

# Improved anticorrosive property of waterborne epoxy coating by ultrasonic blending with small amounts of polyaniline

Huan-Yan Xu (✉ [xuhuanyan@hrbust.edu.cn](mailto:xuhuanyan@hrbust.edu.cn))

Harbin University of Science and Technology <https://orcid.org/0000-0003-4895-5853>

Lu Zhang

Harbin University of Science and Technology

Yun-Fei Wang

Harbin University of Science and Technology

Xu Han

Harbin University of Science and Technology

---

## Research Article

**Keywords:** Waterborne epoxy coating, Polyaniline, Anticorrosion, Electrochemical analysis, Salt spray test

**Posted Date:** June 9th, 2021

**DOI:** <https://doi.org/10.21203/rs.3.rs-599291/v1>

**License:**  This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

---

**Version of Record:** A version of this preprint was published at Journal of the Iranian Chemical Society on January 20th, 2022. See the published version at <https://doi.org/10.1007/s13738-021-02475-7>.

# 1 Improved anticorrosive property of waterborne epoxy coating by 2 ultrasonic blending with small amounts of polyaniline

3 Huan-Yan Xu\*, Lu Zhang, Yun-Fei Wang, Xu Han

4 School of Materials Science and Chemical Engineering, Harbin University of Science and Technology,  
5 Harbin 150040, P. R. China

6 \* Corresponding author

7 Tel: +86-451-86392501; Fax: +86-451-86392555

8 E-mail address: [xuhuanyan@hrbust.edu.cn](mailto:xuhuanyan@hrbust.edu.cn) (H.-Y. Xu)

9 ORCID: 0000-0003-4895-5853

## 10 **Abstract**

11 In order to improve the anticorrosive performance of waterborne epoxy (WEP) coating, small  
12 amounts of polyaniline (PANI) were blended under ultrasonic irradiation to obtain PANI/WEP  
13 composite coatings with high dispersibility of PANI particles. The PANI/WEP composite coatings  
14 were characterized by Fourier transform infrared spectroscopy (FTIR) and field emission scanning  
15 electron microscopy (FESEM). Their adhesive force level and hardness grade were tested based on  
16 the Chinese National Standard GB/T9286-1998 and GB/T6739-1996, respectively. These results  
17 indicated that, compared to the pristine WEP coating, the addition of PANI with suitable content  
18 could completely fill the micropores or microcracks and remarkably improve the hardness grade of  
19 composite coatings. The electrochemical impedance spectra (EIS) and Tafel polarization curves  
20 revealed that the addition of PANI not only could increase the impedance arc, but also could  
21 increase the impedance modulus at low frequency. Then, the salt spray tests were employed to  
22 observe the anticorrosive performance of PANI/WEP composite coatings. Finally, the enhanced  
23 anticorrosive mechanism of WEP coating by the addition of small amounts of PANI was proposed  
24 and discussed. The addition of PANI with suitable content could play an important role of physical  
25 and chemical barriers to improve the anticorrosive performance of waterborne epoxy coating.

## 26 **Key words**

27 Waterborne epoxy coating; Polyaniline; Anticorrosion; Electrochemical analysis; Salt spray test

## 28 **Declarations**

29 Not applicable

## 1 Introduction

2 The phenomenon of metallic corrosion worldwide exists in various fields such as mechanical  
3 equipment, bridge construction, chemical industry, shipping and ocean engineering, which has  
4 resulted in huge economic losses and been greatly concerned by governments and enterprises [1,2].  
5 Many methods have been attempted to protect the metallic surface against corrosion, for example,  
6 polymeric coatings [3], inorganic coatings [4], hydrid coatings [5], self-healing smart coatings [6],  
7 photocathodic protection [7] and so on. Among them, the polymeric coatings are more popularly  
8 used for the protection of metallic surface, which can form a protective barrier to inhibit the  
9 penetration of corrosive media including H<sub>2</sub>O, O<sub>2</sub> and other ions. Well designed polymers usually  
10 exhibit good adhesive property and stability. In addition to this, the coating technologies for  
11 polymers are simple and diverse, such as brush coating, spray coating, bar coating, roller coating,  
12 flow coating, spin coating and dip coating [8]. However, with the on-going deterioration of air  
13 environmental quality and increasing attention to human health, more and more strict laws and  
14 policies on environmental protection have been formulated by governments around the world to  
15 control and restrict the discharge of volatile organic compounds (VOCs). Therefore, the conventional  
16 solvent-based polymeric coatings are seriously suppressed and alternatively replaced by the  
17 emerging waterborne-based ones [9].

18 Various resins can be frequently used as waterborne coating matrix, including epoxy, acrylic,  
19 polyester, urethane and alkyd [10]. Among them, epoxy resin is extensively applied as protective  
20 coating for the metallic anticorrosion, attributed to its wide range of varieties and curing, strong  
21 adhesion, low shrinkage, excellent mechanical and electric properties, superior chemical and  
22 dimensional stability and good microbial resistance [11]. The epoxy resin coating can provide an  
23 effective protective barrier for metallic substrates and thus restrict the metallic corrosion reactions  
24 by inhibiting, shielding and cathodically protecting [12]. However, in comparison with the  
25 solvent-borne epoxy, the water-borne epoxy is not very satisfactory to act as protective coatings in  
26 practical application [13]. Suffered from a longtime exposure to extremely aggressive environment,  
27 pure epoxy resin coating will become brittle and fatigued, consequently suppressing its protection  
28 ability and further blocking its application in the anticorrosion field [14]. Furthermore, the inherent  
29 permeability of small-molecule substances (O<sub>2</sub>, H<sub>2</sub>O and organic vapors) and the destruction or  
30 degradation caused by mechanical or chemical effects can reduce the protective function of

1 coatings [8]. In order to solve these problems, many strategies have been put forward to enhance  
2 the performance of epoxy resin coatings. To approach this goal, various organic/inorganic materials  
3 have been developed as nanofillers, including boron nitride nanosheets [12], silicon nitride  
4 nanoparticles [14], clay [15], modified graphene [16] and conducting polymers [17].

5 In the past few years, the conductive polymers have been increasingly employed as the additive  
6 filler in organic coatings to improve metallic anticorrosion ability, which has become a research  
7 hotspot [18]. The conductive polymers are normally constituted by conjugated electronic structures,  
8 accordingly exhibiting certain performances of both semiconductors and traditional polymers [8].  
9 Therefore, the conductive polymers ordinarily have excellent optical, electrical and electrochemical  
10 properties and thus help to increase the corrosion protection of metallic substrates [14]. Among all  
11 the conducting polymers, polyaniline (PANI), polypyrrole (PPY), polyindole and polythiophene are  
12 more potential in the application of metallic anticorrosion [8]. And, PANI is the most fascinated by  
13 its easy preparation, environmental harmony, chemical and thermal stability, low cost, electrical  
14 conductivity, reversible redox properties and unique doping characteristics [14, 18]. Hence, PANI has  
15 been extensively used in the anticorrosive composite coatings. In general, the conductive  
16 polymers-based anticorrosive coatings can be prepared through two approaches, i. e. direct  
17 electrodeposition and blend with polymeric coating matrix. In terms of the latter, the polymeric  
18 coating blended with a small amount of conductive polymer can show better corrosion resistance  
19 than pristine coatings. However, it is difficult to obtain high solubility or dispersibility of conductive  
20 polymers in the polymeric coating matrix [17]. Likewise, PANI is easy to agglomerate in the matrix  
21 [18]. Undoubtedly, lower dispersibility of PANI in the matrix will result in worse anticorrosive  
22 performance of composite coatings.

23 In order to sweep away this obstacle, an ultrasonic blending method was adopted to realize the  
24 high dispersibility of PANI in water-borne epoxy resin (WEP) coatings with improved anticorrosive  
25 performance. The functional groups of PANI/WEP composite coatings were determined by Fourier  
26 transform infrared spectroscopy (FTIR). The surface and fracture morphologies of PANI/WEP  
27 composite coatings were observed by field emission scanning electron microscopy (FESEM). The  
28 hardness and adhesion of PANI/WEP composite coatings were analyzed as well. The electrochemical  
29 and anticorrosive performances of PANI/WEP composite coatings were analyzed by the  
30 electrochemical workstation and neutral salt spray (NSS) tests, respectively. Then, the effect of

1 addition amount of PANI on the composite coating properties was discussed and the enhanced  
2 anticorrosive mechanism was put forward.

## 3 **2 Materials and methods**

### 4 *2.1 Preparation of water-borne epoxy resin*

5 Firstly, water-borne epoxy resin was prepared and the procedure has been introduced in our  
6 previous paper [19]. Briefly, polyethylene glycol (PEG) and sodium persulfate (SPS) were employed  
7 as the accelerant and catalyst, respectively and added into some amount of epoxy resin (E44).  
8 When the mixture was heated to 175-185 °C, the emulsifier was obtained. Then, the obtained  
9 emulsifier was mixed with deionized water and epoxy resin E44 at a certain weight proportion  
10 under magnetic stirring to prepare the water-based emulsion of epoxy resin.

