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Scanning Electron Microscopy of Carbon Nanotube–Epoxy Interfaces: Correlating Morphology to Sulfate Exposure

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Abstract

Epoxy resins are widely used as protective coatings in civil infrastructure, yet sulfate-rich environments accelerate their deterioration. This study evaluates the effectiveness of multi-walled carbon nanotubes (MWCNTs) in enhancing the sulfate resistance of epoxy resins. Neat and MWCNT-reinforced epoxy specimens (0.25 wt.% and 0.5 wt.%) were fabricated, heat cured at 100 °C and exposed to a solution of sulfuric acid and sodium chloride maintaining a pH of less than 3 for 0, 30, and 60 days. Analytical techniques, including scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS), revealed distinct degradation patterns: the neat epoxy exhibited puncture damage and extensive salt deposition, while the MWCNT-reinforced specimens showed crack propagation mitigated by nanotube bridging. Heat curing introduced micro-voids that exacerbated sulfate ingress. The salt deposition surged to 200 times for the MWCNT-reinforced specimens compared to the neat ones, whereas crack width was higher in the MWCNT reinforced specimen compared to their neat counterparts, given that crack-bridging was observed. These findings highlight the potential of MWCNTs to improve epoxy durability in sulfate-prone environments, though the optimization of curing conditions and dispersion methods is critical.

Keywords: carbon nanotubes; epoxy; SEM characterization; spectroscopy; bridging; MWCNT dispersion in epoxy composites



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1. Introduction

Corrosion resistance is a critical parameter to consider for the design of materials with applications in corrosive environments. This design consideration serves to improve the durability, longevity, and structural integrity of the materials while maintaining beneficial mechanical properties. Harsh environmental conditions containing sulfates pose a threat to these properties when materials are utilized in engineering, commercial, and construction applications. Elemental analyses are conducted in engineering design to identify elemental properties that may improve material resistance to sulfate intrusion. This sulfate intrusion resistance exists due to the parental properties of the elements used and allows for the

boundaries of material science to be scrutinized and extended with the development of hybrid compounds that possess the capabilities of all parental elements [1–3].

Epoxy resins, which are well known for their strength and adhesive capabilities, are of key relevance in corrosion resistance [4]. Additionally, we can potentially enhance this corrosive resistance to sulfate salt. The previously discussed study primarily researched the effects on epoxy resin of adding a component to the matrix. Other researchers have investigated the effects of different environments. Researchers have placed epoxy resin specimens in various harsh environments such as saltwater, freeze–thaw cycles, wet–dry cycles, water with chlorine, and other corrosive environments. Researching the effects of harsh environments is highly important because epoxy resin used in structural applications is exposed to various conditions.

In this study, the researchers exposed epoxy adhesive specimens to different environmental conditions, mainly thermal (TC), freeze–thaw (FT), and wet–dry (WD) cycles and immersion in pure water (PW) and water with chlorides (CW) for periods of exposure that lasted up to 16 months. The researchers concluded from their investigation that the exposed specimens did not experience a change in their chemical composition. The researchers also concluded that the specimens exposed to thermal cycles exhibited a 33% and 15% increase in ultimate tensile stress and the E-modulus, respectively, while the specimens exposed to freeze–thaw cycles showed a decrease in these areas. The researchers proposed that the “thermal cycles might have caused a post-curing phase” [5]. The authors conducted a study to investigate how UV radiation impacts thermoplastic-epoxy-matrix-formed hybrid cables for external strengthening purposes. The results indicate that, “while the neat resin is susceptible to photo-oxidation and a sharp decline in strength, the hybrid FRP shows no significant changes in tensile properties even after nearly 2000 MJ/m²” [6].

Therefore, epoxy could be used in different environments, and unique results can be obtained based on exposure. Hence, the introduction of reinforcing materials such as carbon nanotubes (CNTs), which are tiny cylindrical structures composed of carbon atoms that are 100,000 times thinner than human hair, can improve epoxy resin’s mechanical properties due to their extraordinary strength, lightweight nature and unique electrical and thermal properties [7,8]. This makes CNTs extremely useful in this field of material science [9–11].

There are two types of CNTs; single-walled CNTs (SWCNTs) and multi-wall CNTs (MWCNTs). SWCNTs are composed of a single layer of graphene rolled into a tube with a diameter of roughly 1 µm and a length 1000 times larger than their diameter, forming a thread-like structure. They are widely used in electronics, photonics, and advanced biomedical applications. MWCNTs consist of several concentric layers of graphene rolled into a tube where the core is hollow. These have slightly larger diameters than SWCNTs ranging from 2 nm to 100 nm. Additionally, MWCNTs are extremely robust due to the presence of multiple layers in their geometry; therefore, their use as reinforcement falls into the high-strength composites category [12–15]. Epoxy/carbon nanotube composites offer substantially improved properties compared to traditional fiber-reinforced epoxy composites [16]. Additionally, graphene nano platelets (GNP) at concentrations of 0.25 wt.% and 0.5 wt.% exhibited significant potential for enhancing resin bonding capacity, and 0.25 wt.% GNP mixed epoxy resin outperformed neat epoxy by 181%; it also showed better performance in terms of stiffness [17]. Moreover, one study [18] explained that MWCNTs’ content had a significant effect on the corrosion resistance of the hybrid coating. When the MWCNT content was 2 wt.%, the hybrid coating had the highest anticorrosion and good conductivity, which can potentially be employed for bare carbon steel against the corrosive environment. Figure 1 illustrates the variation in CNTs.

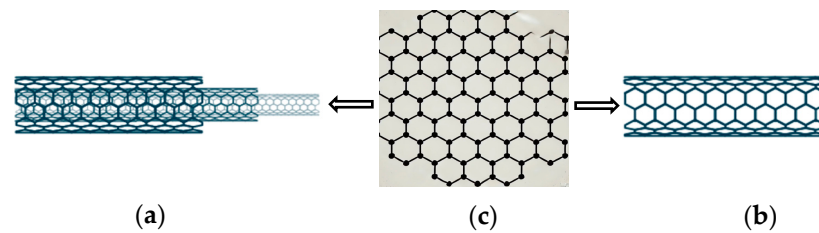


Figure 1. Types of CNTs: (a) MWCNT. (b) SWCNT. (c) Graphene.

Microscopic imaging is vital to viewing CNTs, allowing material scientists to observe their structural, morphological, and functional characteristics. CNTs' electrical conductivity and strength changes significantly due to variations in their geometry (length, width and diameter) [19,20]. Additionally, the roughness, alignment and agglomeration of CNTs can affect their interaction with the reinforced material [21,22]. Therefore, scanning electron microscopes (SEMs) or light microscopy is critical in viewing the characteristics of CNTs. The long-term durability of epoxies under harsh environments restricts their widespread use [23]. Studies on the effects of humid, acidic, and basic environments and temperature variation have been extensively explored [24–28]. These studies considered the aging time of epoxy specimens under these harsh conditions. Depending on the mechanical properties being studied, the ageing times are utilized. Moreover, ref. [29] studied the effects of sulfuric acid media on epoxy resins; however, the oxidation of epoxy resins due to such harsh conditions was not investigated. Additionally, the intrusion of sulfate salts into nanomodified epoxy resin during the ageing process was not discussed. Moreover, ref. [30] determined that the samples immersed in tap water were characterized by a higher strength than in acidic environments; this project produced EDS data to support its claim about the salt deposition and crack bridging phenomena, which makes this study stand out over its counterparts. Finally, ref. [31] found that a corrosion-resistant epoxy-based paint with 10% polyaniline demonstrated a low corrosion rate ($0.35 \mu\text{m}/\text{year}$); proper biocide formulation significantly enhanced antifouling and corrosion resistance, which indicates that the nano-modified epoxy has significant benefits over non-modified ones. Ref. [32] explains that the introduction of carbon nanotubes into an epoxy compound influences the physio-mechanical properties, cross-linking processes, morphology, and heat resistance of reinforced epoxy composites which provides the wide-angle view for this study. Ref. [33] examined alkali-treated and CGO-nanoparticle-incorporated jute fiber-reinforced epoxy composite specimens, revealing valuable insights into their functional properties and structural characteristics. The morphological evidence supported the surface modifications induced by the alkali treatment and the CGO coating, further validating the improved adhesion and interlocking between the fibers and the epoxy matrix, and ultimately leading to even better thermal stability and mechanical properties; this, in turn, aids the study of these materials, as modifications boost the properties of the epoxy and provide the same epoxy with new and reinforced properties.

This study serves to investigate how carbon-nanotube-reinforced and non-reinforced epoxies corrode under harsh, sulfate-rich conditions. The findings of this study will illuminate the possible applications of nanoparticles in the design of materials that can withstand the effects of corrosive environments. The mechanical properties and effects of corrosive environments on epoxy resin bonding structures exposed to a solution of NaCl and H_2SO_4 are investigated. The aging times considered in this study are 0, 30, and 60 days for Phases 0, 1, and 2, respectively. Additionally, SEM and light microscopy analyses are utilized to image the morphological changes that occur due to the harsh conditions outlined in this introduction.

2. Materials and Methods

2.1. Material and Specimen Fabrication

Specimen fabrication was the first objective of this research. Neat specimens, which are unreinforced with CNTs, were used as a control group. Similarly, we utilized functionalized carboxyl group (COOH) MWCNTs from Cheap Tubes, Inc., with an inner diameter ranging between 5 and 10 nm, an outer diameter ranging between 20 and 30 nm and a length between 10 and 30 μm . The content of the COOH group was 1.2% according to the manufacturer. The CNTs were synthesized and functionalized by the manufacturers and graphitized via catalyzed chemical vapor deposition at 2800 °C. According to Cheap Tubes, Inc. (Grafton, VT, USA), the CNTs have a purity greater than 99.9% by weight. Dural 452 MV 1:1 Part A and Part B epoxy resin from Euclid Chemical was utilized. The primary compound in Part A is bisphenol-A poly glycidyl ether resin, which acts as the monomer of the epoxy polymer. Part B is primarily diaminocyclo-hexane, which acts as the hardener in the chemical reaction. Generic acetone thinner was added to the epoxy resin at 25% of the total volume. Type V tensile ‘dog-bone’ specimens were produced in accordance with ASTM D638-22. Figure 2 illustrates the chemical reaction that occurs in the formation of MWCNT-reinforced epoxy resins.



