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The synergic effect of microcapsules and titanium nanoparticles on the self-healing and self-lubricating epoxy coatings: A dual smart application

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Abstract

In the present study, the multi-functional smart epoxy coatings were fabricated by incorporating the 15 wt.% microcapsules containing the linseed oil and various percentage of nano-TiO_2 (4, 8, and 16 wt.%). The self-healing and self-lubricating abilities of these nanocomposite coatings were investigated by corrosion and wear tests. The obtained results showed that the smart coating containing the 16 wt.% nano-TiO_2 had the best function in the corrosion media, due to healing a scratch in form of layer by layer. By using the microscopically analysis, it was found that the linseed oil acted as lubricant agent in the wear test. Adding 4 wt.% nano-TiO_2 had the negative effect on the anti-wear properties, due to forming the nanocomposite debris. However, by increasing the percentage of nano-TiO_2 up to 12 wt.%, the anti-wear properties had the enhancing trend. Improving the mechanical function of coatings, forming the nano-TiO_2/linseed oil self-suspense and trapping the debris by capsule containers were the characterized mechanisms for improving the anti-wear properties. It was also realized that the formation of nano-TiO_2/epoxy skin on the surface of microcapsules and agglomeration of nanoparticles had the negative effect on the wear properties of smart coatings.

Keyword: Nanocomposite, Self-healing, Self-lubricating, Microcapsules, Smart coating

1. Introduction

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The researches on the self-healing materials as one of the smart materials had an incredible growing in the last decade. One of the big major of these materials is the polymeric self-healable coatings and structures especially epoxy based materials [1-4]. The self-healable epoxy coatings were used to protect the coating and substrate. Theses smart system can protect the substrate via healing the created microcracks by healing agents or covering the substrate by inhibitor agents [3, 5]. These agents can be embedded into the epoxy coatings by capsulation of them. The urea-formaldehyde [6], poly methyl methacrylate [7], and polystyrene [8] are the famous polymeric materials for capsulation of these agents.

The epoxy, dicyclopentadiene, hexamethylene diisocyanate and sophorone diisocyanate can form a protective film in the damage area. Needing the catalyst for forming the protective films and the environmental toxicity of these agents are the disadvantages of them, so that, have been restricted their applications [9]. The key of this problem is using the dry oils instead of these agents. These oils are environmental friendly protective agents which can react with the oxygen for forming the protective film. Tung and linseed oils are the famous dry oils, which previously used as healing agents for protecting the substrate from the corrosive agents [10]. Hatami Boura et al. [11] capsulated the linseed oil by using the urea-formaldehyde shell for creating the healing ability in the epoxy coatings. They reported that the coating with the 15 wt.% microcapsules showed the highest corrosion resistance. Also, embedding the microcapsules reduced the permeability of water through the coating. Szabó et al. [12] synthesized microcapsules with the urea-resorcinol-formaldehyde shell for using in the epoxy coatings. They added the co-octoate as drier agent and octadecylamine (ODA) as inhibitor agent into the linseed oil for improving the healing-protecting behaviors of smart coatings. Based on the obtained results, the co-octoate reduced the drying time of linseed oil, whereas the ODA elongated that.

It is no secret that the nanomaterials like nanosilica [13], carbon nanotube [14], nanoclay as well as titanium oxide [16] have attracted much attentions for using as reinforcement into the polymeric materials like epoxy coatings in order to improve the different properties in various applications. Balaskas et al. [17] used the nano-TiO_2 for encapsulation of 8-hydroxyquinoline as inhibitor agent to improve the anti-corrosive properties of epoxy coatings. In another work, Atta et al. [18] studied the effect of titanium dioxide nano-gels and their particles size on the anticorrosion behaviors of epoxy coatings. Wang et al. [19] investigated three structures of nano-TiO_2 on the anti-corrosive properties of those. The obtained results showed that the meso-TiO_2 had the best performance. In the study of Nguyen et al. [20], the effect of nano-TiO_2 on the mechanical and thermal properties of epoxy coatings was investigated. The reported results depicted that these nanoparticles significantly improved the impact properties of those. Tu et al. [21] studied the restraining charge accumulation in the epoxy coating containing the various percentage of nano-TiO_2. The obtained results showed that adding the 5% nano-TiO_2 had the most significant effect on the restraining behavior.

Improving the adhesion between epoxy coatings and substrate was investigated by Sekhavatpour et al. [22] through adding the surface modified nano-TiO_2. The fire performance of epoxy coating including the nano-TiO_2 was studied by Aziz et al. [23]. They reported that the coating with the 4 wt.% nano-TiO_2 had the best thermal insulation. In the light of the above, it can be said that the nano-TiO_2 has been used for different applications in the epoxy coatings. Up to now, the effect of these nanoparticles on the smart epoxy coatings has been not investigated yet. Therefore, it can be said that the first novelty of this work is using nano-TiO_2 and microcapsules at the same time into the epoxy coatings. The second novelty is using the linseed oil in dual smart applications. In other words, this oil acted as healing and lubricant agents under healing and wearing conditions, respectively. Characterizing the interaction between nano-TiO_2 with the lubricant agent like recognizing the self-suspense lubricant behavior and trapping the debris under the wear condition is the third novelty of this work. Also, investigating the effect of adding the nano-TiO_2 on the healing behavior of smart epoxy coating is the fourth novelty of this work.

2. Experimental

2.1. Raw materials

For synthesizing the microcapsules containing the healing agent, the linseed oil, sodium dodecyl sulfate (SDS), gelatin, poly methyl methacrylate (PMMA) (average molecular weight ~15000 g/mol) and dichloromethane (DCM, >99.5 wt.%) were supplied from Sigma Aldrich chemicals. The titanium oxide nanoparticles with the average size of 30 nm and 99.9 % purity were ordered from US Research Nanomaterials. Bisphenol-A epoxy resin (epoxy 828) and triethylenetetramine (TETA) hardener (by Kumho P&B Chemical, Korea) were used as polymeric coatings.

2.2. Preparation of microcapsules

In this research, the microcapsules were synthesized by the promoted solvent evaporation method [24]. Firstly, 2 g linseed oil as healing or lubricant agent was added to 30 ml DCM solvent. In the following, 1 g PMMA was slightly added to this solution. After that, this solution was added dropwise to 200 ml solution containing surfactant (2 wt.% SDS, 1 wt.% gelatin, 97 wt.% deionized water) under the 500 rpm agitation rate. To form the microcapsules, the temperature of solution was increased up to 40 ˚C. After 2.5 h, the DCM solvent was evaporated and the PMMA microcapsules containing the linseed oil were formed. Finally, the microcapsules were washed several times with the deionized water, then filtered and air dried.