### 11 *2.2 Preparation of PANI/WEP composite coatings*

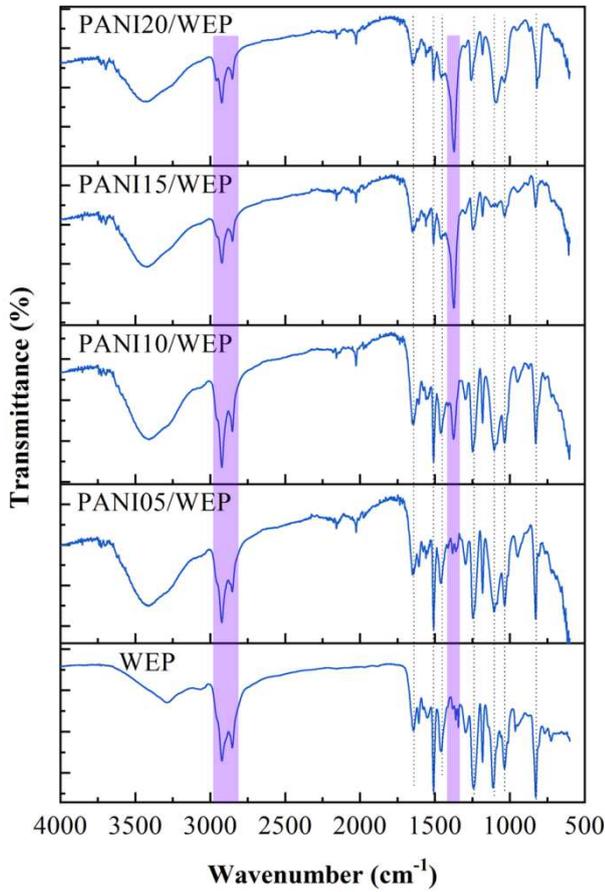
12 A small amount of PANI powder was added into the epoxy resin emulsion as prepared above.  
13 Under the ultrasonic irradiation, the mixed products were fully blended to realize the uniform  
14 dispersion of PANI. Afterwards, polyamide as the curing agent was added and evenly stirred by  
15 mechanical agitation. After the composite product was degassed in a vacuum oven, it was painted  
16 onto a pretreated iron plate. Subsequently, the composite coating was cured at room temperature.  
17 In this study, the coatings with PANI content of 0.5, 1.0, 1.5 and 2.0 wt. % were prepared and  
18 labeled as PANI05/WEP, PANI10/WEP, PANI15/WEP and PANI20/WEP, respectively. Otherwise, the  
19 pure WEP coating without the addition of PANI filler was prepared as the comparative sample and  
20 labeled as WEP.

### 21 *2.3 Characterization methods*

22 FTIR was employed to determine the functional groups of PANI/WEP composite coatings,  
23 operating on a Nicolet Nexus-470 infrared spectrometer. FESEM was used to observe the surface  
24 and fracture morphologies of coatings, operating on a FEISirion200 scanning electron microscope  
25 equipped with a digital camera. The adhesion and hardness of PANI/WEP coatings were tested  
26 based on the Chinese National Standard GB/T9286-1998 and GB/T6739-1996, respectively. A  
27 RST-3000 electrochemical workstation was utilized to analyze the electrochemical performances of  
28 composite coatings including electrochemical impedance spectroscopy (EIS) and Tafel polarization  
29 curves. NSS tests were implemented to investigate the anticorrosive performance of composite  
30 coatings by a salt spray chamber with 5±0.5% NaCl solution (pH=6.5-7.2) as the corrosive medium.

1 **3 Results and discussion**

2 *3.1 Characterizations of PANI/WEP coatings*



3  
4 **Figure 1** FTIR spectra of WEP and PANI/WEP composite coatings

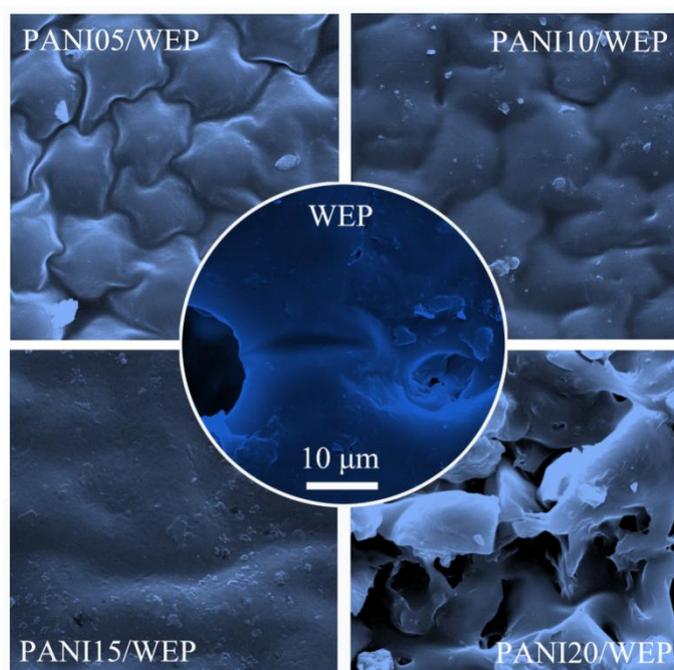
5 **Figure 1** illustrates the FTIR spectra of WEP and PANI/WEP composite coatings, from which we  
6 can know that, for the pristine WEP coating, all the FTIR absorption peaks are assigned to the epoxy  
7 resin cured with polyamide [20]. Due to small amounts of PANI addition, its characteristic FTIR  
8 absorption peaks cannot be found in PANI/WEP composite coatings. FTIR peak positions and their  
9 assignments of these coatings are listed in Table 1. Despite no changes in the peak positions, the  
10 intensities of certain peaks regularly vary with PANI content increasing, especially those at 2931,  
11 2862 and 1370  $\text{cm}^{-1}$ . The peak intensities at 2931 and 2862  $\text{cm}^{-1}$  decrease with PANI content  
12 increasing, which might be attributed to the weakened N–H stretching vibration of amide group in  
13 polyamide structure by increasing PANI content. While, the peak intensity around 1370  $\text{cm}^{-1}$   
14 increases with PANI content increasing, probably also caused by the addition of PANI. It is well  
15 known that one of the characteristic absorption peaks of PANI appears around 1300  $\text{cm}^{-1}$ , assigned  
16 to the stretching vibration of C–N of benzenoid rings in PANI structure [25-28]. Coincidentally, the

1 C–N vibration from amide group in polyamide structure occurs nearby. Therefore, the addition of  
 2 PANI tended to enhance the C–N vibration and thus increase the peak intensity.

3 **Table 1** FTIR peak positions and their assignments of WEP and PANI/WEP composite coatings

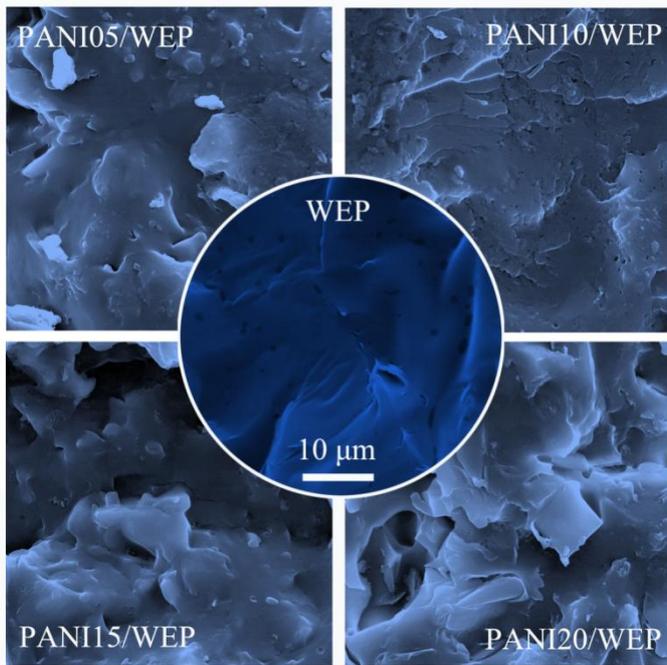
FTIR peak positions (cm <sup>-1</sup> )	Assignments	Refs.
3300-3400	—OH from hydrolyzed epoxy resin	[21]
2931	N–H stretching vibration from polyamide	[22]
2862		
1652	C=O stretching vibration from amide group	[23]
1508	aromatic rings	[22]
1455	C=C of benzene ring	[21]
1370	C–N vibration from amide group	[19]
1245	epoxy groups of epoxy resin	[22]
1185		
1113	C–O–C bending vibration from epoxy resin	[24]
1035		
825	epoxy groups of epoxy resin	[22]

