Materials Research. 2022; 25:e20210413
DOI: https://doi.org/10.1590/1980-5373-MR-2021-0413

Enhancement of Barrier and Mechanical Performance of Steel Coated with Epoxy Filled with Micron and Nano Alumina Fillers

D. Saber[a,*] ***, Abdulaziz H. Alghtani***[b]***, Emad M. Ahmed***[c]***, Bassem F. Felemban*** [b]***, Hafiz T. Ali***[b]***,***

M. Megahed[d]***, Kh. Abd El-Aziz***[b]

[a]*Taif University, College of Engineering, Department of Mechanical Engineering, Industrial Engineering program, P.O. Box 11099, Taif 21944, Saudi Arabia.*
[b]*Taif University, College of Engineering, Department of Mechanical Engineering, P.O. Box 11099, Taif 21944, Saudi Arabia.*
[c]*Taif University, College of Science, Department of Physics, Taif, 21944, Saudi Arabia.*
[d]*Zagazig University, Faculty of Engineering, Department of Mechanical Design and Production Engineering, P.O. Box 44519, Zagazig, Egypt.*

Received: August 12, 2021; Revised: November 05, 2021; Accepted: November 12, 2021

Steel is an essential part of our life as it is used in wide applications as food equipment and heavy construction. The polymeric coating prevents the deterioration of the properties of metals due to rust and corrosion. This study investigated a reinforced polymeric coating to steel for enhancing barrier and mechanical properties. A comparison between different configurations of double-layered polymeric coatings was attained. The results showed that a maximum enhancement of 16.7%, 18.9%, 32.6%, 8.5%, and 5.7% in tensile strength, tensile strain, toughness, flexural strength, and flexural strain, respectively were achieved with a coating of epoxy filled with 1wt% Al_2O_3 microparticles before 1wt% Al_2O_3 nanoparticles on both sides as compared with pure epoxy coating. Adding micro/nanoparticles to epoxy coating enhanced the barrier properties of the coated steel against salt solution and citric acid environment as compared to pure epoxy coated steel.

Keywords*: Micro/nanocomposites coating, Alumina, Steel, Mechanical properties, Food equipment, Barrier properties.*

1. Introduction

Steel as a type of metal has become an essential part of our life as it is used in wide applications like automotive, household appliances, food equipment. The mild steel material was used for food equipment manufacturing purposes because it has good mechanical properties like its strength, ductility, and weldability[1, 2, 3]. Corrosion of steel is considered as a sustained matter that attracted interest as it is the main cause of industrial accidents and also the consumption of metal resources[4,5,6,7]. Metal with polymeric composite barrier liners was used to reduce oxygen and moisture diffusion produced in food packaging [6, 8]. Epoxy resin is one of the widely used polymers utilized to protect mild steel due to its strong adhesion, good chemical resistance, and low shrinkage [4, 9, 10]. To get benefit from its good properties, inorganic particles may improve the stiffness and other properties of the epoxy coatings[11]. Many studies have attempted to improve the toughness of epoxy and other polymers by reinforcing them with micro and nanofiller to promote extrinsic toughening procedures[12-17].

Nanocomposite coating is being investigated to enhance barrier properties for steel [7]. Adding nanofillers to epoxy coatings leads to less coating blistering and delamination. This can be attributed to the high capability of fine particles to fill the cavities. Moreover, the transparency of the polymeric coating will not be disturbed with the existence of nanoparticles with dimensions less than100 nm[18]. The anticorrosion performance and mechanical properties of metals are highly improved by the incorporation of metal oxide nanofillers to epoxy matrices[5, 9, 19, 20]. In addition, alumina (Al_2O_3) fillers characterized by their high mechanical properties have been widely used to enhance related properties of epoxy matrices[4]. Different nanomaterials such as nanopolymers and nanocomposites are included at various levels in the food industry[21]. The coatings containing Al_2O_3 nanofillers showed enhancement in mechanical properties as compared to pure polymer coating[18,22].

Behzadnasab et al.[23] reported that the simultaneous adding of layered nanoclay and small amounts of APS-treated zirconia nanoparticles to epoxy coatings considerably improves the corrosion resistance of the nanocomposite coatings. The optimum amount of nanoparticles was 1 wt% nanoclay and 1 wt% zirconia nanoparticles. However, other combinations reduce the corrosion performance, due to flaws introduced in the coating film. Similarly, epoxy/Molybdenum oxide nanocomposite coating enhanced the mechanical, adhesion, and anticorrosion properties as compared to epoxy coating [9]. Furthermore, Abd El-Lateef and Khalef[24] reported that the optimum percent of ZrO2-TiO_2 is 10wt % but the inclusion of a higher weight

*e-mail: *dselsayed@tu.edu.sa*

percent of ZrO2 resulted in the formation of a weak film with poor barrier properties. Furthermore, Ramezanzadeh and Attar[25] stated that the epoxy coating resistance was significantly enhanced using nano and micro-sized ZnO particles. The barrier properties of the nanocomposite were considerably higher than the microcomposite. Golru et al.[18] studied the impacts of the addition of 1, 2.5 and 3.5 wt% Al_2O_3 nanoparticles of an epoxy/polyamide coated AA-1050 on the anticorrosion properties immersed in a 3.5 wt% NaCl solution and salt spray test. Results revealed that Al_2O_3 nanoparticles could significantly improve the corrosion resistance of the epoxy coating. The rationale for this study is to create a new protective polymeric coating to steel using microparticles and nanoparticles embedded in an adhesive polymer which is the epoxy matrix. Alumina particles in micron size were used with two percentages (1wt% and 2wt%) for their low cost and good mechanical and barrier properties. However, alumina nanoparticles are more expensive, nanocomposite coatings were used with a low percentage (1wt%) for their high mechanical and barrier properties. Combining both nanoparticles and microparticles embedded in an epoxy matrix to get benefit from both reinforcements. The mechanical and barrier performance of micro/nanocomposite double-layers coated steel with different configurations was evaluated. Three different alternating double-layer coatings were designed. The outer layers for all conditions were 1 wt% Al_2O_3 nanoparticles. However, the first layers were differentiated with epoxy, 1wt% Al_2O_3 microparticles, and 2wt% Al_2O_3 microparticles. Mechanical and barrier resistance properties were conducted on the nano/microparticles coated specimens and compared with pure epoxy coated steel.

2. Experimental Work

2.1. Materials

Mild steel was utilized as a substrate provided by Al Ezz-Dekheila Steel Company Alexandria. The chemical composition of the used steel is presented in Table 1. The sheets of steel were cut to the required dimension of the coupons by a laser machine. The coupons were polished to roughen the steel surface. After polishing, the top and bottom side coupons surfaces were cleaned with acetone before coating. Chemicals including sodium hydroxide, citric acid, and acetone were provided by El Nasr Pharmaceutical Chemicals, Egypt. The polymeric coating was Epoxy resin (Kemapoxy RGL150) and was provided by CNB Company, Egypt. The fillers used were aluminum dioxide (Al_2O_3 with a purity of about 99%). The size of nanoparticles and microparticles were 70 nm and 90 µm, respectively.