2.3. Preparation of smart coating

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The distribution of nanoparticles into the epoxy coatings was done as per previous works [25]. Firstly, the 0, 4, 8, 12 and 16 wt.% TiO_2 nanoparticles were added to the epoxy and mixed with the 3-blade mechanical stirrer (Finetech, Korea) with the rotation rate of 1500 rpm for 30 min. After that, the nanoparticles were completely dispersed into the epoxy by using the probe sonicator device (Fapan, Iran) with the power of 120 W and frequency of 24 kHz for 90 min. In the next step, the 15 wt.% synthesized microcapsules were added to the mixture and mixed with that by 3-blade mechanical stirrer with the rotation rate of 300 rpm for 5 min. Finally, the polyamine hardener was added into this mixture. The resin to hardener mixing ratio was 100:10 wt.% according to producer recommendation. Then, the CK 10 steel plates (self-healing samples) with the dimension of 60×40×2 mm^3 and CK 45 steel disk (self-lubricating samples) with diameter of 10 mm were coated by these coatings. The curing time of these smart coatings was about 24 h in the ambient temperature. The conventional epoxy coating and smart coatings containing the 0, 4, 8, 12 and 16 wt.% nano-TiO_2 were named 0M0T, 15M0T, 15M4T, 15M8T, 15M12T, and 15M16T, respectively. The M and T are the sign of microcapsules and titanium oxide nanoparticles, respectively. Also, the used numbers are the weight percentage of microcapsules and nano-TiO_2.

The self-lubricating performance of coatings were studied by using wear test with the pin on disk configuration. The applied load, sliding velocity and distance were 7 N, 0.15 m/s and 300 m, respectively. Also, the steel 52100 was used as counterpart. The wear rate was calculated as per equation 1 [26]:

$$WR=\frac{\Delta m}{\rho d} \tag{1}$$

Where, WR (mm^3/m), Δm (g), ρ (g/mm^3) and d (m) are the wear rate, reduced mass, density and sliding distance, respectively.

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The effect of microcapsules and nano-TiO_2 on the mechanical function was investigated by shore D hardness test (TQC-LD0559, Germany) as per ASTM D2240 standard.

To recognize the effect of nanoparticles on the wear and healing performance, characterize the interaction between nanoparticles-linseed oil, and investigate the synthesized microcapsules, the field emission scanning electron microscopy (FESEM, Mira3 Tescan, Czech) and energy dispersed spectroscopy (EDS) were used.

3. Results and discussion

3.1. Microcapsules

Fig. 1a shows the FESEM micrograph of linseed oil-PMMA microcapsules which is the representative of FESEM observations with the same magnification. At least 10 FESEM images like this were used to characterize the size distribution of microcapsules. Based on Fig. 1b, it can be seen that the synthesized microcapsules have a spherical shape with the rough surface which make them proper for using in the coating applications especially under the wear conditions. The rough surface causes that the microcapsules have a stronger interface with the epoxy coatings, which causes to reduce the producing debris and separating the microcapsules during the wearing situations. Fig. 1c illustrates the size distribution of synthesized microcapsules in this work, which has been extracted from FESEM observations. As can be seen, the microcapsules have size distribution from 20-110 µm. The average size of microcapsules in this work was about the 60 µm. Also, the 40% of microcapsules had the size distribution between 60-70 µm.

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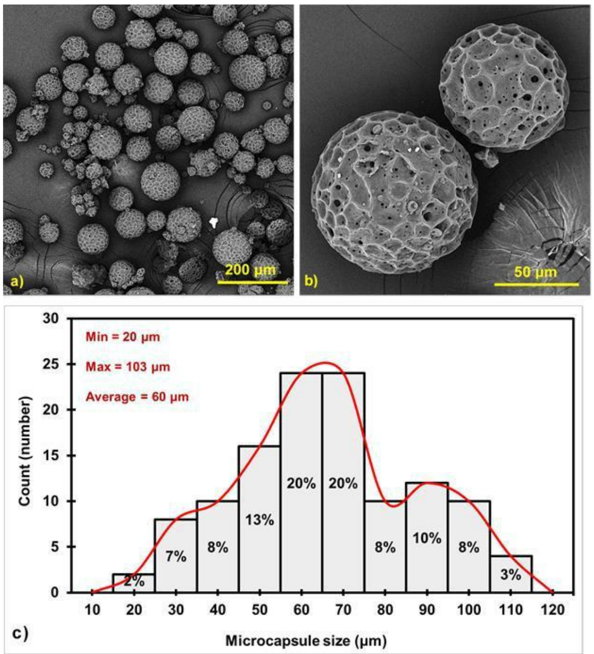

Fig. 1. Characterization of fabricated microcapsules; a and b) FESEM analysis, c) size distribution curve.

3.2. Hardness

The hardness of conventional and smart epoxy coatings are presented in Fig. 2. As can be seen, the conventional epoxy coating (0M0T) had the hardness of 65.4 ˚ShD. By including the 15 wt.% microcapsules into the epoxy coating (15M0T), the hardness of that reduced about 6.3%, which was due to the much lower hardness of microcapsules than the epoxy matrix. Adding the 4, 8 and 12 wt.% titanium dioxide as ceramic nanoparticles into the smart epoxy coating (15M0T) caused to enhance the hardness of that about the 8.2, 10.3 and 11.8, respectively. The maximum hardness obtained in the smart coating with the 12 wt.% nano-TiO_2. Including the 16 wt.% nano-TiO_2 reduced the hardness of smart coating, which can be due to the agglomeration of TiO_2 nanoparticles [27].