Figure 2. Dural 452 MV 1:1 resin and hardener.

For the MWCNT-reinforced specimen, MWCNTs were added into the epoxy resin specimens at 0.25 and 0.5% by weight, as CNT loadings (<1%) significantly enhance the epoxy's performance without agglomeration [23,34]. The MWCNTs were dispersed within the epoxy resin utilizing mechanical stirrers for 30 s. Ultrasonication was then performed with 5 min of de-gassing and 60 min of sonication at 40 °C in a Branson 1800. Finally, the epoxy resin was stirred using (IKA Works, Inc. Staufen, Germany) IKA C- Mag HS-10 digital at 800 rotations per minute and a temperature of 80 °C for an hour. The complete epoxy resin was poured into tensile specimen molds. The specimens were cured in both ambient temperature (AC) and heated temperature (HC) conditions. The ambient temperature was between 28 and 30 °C, whereas, for the heat curing, which took place on a flat rack in a convection lab oven, the specimens were pre-heated to 100 °C for 24 h. Heat curing improves chemical resistance by raising the crosslink density. The specimens were then rested on a flat surface for another 24 h and demolded. Figures 3–7 shows the neat vs. CNT-reinforced composition with AC and HC specimens. Figure 8 shows the homogeneous mixture of CNTs in the specimen. In order to facilitate the even dispersion of MWCNTs inside the epoxy matrix, acetone was added as a dispersing agent in our investigation. By reducing viscosity during mixing, this method enhances nanoparticle dispersion. The specimens were fractured from the neck, representing brittle failure.

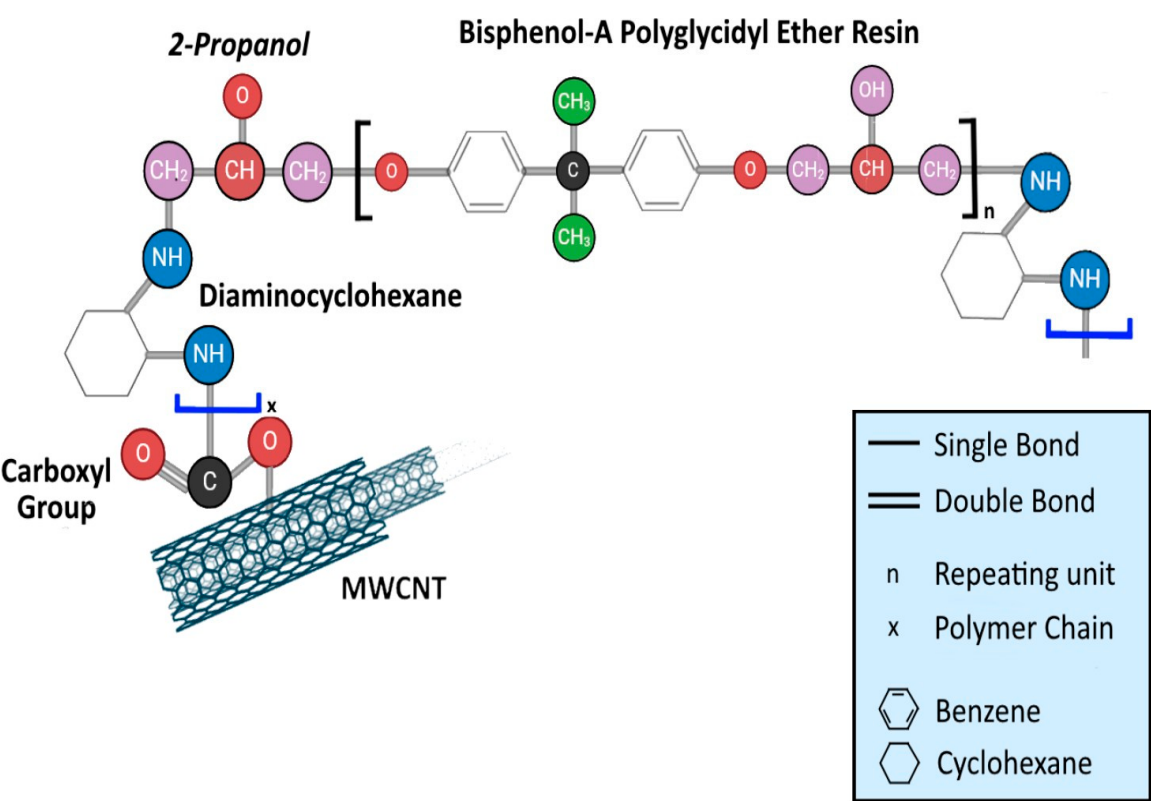


Figure 3. Hypothesized chemical reactions in the formation of MWCNT-reinforced epoxy resin.

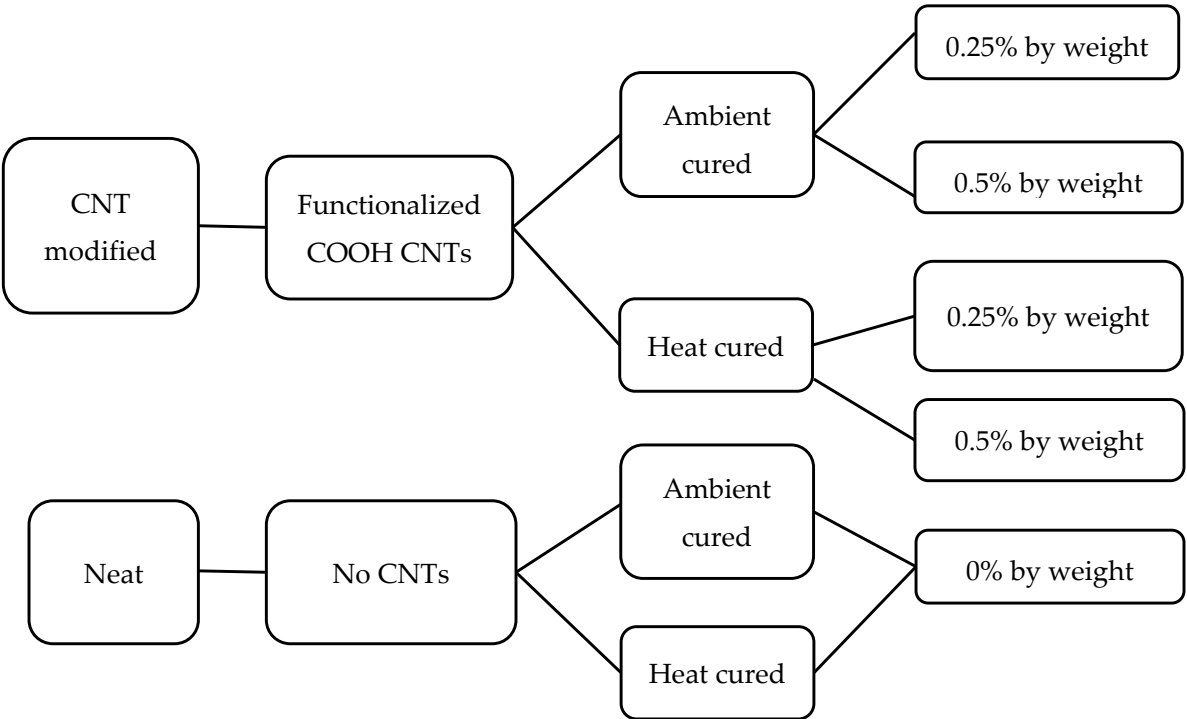


Figure 4. CNT: modified vs. neat specimens’ composition.

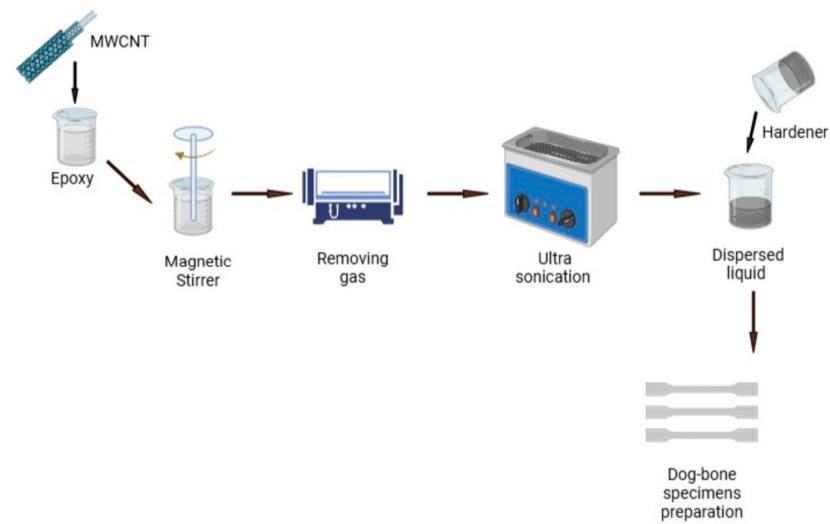


Figure 5. MWCNT-modified ambient-cured specimens.