2.2. Preparation of epoxy micro/nanocomposite coating

The epoxy coating was prepared by adding hardener carefully to the epoxy and mixed thoroughly with a ratio of 1:2 by mass of epoxy matrix. Micro/nanoparticles were added to epoxy by the sonication method. Sonicating was conducted with Hielscher ultrasonic processor UP 200 S. The conditions of sonication were 0.5 cycles per second with an amplitude of 40% for 2 hrs as recommended by[26, 27]. To protect the epoxy resin from degradation, micro/nanoparticles with epoxy mixture were cooled by putting it on an ice water bath during operating sonication[14]. Afterward, the blend and the hardener were mixed together with the recommended ratio. This preparation was performed at a temperature of 25°C. The coating layers were performed on steel by a metallic roller that was used to remove excess resin to reduce void content and any entrapped air bubbles. The polymeric coating on one side of the steel coupon is left for 24 hrs to cure. Subsequently, the second layer on the same side was laid and left for 24 hrs to cure. The same technique was done for the other two layers on the bottom side of the coupons. The quantity (volume) of each layer of epoxy resin and epoxy filled with micro/nanoparticles that was spread during the manufacturing process was the same. This indicates that the thickness of the composite layers is approximately the same. The film thickness of each layer is 110 µm. The final types of micro/nanocoatings on steel substrate were constructed as illustrated in Figure 1.

2.3. Materials characterizations

2.3.1. Tensile test

The tensile properties of the steel coated with micro/nanocomposites coupons were tested according to ASTM D3039. The various test coupons were cut into strips (250x25 mm^2). The tensile test was achieved with a computerized universal testing machine (Jinan Test Machine WDW 100 kN). The cross-head speed was set at 2 mm/min. The stress-strain curve was recorded by a computer data acquisition system. All tests were performed at ambient temperature.

2.3.2. Three-point flexural test

Three-point flexural tests were conducted according to JISK7055. Different test coupons were cut into strips (170x15 mm^2). The flexural strength and flexural strain, σ_f and ε_f were calculated, respectively as follows[28]:

$$\sigma_f = 3P_f L / 2bh^2 \quad (1)$$

$$\varepsilon_f = 6Dt / L^2 \quad (2)$$

where L denotes the support span length, P_f is the maximum flexural load and D represents the maximum deflection of the middle of the strips.

Table 1. Chemical composition of steel in mass %.

C	Si	Mn	P	S	Fe
0.19	0.03	0.85	0.01	0.005	Remainder

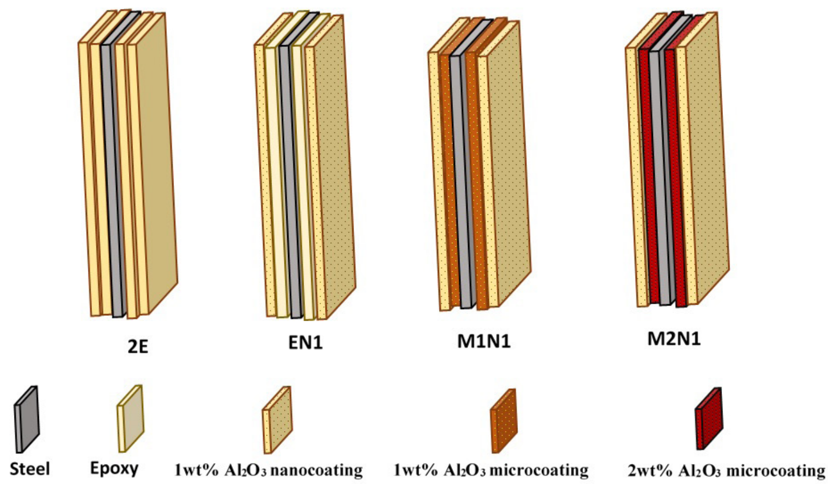

Figure 1. The final types of micro/nano coatings on steel substrate.

2.2.3. Hardness

Barcol hardness test is a means of evaluating the hardness of reinforced and non-reinforced rigid plastics. The hardness value determines the resistance of polymeric materials as penetrated by the indenter. The composite layers are placed beneath the indenter of the Barcol hardness tester and a uniform pressure is applied to the coupons until the dial indicator reaches a maximum value. The hardness was determined via the PCE-1000N Hardness instrument at ten different places of the micro/ nanocomposite coated steel and the average value was taken.

2.3.4. Barrier resistance

Some test coupons were immersed in salt solution and in citric acid solution to estimate the corrosion performance of the micro/nanocomposite coated steel. Citric acid is one of the most versatile, inexpensive, and widely used organic acidulates, and it is commonly applied to the production of fruit-flavored beverages, lemon juice, and food. Citric acid serves to adjust the pH of jellies, jams, or preserve mixtures to the optimum range, where pectin can act most effectively. Certain foods such as guava, mangos, blackberries, cherries, sweet peaches, and sweet plums would not naturally contain sufficient acids to give the proper pH. In particular, citric acid is highly favored by the food industry on account of its light fruity taste, solubility, low cost, and abundant supply[29, 30]. Citric acid solution with a concentration of 2 N was prepared by double distilled water[31]. The salt solution was performed as 3.5 wt% NaCl dissolved in water. Uptake tests were carried out according to ASTM D5229 / D5229M - 14. The coupons were periodically withdrawn from the solutions, wiped dry, and weighed using an analytical balance of accuracy up to 10^{-4} g to observe the weight change during the absorption process. The solution content M(t) absorbed by micro/nanocomposite coating was then calculated as the mass gain percent refer to its initial weight (w_0) as follows[32]:

$$M(t) = \left(\frac{w_t - w_0}{w_0}\right) \times 100 \quad (3)$$

Where w_t is the coupon mass after time t. Coupons were immersed for up to 21 days.

Composite materials absorb water when exposed to a wet environment that is assumed to enter into the composite material obeying the diffusion laws as Fick's laws. Fick's law predicts the linearity of the quantity of water uptake with the square root of time, and then gradually a decrease is attained until an equilibrium is achieved. The diffusion of water in composite material was studied using Fick's model by applying Equation 4[33].

$$D = \pi\left(\frac{h}{4M_\infty}\frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}}\right)^2 \quad (4)$$

where D is the diffusion coefficient, M_∞ is the weight of absorbed water when fully saturated, h is the specimen thickness, M_1 and M_2 are the solution uptake contents at times t_1 and t_2, respectively. These times are selected at an early stage of the uptake process, where the weight change can vary linearly with the square root of time.