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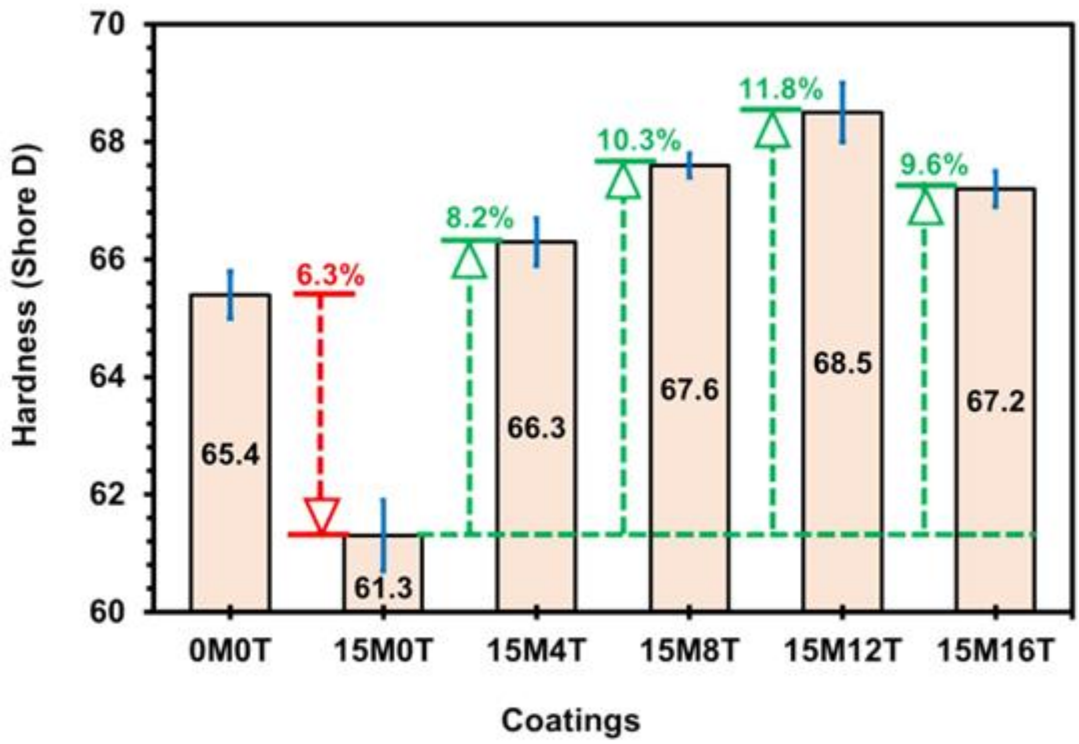

Fig. 2. The hardness of various coatings.

The improvement in the hardness can be explained by crack pinning and plastic deformation theories. In the lower content, the nano- TiO_2 particles act as obstacles to crack growth by pinning. But, in higher content of those, reducing the matrix deformation is the reason of mechanical properties improvement [28, 29]. To conform the agglomeration of nanoparticles in the sample of 15M16T, the FESEM analysis was used which can be seen in Fig. 3. Given up other literatures [30, 31], by increasing the percentage of nanoparticles, the sonication device has not enough power for dispersing the nanoparticles. In the other hand, the distance between nanoparticles is reduced. Therefore, the nanoparticles tend to agglomerate, consequently, they cannot homogeneously disperse into the epoxy matrix, which cause to reduce the effect of them on the improvement of mechanical properties like hardness.

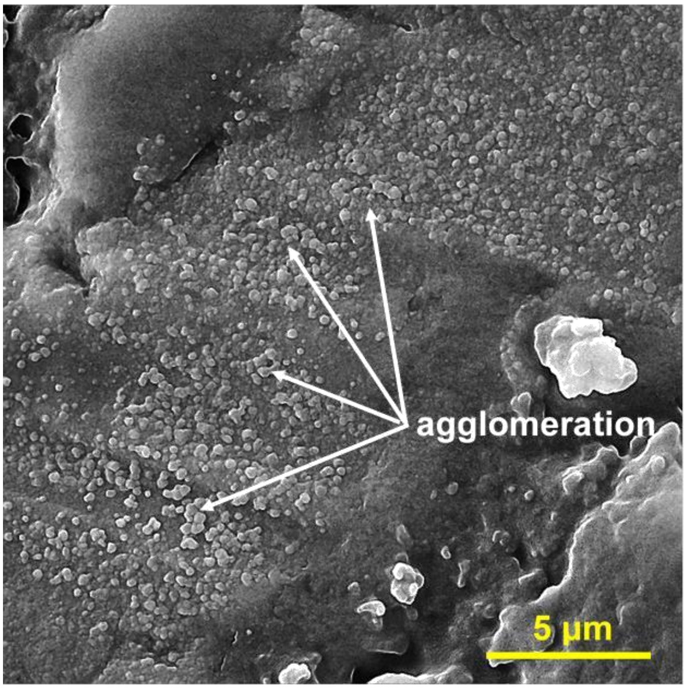

Fig. 3. Characterization of agglomerated nanoparticles in the smart coating containing 16 wt.% nano-TiO_2.

3.3. Tribological investigations

The obtained results from wear test have been reported in Fig. 4. According this figure, the conventional epoxy coating (0M0T) had the wear rate of $9.75\times10^{-3}mm^3/m$. Adding the microcapsules containing the linseed oil (15M0T) caused to decrease the wear rate, so that, the wear rate was became a quarter of the initial amount that. By increasing the weight percentage of nano-TiO_2, the wear rate showed the reducing trend. The smart coating containing 12 wt.% nano-TiO_2 had the minimum wear rate ($1.10\times10^{-3}mm^3/m$). Also, the wear rate of sample with the 16 wt.% nano-TiO_2 ($4.30\times10^{-3}mm^3/m$) was more than the coatings with 8 and 12 wt.% nano-TiO_2. To more discus and deep investigation on the wear behavior of coatings, the coefficient of friction (COF) and FESEM results should be studied.