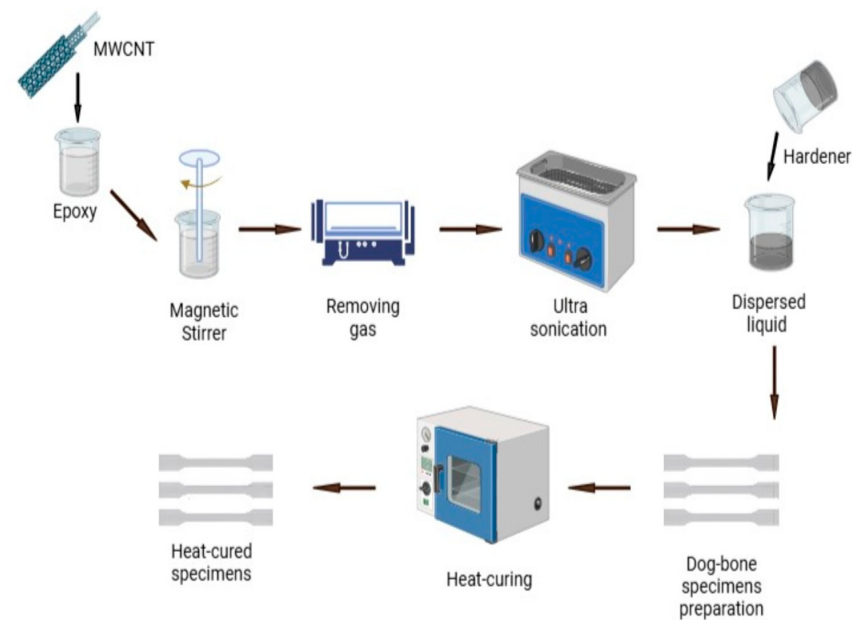


Figure 6. MWCNT-modified heat-cured specimens.

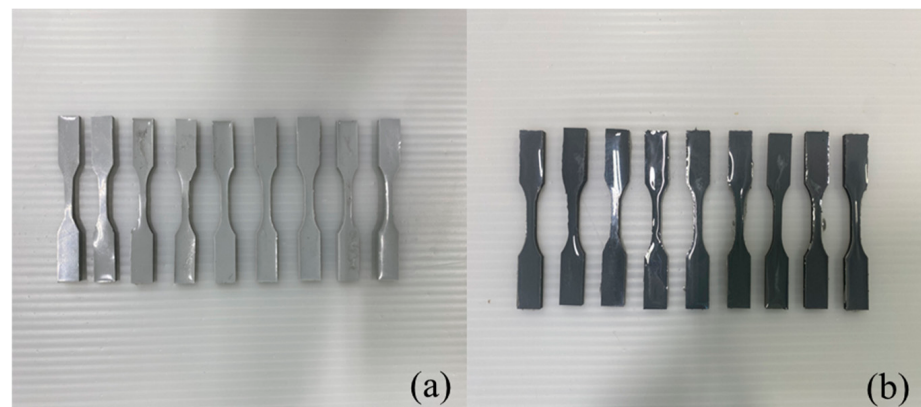


Figure 7. (a) Neat and (b) nanomodified specimens.

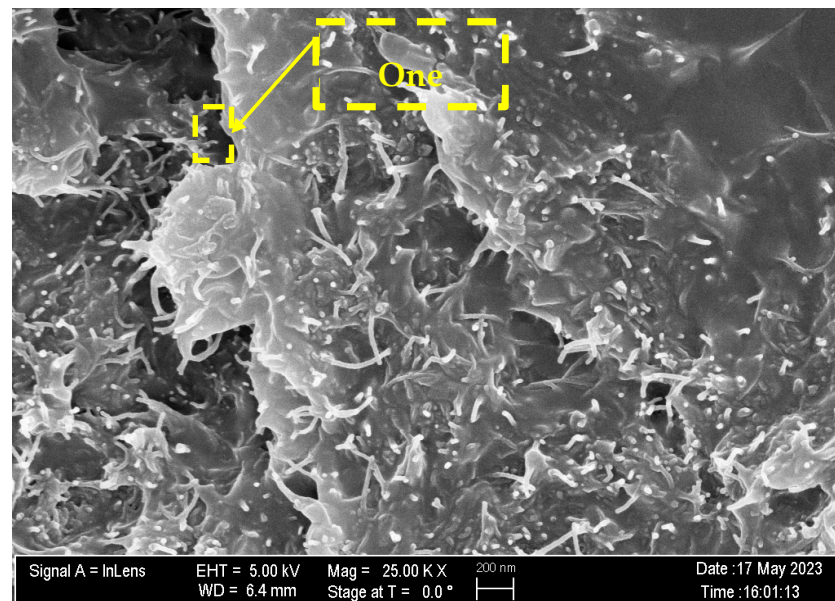


Figure 8. Homogeneous dispersion of CNTs in the specimen.

2.2. Aging Process

In order to simulate the real-world environmental deterioration of structural epoxy components, the specimens were exposed to a harsh acidic solution for varying timeframes. Three phases of exposure were utilized: Phase 0 at 0 days of exposure, Phase 1 at 30 days of exposure, and Phase 2 at 60 days of exposure. The 0-, 30-, and 60-day aging periods were chosen to capture both the initial degradation behavior and the progression of damage over time in epoxy systems exposed to aggressive chemical environments. While the 60-day period enables the observation of more advanced deterioration processes, such as deeper sulfate ingress and matrix damage, the 30-day interval indicates early-stage exposure effects, which are frequent enough to trigger microstructural alterations such as crack development or salt deposition. The solutions were created by mixing NaCl and H₂SO₄ into a beaker of deionized water and stirred until a pH under 3.0 was maintained. Then, 60 mL plastic vials were utilized to submerge the epoxy specimens under the NaCl and H₂SO₄ deionized water solution. Specimens were labelled as 0.25% AC, 0.25% HC, 0.5% AC, 0.5% HC, and neat specimens. Three specimens for each phase were prepared. The pH levels of the acidic solution were maintained under 3.0 throughout the aging process as shown in Figure 9. The chemical reactions occurring in the acidic solution environment are given as:

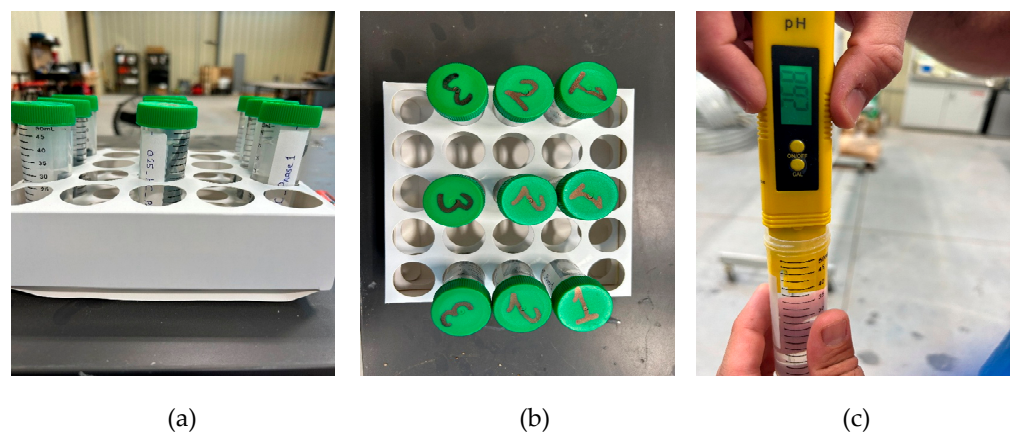
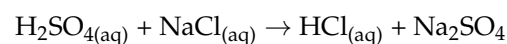


Figure 9. (a,b) Specimen identification and (c) pH maintained at less than 3.0.

2.3. Microscopic Analysis

Once the specimens were ready for evaluation, they were pulled apart by hand to tensile failure, exposing the cross section for surface microscopy analysis. A light microscope, the Keyence VHX 7000 Digital Microscope (KEYENCE CORPORATION OF AMERICA, Itasca, IL, USA), was used for low-magnification surface imagery and 3D surface composition. An SEM analysis of the specimen failure surface and energy-dispersive spectroscopy (EDS) were conducted for higher magnifications and elemental analysis, respectively. The SEM used is shown in Figure 10. The Thermo Fisher Quattro S (Thermo Fisher Scientific, Waltham, MA, USA) was utilized for both of these analyses. The EDS utilizes X-rays produced by the SEM to identify the elements present in the specimen.

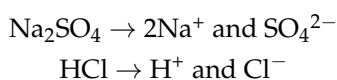


Figure 10. Scanning electron microscope.

3. Result and Discussion

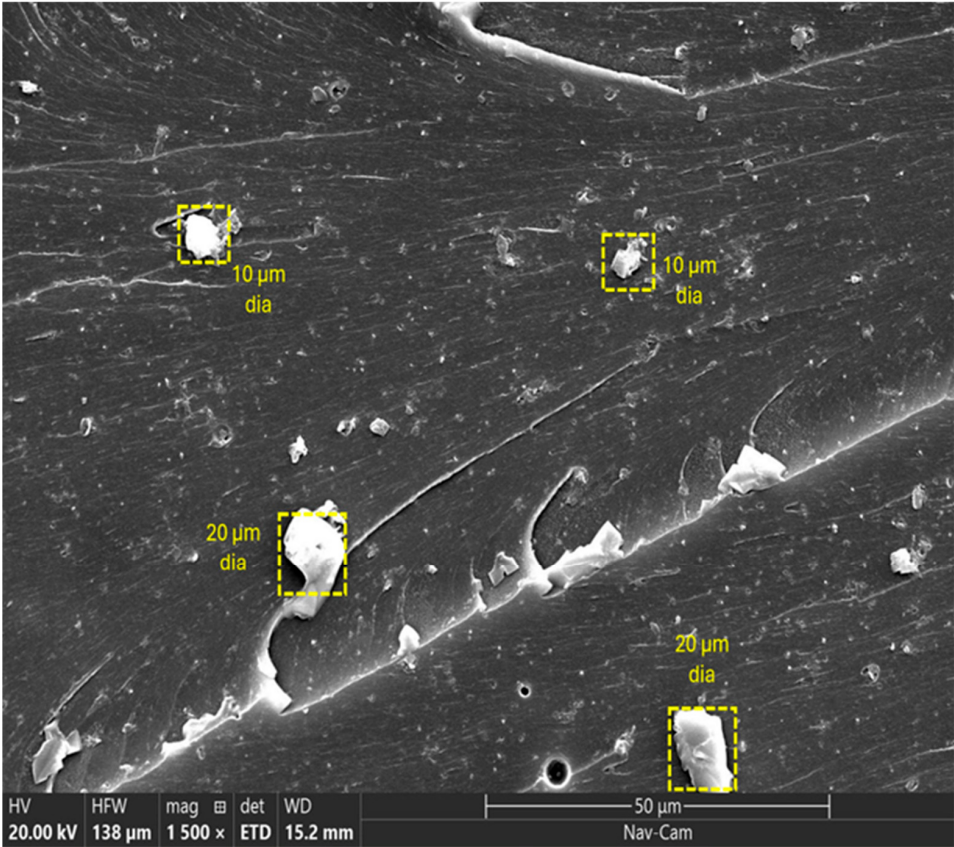
3.1. Salt Deposition

Salt deposition refers to the Na_2SO_4 that has been produced during the chemical reaction between H_2SO_4 and NaCl . Salt deposition is crucial as it provides evidence of a reaction as a by-product, as given in the equation below. Given that the acid and salt do not react with each other, Na_2SO_4 is produced, which is deionized to form Na^+ and SO_4^{2-} ions. The chemical equation of this process is given as:

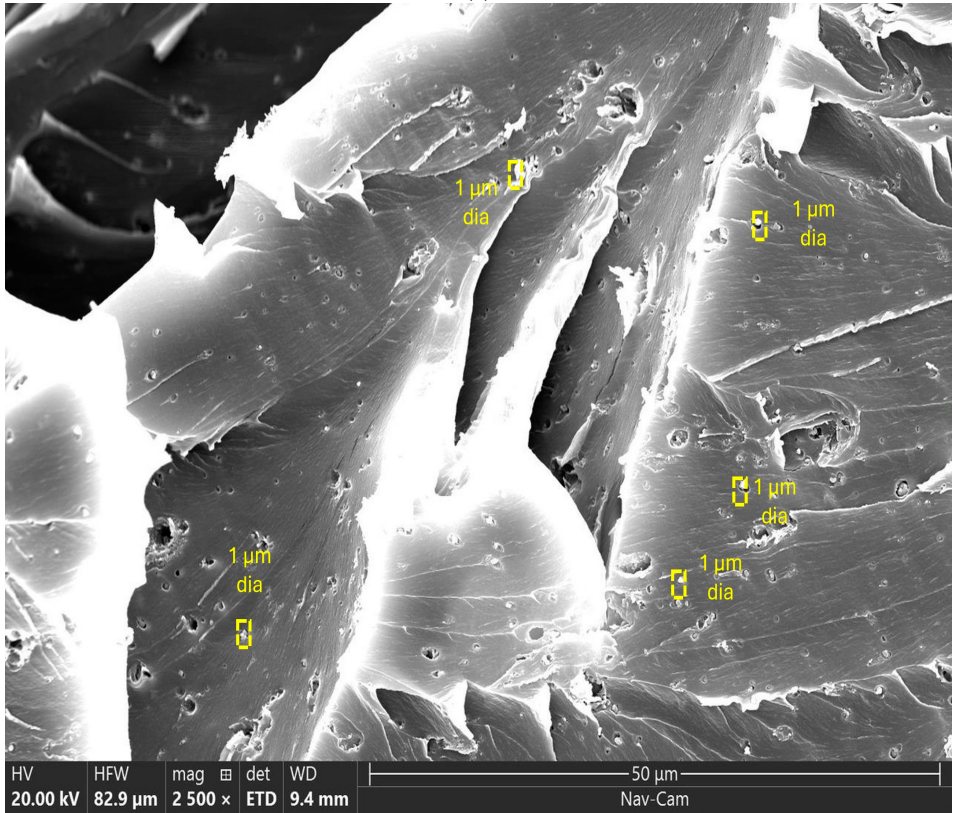


The SEM images of Phase 1 vs. Phase 2 for the neat specimens are shown in Figure 11. The size of the salt in the Phase 1 neat specimens is nearly $15\text{ }\mu\text{m}$, whereas, in Phase 2, the salts are nearly $1\text{ }\mu\text{m}$, which indicates that the deposition has been significantly reduced. The punctures on the surface of Phase 2 neat specimens are large; however, there were no observed punctures on the Phase 1 specimens. It can be determined that the salt deposition has significantly decreased between 30 and 60 days of exposure.

Salt deposition images for the SEM Phase 1 vs. Phase 2 MWCNT-reinforced specimens, both for 0.25% and 0.5%, are shown in Figure 12. Here, the case was exactly the opposite of that seen for the neat specimens. The salt depositions were greater in Phase 2 as compared to Phase 1. The average size of the salt deposited in Phase 1 was determined to be nearly $1\text{ }\mu\text{m}$, which was much less than the $20\text{ }\mu\text{m}$ on the Phase 2 specimens, indicating that salt deposition was at a maximum during the longer as compared to the shorter aging periods. In order to investigate this further, EDS analysis was utilized, with the elemental analysis of the specimens being used to observe any signs of Na, S and O_2 , as shown in Figure 13.

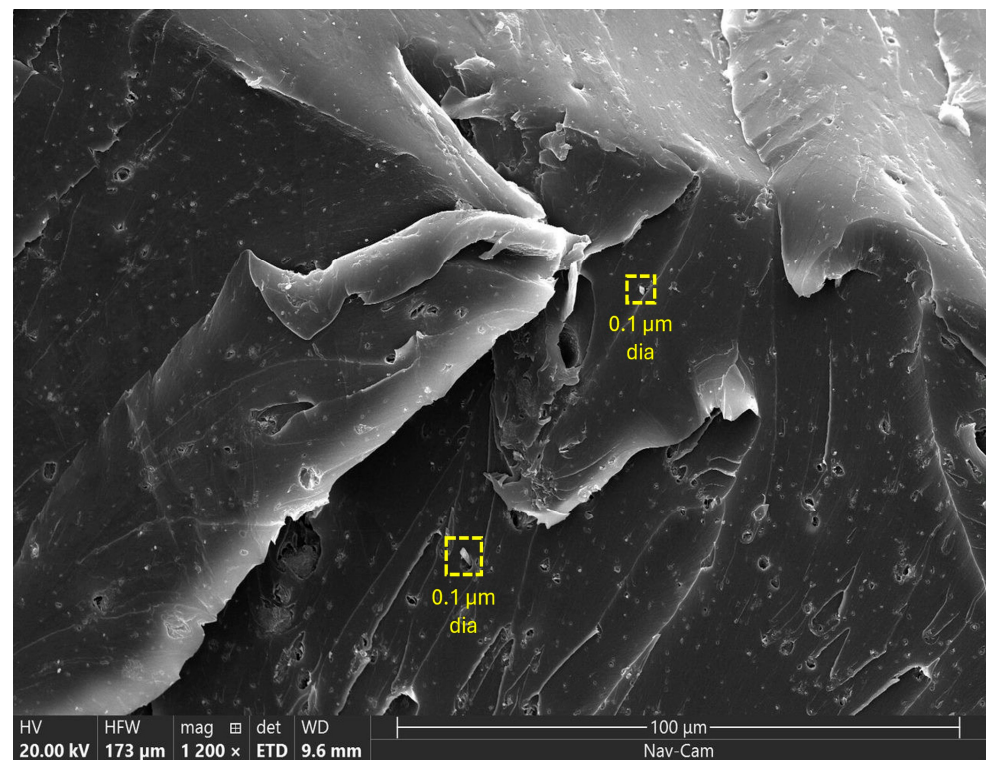


(a)

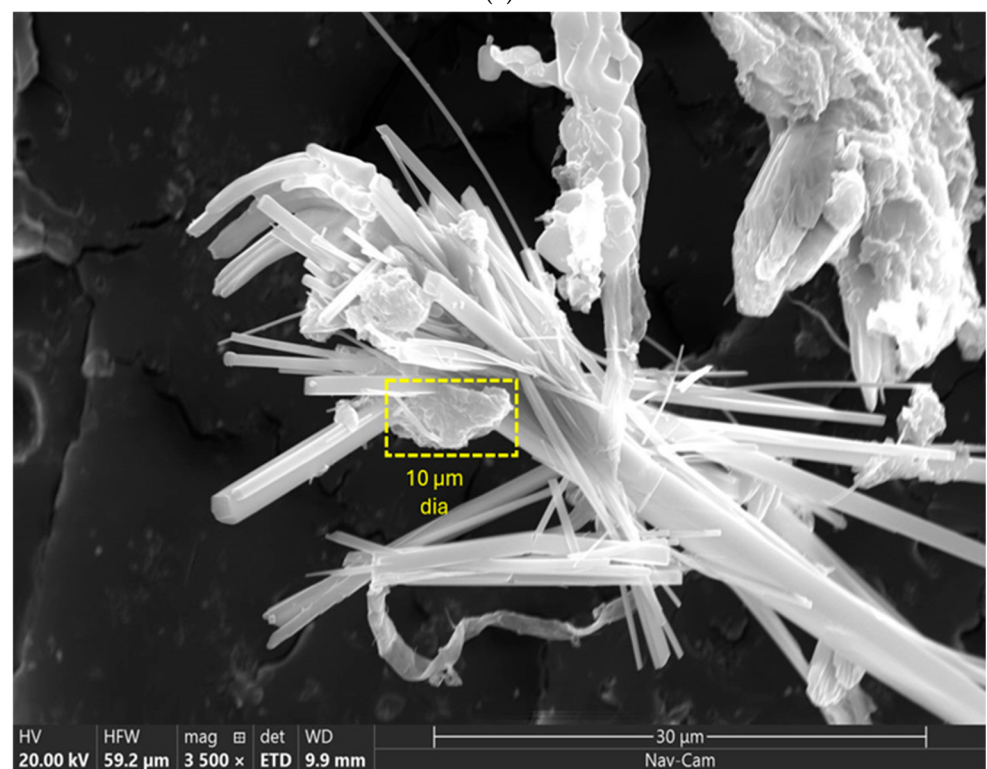


(b)

Figure 11. (a) 1500× magnified, Phase 1 aged neat specimen; (b) 2500× magnified, neat Phase 2 aged specimen.



