3AlC_2 phase with LiF/HCl. Initially, 1 g LiF was dissolved in 20 mL 9 M HCl, and the mixture was well-mixed at room temperature for several

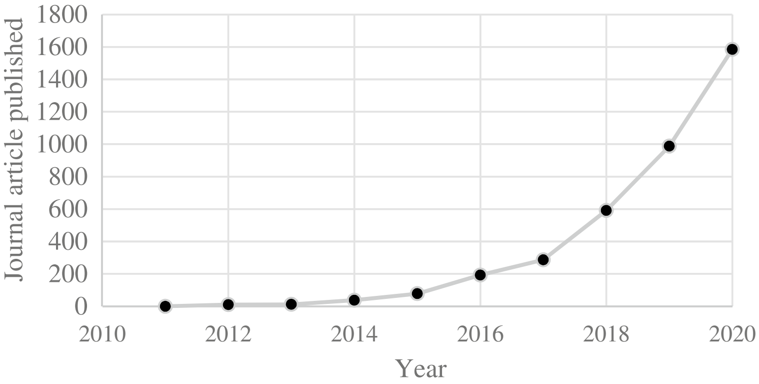

Fig. 14.1 Journal article published from 2011 to 2020 using "MXenes" as keyword obtained from Lens.org on 23rd May 2021

minutes. The solution was prepared by slowly adding 1 g Ti_3AlC_2 into it. Then, the reaction was stirred continuously for 24 h at 35 °C. The etched powder was rinsed with deionised water and left to dry at room temperature. Sonication with Ar resulted in Ti_3C_2 aqueous solutions that were then centrifuged for one hour at 3500 rpm.

Deposition techniques include CVD, ALD, and photo-deposition. CVD has multiple volatile precursors that cause a film to be formed on the substrate's surface. A semiconductor, nanocomposite, alloy or metal can be used as the deposited material. ALD splits the CVD reaction into two halves, ensuring that the precursor materials do not come into contact during the reaction. ALD film growth is constrained and self-dependent on surface reactions, allowing for atomic-scale deposition control. By keeping the precursors separated during the coating process, a monolayer as fine as 0.1 can be fabricated. ALD has various advantages over other processes, including the formation of pinhole-free, chemically linked and substrate conformal layers.

Zhang et al. have successfully employed ALD to develop Pt–TBA–$Ti_3C_2T_x$, which was later used in hydrogen evolution reactions [8]. Electrodeposition processes could be used to create MXene hybrids incorporating C-based materials, transition metal phosphides, oxides and metals. The photo-deposition can be used to apply metallic NPs, such as Cu and Pt, over MXene surface. The deposition methods are regulated and more encapsulating for the fabrication, but the higher cost of production is not preferred.

Solution processing is one of the most frequent processing procedures for synthesising MXene-reinforced polymer composites due to the hydrophilic character of MXene nanosheets created by the presence of a significant number of functional groups.

Premodified MXene and polymer nanoparticles are typically dispersed in polar fluids such as dimethylsulfoxide (DMSO), water and N, N-dimethylformamide to improve dispersibility. The major components are blended together to create a homogeneous slurry. So far, MXenes have been successfully combined with polyurethane, cellulose, polyethylene oxide and a few other materials. This approach can be used to hybridise a wide range of inorganic materials with MXenes. Poor mechanical properties, the creation of substantial amounts of environmental waste associated with the resulting composites and the difficulty in removing solvents using evaporation, which usually limits the use of solution mixing, are all significant disadvantages of this method.