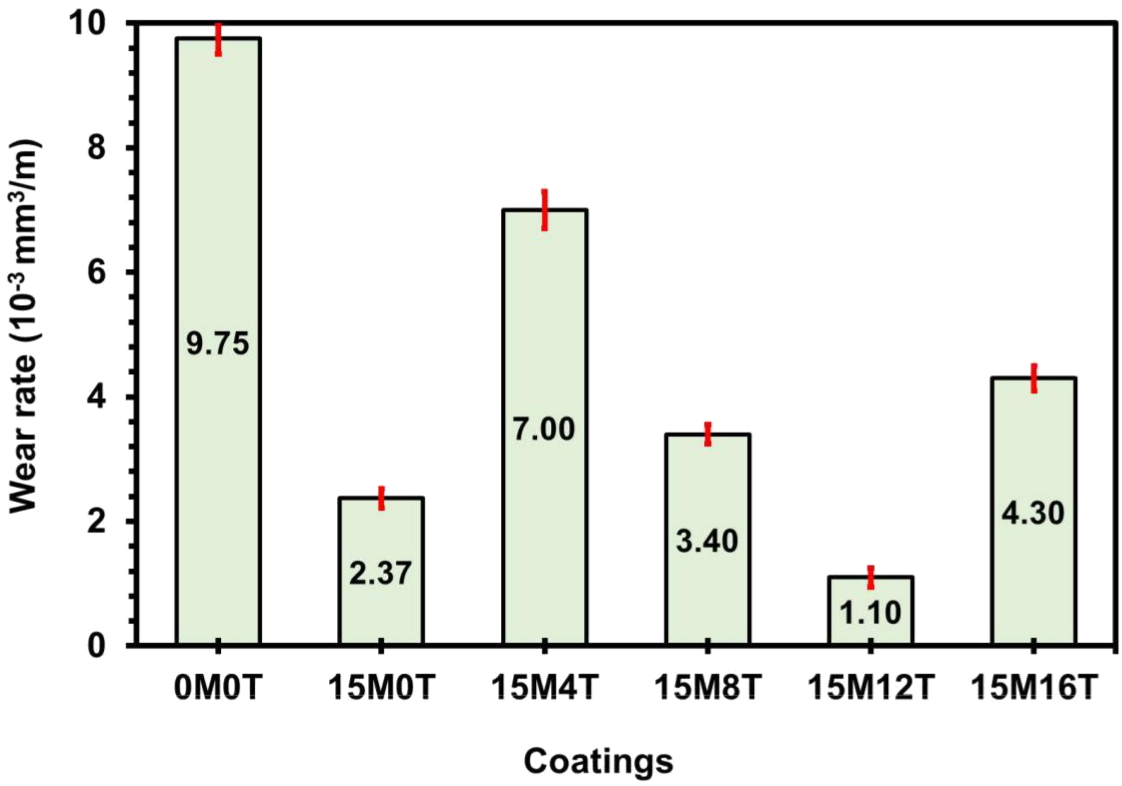

Fig. 4. The wear rate of various coatings.

Fig. 5 shows the COF of coatings in various sliding distances. Given up this figure, the conventional epoxy (0M0T) had the 0.4 COF. By adding the capsulated linseed oil (15M0T), the COF was reduced, so that, it reduced down to 0.1. This reduction trend can be explained by FESEM observations (Fig. 6). Based on Fig. 6a, it can be seen that the friction surface morphology of conventional epoxy had the rough surface with the deep furrow, which showed the fatigue wear behavior in this sample [32]. The surface of smart epoxy coating (15M0T) showed the smoother worn surface. Also, the created polymeric film on the surface of this sample can be observed. Actually, during the wearing, the microcapsules firstly were ruptured. After that, the linseed oil diffused into the contact area and created the self-lubricant polymeric film. The formation of this film reduced the COF and created debris, so that, the wear rate showed the decreasing trend. The microcapsules had another impressive effect on the wear

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behavior of smart coatings, which can be seen in Fig. 7. Based on this figure, it can be explained that after the rupturing and empting the linseed oil, the created cavities from microcapsules can act as containers for trapping the debris during the wear test. Therefore, the effect of debris on the wear of coating was reduced, consequently, the anti-wear properties can improve.

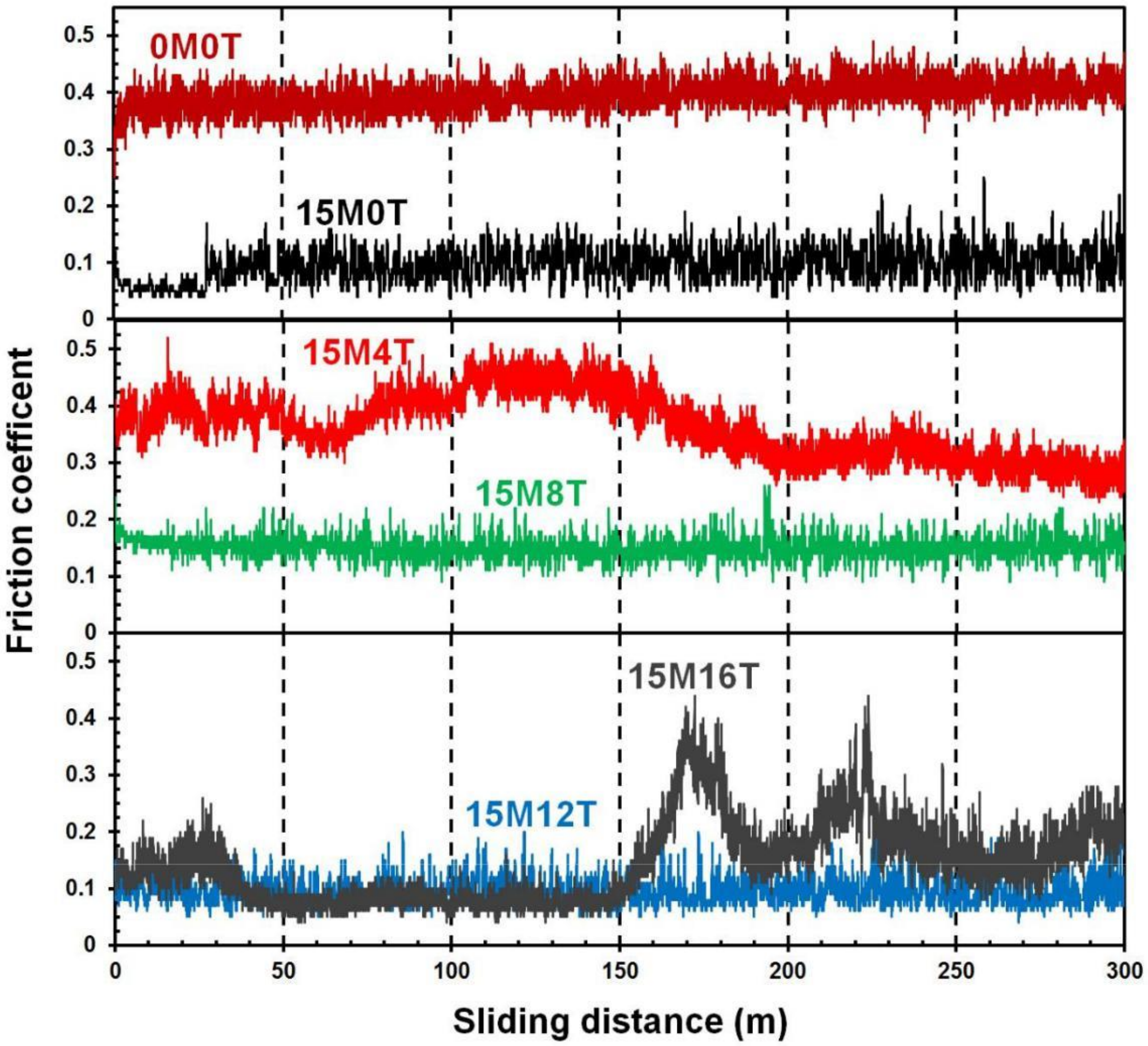

Fig. 5. The friction coefficient of various coatings in different sliding distances.