4



5

6 **Figure 2** Surface morphologies WEP and PANI/WEP composite coatings

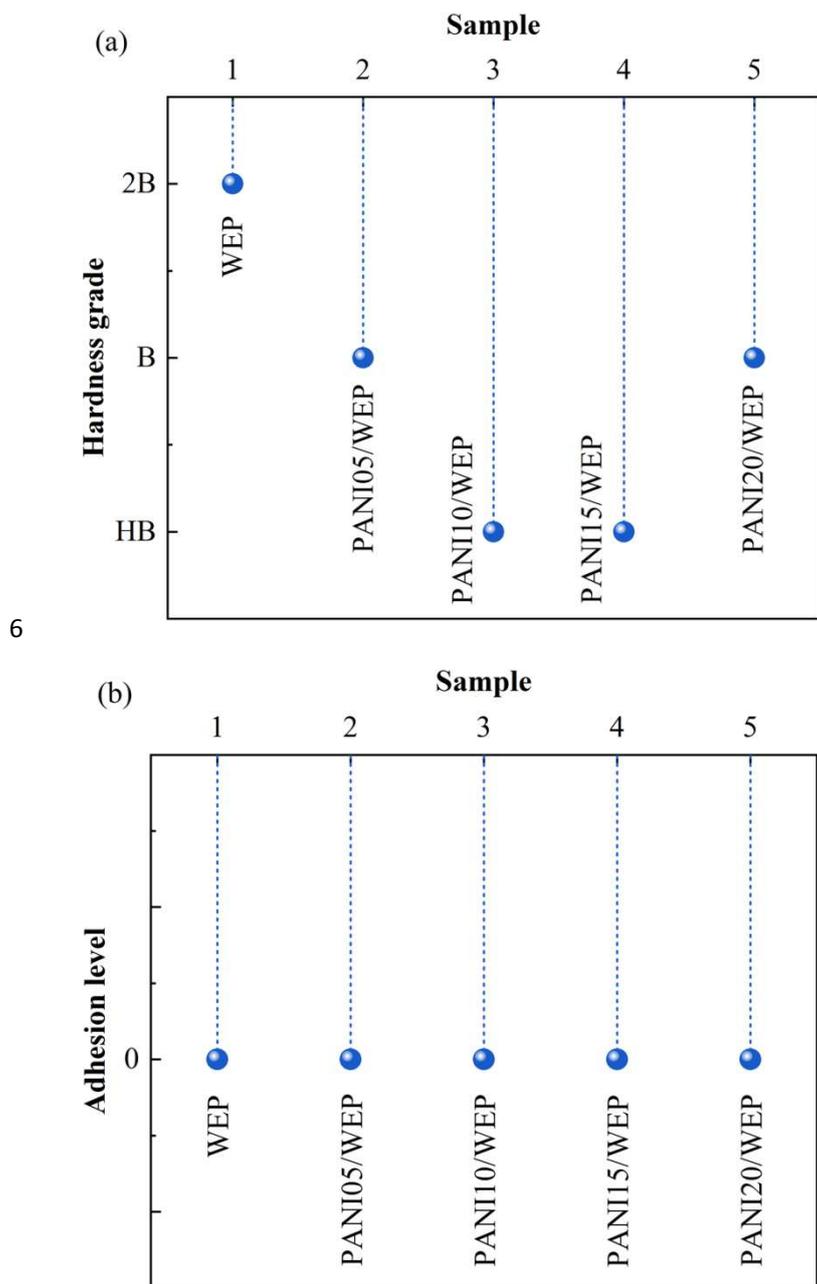


1  
2 **Figure 3** Fracture morphologies WEP and PANI/WEP composite coatings

3 The surface morphologies of WEP and PANI/WEP composite coatings are presented in [Figure 2](#),  
4 where it can be seen that there exist many micropores in WEP coating, which might be formed  
5 during the curing process of WEP. This is an unavoidable drawback for WEP [\[11\]](#). These micropores  
6 could become the tunnels for the permeability of corrosive substances, accordingly hindering the  
7 protective barrier function of WEP. After the addition of PANI with suitable content, these  
8 micropores can be filled, just like PANI05WEP, PANI10WEP and PANI15WEP coatings. However, large  
9 amounts of wrinkle-like microcracks appear in PANI05WEP coating, which will remarkably suppress  
10 its anticorrosive and mechanical performances. For PANI20WEP coating, its surface is not smooth  
11 and compact, suggesting that excessive PANI might impose restriction on the curing of WEP. Similar  
12 observation results can be seen in the fracture morphologies of WEP and PANI/WEP composite  
13 coatings, as shown in [Figure 3](#). Many micropores appear in WEP coating and PANI particulates  
14 uniformly disperse in PANI05WEP, PANI10WEP and PANI15WEP coatings. As expected, large  
15 numbers of micropores exist in PANI20WEP coating.

16 [Figure 4](#) shows the hardness grades and adhesive force levels of WEP and PANI/WEP composite  
17 coatings. According to the Chinese National Standard GB/T9286-1998 and GB/T6739-1996,  
18 PANI10WEP and PANI15WEP coatings exhibit the highest hardness grade among these five coatings  
19 and all the coatings have the adhesive force level of “0” that is the highest level of the given

1 standard. These results indicate that the addition of PANI can improve the hardness grade of  
2 composite coating compared to the pristine WEP coating. Due to the existence of lots of  
3 microcracks or micropores in PANI05WEP and PANI20WEP coatings, their hardness grades are lower  
4 than those of PANI10WEP and PANI15WEP coatings. Otherwise, the addition of PANI can not affect  
5 the adhesive property of WEP.



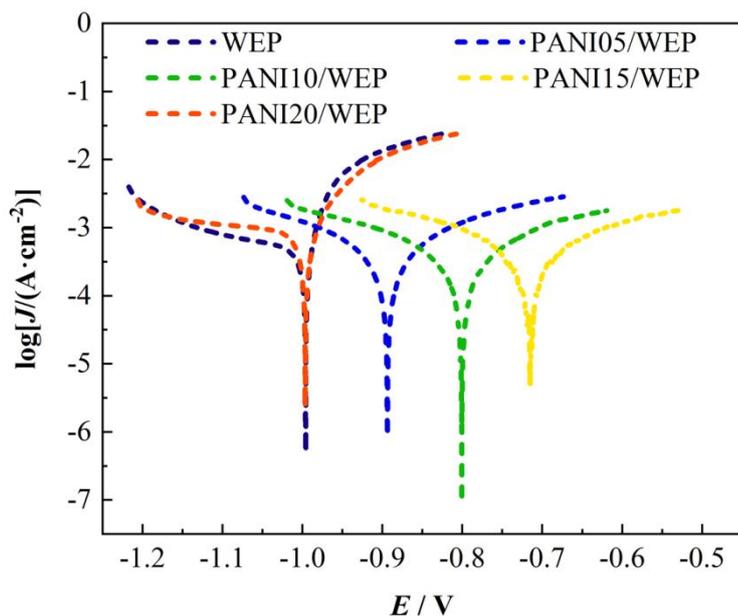
6  
7  
8 **Figure 4** Hardness grades (a) and adhesive force levels (b) of WEP and PANI/WEP composite  
9 coatings

10 *3.2 Electrochemical properties of PANI/WEP coatings*

1 Generally speaking, the anticorrosive nature of a coating is closely related with its  
 2 electrochemical performance. In order to have a deeper insight into the anticorrosive nature of  
 3 PANI/WEP composite coatings, their electrochemical properties were characterized by Tafel  
 4 polarization curve and ESI spectra in this study. Figure 5 gives the Tafel polarization curves of WEP  
 5 and PANI/WEP composite coatings. Based on these curves, the corrosive potential and current  
 6 density of corresponding coatings can be determined by the curve extrapolation method, i. e. the  
 7 point of intersection of the straight line portions of anodic and cathodic curves [29-32]. The results  
 8 are listed in Table 2, from which we can know that the addition of PANI with suitable content (0.5,  
 9 1.0 and 1.5 wt. %) can make the corrosive potential shift towards the anodic direction and  
 10 dramatically decrease the corrosive current density of the coatings. However, when the PANI  
 11 content was increased to 2.0 wt. %, the corrosive potential and current density of PANI20WEP are  
 12 comparable to those of WEP. It is widely accepted that the larger corrosive potential and smaller  
 13 corrosive current density indicate the better anticorrosive performance of a coating [16, 19, 31-34].  
 14 For this reason, it can be concluded that, among all the composite coatings, the anticorrosive  
 15 performance of PANI15WEP is the best; while, that of PANI20WEP is the worst. The possible  
 16 explanation for this phenomenon might be that PANI with suitable content can act as the filler to  
 17 eliminate the micropores and microcracks in the coatings; but excessive PANI might suppress the  
 18 curing of WEP and consequently generate large amounts of micropores, just as shown in the SEM  
 19 images. When the micropores or microcracks were occupied, the migration pathway of corrosive  
 20 substances could be interrupted and thus the corrosive potential increased and corrosive current  
 21 density decreased. As a result, the anticorrosive performance of composite coatings with suitable  
 22 PANI content could be improved.

23 **Table 2** The corrosive potential and current density of different coatings obtained from Tafel curves

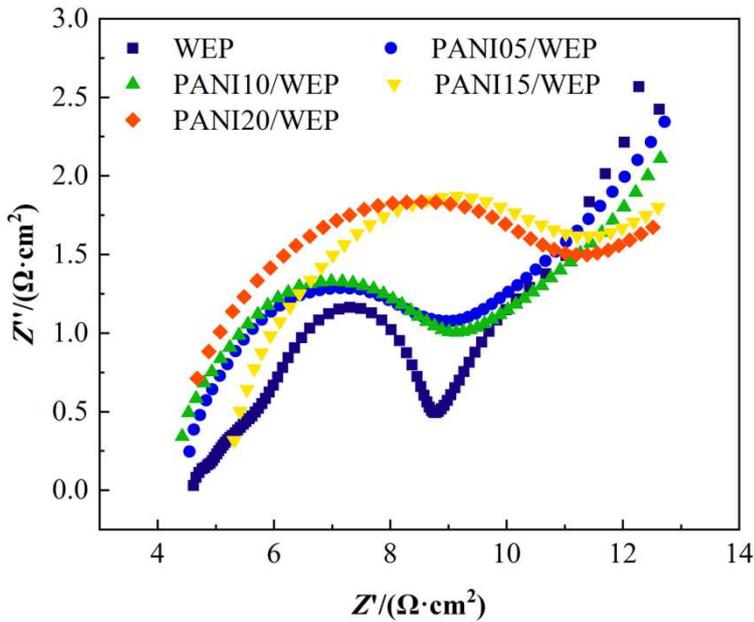
Sample	Corrosive potential (V)	Corrosive current density (A·cm <sup>-2</sup> )
WEP	-1.17	1.55×10 <sup>-3</sup>
PANI05WEP	-0.92	5.89×10 <sup>-4</sup>
PANI10WEP	-0.81	4.90×10 <sup>-4</sup>
PANI15WEP	-0.72	5.75×10 <sup>-4</sup>
PANI20WEP	-1.17	1.48×10 <sup>-3</sup>



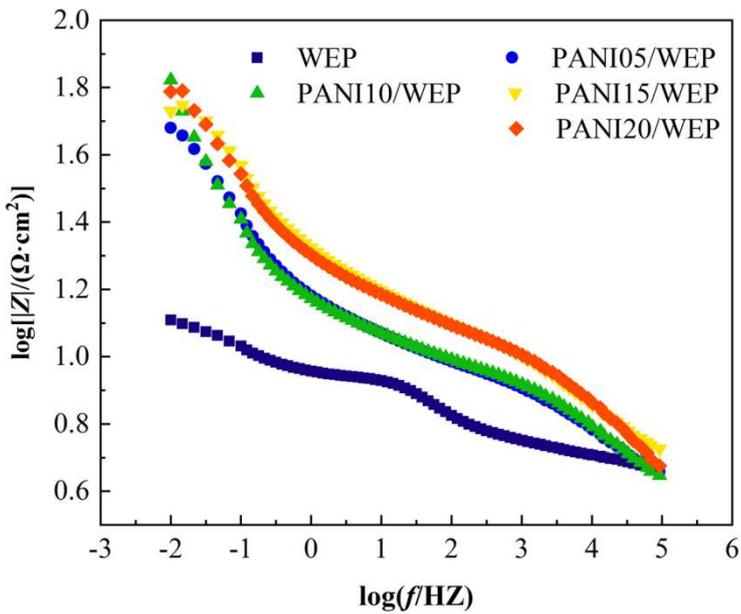
2 **Figure 5** Tafel polarization curves of WEP and PANI/WEP composite coatings