The hydrothermal and solvothermal processes take advantage of the connection between the mineraliser, liquid solvent and precursor molecule, particularly when temperature and pressure are enhanced. It provides the simplest and most cost-effective methods for synthesising diverse secondary materials with different morphologies following the processing conditions. The procedures for solvothermal and hydrothermal are similar apart from for the solvents used in the synthesis process. The chemical reaction takes place in a sealed autoclave above the boiling point in a suitable solvent containing the reaction mixture. As the temperature and pressure rise above the critical point of the solvent, a supercritical fluid phase form is formed. The supercritical fluid phase incorporates both gas and liquid specificities, and there is no surface tension at the solid–supercritical fluid interface. Supercritical fluids had higher viscosities and dissolved a chemical compound that is insoluble at room temperature. One of the method's significant drawbacks is the aggressive corrosion caused by water molecules or hydroxyl units at high temperature and pressure settings, which results in unexpected modifications. MXenes were hybridised with a variety of inorganic compounds, including transition metal oxides, nitrides, phosphides, perovskites and chalcogenides.

14.3 Applications of MXenes

MXenes' versatile and desirable properties make them a potential choice in a wide range of applications. The unique morphological features and high Young's modulus make it attractive in composite formation. On the other hand, these properties drive them as a strong candidate for many applications like catalysis, sensors and energy storage. MXenes performs similarly to or better than most currently utilised products in various instances, such as electromagnetic interference shielding. They are also found in several other fields, for example opto/spintronic, environmental, tribologic and biomaterial. Figure 14.2 shows a 3D model of crystal structures Ti_3AlC_2 max phase, presented isometric and front view. Recently, MXenes have emerged as corrosion inhibitors in coating [7, 9]. Figure 14.3 shows the major industrial applications of MXene composites. They are widely used in energy storage, tribology, biomedical, sensors, catalysis and EMI shielding.

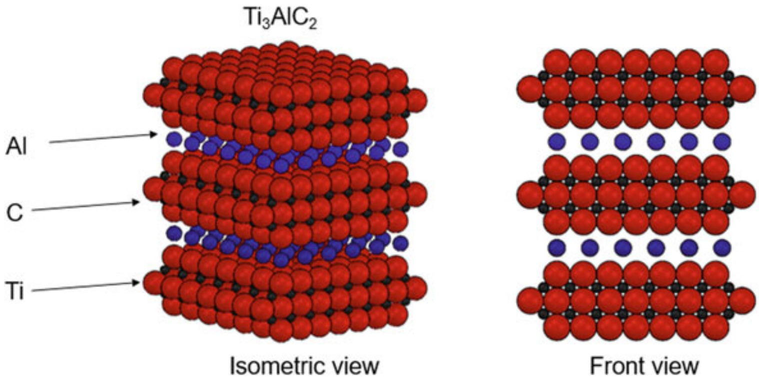

Fig. 14.2 3D model of crystal structures Ti_3AlC_2 max phase (not drawn to scale)