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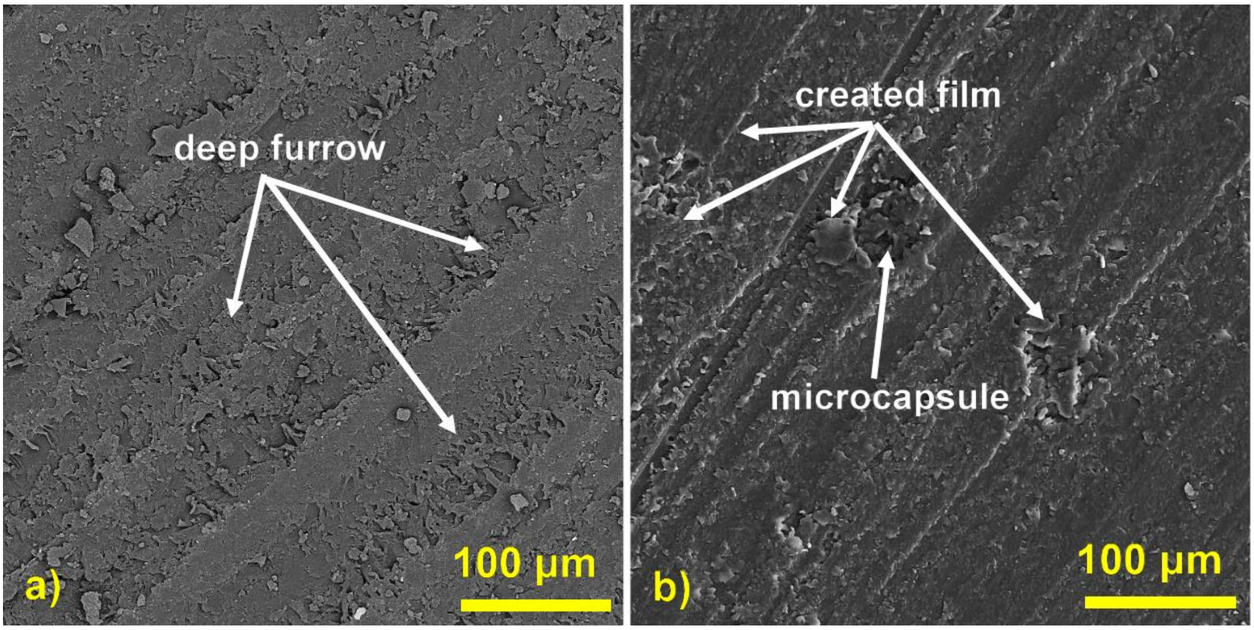

Fig. 6. The worn surface of; a) conventional epoxy coating, b) smart epoxy coating without nano-TiO_2.

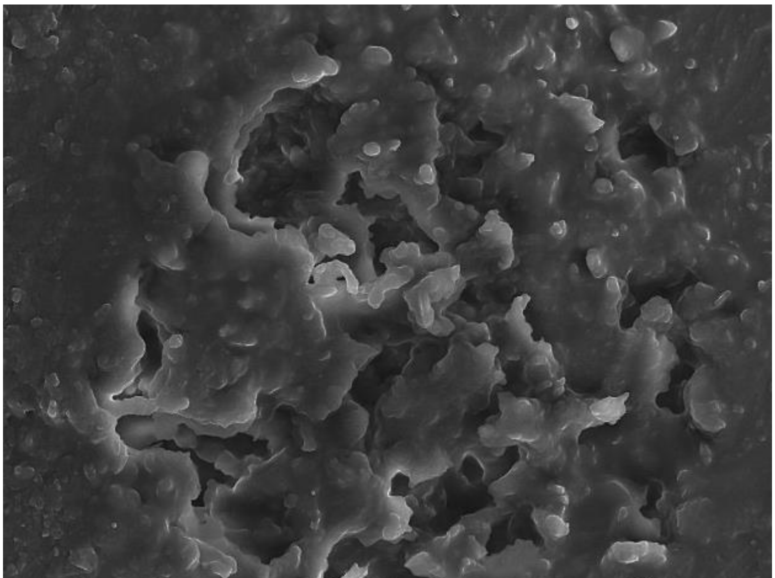

Fig. 7. The filled microcapsules by debris in the smart coating without nano-TiO_2.

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According to Fig. 5, in the smart coating with 4 wt.% nano-TiO_2 (15M4T), the COF was 0.38 between the sliding distance of 0-100 m, which was higher than the COF of 15M0T sample (0.1). By continuing the wear in the sliding distance of 100-150 m, the COF increased and reached to the 0.49. In the following, by increasing the sliding distance, the COF had the reducing trend and decreased to the 0.27. In the low content of nanoparticles, these particles have not the homogenous dispersion into the epoxy matrix. When the cracks reach these nanoparticles, the crack path is changed by nanoparticles. Forasmuch as, the content of nanoparticles is low, they cannot attenuate the crack propagation energy. Therefore, the nanocomposite debris can be created during the wear test. Although, the linseed oil acts as lubricant agent, but the effect of these nanocomposite debris is higher than the lubricant agent. Hence, the COF and wear rate were increased. By continuing the wear test, the more microcapsules were ruptured and created the sites for trapping the debris. Fig. 8, shows the sites where trapped the debris. The EDS method showed the Ti element into these debris, which confirmed the formation of nanocomposite debris during the wearing.

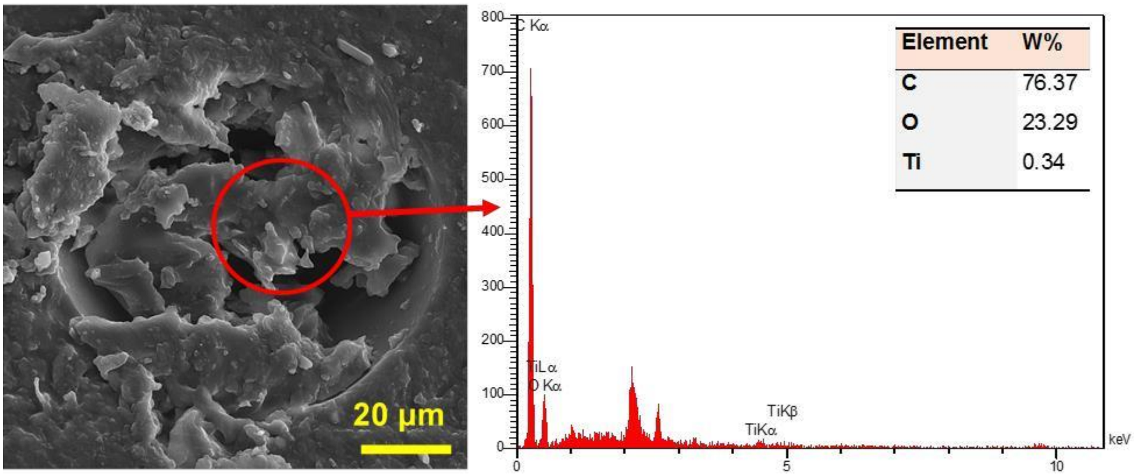

Fig. 8. The filled microcapsules by nano-TiO_2/epoxy nanocomposite debris in the smart coating containing 4 wt.% nano-TiO_2.