3 Furthermore, EIS is another important electrochemical technique to investigate the  
 4 anticorrosive nature of polymeric coatings. In this study, the impedance spectra of WEP and  
 5 PANI/WEP composite coatings were obtained in 3.5 wt.% NaCl solution at room temperature. The  
 6 Nyquist plots of WEP and PANI/WEP composite coatings are presented in [Figure 6](#), where it can be  
 7 seen that all the PANI/WEP composite coatings exhibit greater impedance arc than pristine WEP  
 8 coating. This means that the addition of PANI can endow these composite coatings with higher  
 9 impedance against the electrochemical reactions that happened at the interface between polymeric  
 10 coating and metallic substrate. PANI belongs to a kind of conducting polymer with excellent  
 11 electrochemical properties and was widely used as the filler in anticorrosive coatings [\[14, 18\]](#). PANI  
 12 not only acts as the protective barrier for the metallic surface, but also provides the electrochemical  
 13 protection for anode and cathode related with the corrosive reactions [\[14\]](#). PANI can transfer the  
 14 electrons towards the interior of coating and keep them away from the coating-metal interface,  
 15 accordingly impeding the redox reactions of metallic corrosion and improving the anticorrosive  
 16 performance. The Bode modulus plots of WEP and PANI/WEP composite coatings are illustrated in  
 17 [Figure 7](#). The anticorrosive performance of polymeric coating can also be evaluated by the Bode  
 18 modulus value at  $f = 0.01$  Hz. In the same way, all the PANI/WEP composite coatings have larger  
 19 Bode modulus value at  $f = 0.01$  Hz than pristine WEP coating. Larger Bode modulus suggests better  
 20 anticorrosive performance of polymeric coating [\[19, 34\]](#). In brief, the addition of PANI not only could  
 21 increase the impedance arc, but also could increase the impedance modulus at  $f = 0.01$  Hz. Hence,

1 from the view point of electrochemical analyses, PANI can remarkably improve the anticorrosive  
2 performance of waterborne epoxy coating.



3  
4 **Figure 6** Nyquist plots of WEP and PANI/WEP composite coatings



5  
6 **Figure 7** Bode plots of WEP and PANI/WEP composite coatings

### 7 3.3 Enhanced anticorrosive mechanism of PANI/WEP coatings

8 The photographs of PANI/WEP composite coatings before and after salt spray tests are  
9 displayed in [Figure 8](#), from which we can see that the large-area brown rusty spots appear on  
10 PANI05WEP and PANI10WEP coatings after 40-hour salt spray test. In addition, the delamination on

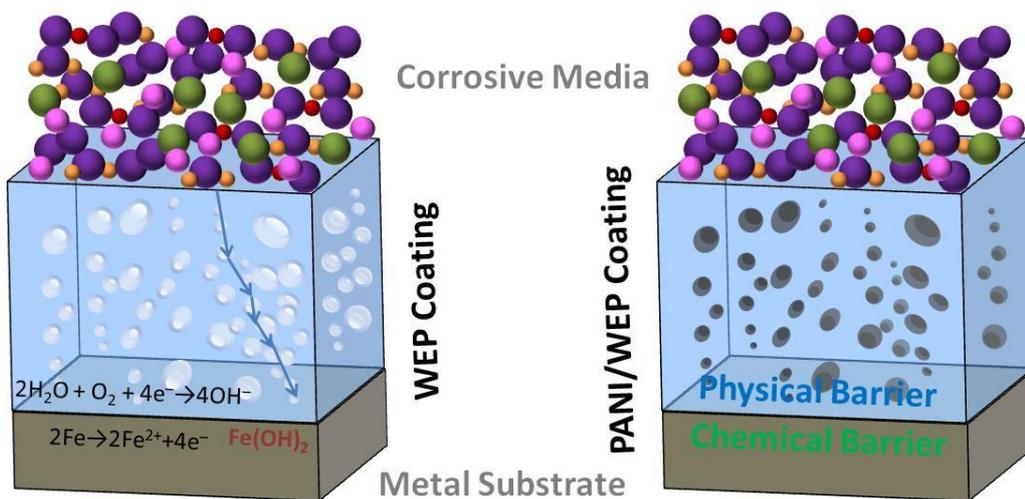
1 the edge of PANI20WEP coating can be observed. Therefore, PANI15WEP coating exhibits the best  
2 anticorrosive performance among these composite coatings. According to the aforementioned  
3 characterization and discuss, PANI15WEP coating is compact without micropores or microcracks on  
4 its surface and with the uniform dispersion of PANI particles in its interior; meanwhile, PANI15WEP  
5 coating has excellent electrochemical properties against the corrosive reactions, such as corrosive  
6 potential, corrosive current density and electrochemical impedance.



7  
8 **Figure 8** Photographs of PANI/WEP composite coatings before and after salt spray tests

9 Here, the enhanced anticorrosive mechanism of WEP coating by the addition of small amounts  
10 of PANI is proposed and illustrated in [Figure 9](#). It has been proved that, when a low concentration of  
11 conducting polymers was added into organic coating matrix, the obtained composite coating could  
12 show better corrosion resistance than the corresponding pristine coating [17]. As a typical  
13 representative of conducting polymers, PANI has been extensively used as the filler to improve the  
14 anticorrosive performance of polymeric coatings. However, researchers still could not reach a  
15 consensus on the enhanced anticorrosive mechanism by PANI, attributed to the complicated  
16 affecting factors such as dosage, doping, modification and redox state of PANI. Up to now, five  
17 widely accepted anticorrosive mechanisms are suggested as follows: 1) anode protection by the

1 oxidation of PANI to form a new product layer on the metallic surface; 2) cathode separation by  
 2 transferring the electrons generated by the corrosive reactions at the coating-metal interface to the  
 3 interior of coating; 3) release of corrosion inhibitors by the doping of PANI with suitable inhibitors; 4)  
 4 suppressed penetration of corrosive media by reducing the porosity to form more compact coating;  
 5 and 5) electric field effect by the contact between metal and PANI to hinder the migration of  
 6 electrons from metal to oxidant [35]. In this study, an ultrasonic blending method was adopted to  
 7 realize the uniform dispersion of PANI particles in WEP matrix. This could guarantee the complete  
 8 fill of micropores or microcracks which were probably generated during the curing or drying process.  
 9 The more compact coating could play an important role in the protective barrier to suppress the  
 10 penetration of corrosive media such as H<sub>2</sub>O, O<sub>2</sub> and other ions. This belongs to the physical barrier  
 11 effect. On the other hand, PANI as a kind of conducting polymer could effectively transfer the  
 12 electrons to the inside of the composite coating and accordingly interrupt the redox reactions  
 13 related with metallic corrosion. At the same time, the electric field between PANI and metal could  
 14 block the electron migration from metal to oxidant and thus prevent the transformation of Fe to  
 15 Fe<sup>2+</sup>. These can be regarded as the chemical barrier effects. The dual barrier effect of PANI endowed  
 16 the composite coatings with enhanced anticorrosive performance.



17  
 18 **Figure 9** Enhanced anticorrosive mechanism of WEP coating by the addition of PANI

19 **4 Conclusions**

20 An ultrasonic blending method was adopted to realize the high dispersibility of PANI particles in  
 21 WEP coatings with improved anticorrosive performance. There existed many micropores in WEP  
 22 coating; while, after the addition of PANI with suitable content, these micropores could be filled.

1 Moreover, PANI could improve the hardness grade of composite coatings compared to the pristine  
2 WEP coating. The Tafel results indicated that the addition of PANI with suitable content (0.5, 1.0 and  
3 1.5 wt. %) could make the corrosive potential shift towards the anodic direction and dramatically  
4 decrease the corrosive current density of the coatings. PANI not only could increase the impedance  
5 arc, but also could increase the impedance modulus at  $f = 0.01$  Hz. Hence, from the view point of  
6 electrochemical analyses, PANI could remarkably improve the anticorrosive performance of  
7 waterborne epoxy coating.