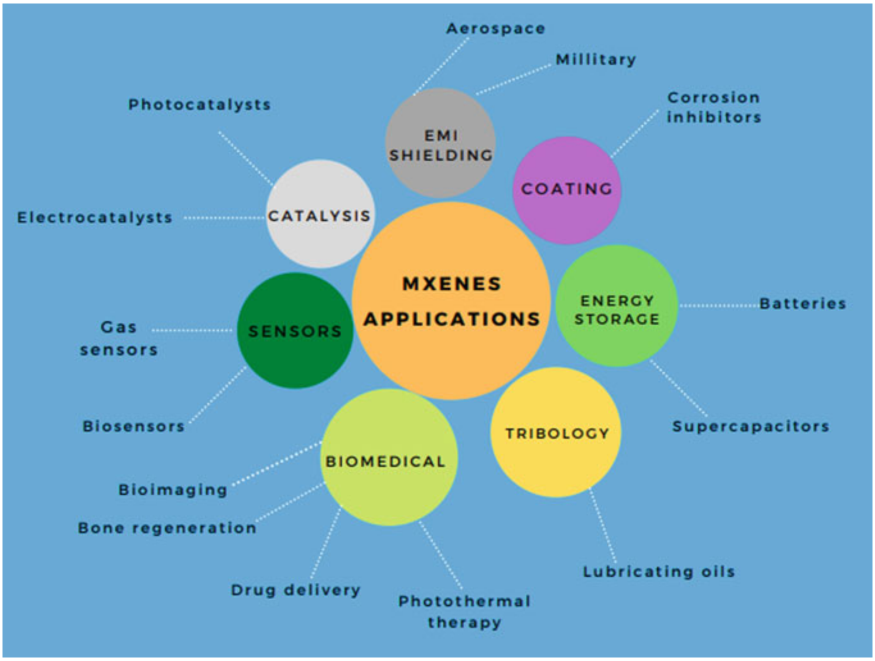

Fig. 14.3 Applications of MXenes from literature

14.4 Tensile Properties of MXenes/Nanocomposites

Figure 14.4 shows the increase in the percentage of the tensile strength for MXenes/nanocomposites obtained from the literature. Zhi et al. studied the MXene-filled polyurethane nanocomposites prepared via an emulsion method [10]. An

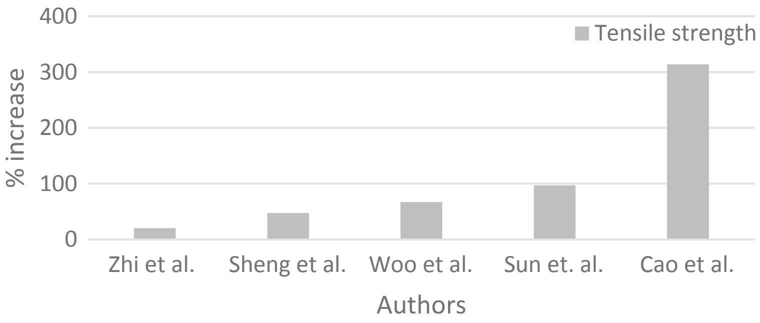

Fig. 14.4 Percentage increase in tensile strength of MXenes/nanocomposites [8, 10–13]

increase of 20% was observed with the addition of 0.5 wt% MXenes into polyurethane. Sheng et al. [8], Woo et al. [11] and Sun et al. [12] reported an increase of tensile properties of 39%, 49% and 89%, respectively. The highest tensile strength of 314% was observed by Cao et al. in the case of MXene/cellulose nanofiber composite [13]. Their works demonstrate that by incorporating MXene into polymers, MXenes significantly improve tensile strength's mechanical properties at a low mass content.

Figure 14.5 shows the percentage increase in elastic modulus of MXenes/nanocomposites. It can be observed that a minimum increase (35%) in elastic modulus was reported by Liu et al. [14]. Sheng et al. [8] reported 40% increase in elastic modulus in their research. Liu et al. in their new study have reported an improvement of 46% in elastic modulus [15]. On the other hand, Saharudin et al. [4] stated that a 49% of the increase in elastic modulus was reported. Last but not least, Wei et al. [5] reported the highest elastic modulus where an 89% increase was observed in their study.

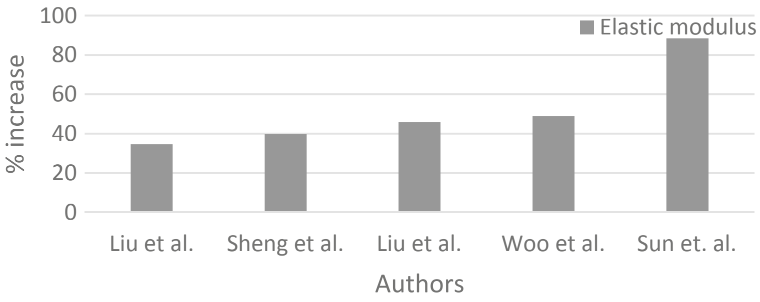

Fig. 14.5 Percentage increase in elastic modulus of MXenes/nanocomposites [8, 11, 12, 14, 15]

14.5 Corrosion Properties of MXenes/Nanocomposites

Yan et al. studied [16] anti-corrosion behaviour of an inorganic–organic multilayer protection system composed of nitriding layer and epoxy coating with Ti_3C_2Tx MXene. The results demonstrated that two orders of magnitude enhanced the electrochemical impedance during 4 weeks of immersion in 3.5 wt% NaCl solution, and the wear rate was decreased by 96.26%. Wu et al. [17] studied the improved corrosion resistance of AZ31 Mg alloy coated with MXenes/MgAl-LDHs composite layer modified with yttrium. The corrosion tests indicated that the composite coating modified with yttrium had an excellent anti-corrosion performance ($E_{\text{corr}} = -0.36$ VSCE, $I_{\text{corr}} = 9.12 \times 10^{-9}$ A cm^{-2}) and self-healing ability.