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The inclusion of 8 wt.% nano-TiO_2 caused to reduce the COF (0.14). But, it has higher COF in comparison with the 15M0T sample (0.1). By adding the 12 wt.% nano-TiO_2 (15M12T), it can be seen that the COF recued down to 0.08, which was minimum COF. Also, the wear rate in this sample was about a half of that in 15M0T sample. In practical, two factors had the influence on this improvement. Firstly, the nanoparticles caused to improve the mechanical properties and controlling the crack behaviors which the obtained results from hardness test confirmed this assumption. Also, by improving the mechanical properties of coatings, the possibility of fabricating the debris is reduced, consequently, the anti-wear properties improve. Based on the literatures [33], during the wearing, the nanoparticles can be separated from matrix and created the separation film between counterface and samples. To recognize effective mechanisms, the FESEM analysis from 15M12T sample was done, which can be seen in Fig 9. Based on this figures, the nanoparticles were entered into the linseed oil and crated the nano-TiO_2/linseed oil self-suspense lubricant, which had noteworthy influence on the anti-wearing properties. The similar improvement on the tribological behaviors by nano-TiO_2 self-suspense systems was previously reported by Zhang et al. [34].

According to the Fig. 5, it can be realized that in the sample with the 16 wt.% nano-TiO_2, the COF has been increased in compared with the 15M12T sample, which can be due to the agglomeration of nanoparticles (seen Fig. 3). Based on other literatures [35], the agglomerated nanoparticles can effect on the wear properties by two mechanisms. The first of that is reducing the mechanical properties and increasing the produced debris during the wearing. These debris can act as abrasive particles, which increase the wearing. The second mechanism is entering the higher percentage of nanoparticles into the nano-TiO_2/linseed oil self-suspense system. Wu et al.

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[36] in their study mentioned that in thigh content of nanoparticles, the thickness of self-suspense film was increased, which reduced the movement of nanoparticles between counterface and sample. This reduction increased the wear rate and COF. Fig. 10 shows the FESEM analysis of 15M16T sample after wear test. By using the higher magnification and EDS analysis, it was realized that the mixture of epoxy-TiO_2 nanoparticles covered the microcapsules in form of nanocomposites. The existence of this nanocomposite skin can increase the mechanical properties of microcapsules. Hence, it can be said that during the wearing, the rupturing time of the microcapsule in this sample was higher than other samples. Increasing the rupturing time reduced the releasing the linseed oil as lubricant, which enhanced the COF in this sample.

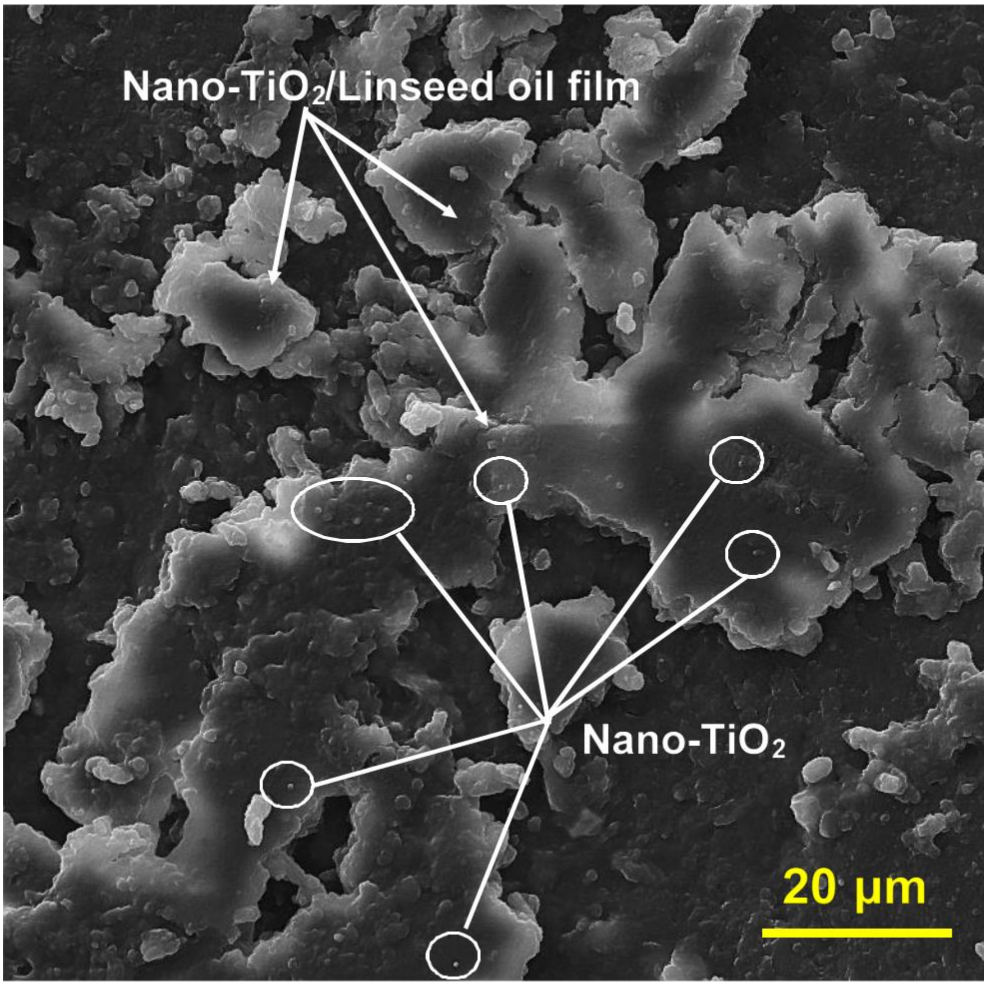

Fig. 9. The characterized nano-TiO_2/linseed oil film on the surface of coating containing 12 wt.% TiO_2.