3. Results and Discussions

3.1. Tensile properties

Figure 2 shows the tensile stress-strain curves of pure epoxy and steel lined with epoxy filled with Al_2O_3 micro/ nanoparticles. These curves revealed that the various coating constituents led to several tensile behaviors. Also, adding either nanofillers or microfillers to epoxy coating increased both the tensile strength and tensile strain. The addition of 1wt% Al_2O_3 microparticles before 1wt% Al_2O_3 nanoparticles to the epoxy coating exhibited the highest tensile strength and tensile strain. Figure 3 shows the ultimate tensile strength of steel coated with micro/nanocomposites. Peak improvement of 16.7% in tensile strength was achieved with epoxy filled with 1wt% Al_2O_3 microparticles before 1wt%

Al_2O_3 nanoparticles on both sides (M1N1) as compared to pure epoxy coating. Moreover, a maximum tensile strain of 18.9% was obtained with the same specimen M1N1. However, increasing the weight percentage of the first layers to 2wt% micron Al_2O_3 particles before 1wt% nano Al_2O_3 particles (M2N1) decreased the tensile strength as compared to M1N1. However, the tensile strain of M2N1 increased as compared to M1N1 as shown in Figure 4. An enhancement of 7% and 3.2% in tensile strength was attained with EN1 and M2N1, respectively as compared to pure epoxy coating. However, an enhancement of 9.7% and 13.7% were attained in the tensile strain with EN1 and M2N1, respectively as compared to pure epoxy coating.

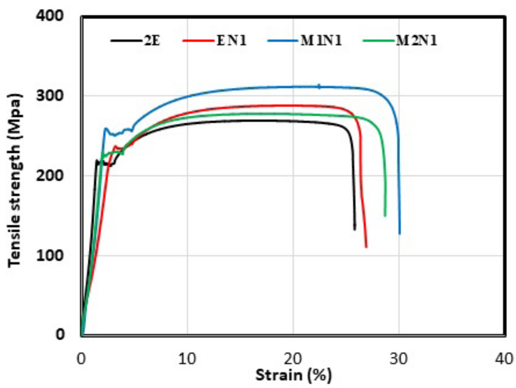

Figure 2. Tensile stress-strain curves of steel lined with epoxy filled with Al_2O_3 micro/nanoparticles.

Figure 5 indicates the toughness of steel lined with pure epoxy and epoxy filled with Al_2O_3 micro/nanoparticles. The toughness is the ability of the material to absorb energy without fracture which its value is obtained from the tensile test[34]. All additives of either nanofillers or microfillers to epoxy coating increased the toughness of the coupons. A significant enhancement of 32.6% was observed with M1N1 coated specimens. Moreover, an improvement of 7.3% and 14.3% was attained with EN1 and M2N1, respectively as compared to pure epoxy coating.

The addition of 1wt% Al_2O_3 microparticles before 1wt% Al_2O_3 nanoparticles exhibited the highest tensile strength and tensile strain as compared to pure epoxy coating. This is followed by a decrease in tensile strength and strain with a further increase in Al_2O_3 microparticles to 2wt% before 1wt% Al_2O_3 nanoparticles. This may be attributed to the good dispersion of the first layers of 1wt% micron Al_2O_3 particles in epoxy coating. Enhancing the mechanical properties depends on the good dispersion of Al_2O_3 microparticles inside the epoxy matrix[35,36]. Dispersing of Al_2O_3 microparticles into epoxy homogenously gains the full benefit of its interfacial area with the epoxy matrix[37]. Due to epoxy highly cross-linked structure, poor durability was

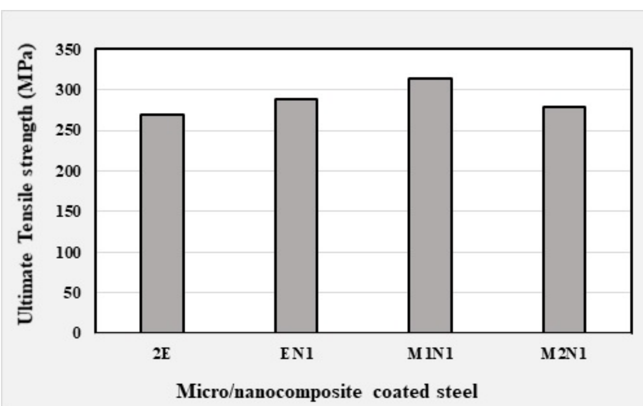

Figure 3. Ultimate tensile strength of steel lined with epoxy filled with Al_2O_3 micro/nanoparticles.

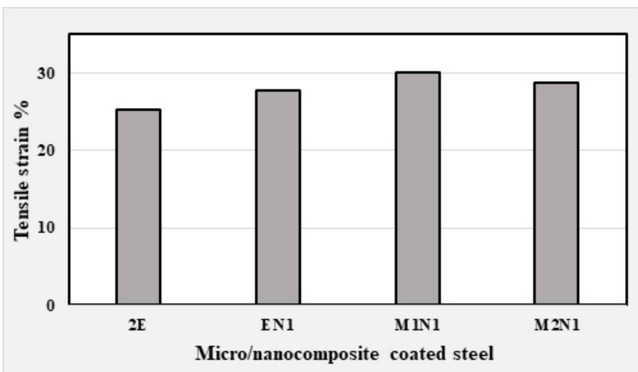

Figure 4. Tensile strain of steel lined with epoxy filled with Al_2O_3 micro/nanoparticles.

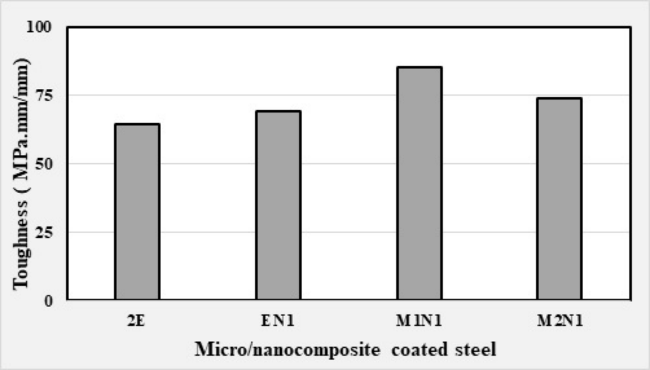

Figure 5. The toughness of steel lined with epoxy filled with Al_2O_3 micro/nanoparticles.

demonstrated to crack initiation and propagation. The good interfacial bond oriented the crack growth path through the micro/nanophase epoxy matrix. This long traveling path of the propagation of crack consumed high energy and hence improved the mechanical properties as compared to 2E specimen. So, the Al_2O_3 micro/nanoparticles might act as crack stoppers and increased the capability of the material to absorb energy by forming tortuous pathways for crack growth which resulting in an increasing in tensile properties. In addition, when microcracks due to the tensile loads were met with Al_2O_3 micro/nanoparticles, they might be stabilized by crack bridging of Al_2O_3 micro/nanoparticles[38] . Micro/Nanoparticles hindered the development and propagation of micro-cracks in epoxy coatings. Epoxy filled with micro/nanoparticles offered more effective stress transfer, hence reducing the local stress concentration throughout the epoxy matrix[39].