Yan et al. [18] studied the Ti_3C_2 MXene nanosheets towards high-performance corrosion inhibitor for epoxy coating. The results reveal that epoxy coatings with Ti_3C_2 nanosheets have strong corrosion resistance due to the intrinsic properties of 2D Ti_3C_2 nanosheets and the establishment of a barrier against corrosive media. They achieved a protective efficiency up to 99%. Therefore, the Ti_3C_2 can enhance corrosion protective performance. Nie et al. studied the MXene-hybridised silane films for metal anti-corrosion and antibacterial applications. They have reported that, after three days of NaCl spray time on aluminium alloy, the corrosion area for Al coated with MXene was 0% compared to chromium and silane films [19].

Shen et al. studied GO-Ti_3C_2 two-dimensional heterojunction nanomaterial for anti-corrosion enhancement of epoxy zinc-rich coatings [7]. Hybride additives of GO-Ti_3C_2 were incorporated into the ZRC coating to improve the utilisation rate of zinc particles. Both GO and Ti_3C_2 provided a barrier for corrosion inhibition. At the end of immersion, R_c value of ZRC/GO-Ti_3C_2 coating was 3.047×10^4 Ω cm^2, it was one order of magnitude better than ZRC coating.

Zhao et al. investigated air-stable titanium carbide MXene nanosheets for corrosion protection [20]. It was discovered that the $Z_{\text{f=0.01 Hz}}$ values of the IL@MXene$_{0.5}$ coating remained nearly unchanged after ten days of immersion. This can be associated with its high coating stability. The self-healing characteristics of the IL@MXene-WEP coating were also validated via the scanning vibrating electrode approach. The improved protective performance was due to the synergistic effects of the outstanding barrier property provided by well-dispersed MXene nanosheets and the self-repairing property caused by IL passive films. This research also provides a good technique for the design and preparation of MXene smart anti-corrosion coatings.

Cai et al. studied in situ assembly of $Ti_3C_2T_x$ MXene@MgAl-LDH heterostructure towards anti-corrosion and antiwear application [21]. As-prepared Ti_3C_2Tx MXene@MgAl-LDH/epoxy coating (C-MXene@LDH) exhibits satisfactory corrosion/wear protection and certain self-healing performance. The corrosion resistance of $Ti_3C_2T_x$ MXene@MgAl-LDH can be attributed to the synergy of good dispersibility, barrier effect and corrosion inhibitor release.

Song et al. studied the thermal and corrosion behaviour of MXenes/Cu composites [22]. The results show that Ti_3C_2/Cu composites have better corrosion resistance than TiC/Cu composites. This can be associated with the outstanding electrical conductivity and easily oxidised property of Ti_3C_2. However, the thermal conductivity of Ti_3C_2/Cu composite with the content of 2 wt% Ti_3C_2 improves about 15% compared to TiC/Cu composites even with the same content, resulting from the low inherent thermal conductivity of filler. Besides that, at the interfacial contact resistance measurement the electric resistance of Ti_3C_2/Cu composites increases around 100% compared to pure Cu, with the content of Ti_3C_2 at 2 wt%. Meanwhile, the anti-corrosion performance of the Ti_3C_2/Cu composites was improved over pure Cu. This work will broaden the application field of Ti_3C_2 and lay the foundation for future research. The E_{corr} of 2.0 wt% Ti_3C_2/Cu composite is 0.048 V higher than that of 2.0 wt% TiC/Cu composite, verifying that Ti_3C_2/Cu composite has better corrosion resistance compared to TiC/Cu composite. Additionally, Ti_3C_2/Cu composites have improved anti-corrosion performance compared to pure Cu.