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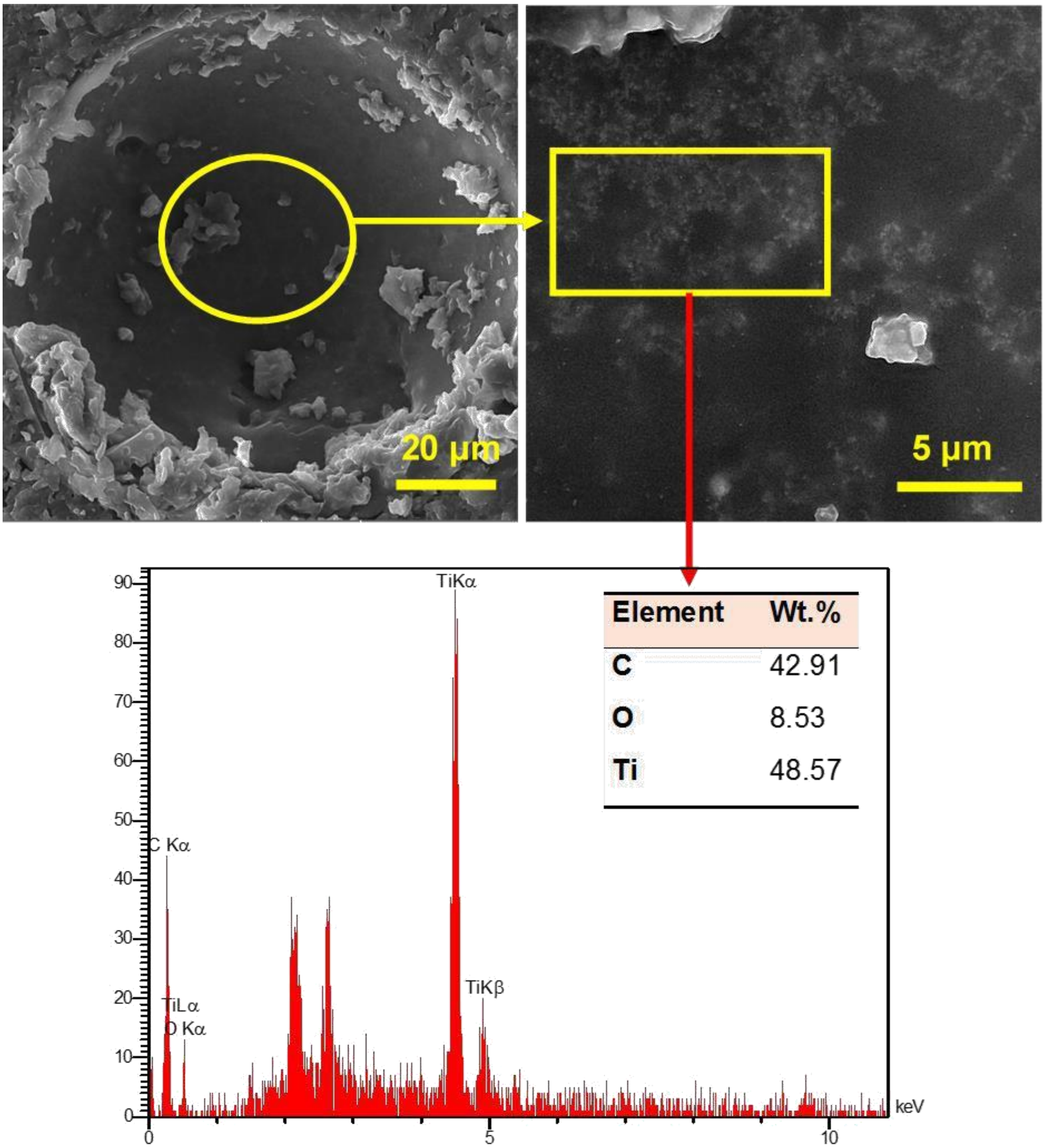

Fig. 10. The characterized the nano-TiO_2/epoxy nanocomposite skin on the surface of microcapsules.

3.4. Healing ability

Fig. 11 shows the visual appearance of scratched area in various coatings. The selected immersion times were 1, 3, 5, 7 and 9 days. Based on this figure, it can be realized that after 3 days, the rusting was started in the conventional sample (0M0T). But, the in the smart coatings, the rusting has not occurred. After the 5 days, the rusted area in the 0M0T sample was increased. Also, the 15M0T sample showed the negligible rusting. In the samples containing the nano-TiO_2, the rusting cannot be still observed. After the immersion time of 9 days, it can be seen that a major part of 0M0T sample was rusted. Also, the rusting in the 15M0T sample has propagated. But, the rusting cannot be still seen in the sample with 16 wt.% nano-TiO_2. To recognize the effect of nanoparticles and microcapsules on the healing ability of smart coatings, the FESEM analysis from the surface of 0M0T, 15M0T and 15M16T samples was done (Fig. 12).

Based on Fig. 12, it can be seen that the created scratch or damage area had about 600 μm width. This damage area created the proper site for permeating the water and rusting the substrate. Although, by creating the scratch in the 15M0T sample, the microcapsules were ruptured and the healing agent diffused into the damaged area. However, it seems that the damaged area could not be completely filled. Therefore, the water can still penetrated into the damaged area. But, it can be said that the volume of rusting has been reduced. In the sample with the 16 wt.% nano-TiO_2, it can be seen that the damaged area completely filled by linseed oil. Based on literatures [19], it can be said that the nano-TiO_2 can effect on the rusting behavior by two mechanisms. Firstly, when the water molecules reach the nanoparticles, the penetrating path has been obstructed by them. Therefore, these molecules changed their path, consequently, the penetration time is increased, which reduces the rusting. The second mechanism can be the effect of nanoparticles on the diffusion of healing agent. In other words, after the creating the scratch, the healing agent suddenly diffuses into the damaged area. But, the surface of healing agent can react with the surrounding oxygen, which causes to form solid film. Therefore, the healing agent may be viscose, so that, it cannot fill the whole of scratch in the length direction.

In the 15M16T sample, the nanoparticles reduce the healing agent diffusion. Therefore, the released healing agents from different microcapsules had various diffusing rates, so that, they reacted with oxygen in the scratch area in different times. This phenomenon caused to completely fill the scratch in form of layer by layer, which can be seen in Fig. 12c.

In order to comprehensively understand the healing-protecting behaviors of fabricated smart epoxy coatings in this research, the similar research works have been listed in Table 1. In all numbered works in Table. 1, the used healing agent was the capsulated linseed oil. Suryanarayana et al. [10] added the 10 wt.% urea-formaldehyde microcapsules with the average diameter of 50 μm into the epoxy coatings. The obtained results showed that after 3 days immersion time, the created scratch was healed, so that, there was not seen rusting on the surface of steel. In the study of Hatami Boura et al. [11] fabricated the smart coatings containing the 10 and 15 wt.% capsulated linseed oil with the average diameter of 50 μm. The obtained results showed the coating containing the 10 wt.% microcapsules could not protect the surface of steel from rusting after 10 days. But, in the coating including 15 wt.% microcapsules, the rusting was partially observed on the surface of substrate. This means that, these coatings with these microcapsules had not proper capability to heal the damaged areas. For solving this problems, they used microcapsules with sub-micron sizes, which completely changed the healing behavior, so that, the completely protecting was seen on the surface of steel plate.