However, further increase in the weight percentage of Al_2O_3 microparticles to 2wt% cause the formation of agglomeration which in turn decreases the tensile strength and strain as compared to M1N1. These agglomerations possess a higher surface area that helps in the formation of enclosed air bubbles from the atmosphere. Consequently, this causes a reduction in the tensile properties of the polymeric matrix composite[40, 41]. Also, the presence of particles agglomerations leads to stress concentration and may cause premature failure[42]. Moreover, an increase in matrix viscosity due to the increase in Al_2O_3 microparticles content, which in turn allowed small air-bubbles to be trapped in the matrix during the mixing process forming tiny voids in the samples. This in turn results in specimens failure at relatively low stress[38].

3.2. Flexural properties

Figure 6 shows the flexural stress-strain curves of steel lined with pure epoxy and epoxy filled with Al_2O_3 micro/nanoparticles. Also, adding either nanofillers or microfillers to epoxy coating increased both the flexural strength and strain. The addition of 1wt% Al_2O_3 microparticles before 1wt% Al_2O_3 nanoparticles exhibited the maximum flexural strength and strain. Figures 7 and 8 show the mean values of flexural strength and strain of steel lined with epoxy filled with Al_2O_3 micro/nanoparticles. An enhancement of 3.9%, 8.5, and 1.7% in flexural strength was attained with

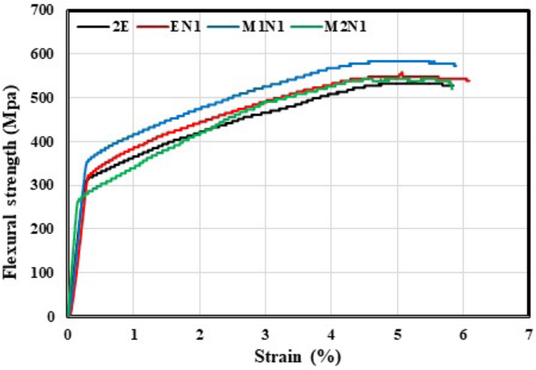

Figure 6. Flexural stress-strain curves of steel lined with epoxy filled with Al_2O_3 micro/nanoparticles.

EN1, M1N1, and M2N1, respectively as compared to the 2E specimen. However, an improvement of 2.9%, 5.7%, and 2.3% in flexural strain was attained with EN1, M1N1, and M2N1 as compared to the 2E specimen.

3.3. Hardness

Figure 9 shows the hardness of steel lined with micro/nanocomposites. The several coating configurations led to different hardness values. Increasing the weight percentage of the first layers to 2wt% Al_2O_3 microparticles before 1wt% Al_2O_3 nanoparticles (M2N1) led to a maximum significant enhancement of 39.4% in hardness as compared to 2E. This may be concluded as, during the hardness test, when the indenter goes downward, it faced increased resistance from the filled coated material[43]. This high resistance was owing to the increase of the weight content of Al_2O_3 particles that have a high hardness value. As the mass percentage of filler increased, the filler particles filled in the gap and voids in the polymeric matrices and formed a denser structure, and therefore hardness increased[44]. An enhancement of 12.3% and 14.9% in hardness was attained with EN1 and M1N1, respectively as compared to the 2E specimen. The enhancement in scratch and abrasive resistance was owing to the dispersion hardening of alumina nanoparticles in polymeric coatings[22]. The high hardness value could

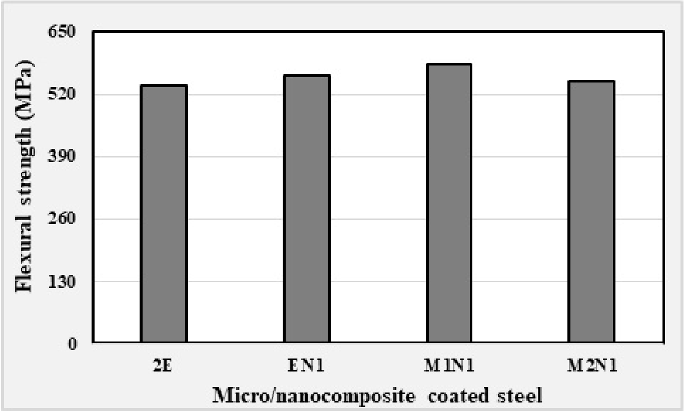

Figure 7. Flexural strength of steel lined with epoxy filled with Al_2O_3 micro/nanoparticles.

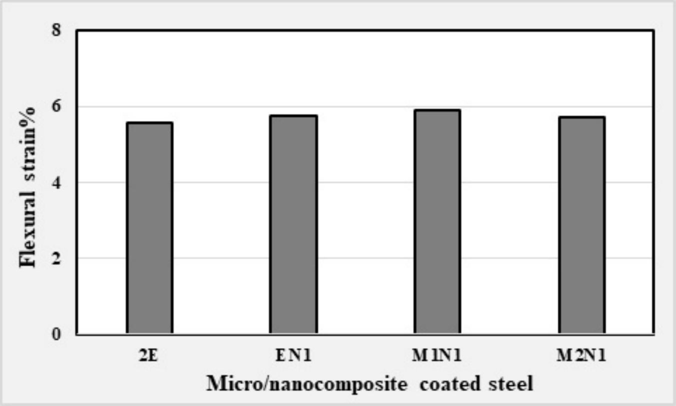

Figure 8. Flexural strain of steel lined with epoxy filled with Al_2O_3 micro/nanoparticles.

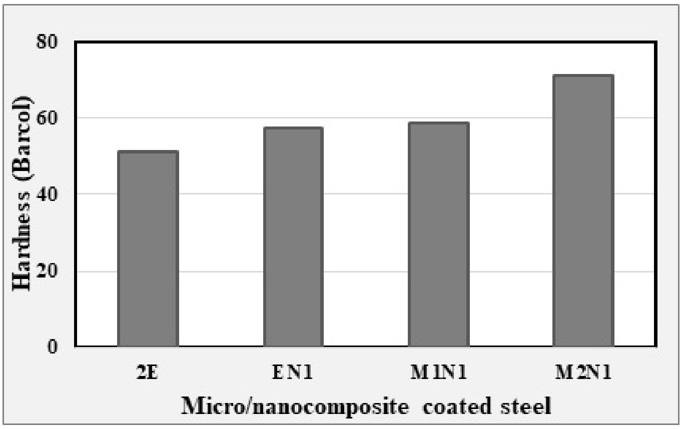

Figure 9. Hardness of steel lined with epoxy filled with Al_2O_3 micro/nanoparticles.

be attained for metallic coatings by inducing the hard nanocrystalline phases[45].