Sheng et al. reported with 0.4 wt% MXene, the WPU/ Ti_3C_2 MXene composite coatings reach the lowest corrosion current of 2.143×10^{-6} A/cm^2 [23]. A decrease of one order of magnitude compared with blank WPU (1.599×10^{-5} A/cm^2) was achieved, and it has an excellent UV-blocking property [23]. Moreover, measurement against corrosion shows that the WPU Ti_3C2@Si has an exceptional resistance. It was found that the 0.1%Ti_3C_2@Si/ WPU exhibits the lowest corrosion current density (2.67×10^{-9} A/cm^2) and the largest corrosion resistance (3.05×10^6 Ω). After 42 days' immersion, the lowest frequency impedance of 0.1%Ti_3C_2@Si/WPU composite coating was 3.68×10^6 Ω cm^2 [24]. This research is also important for future anti-corrosion applications (Table 14.1).

Table 14.1 Recent literature of corrosion studies in NaCl environment

Ref	Year	Metal type	Exposure	Findings
[16]	2021	Al alloy	28 days	Wear rate decrease 96.26%
[17]	2021	Mg alloy	15 days	$E_{corr} = -0.36$ V SCE, $I_{corr} = 9.12 \times 10^{-9}$ A cm^{-2}
[7]	2021	Steel	50 days	Rc value of ZRC/GO-Ti_3C_2 coating was 3.047×10^4 Ω cm^2
[20]	2021	Steel	10 days	$Z_{f=0.01\ Hz}$ value remains unchanged
[21]	2021	Q345 steel	21 days	The wear rate of C-MXene is 0.0546 μm^3/N μm, reduced by 41.35% compared to that of EP
[23]	2021	Q235 mild steel	Not available	MXene composite coatings reach the lowest corrosion current of 2.143×10^{-6} A/cm^2
[24]	2021	Q235 mild steel	42 days	Largest corrosion resistance (3.05 × 106 Ω)
[22]	2020	Copper	Not available	E_{corr} of 2.0 wt% Ti_3C_2/Cu composite is 0.048 V
[19]	2020	Al alloy	3 days	Corrosion area 0%
[18]	2019	Q345 steel	15 days	Protective efficiency 99%

14.6 Conclusion

This work has provided an overview of applications, tensile properties and corrosion resistance studies of MXenes/nanocomposites. This review also introduces MXene as potential corrosion inhibitors. The composite coating with MXenes exhibits the highest corrosion potential and the lowest corrosion current density, and superior polarisation resistance, which is attributed to the intrinsic properties of Ti_3C_2 and its strong barrier effect. 2D MXene with good anti-corrosion function was proven. Recent research into MXenes as corrosion inhibitors has paved the way for MXene to be used as a high-performance anti-corrosion additive in the real world.

Acknowledgements The authors wish to thank the Centre of Research and Innovation (CoRI), Universiti Kuala Lumpur, for the Research Cluster grant awarded to Composites & Simulation Cluster (CSC) and UniKL MIDI for the research facilities provided.