(a)



(b)

Figure 12. Salt deposition (a) 1200× magnified; Phase 1 aged neat heat-cured specimen. (b) 3500× magnified, Phase 2 aged 0.5%-MWCNT-reinforced heat-cured specimen.

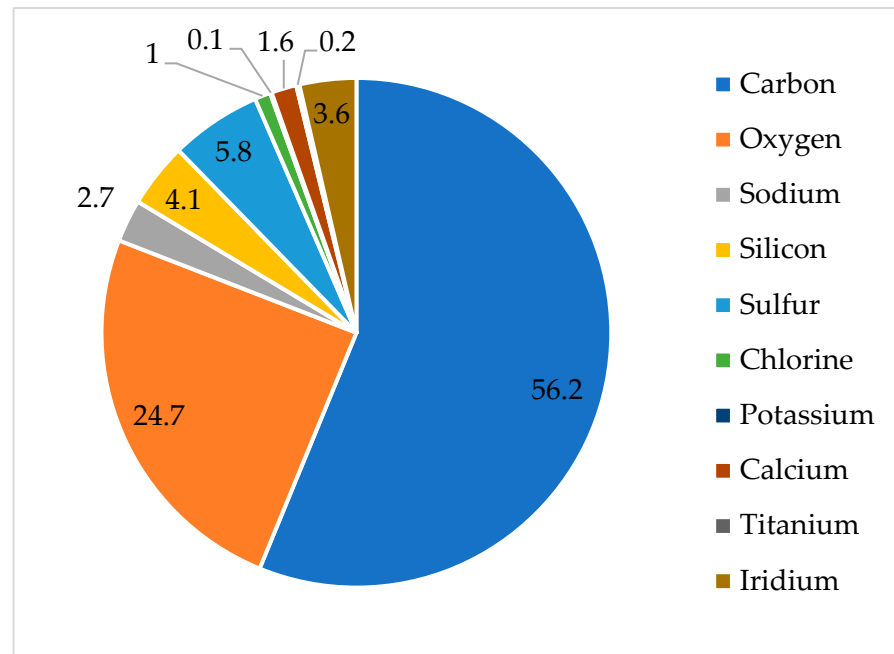


Figure 13. EDS results for salt deposition theory for the MWCNT-modified specimen.

The salt deposition was high, as the Na, S and O concentrations were 2.7%, 5.8%, and 24.7%, respectively, which indicates that the selected point features salt deposits. Additionally, other elements such as C (carbon) were produced from epoxy and MWCNTs. Cl, K, Ca, Ti are the impurities present in the specimens; finally, the presence of Ir as iridium is due to the sputter coating that was added to the specimens before investigation in the SEM. This is also shown in Figure 14 for the specimens and Figure 15 for the EDS results.

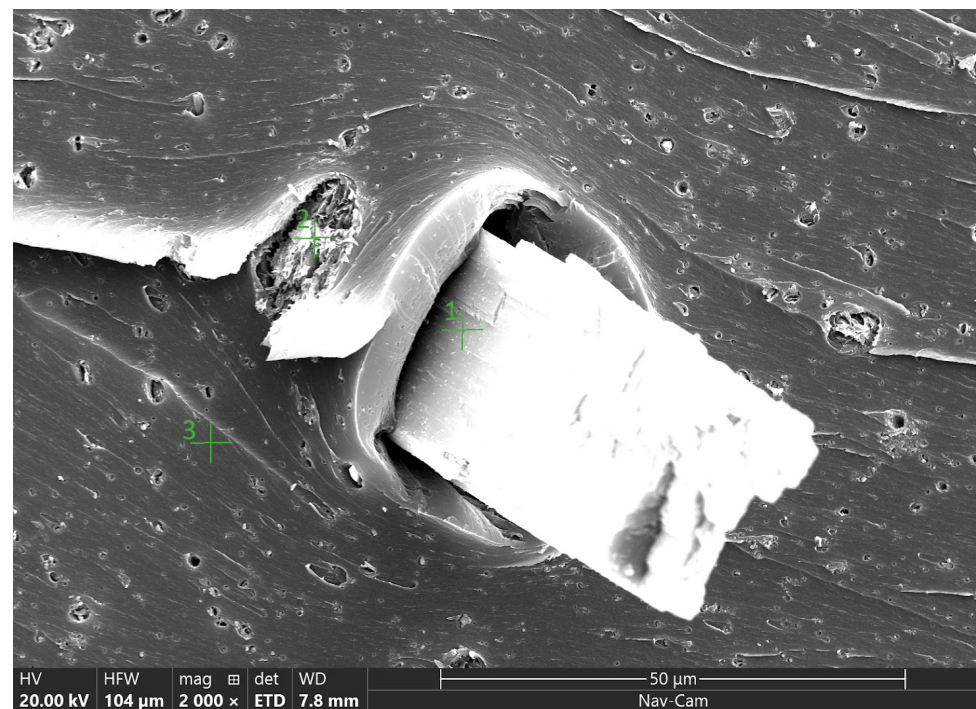


Figure 14. Salt deposition, 2500 $\times$ magnified; Phase 1 neat room-temperature-cured specimen. Point 1,2 and 3 are the EDS point of observations.

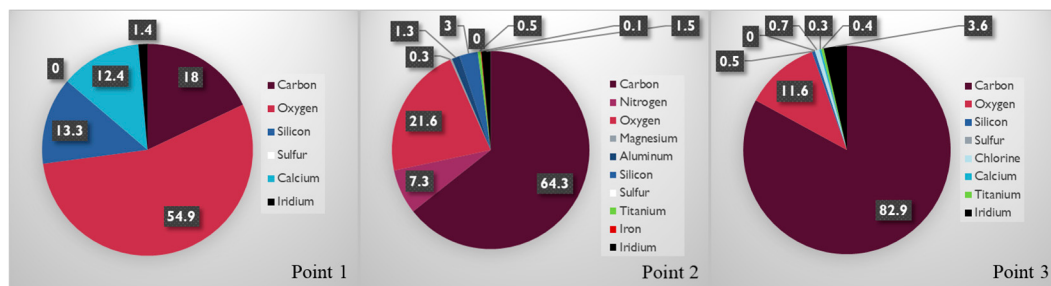
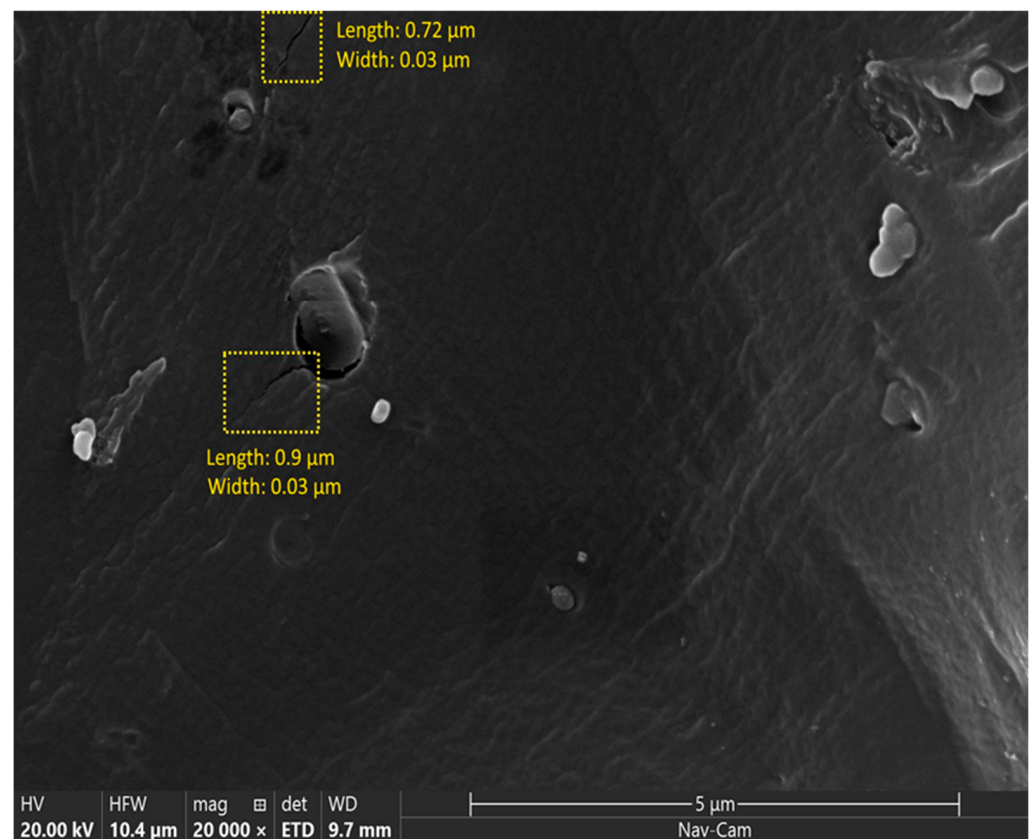


Figure 15. EDS results for salt deposition theory for the neat specimen.