3.4. Failure mode

Figure 10 shows the damage mechanism in steel coated by epoxy and epoxy filled with Al_2O_3 micro/nanoparticles after being subjected to tensile loading. The pure epoxy coating separated from the steel substrate during tensile fracture as shown in Figure 10. Adding 1 wt% Al_2O_3 nanoparticles into the epoxy matrix in the exterior layers improved slightly the adhesion of the coating to steel as compared to 2E specimen. However, adding 1 wt% Al_2O_3 microparticles into the epoxy matrix that represented the first layer coated steel on both sides followed by 1 wt% Al_2O_3 nanoparticles into the epoxy matrix as exterior layers enhanced the adhesion to steel substrate thus revealing the good tensile properties of this

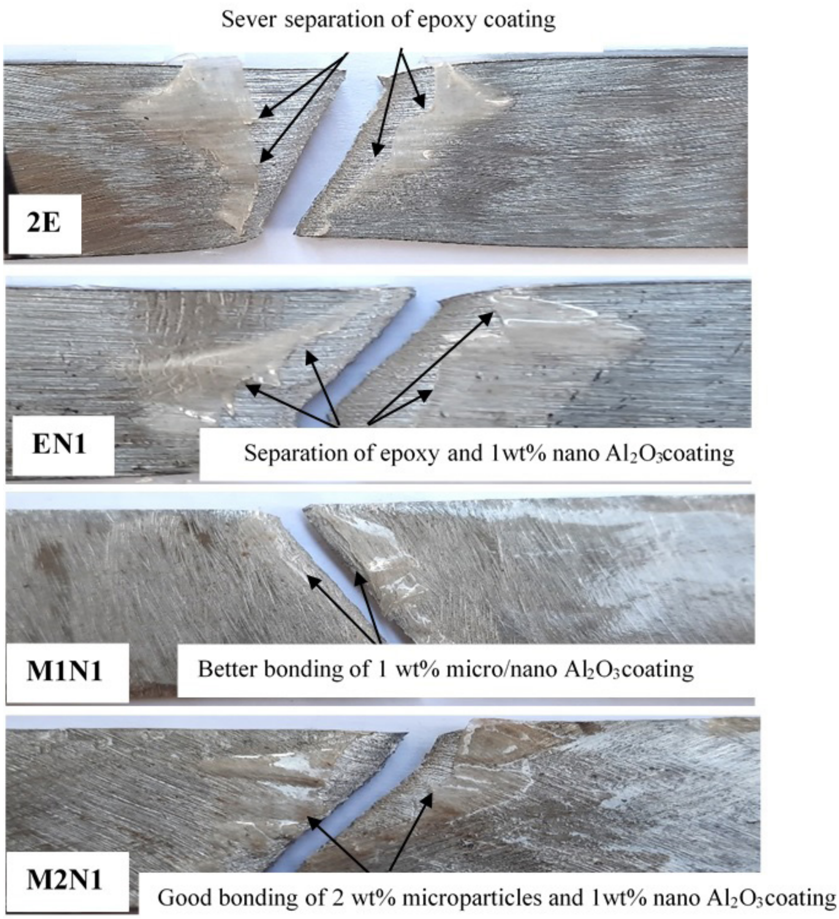

Figure 10. The damage mechanism in steel coated by epoxy and epoxy filled with micro/nano Al_2O_3 particles after being subjected to tensile loading.

type of coating. Adding 2 wt% Al_2O_3 microparticles into epoxy matrix that represented the first layer coating on both sides followed by 1 wt% Al_2O_3 nanoparticles into the epoxy matrix enhanced also the coating adhesion. The increase in micron-sized weight percentage to 2 wt% in the first layer decreased the adhesion of the coatings as compared to M1N1.

Adding 2 wt% Al_2O_3 microparticles to the epoxy matrix as the first layer increased the adhesion of this layer to the steel substrate. The second layers from both sides of epoxy filled with 1wt% Al_2O_3 nanoparticles were characterized by good adhesion to the first layers of epoxy filled with 2 wt% Al_2O_3 microparticles on both sides. So, after being subjected to tensile loadings, good bonding was observed for the two composite layers from both sides to steel. However, for EN1 specimens, the first layers of unfilled epoxy were separated from the steel surface after tensile loading. This in turn led to the separation of the second layers of epoxy filled with 1wt% nanoparticles as the second layers had adhered to the first layers of epoxy coatings.

3.5. Barrier resistance

Figure 11 shows the barrier properties of steel coated by epoxy and epoxy filled with Al_2O_3 micro/nanoparticles when immersed in 3.5wt% NaCl. Moreover, Figure 12 shows the barrier properties of steel coated by epoxy and epoxy filled with Al_2O_3 micro/nanoparticles when immersed in citric acid solution. The salt solution and citric acid absorption content increased as the immersion time increased until equilibrium saturation was achieved. It is clear that the coating with double layers filled with either nanoparticles or microparticles increased the barrier properties of steel against salt solution and citric acid solution as compared with pure epoxy coating. The least water absorption was detected for M1N1 composite coating, followed by M2N1 composite coating. This indicated that further increase of microparticles led to a slight decrease in barrier properties. Table 2 and Table 3 show Fickian Diffusion coefficient values of steel coated by epoxy and epoxy filled with Al_2O_3 micro/nanoparticles when immersed in 3.5wt% NaCl and citric acid solution, respectively. It was observed that the addition of 1wt% and 2 wt% of Al_2O_3 microparticles to the epoxy matrix in the first layers decreased the diffusion coefficient as compared to 2E as the specimens immersed in 3.5wt% NaCl and citric acid solution. The highest diffusion coefficient was observed for steel coated with pure epoxy coating. From Tables 2 and 3, the diffusion coefficient of specimens immersed in citric acid was greater than ones immersed in the salt solution.

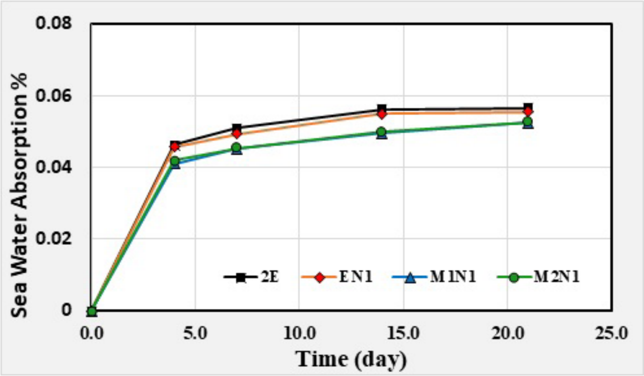

Figure 11. The barrier properties of steel coated by epoxy and epoxy filled with micro/nano Al_2O_3 particles when immersed in 3.5wt%NaCl.