## 8 **References**

- 9 1. Y.K. Cai, Y.M. Xu, Y. Zhao, X.B. Ma, Atmospheric corrosion prediction: a review. *Corros. Rev.* **38**,  
10 299-321 (2020)
- 11 2. N. Guo, Y. Wang, X.R. Hui, Q.U. Zhao, Z.S. Zeng, S. Pan, Z.W. Guo, Y.S. Yin, T. Liu, Marine bacteria  
12 inhibit corrosion of steel via synergistic biomineralization. *J. Mater. Sci. Technol.* **66**, 82-90 (2021)
- 13 3. T. Liu, J. Wei, L. Ma, S. Liu, D. Zhang, H. Zhao, Effect of polyaniline-based plate on the  
14 anticorrosion performance of epoxy coating. *Prog. Org. Coat.* **151**, 106109 (2021)
- 15 4. X. Yang, R.H. Zhang, J.B. Pu, Z.Y. He, L.P. Xiong, 2D graphene and h-BN layers application in  
16 protective coatings. *Corros. Rev.* **39**, 93-107 (2021)
- 17 5. J. Zhang, Z.Y. Liu, L.H. Zhang, J. Ma, D. Sun, D. Zhang, J.R. Liu, H.N. Bai, B. Wang, Preparation of  
18 polyvinylpyrrolidone/graphene oxide/epoxy resin composite coatings and the study on their  
19 anticorrosion performance. *J. Appl. Polym. Sci.* **138**, e50596 (2021)
- 20 6. G. Cui, Z.X. Bi, S.H. Wang, J.G. Liu, X. Xing, Z.L. Li, B.Y. Wang, A comprehensive review on smart  
21 anti-corrosive coatings. *Prog. Org. Coat.* **148**, 105821 (2020)
- 22 7. H.X. Guo, L.L. Li, C. Su, D.M. Yu, Z.Y. Liu, Effective photocathodic protection for 304 stainless steel  
23 by PbS quantum dots modified TiO<sub>2</sub> nanotubes. *Mater. Chem. Phys.* **258**, 123914 (2021)
- 24 8. T.Y. Peng, R.H. Xiao, Z.Y. Rong, H.B. Liu, Q.Y. Hu, S.H. Wang, X. Li, J.M. Zhang, Polymer  
25 nanocomposite-based coatings for corrosion protection. *Chem.-Asian J.* **15**, 3915-3941 (2020)
- 26 9. C.Y. Jiao, L. Sun, Q. Shao, J.Y. Song, Q. Hu, N. Naik, Z.H. Guo. Advances in waterborne acrylic resins:  
27 synthesis principle, modification strategies, and their applications. *ACS Omega* **6**, 2443-2449 (2021)
- 28 10. Y.J. He, G. Li, K.-H. Hwang, Y. Boluk, P.M. Claesson, Nano-scale mechanical and wear properties  
29 of a corrosion protective coating reinforced by cellulose nanocrystals-Initiation of coating  
30 degradation. *Appl. Surf. Sci.* **537**, 147789 (2021)

- 1 11. C. Verma, L.O. Olasunkanmi, E.D. Akpan, M.A. Quraishi, O. Dagdag, M.E. Gouri, E.M. Sherif, E.E.  
2 Ebenso, Epoxy resins as anticorrosive polymeric materials: a review. *React. Funct. Polym.* **156**,  
3 104741 (2020)
- 4 12. D. Pan, X.D. Zhang, G. Yang, Y. Shang, F.M. Su, Q. Hu, R.R. Patil, H. Liu, C.T. Liu, Z.H. Guo,  
5 Thermally conductive anticorrosive epoxy nanocomposites with tannic acid-modified boron nitride  
6 nanosheets. *Ind. Eng. Chem. Res.* **59**, 20371-20381 (2020)
- 7 13. M. Faccini, L. Bautista, L. Soldi, A.M. Escobar, M. Altavilla, M. Calvet, A. Domènech, E. Domí  
8 nguez, Environmentally friendly anticorrosive polymeric coatings. *Appl. Sci.* **11**, 3446 (2021)
- 9 14. H.F. Wang, Q. Qi, Y.X. Zhang, S.G. Chen, B.B. Dong, S.D. Zhu, Q. Hu, Z.H. Guo, Anticorrosive epoxy  
10 nanocomposite coatings filled with polyaniline-functionalized silicon nitride particles. *Ind. Eng.*  
11 *Chem. Res.* **59**, 16649-16659 (2020)
- 12 15. R.R. Henriques, B.G. Soares, Sepiolite modified with phosphonium ionic liquids as anticorrosive  
13 pigment for epoxy coatings. *Appl. Clay Sci.* **200**, 105890 (2021)
- 14 16. J.H. Li, G. Niu, W. Bai, Y.J. Ma, Q.R. Xiong, C.Y. Qin, J.J. Zhang, R.H. An, W. Ren, Significant  
15 improvement of anticorrosion properties of zinc-containing coating using sodium polystyrene  
16 sulfonate noncovalent modified graphene dispersions. *Coatings* **10**, 1150 (2020)
- 17 17. L.G. Zhang, S.H. Qiu, B. Zhu, H.C. Zhao, PEDOT-hydroxypropyl- $\beta$ -cyclodextrin inclusion complex  
18 as additive for epoxy coating with enhanced anticorrosion performance. *Int. J. Electrochem. Sci.* **16**,  
19 210443 (2021)
- 20 18. S.Q. Yang, S. Zhu, R.Y. Hong, Graphene oxide/polyaniline nanocomposites used in anticorrosive  
21 coatings for environmental protection. *Coatings* **10**, 1215 (2020)
- 22 19. H.Y. Xu, B. Li, X. Han, Y. Wang, X.R. Zhang, S. Komarneni, Synergic enhancement of the  
23 anticorrosion properties of an epoxy coating by compositing with both graphene and halloysite  
24 nanotubes. *J. Appl. Polym. Sci.* **136**, 47562 (2019)
- 25 20. S. Kocaman, G. Ahmetli, A study of coating properties of biobased modified epoxy resin  
26 with different hardeners. *Prog. Org. Coat.* **97**, 53-64 (2016)
- 27 21. J.H. Liu, Q. Yu, M. Yu, S.M. Li, K. Zhao, B. Xue, H. Zu, Silane modification of titanium  
28 dioxide-decorated graphene oxide nanocomposite for enhancing anticorrosion performance of  
29 epoxy coatings on AA-2024. *J. Alloy. Compd.* **744**, 728-739 (2018)
- 30 22. F. Ali, N. Ali, M. Altaf, A. Said, S.S. Shah, M. Bilal, Epoxy polyamide composites reinforced with

- 1 silica nanorods: fabrication, thermal and morphological investigations. *J. Inorg. Organomet. Polym. Mater.* **30**, 3869-3877 (2020)
- 2
- 3 23. D. Balgude, A. Sabnis, S.K. Ghosh, Investigation of cardanol-based reactive polyamide as a  
4 crosslinker in epoxy zinc-rich primer. *J. Coat. Technol. Res.* **14**, 583-595 (2017)
- 5 24. Y. Wang, C.M. Chien, S.M. Chiao, T.Y. Lee, Reactive compatibilization of polyetherimide with  
6 polyamide 6,6: part 2. effect of epoxy-functionalized polyamide. *Polym. Bull.* **73**, 2779-2804 (2016)
- 7 25. S. Fazli-Shokouhi, F. Nasirpouri, M. Khatamian. Epoxy-matrix  
8 polyaniline/p-phenylenediamine-functionalised graphene oxide coatings with dual anti-corrosion  
9 and anti-fouling performance. *RSC Adv.* **11**, 11627-11641 (2021)
- 10 26. A. Alipour, M.M. Lakouraj, H. Tashakkorian. Study of the effect of band gap and  
11 photoluminescence on biological properties of polyaniline/CdS QD nanocomposites based on  
12 natural polymer. *Sci. Rep.* **11**, 1913 (2021)
- 13 27. R.T. Liu, S.Y. Zhang, C. Zhao, D. Yang, T.T. Cui, Y.D. Liu, Y.G. Min, Regulated surface morphology  
14 of polyaniline/polylactic acid composite nanofibers via various inorganic acids doping for enhancing  
15 biocompatibility in tissue engineering. *Nanoscale Res. Lett.* **16**, 4 (2021)
- 16 28. I. Hasan, I.I. BinSharfan, R.A. Khan, A. Alsalmeh, L-ascorbic acid-g-polyaniline mesoporous silica  
17 nanocomposite for efficient removal of crystal violet: a batch and fixed bed breakthrough studies.  
18 *Nanomaterials* **10**, 2402 (2020)
- 19 29. C.-H. Chang, T.-C. Huang, C.-W. Peng, T.-C. Yeh, H.-I. Lu, W.-I. Hung, C.-J. Weng, T.-I. Yang, J.-M.  
20 Yeh, Novel anticorrosion coatings prepared from polyaniline/graphene composites. *Carbon* **50**,  
21 5044-5051 (2012)
- 22 30. D. Prasai, J.C. Tuberquia, R.R. Harl, G.K. Jennings, K.I. Bolotin, Graphene: corrosion-inhibiting  
23 coating. *ACS Nano* **6**, 1102-1108 (2012)
- 24 31. N.K. Rawat, A. Ghosal, S. Ahmad, Influence of microwave irradiation on various properties of  
25 nanopolythiophene and their anticorrosive nanocomposite coatings. *RSC Adv.* **4**, 50594-50605  
26 (2014)
- 27 32. W. Shang, F. Wu, Y. Wen, C. He, X. Zhan, Y. Li, Corrosion resistance and mechanism of graphene  
28 oxide composite coatings on magnesium alloy. *Ind. Eng. Chem. Res.* **58**, 1200-1211 (2019)
- 29 33. H. Guo, B. Chao, Z. Zhao, D. Nan, Preparation of aniline trimer modified graphene oxide new  
30 composite coating and study on anticorrosion performance *Mater. Res. Express* **7**, 125601 (2020)

1 34. H.Y. Xu, D. Lu, X. Han, Graphene-induced enhanced anticorrosion performance of waterborne  
2 epoxy resin coating. *Front. Mater. Sci.* **14**, 211-220 (2020)

3 35. F.J. Gao, J. Mu, Z.X. Bi, S. Wang, Z.L. Li, Recent advances of polyaniline composites in  
4 anticorrosive coatings: a review. *Prog. Org. Coat.* **151**, 106071 (2021)