3.2. Degradations

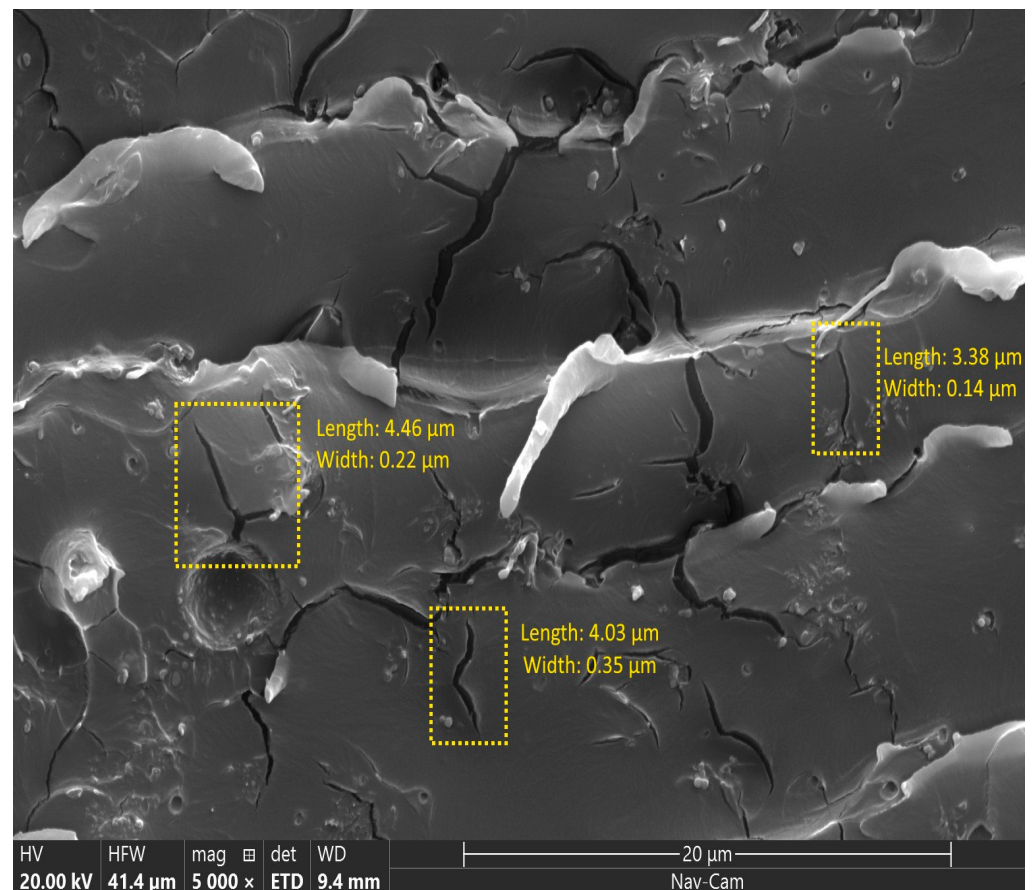
3.2.1. Cracks

Crack degradations were observed in the reinforced aged specimens. However, neat specimens did not exhibit noticeable crack degradations throughout the aging process. Figure 16a shows the crack propagation in reinforced specimens (0.25% and 0.5%) for Phase 1 and Figure 16b shows the same for Phase 2 exposure. Approximate lengths and widths of the highlighted cracks are noted. The average crack width is $0.92 \pm 0.154 \mu\text{m}$ for the Figure 16a and $3.96 \pm 0.31 \mu\text{m}$ for Figure 16b. Phase 2 cracks are wider and exhibit much longer propagation lengths when compared to Phase 1. Cracks appear to propagate from defects in the epoxy matrix surface, such as punctures, epoxy flakes and salt crystals. Pores in the epoxy matrix are caused by the heat curing process, producing more locations from which cracks can propagate. The presence of MWCNT reinforcement may have also caused crack bridging, illustrated by the crack propagation outwards from the edges rather than widening for the Phase 1 and Phase 2 specimens.



(a)

Figure 16. Cont.



(b)

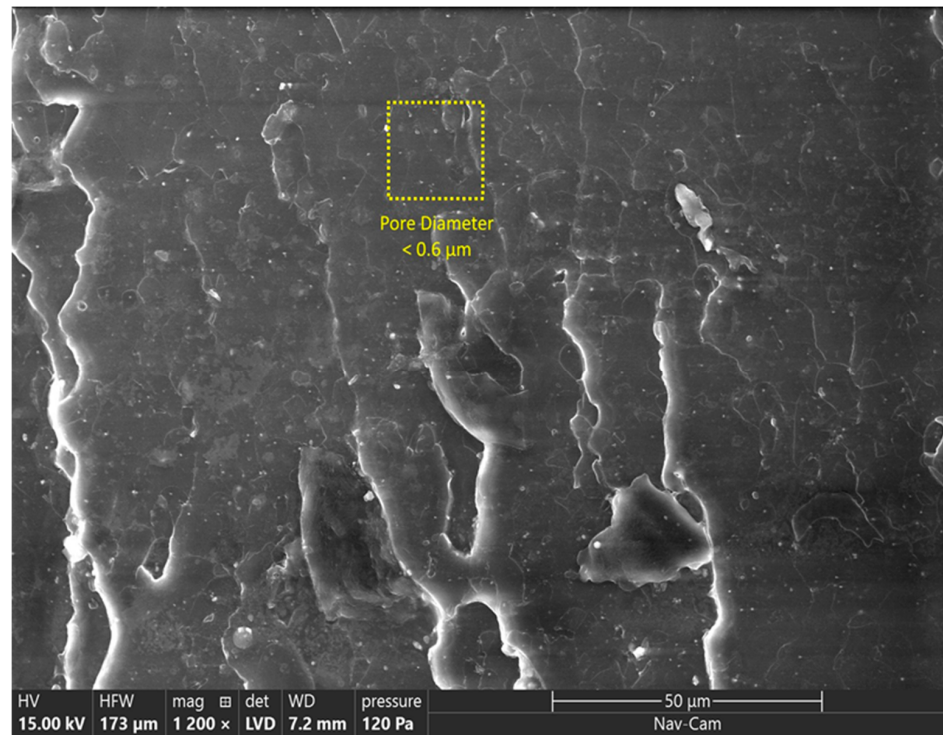
Figure 16. Crack propagation: (a) 20,000 $\times$ magnified, Phase 1 MWCNT-reinforced specimen. (b) 5000 $\times$ magnified, Phase 2 MWCNT-reinforced specimen.

3.2.2. Punctures

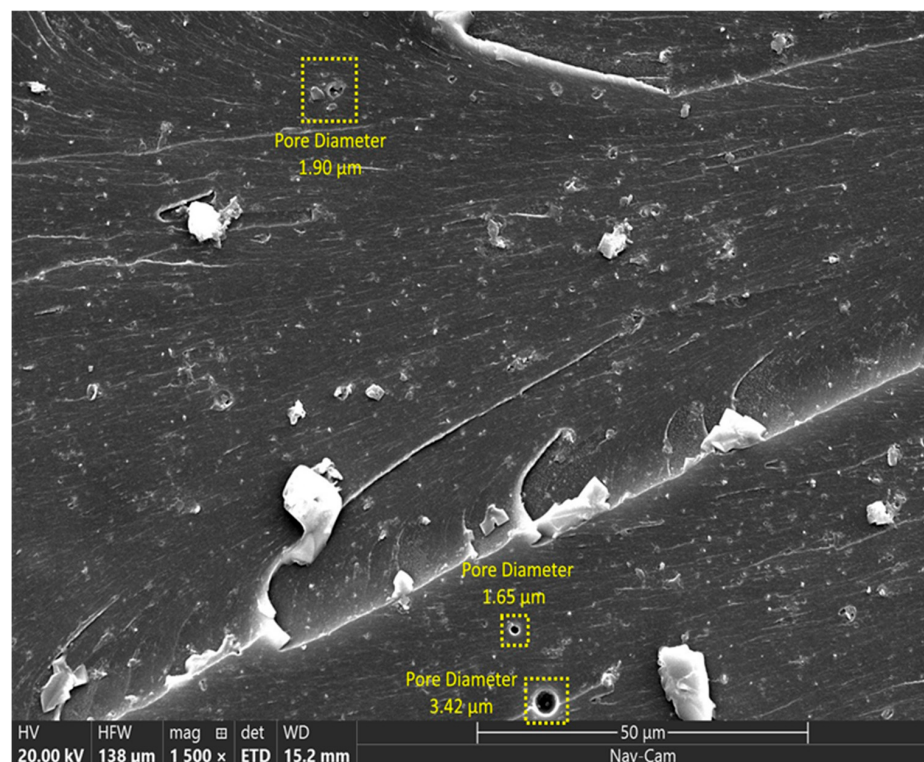
Crack degradations were observed in the reinforced aged specimens. Puncture degradations refer to a noticeable gap that can be seen through the SEM. These gaps create an initiation point for the cracks that can potentially propagate throughout the specimen. These gaps were observed in all specimens throughout the aging process. These punctures appear as white circular pores on the observed surface of the specimen. Figure 17 highlights major and minor punctures observed for neat epoxy specimens where Figure 17a shows Phase 0, Figure 17b shows Phase 1, and Figure 17c shows Phase 2 specimens. As the samples progressed throughout the aging process, punctures grew, and the edges of these punctures became rougher and sharper. Acidic deterioration is the most likely cause of this process of the worsening and widening of punctures, as well as the presence of salt crystals in the larger pores indicating acid salt deposition within the specimen. The neat specimens had surface puncture diameters less than 0.6 μm at Phase 0, 0.2 μm at Phase 1, and 0.4 μm at Phase 2. Due to the variation in the sizes of the punctures, it is difficult to directly compare sizes; however, it can be observed that the punctures increase in size as the specimens are aged for longer.

Figure 18 highlights the punctures observed in the MWCNT-reinforced epoxy specimens for 0.25% and 0.5%, where Figure 18a shows Phase 0, Figure 18b shows Phase 1, and Figure 18c shows Phase 2 specimens. The reinforced specimens' puncture diameters were observed to be about 1–2.5 μm at Phase 0, 1.5–3.5 μm at Phase 1, and 1–4.5 μm at Phase 2. Like the neat specimens, puncture sizes varied significantly and cannot easily be directly compared. Generally, MWCNT-reinforced specimen punctures grew as aging began; how-

ever, their growth slowed down or stopped altogether between Phase 1 and Phase 2. A likely explanation for this is the presence of MECNT tubes mitigating puncture growth and instead causing microcracks to propagate from these punctures. Compared to the neat specimens, the MWCNT-reinforced specimens appear to have fewer puncture degradations and instead have many microcracks, which propagate from pre-existing pores.