Szabó et al. [12] added 5wt.% microcapsules with diameter of 10 μm into the epoxy coatings. Also, they used cobalt octoate as drier material and octadecylamine as corrosion inhibitor into their coatings. The obtained results showed the coating containing 5 wt.% capsulated linseed oil could not protect the substrate. By adding the drier material approximately healing was observed, which could protect the substrate against the corrosive

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agent. Also, it was seen that the adding the inhibitor agent could not completely protect the substrate.

In the current study, the samples with 15 wt.% microcapsules could the partially healed the created scratch after the immersion time of 9 days. Adding the 12 wt.% nano-TiO_2 caused to increase the healing-protecting behavior of this smart coating. Also, in the samples containing the 16 wt.% nano-TiO_2 the completely protection was seen. This improvement can be due to the anticorrosive properties of these nanoparticles, which previously mentioned by Wang et al. [19]. In other words, the nanoparticles act as obstacles against diffusing the corrosive agent, so that, reduces the diffusing rate of that, resulted to improve the protection behavior in epoxy coatings.

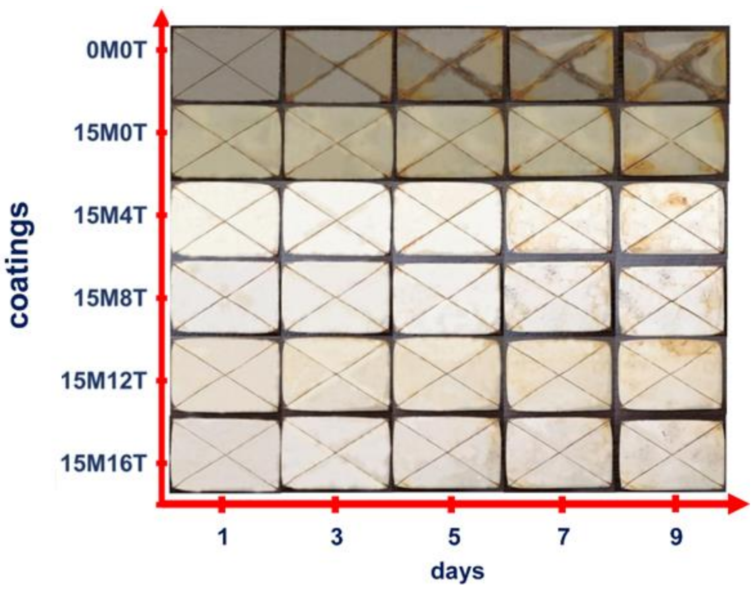

Fig. 11. The trend of corrosion protection in steel plates with various coatings in the different immersion times.

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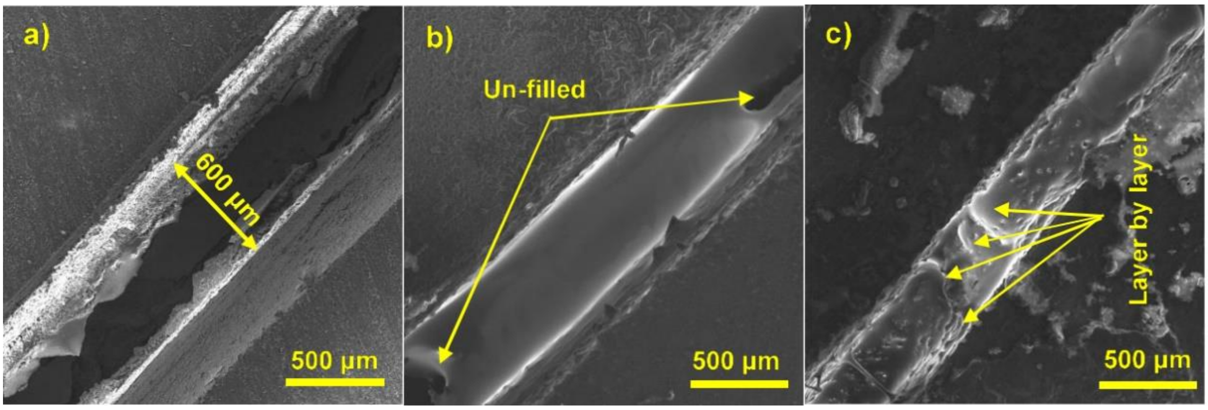

Fig. 12. FESEM analysis from scratch area in epoxy coatings; a) conventional coating, b) unfilled area in coating without nano-TiO_2, c) healed area by layer by layer method in coating containing 16 wt.% nano-TiO_2.

Table 1. Comparing the healing and protective behaviors of smart epoxy self-healing coating containing the capsulated linseed oil.

Microcapsule content (%)	Second agent	Microcapsule shell	Maximum immersion time (day)	Healing behavior	Corrosion behavior	Ref
15	-	Poly methyl methacrylate	9	Partially healed	Partially corroded	Current work
15	12 wt.% Nano-TiO_2	Poly methyl methacrylate	9	Approximately healed	Protected	Current work
15	16 wt.% Nano-TiO_2	Poly methyl methacrylate	9	healed	Protected	Current work
10	-	Urea-formaldehyde	3	healed	Protected	[10]
10	-	Urea-formaldehyde	10	Un-healed	Corroded	[11]
15	-	Urea-formaldehyde	10	Partially healed	Partially corroded	[11]

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5	-	Urea-resorcinol-formaldehyde	4	Un-healed	Corroded	[12]
5	Cobalt octoate	Urea-resorcinol-formaldehyde	4	Approximately healed	Protected	[12]
5	Octadecylamine	Urea-resorcinol-formaldehyde	4	Partially healed	Partially corroded	[12]

4. Conclusion

In this study, the simultaneous effect of microcapsules and nano-TiO_2 on the self-healing and self-lubricating functions of epoxy coatings was investigated. These smart functions were created into the coatings by using the microcapsules containing the linseed oil. The healing and lubricating functions were evaluated by corrosion and wear test. Also, the field emission scanning electron microscopy (FESEM) was used to characterize the effective factors. The obtained results from corrosion test showed that the smart coating with the 16 wt.% nano-TiO_2 had the best performance, as compared with the other coatings. The wear rate and coefficient of friction (COF) in the smart coating containing the 4 wt.% nano-TiO_2 were increased as compared with epoxy smart coating without nanoparticles. Forming the nanocomposite debris was the reason of this negative influence. The minimum COF and wear rate were seen in the smart coatings with 12 wt.% nano-TiO_2. Reducing the formed debris due to improving the mechanical performance, forming the nano-TiO_2/linseed oil self-suspense and trapping the debris into the capsule containers were the reason of these improvements. The COF and wear rate in the coatings with the 16 wt.% nano-TiO_2 were slightly increased, which were due to the formation of nano-TiO_2/epoxy skin on the surface of microcapsules and agglomeration of nanoparticles into the epoxy coating.

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