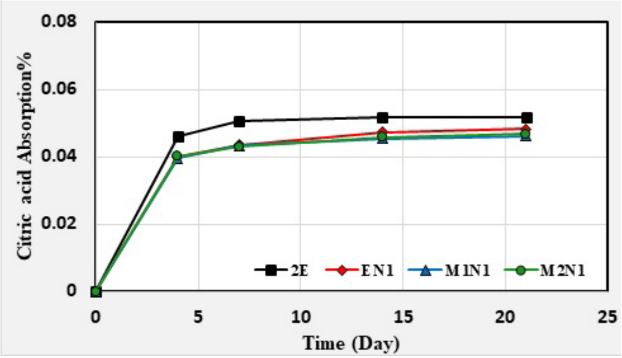

Figure 12. The barrier properties of steel coated by epoxy and epoxy filled with micro/nano Al_2O_3 particles when immersed in citric acid solution.

Nanofillers as alumina, titania, silica are considered well-known materials utilized in coating[7]. As reported by Saji and Thomas that the epoxy filled with MoO_3 nanofillers coated steel significantly improved the barrier capacity of epoxy by preventing the transportation of H_2O and ions into the epoxy matrix and reduce the opportunities of deterioration and blistering of the coating film[9]. The nano-sized inclusion reduce the rate of absorption of water due to the barrier properties of these nanoparticles thus improve the properties of these plasticized nanocomposites[27,46]. These nano-fillers close the pores inside the epoxy matrix, permitting interconnecting with molecule chains, thus increasing the density of polymer cross-linking hence reducing the free volume[47]. Similarly, reducing water absorption by adding nanoparticles to the polymeric matrix was attained by[48,49,50]. Moreover, Nguyen-Tri et al.[45] attributed the good barrier properties to the inclusion of nanofillers into the organic polymeric that decreased the voids and zigzagging the path of diffusion for deleterious species. Therefore, the coating films including nanofillers were expected to have significant barrier behavior for corrosion protection and lower the trend for the coating film to blister or delaminate. Nanofillers modify the surface energy of the inherently hydrophobic siloxane polymers thus enhancing the performance of nanocomposite coating soaked in aggressive media[18]. The fillers efficiently blocked the corrosion medium and enhanced the anticorrosive performance of the composite coating[4].

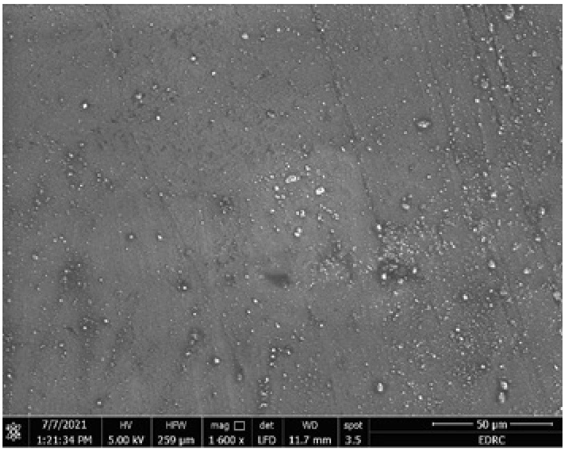

Figure 13. SEM showing the distribution of alumina nanoparticles in M2N1 composites.

Figure 13 shows a scanning electron microscopy micrograph of the layer in M2N1 specimen. From the Figure, a relatively good distribution of Al_2O_3 nanoparticles was observed. This good distribution of Al_2O_3 nanoparticles in epoxy resin revealed the good tensile and flexural behavior over 2E. The homogeneity, amount and distribution of nanoparticles can greatly affect the mechanical properties

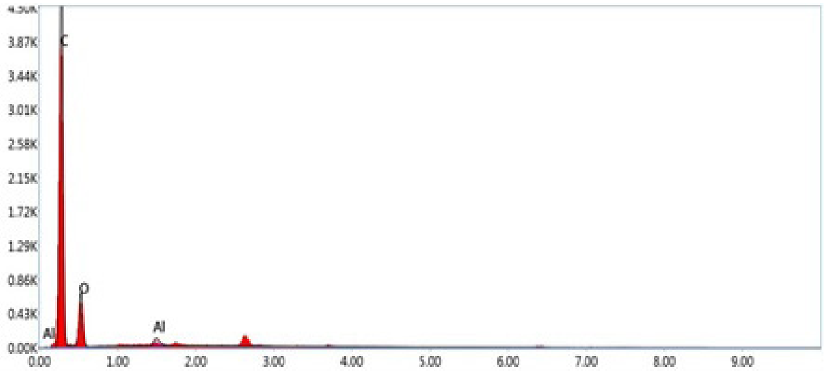

Figure 14. EDX of coated M2N1 composites on steel substrate.

Table 2. Fickian Diffusion coefficient values of steel coated by epoxy and epoxy filled with micro/nano Al_2O_3 particles when immersed in 3.5 wt%NaCl.

Steel lined with different species of composite coatings	Fickian Diffusion coefficient (mm^2/s)
2E	$2.26x10^{-7}$
EN1	$2.05x10^{-7}$
M1N1	$1.96x10^{-7}$
M2N1	$1.99x10^{-7}$

Table 3. Fickian Diffusion coefficient values of steel coated by epoxy and epoxy filled with micro/nano Al_2O_3 particles when immersed in citric acid solution.

Steel lined with different species of composite coatings	Fickian Diffusion coefficient (mm^2/s)
2E	$3.14x10^{-7}$
EN1	$2.53x10^{-7}$
M1N1	$2.91x10^{-7}$
M2N1	$1.59x10^{-7}$

of nanocomposites[50] Figure 14 shows the EDX of coated M2N1 composites on the steel substrate. The elements that are more presented in the composite coating are carbon and oxygen.

4. Conclusions

In this study, the mechanical and barrier properties of steel coated with epoxy filled with alumina particles in micron and nanosized were investigated. Double layers of pure epoxy coated steel were compared with the other three different sequences of double micro/nanocomposites layers coated steel. Tensile, flexural, hardness, and barrier properties of the coated coupons were studied. The results showed that a maximum enhancement of 16.7%, 18.9%, 32.6%, 8.5%, and 5.7% in tensile strength, tensile strain, toughness, flexural strength, and flexural strain, respectively were achieved with a coating of epoxy filled with 1wt% Al_2O_3 microparticles before 1wt% Al_2O_3 nanoparticles on both sides as compared with pure epoxy coating. However, a maximum enhancement in hardness of 39.4% was obtained with a coating of epoxy filled with 2wt% Al_2O_3 microparticles before 1wt% Al_2O_3 nanoparticles on both sides as compared with pure epoxy coating. Adding micro/nanoparticles to epoxy coating enhanced the barrier properties of the coating against salt solution and citric acid environment as compared to pure epoxy coated.