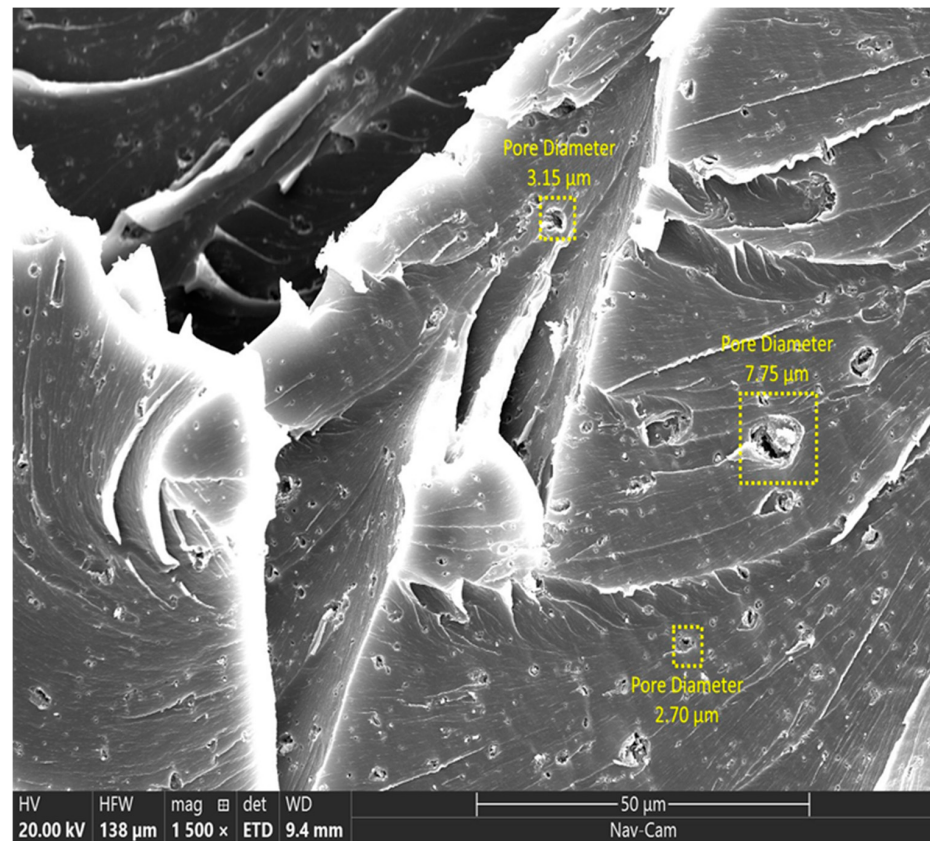


(a)



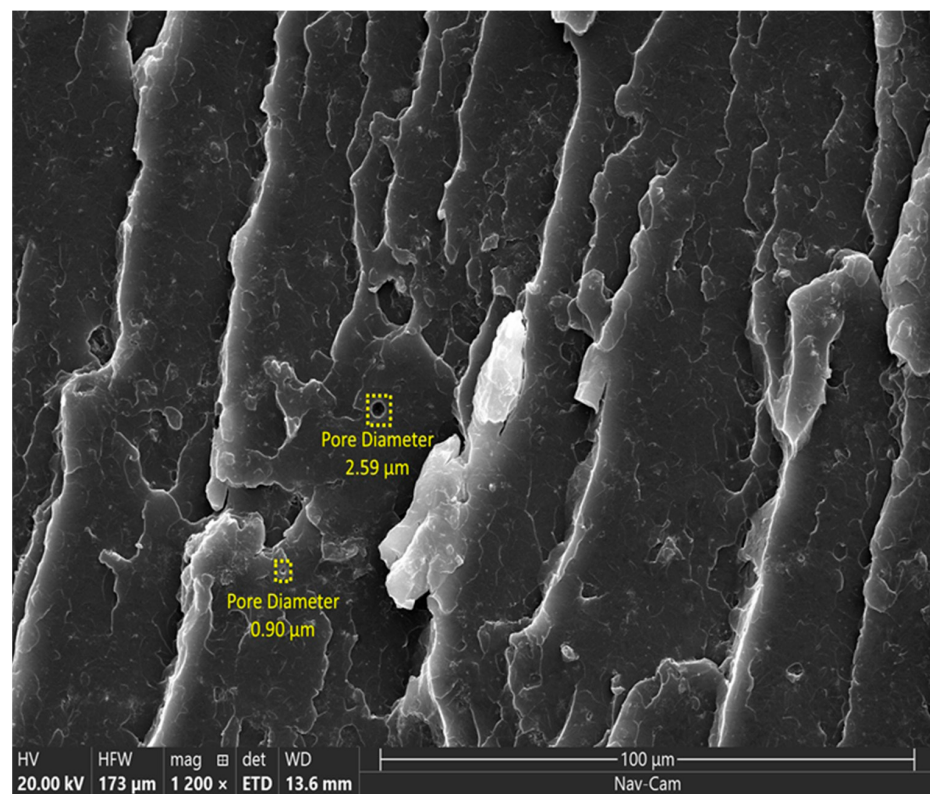
(b)

Figure 17. Cont.



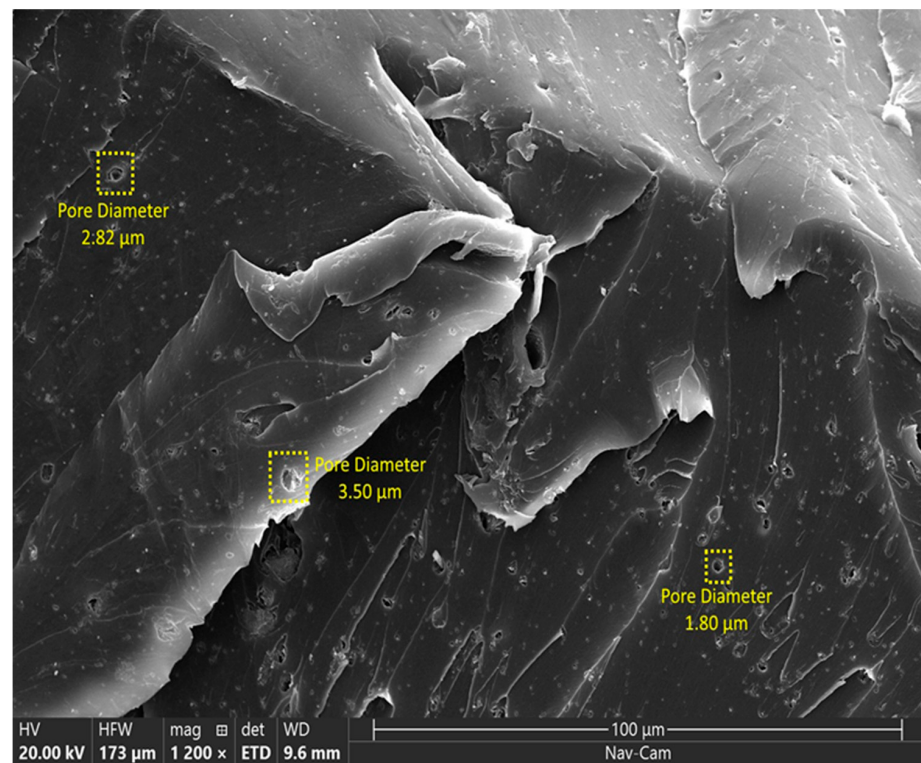
(c)

Figure 17. Surface punctures: (a) 1200 $\times$ magnified unaged neat heat-cured specimen. (b) 1500 $\times$ magnified Phase 1 neat heat-cured specimen. (c) 1500 $\times$ magnified Phase 2 neat heat-cured specimen.

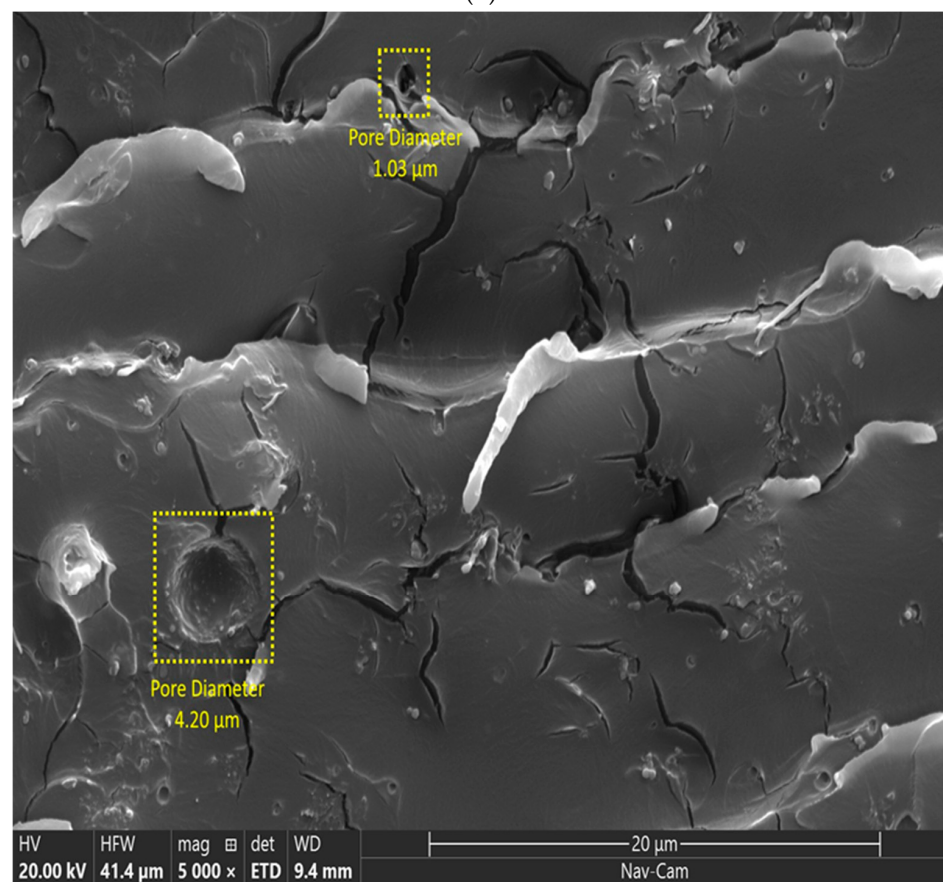


(a)

Figure 18. *Cont.*



(b)