5

6

# Figures

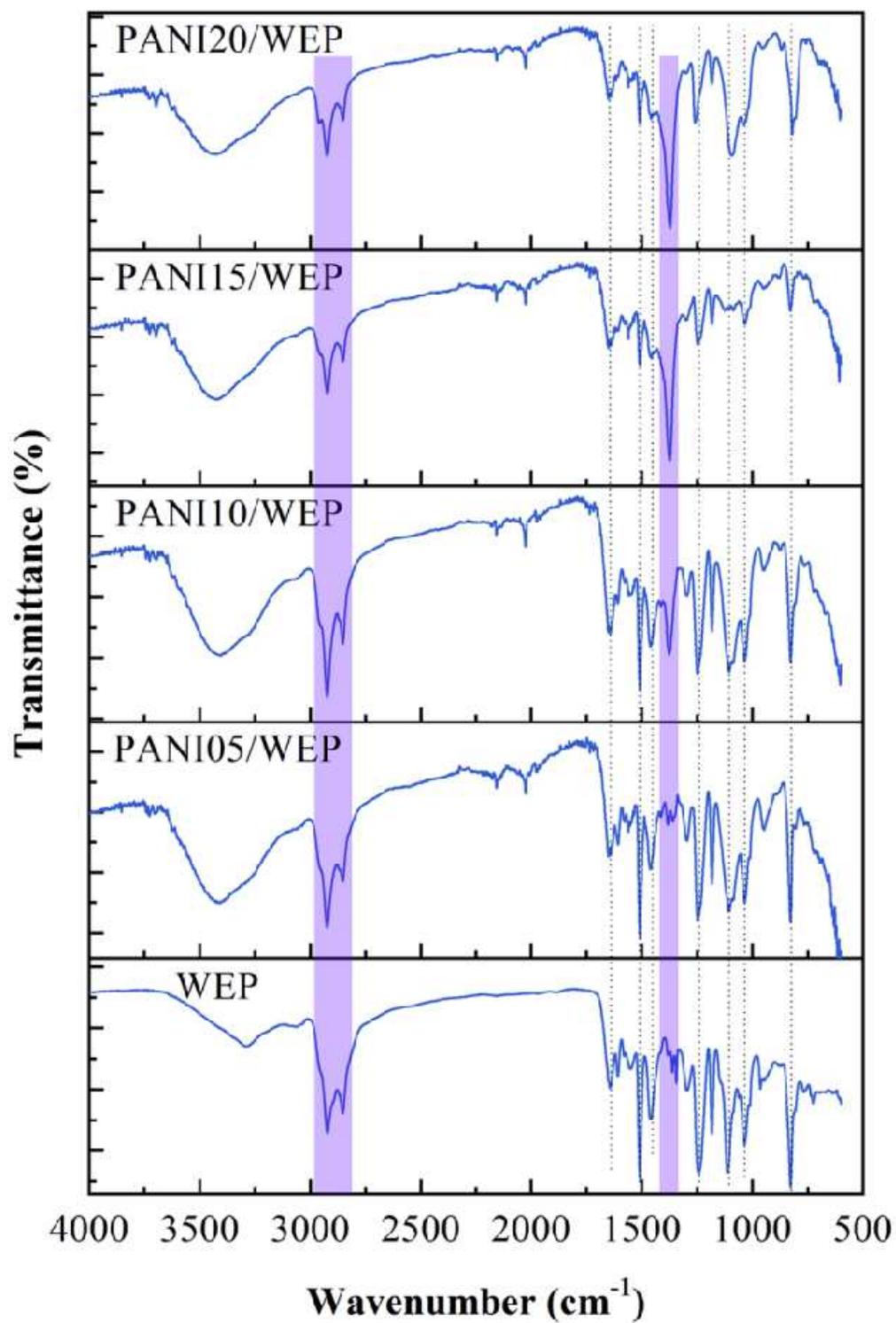


Figure 1

FTIR spectra of WEP and PANI/WEP composite coatings

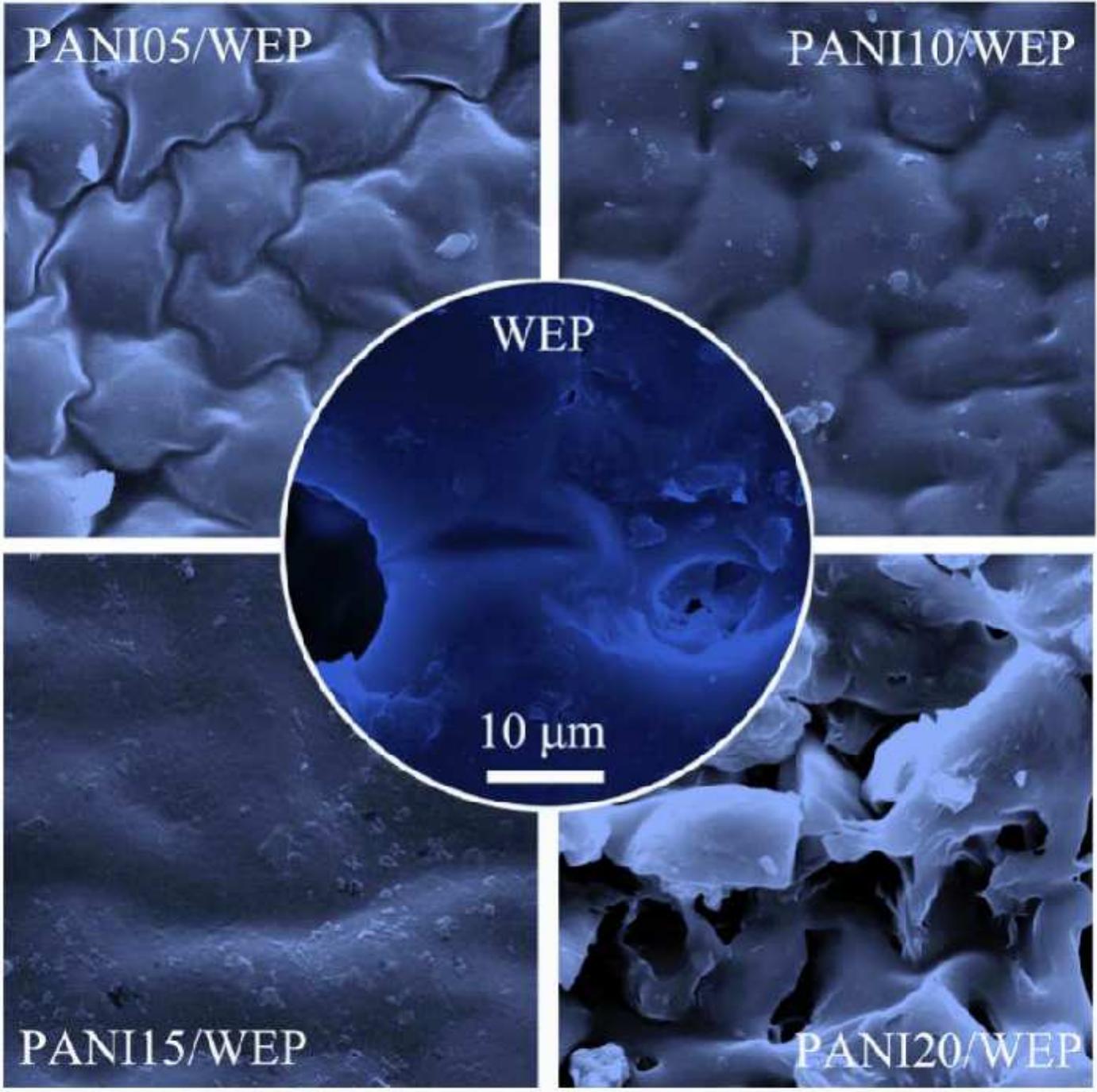


Figure 2

Surface morphologies WEP and PANI/WEP composite coatings