5. Acknowledgements

The authors would like to thank Taif University for its financial support. This research was fully funded by the Deanship of Scientific Research, Taif University, KSA. [Research group number 1-441-92]

6. References

1. Hamzat AK, Adediran IA, Alhems LM, Riaz M. Investigation of corrosion rate of mild steel in fruit juice environment using factorial experimental design. Int J Corros. 2020;2020:5060817. http://dx.doi.org/10.1155/2020/5060817.
2. Oladele SK, Okoro HK. Investigation of corrosion effect of mild steel on orange juice. Afr J Biotechnol. 2011;10:3152-6. http://dx.doi.org/10.5897/ajb10.1426.
3. Fayomi OSI, Popoola API. Corrosion propagation challenges of mild steel in industrial operations and response to problem definition. J Phys Conf Ser. 2019;1378:1-8. http://dx.doi.org/10.1088/1742-6596/1378/2/022006.
4. Zhang J, Zhang W, Wei L, Pu L, Liu J, Liu H, et al. Alternating multilayer structural epoxy composite coating for corrosion protection of steel. Macromol Mater Eng. 2019;304(12):1900374. http://dx.doi.org/10.1002/mame.201900374.
5. Raj XJ. Investigation into the effect of Cr2O3 nanoparticles on the protective properties of epoxy coatings on carbon steel in 3.5% NaCl solution by scanning electrochemical microscopy. Prot Met Phys Chem Surf. 2019;55:80-8. http://dx.doi.org/10.1134/S2070205119010167.
6. Xu H, Zhang Y. A review on conducting polymers and nanopolymer composite coatings for steel corrosion protection. Coatings. 2019;9(12):807. http://dx.doi.org/10.3390/coatings9120807.
7. Radhamani AV, Lau HC, Ramakrishna S. Nanocomposite coatings on steel for enhancing the corrosion resistance: a review. J Compos Mater. 2020;54:681-701. http://dx.doi.org/10.1177/0021998319857807.
8. Ali MM, Magee JC, Hsieh PY. Corrosion protection of steel pipelines with metal-polymer composite barrier liners. J Nat Gas Sci Eng. 2020;81:103407. http://dx.doi.org/10.1016/j.jngse.2020.103407.
9. Xavier JR. Investigation on the anticorrosion, adhesion and mechanical performance of epoxy nanocomposite coatings containing epoxy-silane treated nano-MoO3 on mild steel. J

Adhes Sci Technol. 2020;34(2):115-34. http://dx.doi.org/10.1080/01694243.2019.1661658.

10. Armelin E, Pla R, Liesa F, Ramis X, Iribarren JI, Alemán C. Corrosion protection with polyaniline and polypyrrole as anticorrosive additives for epoxy paint. Corros Sci. 2008;50:721-8. http://dx.doi.org/10.1016/j.corsci.2007.10.006.
11. Boomadevi Janaki G, Xavier JR. Evaluation of mechanical properties and corrosion protection performance of surface modified nano-alumina encapsulated epoxy coated mild steel. J Bio Tribo-Corros. 2020;6:20. https://doi.org/10.1007/s40735-019-0316-7.
12. Kim HJ, Jung DH, Jung IH, Cifuentes JI, Rhee KY, Hui D. Enhancement of mechanical properties of aluminium / epoxy composites with silane functionalization of aluminium powder. Compos Part B. 2012;43(4):1743-8. http://dx.doi.org/10.1016/j.compositesb.2011.12.010.
13. Zunjarrao SC, Singh RP. Characterization of the fracture behavior of epoxy reinforced with nanometer and micrometer sized aluminum particles. Compos Sci Technol. 2006;66(13):2296-305. http://dx.doi.org/10.1016/j.compscitech.2005.12.001.
14. Megahed AAE-W, Megahed M. Fabrication and characterization of functionally graded nanoclay/glass fiber/epoxy hybrid nanocomposite laminates. Iran Polym J. 2017;26(9):673-80. http://dx.doi.org/10.1007/s13726-017-0552-y.
15. Megahed M, Megahed AA, Agwa MA. Mechanical properties of on/off-axis loading for hybrid glass fiber reinforced epoxy filled with silica and carbon black nanoparticles. Mater Technol. 2018;33(6):398-405. http://dx.doi.org/10.1080/10667857.2018.1454022.
16. Manjunath M, Renukappa NM, Suresha B. Influence of micro and nanofillers on mechanical properties of pultruded unidirectional glass fiber reinforced epoxy composite systems. J Compos Mater. 2016;50(8):1109-21. http://dx.doi.org/10.1177/0021998315588623.
17. Megahed M, Fathy A, Morsy D, Shehata F. Mechanical Performance of glass/epoxy composites enhanced by micro- and nanosized aluminum particles. J Ind Text. 2019;51(1):224-243. http://dx.doi.org/10.1177/1528083719874479.
18. Sharifi Golru S, Attar MM, Ramezanzadeh B. Studying the influence of nano-Al2O3 particles on the corrosion performance and hydrolytic degradation resistance of an epoxy/polyamide coating on AA-1050. Prog Org Coat. 2014;77(9):1391-9. http://dx.doi.org/10.1016/j.porgcoat.2014.04.017.
19. Rajitha K, Mohana KNS, Mohanan A, Madhusudhana AM. Evaluation of anti-corrosion performance of modified gelatin-graphene oxide nanocomposite dispersed in epoxy coating on mild steel in saline media. Colloids Surf A Physicochem Eng Asp. 2020;587:124341. http://dx.doi.org/10.1016/j.colsurfa.2019.124341.
20. Sørensen PA, Kiil S, Dam-Johansen K, Weinell CE. Anticorrosive coatings: a review. J Coat Technol Res. 2009;6(2):135-76. http://dx.doi.org/10.1007/s11998-008-9144-2.
21. Bujang A, Rahman FA, Omar SRS. Nanotechnology in the food processing and packaging: an overview of its halalan tayyiban aspect. Malaysian J Consum Fam Econ. 2020;24:1-14.
22. Wang Y, Lim S, Luo JL, Xu ZH. Tribological and corrosion behaviors of Al2O3/polymer nanocomposite coatings. Wear. 2006;260(9-10):976-83. http://dx.doi.org/10.1016/j.wear.2005.06.013.
23. Behzadnasab M, Mirabedini SM, Esfandeh M. Corrosion protection of steel by epoxy nanocomposite coatings containing various combinations of clay and nanoparticulate zirconia. Corros Sci. 2013;75:134-41. http://dx.doi.org/10.1016/j.corsci.2013.05.024.
24. Abd El-Lateef HM, Khalaf MM. Corrosion resistance of ZrO2-TiO2 nanocomposite multilayer thin films coated on carbon steel in hydrochloric acid solution. Mater Charact. 2015;108:29-41. https://doi.org/10.1016/j.matchar.2015.08.010.
25. Ramezanzadeh B, Attar MM. Studying the effects of micro and nano sized ZnO particles on the corrosion resistance and deterioration behavior of an epoxy-polyamide coating on hot-dip galvanized steel. Prog Org Coat. 2011;71(3):314-28. http://dx.doi.org/10.1016/j.porgcoat.2011.03.026.
26. Megahed M, Agwa MA, Megahed AA. Effect of ultrasonic parameters on the mechanical properties of glass fiber reinforced polyester filled with nano-clay. J Ind Text. 2020;2020. http://dx.doi.org/10.1177/1528083720918348.
27. Megahed AA, Agwa MA, Megahed M. Can ultrasonic parameters affect the impact and water barrier properties of nano-clay filled glass fiber/polyester composites? J Ind Text. 2020;2020. http://dx.doi.org/10.1177/1528083720960733.
28. Ali-Eldin SS, Abd El-Moezz SM, Megahed M, Abdalla WS. Study of hybridization effect of new developed rice straw mat/ glass fiber reinforced polyester composite. J Nat Fibers. 2019; 18(8):1194-1206. http://dx.doi.org/10.1080/15440478.2019.1688749.
29. Ciriminna R, Meneguzzo F, Delisi R, Pagliaro M. Citric acid: emerging applications of key biotechnology industrial product. Chem Cent J. 2017;11(1):1-9. http://dx.doi.org/10.1186/s13065-017-0251-y.
30. Swain MR, Ray RC, Patra JK. Citric acid: Microbial production and applications in food and pharmaceutical industries. In: Vargas DA, Medina JV, editors. Citric Acid: Synthesis, Properties and Applications Hauppauge, N.Y : Nova Science 2012:97–118.
31. Matheswaran P, Ramasamy AK. Corrosion inhibition of mild steel in citric acid by aqueous extract of Piper Nigrum L. E-J Chem. 2012;9(1):75-8. http://dx.doi.org/10.1155/2012/803098.
32. Agwa MA, Megahed M, Megahed AA. Enhancement of water barrier properties and tribological performance of hybrid glass fiber/epoxy composites with inclusions of carbon and silica nanoparticles. Polym Adv Technol. 2017;28(9):1115-24. http://dx.doi.org/10.1002/pat.4004.
33. Abdelhaleem AMM, Megahed M, Saber D. Fatigue behavior of pure polypropylene and recycled polypropylene reinforced with short glass fiber. J Compos Mater. 2018;52(12):1633-40. http://dx.doi.org/10.1177/0021998317729888.
34. Megahed M. Abd El-Baky MA, Alsaeedy AM, Alshorbagy AE. An experimental investigation on the effect of incorporation of different nanofillers on the mechanical characterization of fiber metal laminate. Compos, Part B Eng. 2019;176:107277. http://dx.doi.org/10.1016/j.compositesb.2019.107277.
35. Santos JC, Vieira LMG, Panzera TH, Schiavon MA, Christoforo AL, Scarpa F. Hybrid glass fibre reinforced composites with micro and poly-diallyldimethylammonium chloride (PDDA) functionalized nano silica inclusions. Mater Des. 2015;65:543-9. http://dx.doi.org/10.1016/j.matdes.2014.09.052.
36. Alateyah AI, Imam A, Ibn M, Islamic S, Arabia S, Dhakal HN, et al. Processing, Properties, and Applications of Polymer Nanocomposites Based on Layer Silicates : A Review. Adv Polym Technol. 2013;32(4):1-49. http://dx.doi.org/10.1002/adv.21368.
37. Agwa MA, Youssef SM, Ali-Eldin SS, Megahed M. Integrated vacuum assisted resin infusion and resin transfer molding technique for manufacturing of nano-filled glass fiber reinforced epoxy composite. J Ind Text. 2020;2020. http://dx.doi.org/10.1177/1528083720932337.
38. Melaibari AA, Attia MA, Abd El-baky MA. Understanding the effect of halloysite nanotubes addition upon the mechanical properties of glass fiber aluminum laminate. Fibers Polym. 2021;22(5):1416-33. http://dx.doi.org/10.1007/s12221-021-0656-z.
39. Megahed M, Megahed AA, Agwa MA. The influence of incorporation of silica and carbon nanoparticles on the mechanical properties of hybrid glass fiber reinforced epoxy. J Ind Text. 2019;49(2):181-99. http://dx.doi.org/10.1177/1528083718775978.