References

1. Saharudin MS, Wei J, Shyha I et al (2016) The degradation of mechanical properties in halloysite nanoclay-polyester nanocomposites exposed in seawater environment. J Nanomater 2016:1–12
2. Shyha I, Fo G, Huo D et al (2018) Micro-machining of nano-polymer composites reinforced with graphene and nano-clay fillers. Key Eng Mater 786:197–205
3. Wei J, Saharudin MS, Vo T et al (2018) Effects of surfactants on the properties of epoxy/graphene nanocomposites. J Reinf Plast Compos 37:960–967
4. Saharudin MS, Atif R, Inam F (2017) Effect of Short-term water exposure on the mechanical properties of halloysite nanotube-multi layer graphene reinforced polyester nanocomposites. Polymers (Basel) 9:1–27
5. Wei J, Saharudin MS, Vo T et al (2017) N, N-Dimethylformamide (DMF) usage in epoxy/graphene nanocomposites: problems associated with reaggregation. Polymers (Basel) 9:193
6. Tamalmani K, Husin H (2020) Review on corrosion inhibitors for oil and gas corrosion issues. Appl Sci 10:1–16
7. Shen L, Zhao W, Wang K et al (2021) GO-Ti3C2 Two-dimensional heterojunction nanomaterial for anticorrosion enhancement of epoxy zinc-rich coatings. J Hazard Mater 417:126048
8. Sheng X, Zhao Y, Zhang L et al (2019) Properties of two-dimensional Ti3C2 Mxene/thermoplastic polyurethane nanocomposites with effective reinforcement via melt blending. Compos Sci Technol 181:107710
9. Aghamohammadi H, Amousa N, Eslami-Farsani R (2021) Recent advances in developing the MXene/polymer nanocomposites with multiple properties: a review study. Synth Met 273:116695
10. Zhi W, Xiang S, Bian R et al (2018) Study of MXene-filled polyurethane nanocomposites prepared via an emulsion method. Compos Sci Technol 168:404–411
11. Woo JH, Kim NH, Kim SII et al (2020) Effects of the addition of boric acid on the physical properties of MXene/polyvinyl alcohol (PVA) nanocomposite. Compos Part B Eng 99:108205
12. Sun Y, Ding R, Hong SY et al (2021) Mxene-Xanthan nanocomposite films with layered microstructure for electromagnetic interference shielding and joule heating. Chem Eng 410:128348

13. Cao W, Chen F, Zhu Y et al (2018) Binary strengthening and toughening of mxene/cellulose nanofiber composite paper with nacre-inspired structure and superior electromagnetic interference shielding properties. ACS Nano 12:4583–4593
14. Liu L, Ying G, Wen D et al (2021) Aqueous solution-processed Mxene (Ti3C2TX) for non-hydrophilic epoxy resin-based composites with enhanced mechanical and physical properties. Mater Des 197:1–11
15. Liu L, Ying G, Sun C et al (2021) MXene (Ti3C2Tx) Functionalized short carbon fibers as a cross-scale mechanical reinforcement for epoxy composites. Polymers (Basel) 13:1–13
16. Yan H, Cai M, Wang J et al (2021) Insight into anticorrosion/antiwear behavior of inorganic-organic multilayer protection system composed of nitriding layer and epoxy coating with Ti3C2Tx Mxene. Appl Surf Sci 536:147974
17. Wu Y, Wu L, Yao W et al (2021) Improved corrosion resistance of AZ31 Mg alloy coated with Mxenes/Mgal-Ldhs composite layer modified with yttrium. Electrochim Acta 374:137913
18. Yan H, Li W, Li H et al (2019) Ti3C2 Mxene nanosheets toward high-performance corrosion inhibitor for epoxy coating. Prog Org Coatings 135:156–167
19. Nie Y, Huang J, Ma S et al (2020) Mxene-hybridized silane films for metal anticorrosion and antibacterial applications. Appl Sur Sci 527:146915
20. Zhao H, Ding J, Zhou M et al (2021) Air-stable titanium carbide MXene nanosheets for corrosion protection. ACS Appl Nano Mater 4:3075–3086
21. Cai M, Fan X, Yan H et al (2021) In situ assemble Ti3C2Tx Mxene@Mgal-LDH heterostructure towards anticorrosion and antiwear application. Chem Eng J 419:130050
22. Song G, Deng Q, Wang B et al (2020) Thermal and corrosion behavior of Ti3C2/copper composites. Compos Commun 22:1–6
23. Sheng X, Li S, Huang H et al (2021) Anticorrosive and UV-blocking waterborne polyurethane composite coating containing novel two-dimensional Ti3C2 mxene nanosheets. J Mater Sci 56:4212–4224
24. Zhang F, Liu W, Wang S et al (2021) Surface functionalization of Ti3C2Tx and its application in aqueous polymer nanocomposites for reinforcing corrosion protection. Compos Part B Eng 217:108900