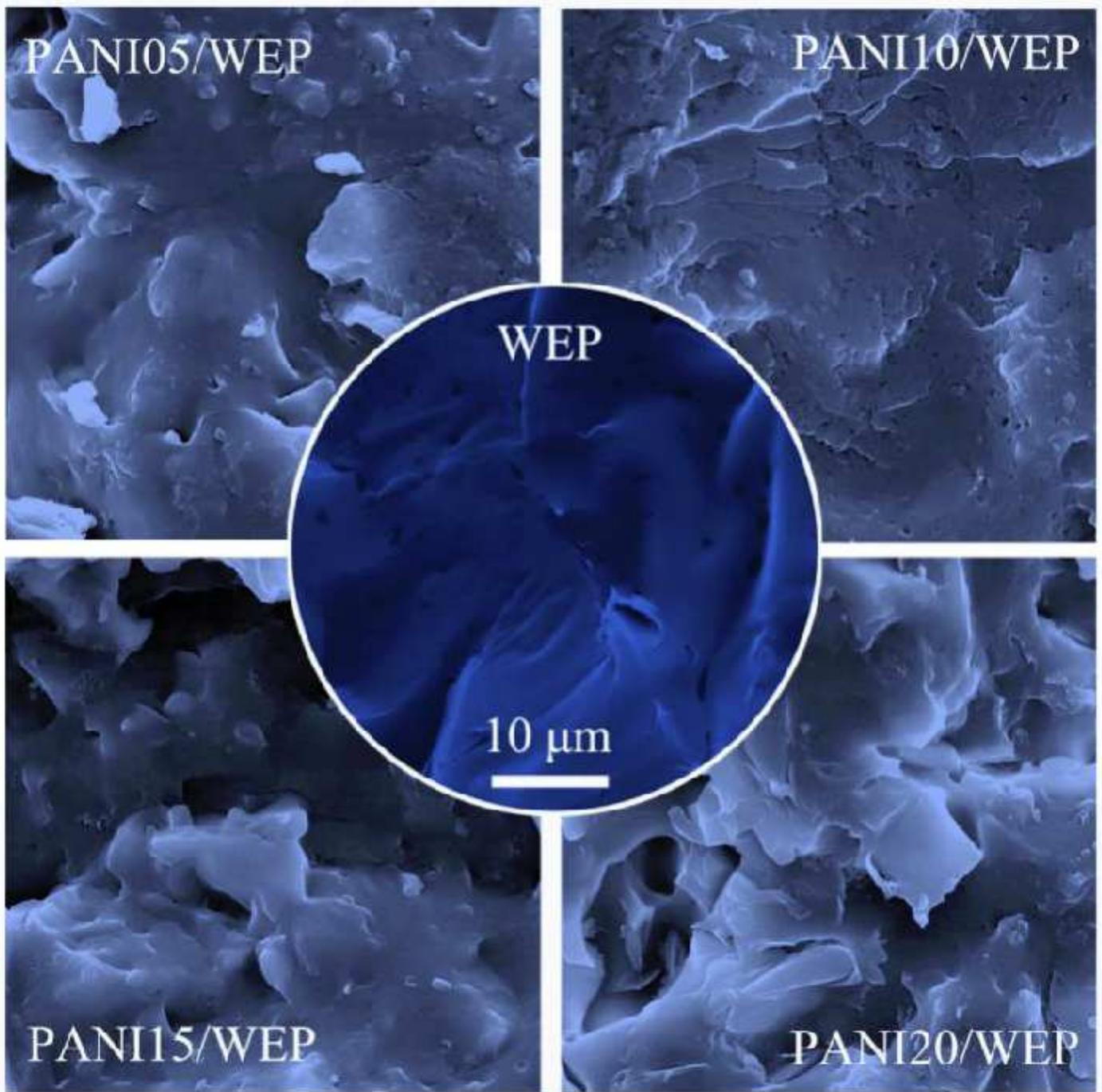
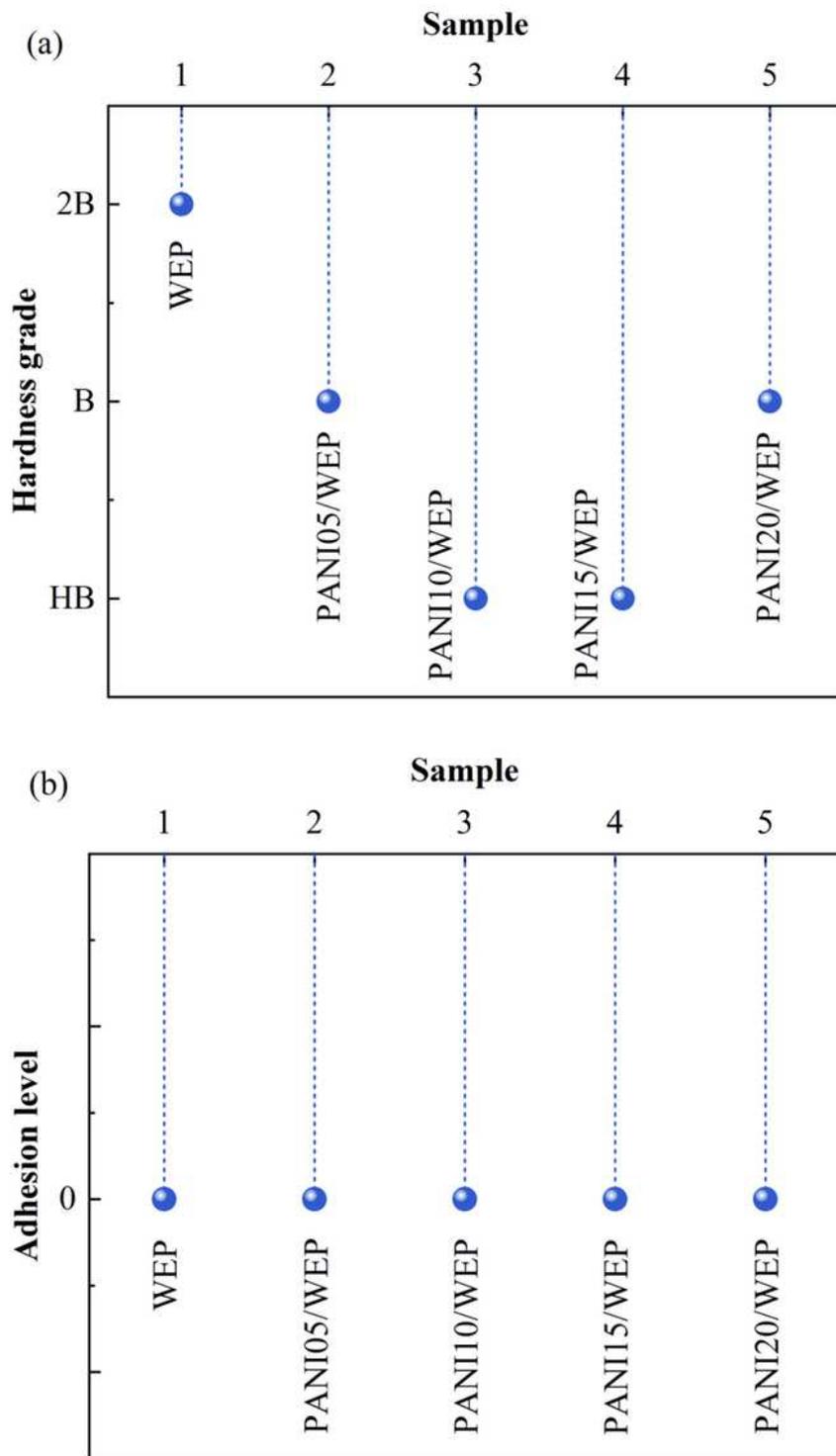


Figure 3

Fracture morphologies WEP and PANI/WEP composite coatings



**Figure 4**

Hardness grades (a) and adhesive force levels (b) of WEP and PANI/WEP composite coatings