40. Megahed M, Youssef SM, Ali-Eldin SS, Agwa MA. Upgraded mechanical properties of diluent nano-filled glass/epoxy composites fabricated by vacuum assisted resin infusion. Fibers Polym. 2021;22(4):1063-81. http://dx.doi.org/10.1007/s12221-021-0210-z.
41. Shen MY, Chang TY, Hsieh TH, Li YL, Chiang CL, Yang H, et al. Mechanical properties and tensile fatigue of graphene nanoplatelets reinforced polymer nanocomposites. J Nanomater. 2013;2013:1-9. http://dx.doi.org/10.1155/2013/565401.
42. Gurusideswar S, Velmurugan R, Gupta NK. Study of rate dependent behavior of glass/epoxy composites with nanofillers using non-contact strain measurement. Int J Impact Eng. 2017;110:324-37. http://dx.doi.org/10.1016/j.ijimpeng.2017.05.013.
43. Megahed M, Attia MA, Abdelhameed M, El-Shafei AG. Tribological characterization of hybrid metal matrix composites processed by powder metallurgy. Acta Metall Sin. 2017;30:781-790. https://doi.org/10.1007/s40195-017-0568-5.
44. Megahed AA, Agwa MA, Megahed M. Improvement of hardness and wear resistance of glass fiber-reinforced epoxy composites by the incorporation of silica/carbon hybrid nanofillers. Polym Plast Technol Eng. 2018;57(4):251-9. http://dx.doi.org/10.1080/03602559.2017.1320724.
45. Nguyen-Tri P, Nguyen TA, Carriere P, Ngo Xuan C. Nanocomposite coatings: preparation, characterization, properties, and applications. Int J Corros. 2018;2018:1-19. http://dx.doi.org/10.1155/2018/4749501.
46. Starkova O, Buschhorn ST, Mannov E, Schulte K, Aniskevich A. Water transport in epoxy / MWCNT composites. Eur Polym J. 2013;49(8):2138-48. http://dx.doi.org/10.1016/j.eurpolymj.2013.05.010.
47. Yousri OM, Abdellatif MH, Bassioni G. Effect of Al2O3 nanoparticles on the mechanical and physical properties of epoxy composite. Arab J Sci Eng. 2018;43(3):1511-7. http://dx.doi.org/10.1007/s13369-017-2955-7.
48. Chow WS. Water absorption of epoxy/glass fiber/organo-montmorillonite nanocomposites. Express Polym Lett. 2007;1(2):104-8. http://dx.doi.org/10.3144/expresspolymlett.2007.18.
49. Alamri H, Low IM. Effect of water absorption on the mechanical properties of nanoclay filled recycled cellulose fibre reinforced epoxy hybrid nanocomposites. Compos, Part A Appl Sci Manuf. 2013;44:23-31. http://dx.doi.org/10.1016/j.compositesa.2012.08.026.
50. Chang HL, Chen CM, Chen CH. Effects of nano-silica addition on water absorption of glass fiber/epoxy composite. Adv Mat Res. 2013;853:40-5. http://dx.doi.org/10.4028/www.scientific.net/AMR.853.40.