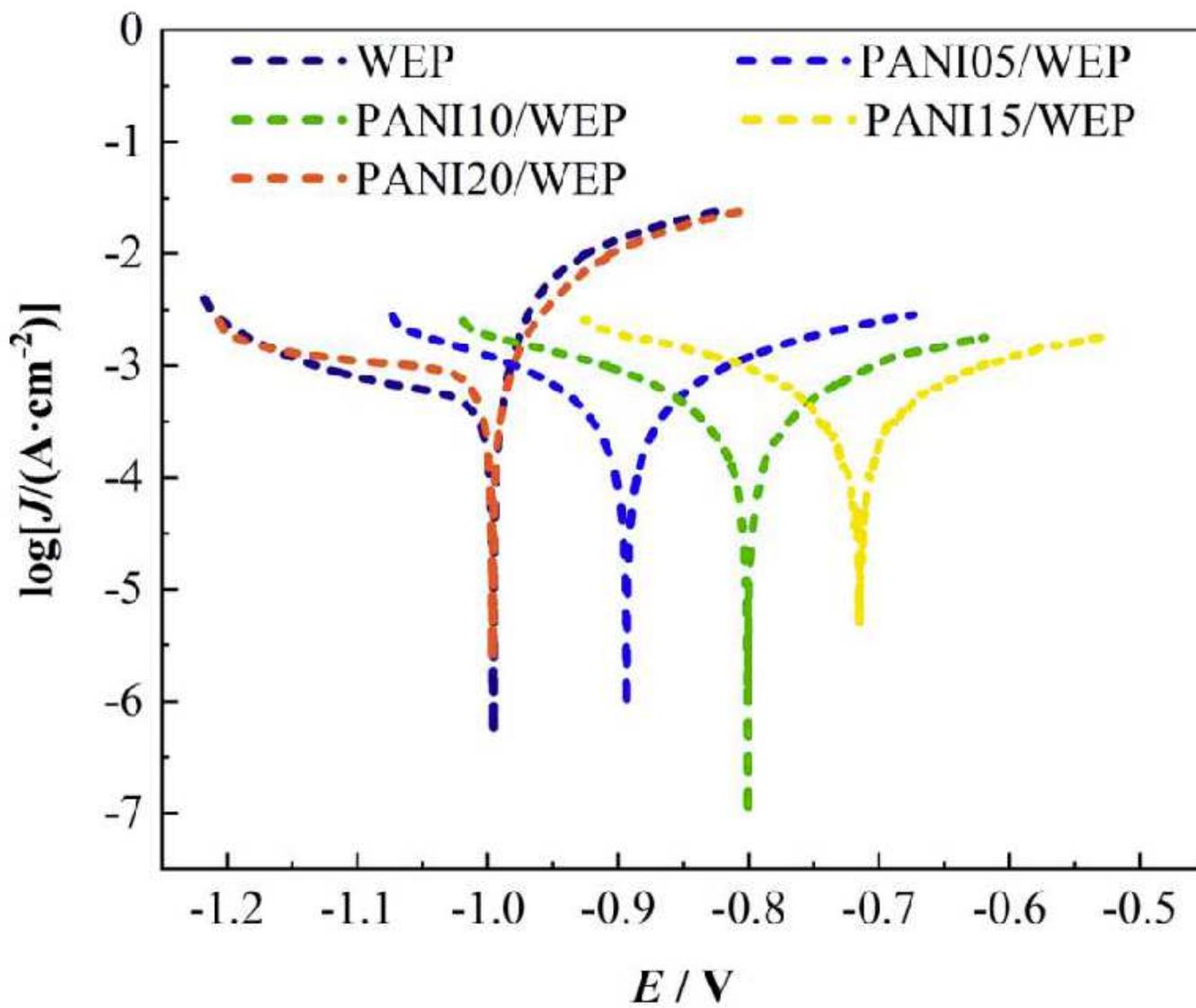


Figure 5

Tafel polarization curves of WEP and PANI/WEP composite coatings

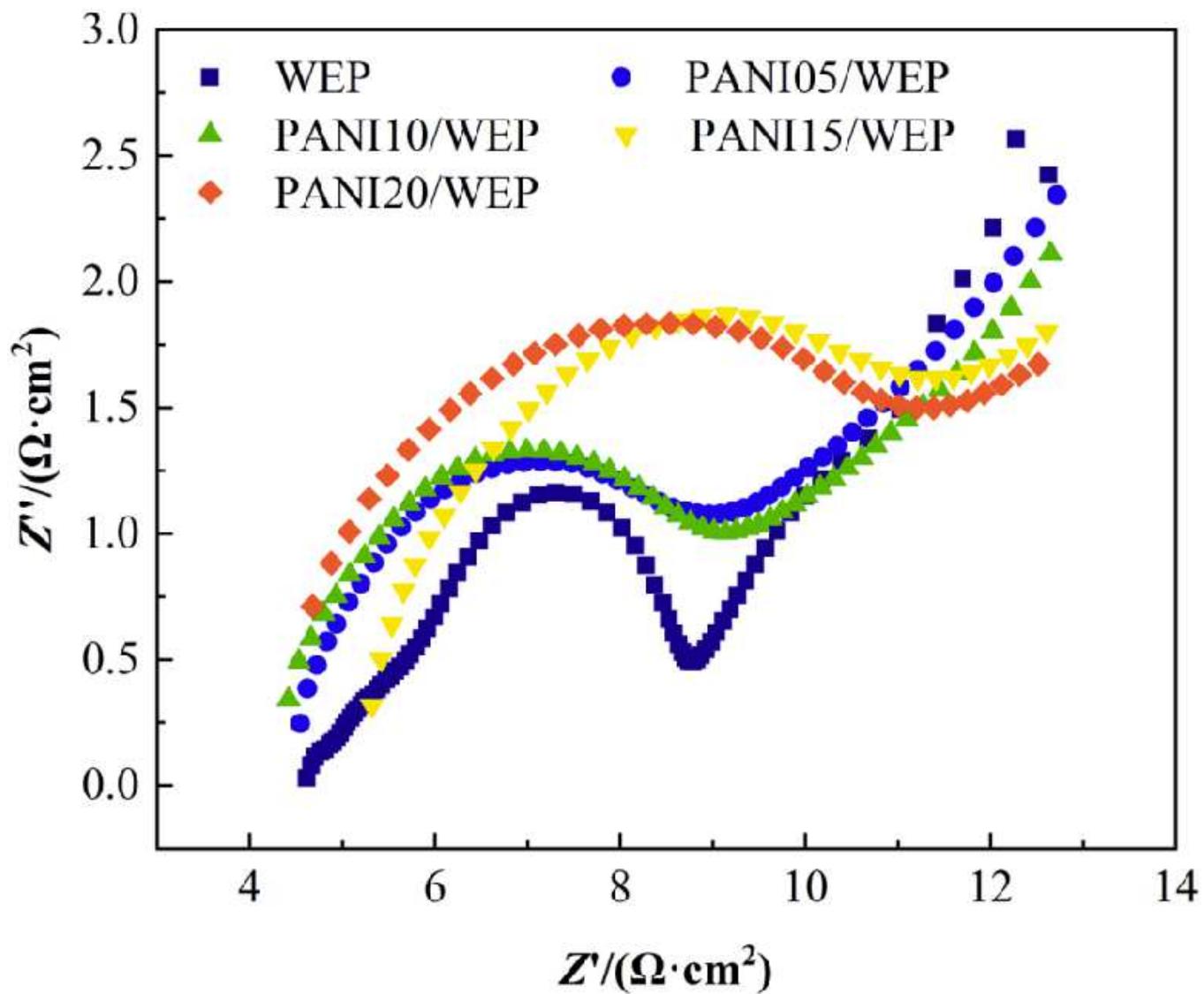


Figure 6

Nyquist plots of WEP and PANI/WEP composite coatings

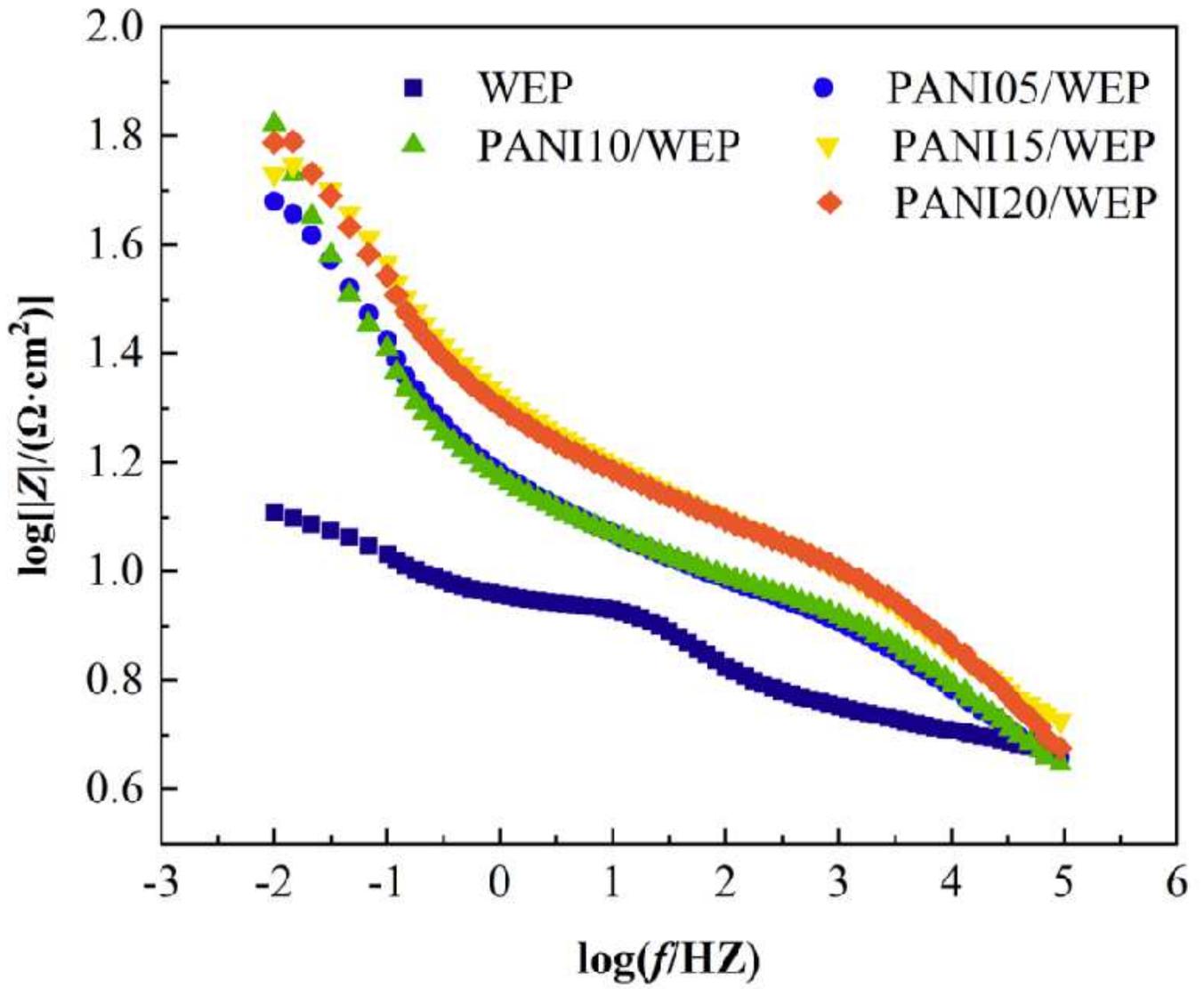


Figure 7

Bode plots of WEP and PANI/WEP composite coatings



Figure 8

Photographs of PANI/WEP composite coatings before and after salt spray tests

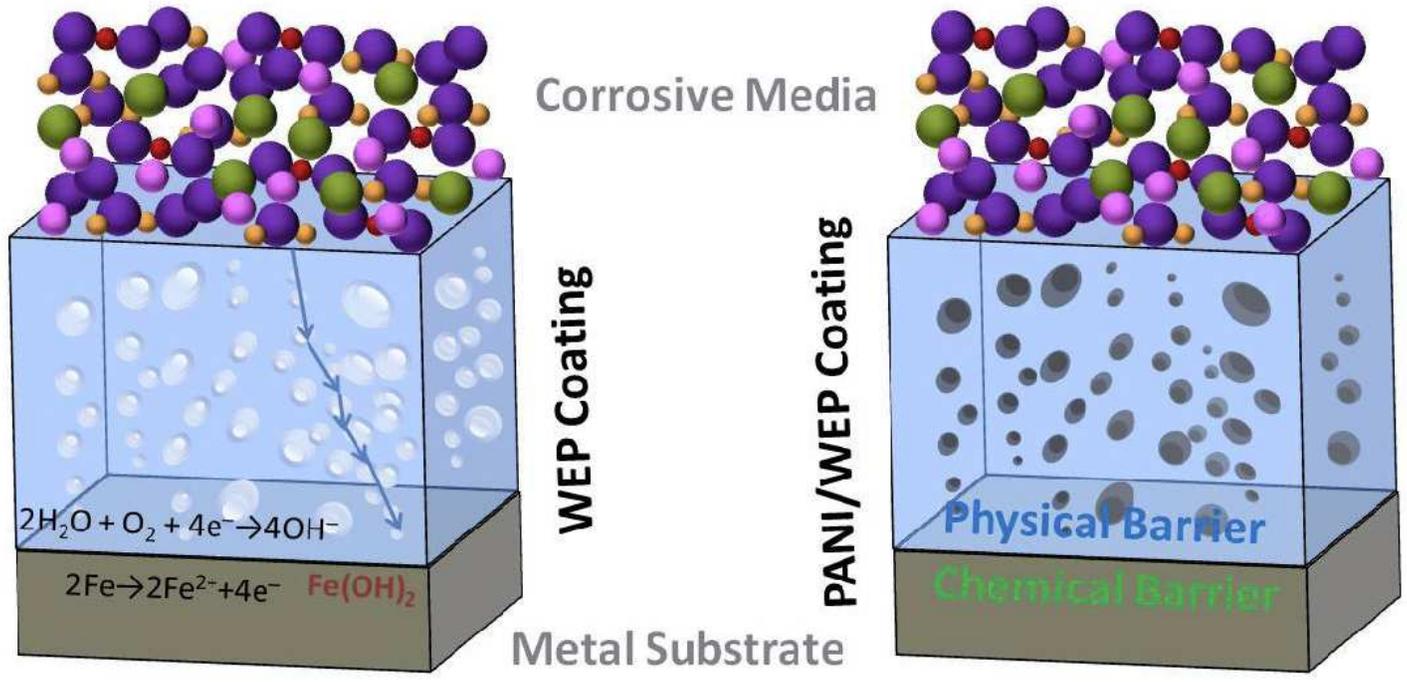


Figure 9

Enhanced anticorrosive mechanism of WEP coating by the addition of PANI