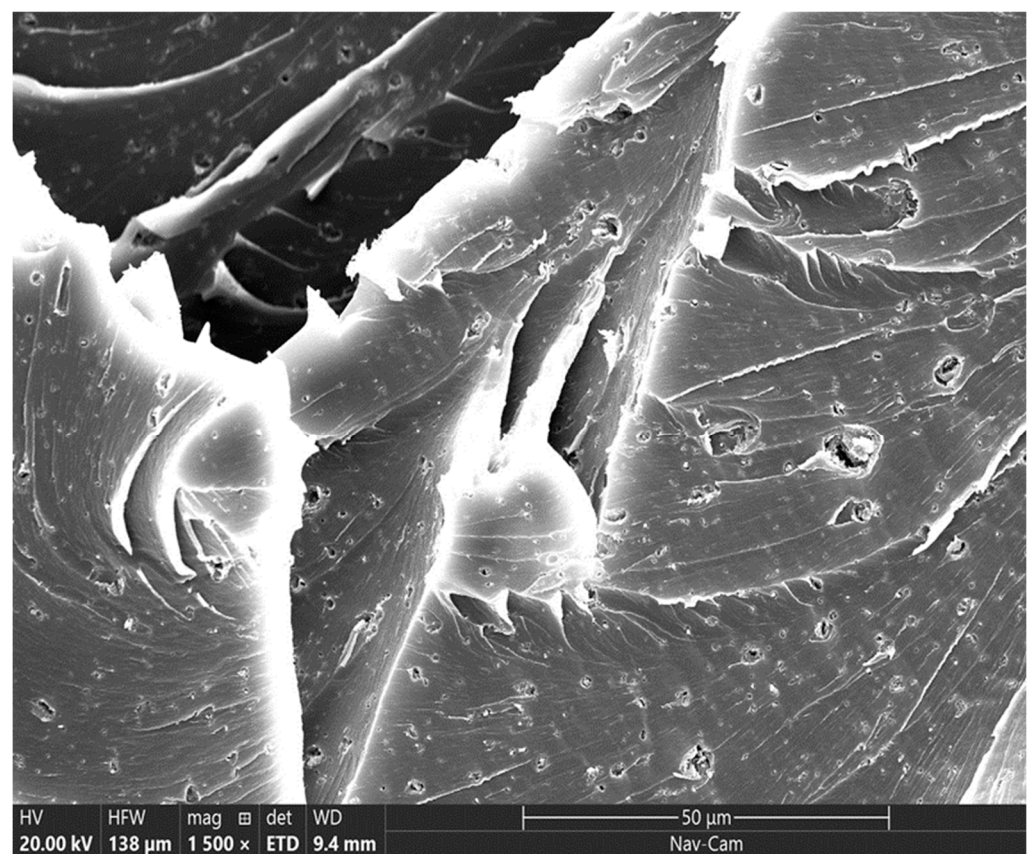


(c)

Figure 18. Surface puncture: (a) 1200× magnified Phase 0 MWCNT-reinforced heat-cured specimen. (b) 1200× magnified Phase 1 MWCNT-reinforced heat-cured specimen. (c) 1200× magnified Phase 2 MWCNT-reinforced heat-cured specimen.

3.3. Neat vs. MWCNT-Reinforced Specimens

The proper comparison between neat and MWCNT-reinforced Phase 2 specimens is shown in Figure 19b. The neat Phase 2 specimens have multiple punctures on the surface, which might be due to the deterioration that can occur after aging in the sulfate solution. However, the Phase 2 reinforced specimens shown in Figure 19b have significant salt deposition and crack propagation, which is a clear sign of the degradation of the specimen. The images of the reinforced specimens were taken at the edge of the specimen, where significant salt deposition is observed. Surface punctures can also be observed on the neat specimens, while none are observed on the MWCNT-reinforced specimens, suggesting that the MWCNTs reduce deterioration. Early in the exposure period, the neat epoxy shows rapid surface deterioration and puncture damage, which could enable the deposited salts to be removed or washed away with further immersion, especially in places with significant material loss. Over time, even when internal deterioration persists, this may lead to a decreased surface concentration of salts. The MWCNT-reinforced samples, on the other hand, show enhanced structural cohesiveness because of crack-bridging effects, which preserve surface integrity. Because of the comparatively intact matrix, which permits more consistent deposition without major loss or delamination, these samples may consequently experience gradual salt accumulation on their surface.



(a)

Figure 19. Cont.

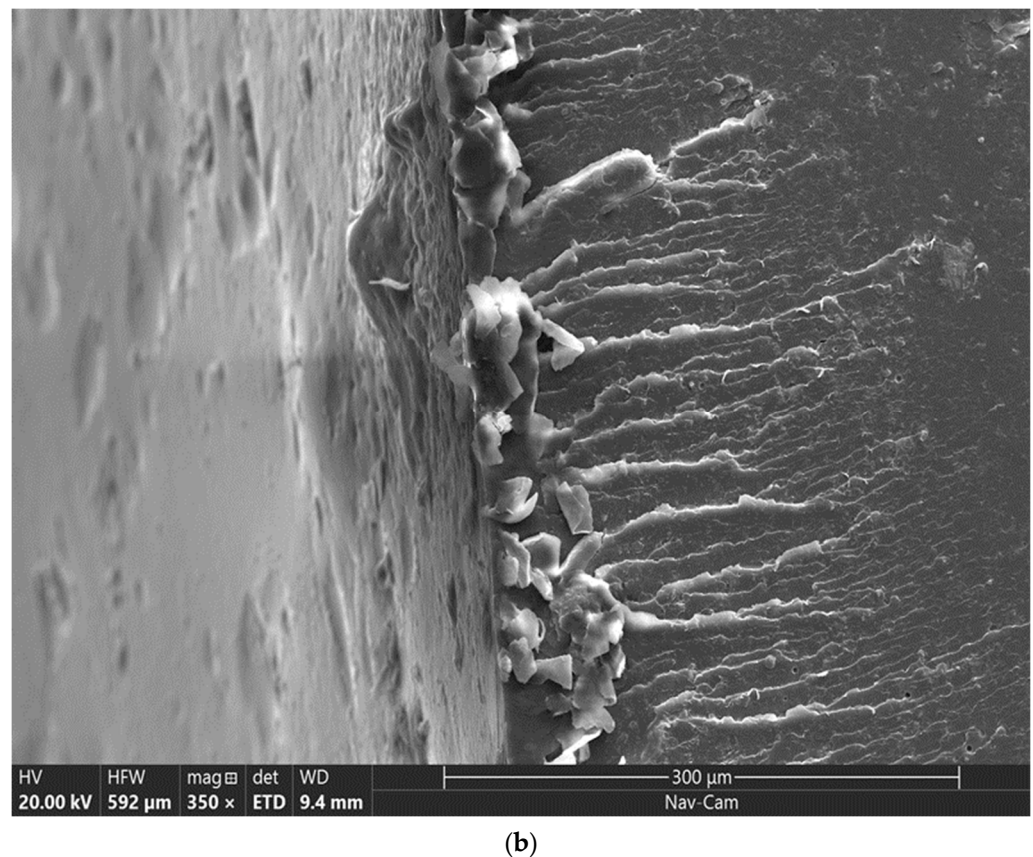


Figure 19. Phase 0 neat vs. MWCNT-reinforced specimens comparison: (a) Phase 2 neat. (b) Phase 2 MWCNT-reinforced specimens.

4. Conclusions

It can be concluded from the results and discussion that the epoxy resin specimens exhibit corrosion due to acid reactions. This is a clear sign of the degradation of the specimens due to the harsh environments they were in. The Phase 1 and Phase 2 specimens underwent significant changes. The Phase 1 specimens were observed to have larger salt depositions ($15\text{ }\mu\text{m}$) on the surface. The Phase 2 specimens were shown to exhibit a decrease in the deposited salt sizes down to $1\text{ }\mu\text{m}$, with punctures taking their place. Additionally, the Phase 1 reinforced specimens' salt deposition sizes were comparatively low at $0.1\text{ }\mu\text{m}$, as compared to $20\text{ }\mu\text{m}$ on the Phase 2 specimens. This result was validated using EDS, which showed 2.7% of Na, 5.1% of S, and 24.7% of O_2 , indicating the presence of Na_2SO_4 . A significant percentage of oxygen was discovered. The presence of oxygen might be due to the oxidation of the epoxy matrix (contamination/absorbed moisture); it might also be because of the limitations of EDS, where light elements such as oxygen can be overestimated due to poor background subtraction due to rough or porous regions.

There was also considerable crack propagation in the reinforced aged specimens. The neat specimens, however, did not exhibit noticeable crack degradations throughout the aging process. Phase 2 cracks show much longer propagation lengths and wider cracks when compared to Phase 1. MWCNT reinforcement may have caused crack bridging, evidenced by the cracks propagating outward at the edge of the cracks rather than widening further. As the samples progressed through the aging process, punctures grew, and the edges of these punctures were observed to be rougher and sharper. Acidic deterioration is the most likely cause of this progressive worsening and widening of punctures, as well as the presence of salt crystals in larger pores, indicating sulfate salt deposition within the specimen. Neat specimens had surface puncture diameters less than $0.6\text{ }\mu\text{m}$ for Phase 0,

2.0 μm for Phase 1, and 4.0 μm for Phase 2. However, the case was slightly different for the MWCNT-reinforced specimens, likely due to the MWCNT mitigating puncture growth and causing microcrack propagation from the punctures instead. All the numerical results are summarized in Table 1 below.

Table 1. Summary of results for neat vs. reinforced specimens.

Phase 1		Phase 2	Remarks
Salt crystals			
Neat	Significant (15 ± 5.77) μm dia	Low (1 ± 0.24) μm dia	Salt crystals decreased in size 15 times
Reinforced	Very Low (0.1 ± 0.003) μm dia	Significant (20 ± 3.26) μm dia	Salt crystals increased in size by 200 times
Crack degradation			
Neat	-	-	No significant cracks
Reinforced	Width of (0.03 ± 0) μm	Width of (0.24 ± 0.01) μm	Cracks increased 5 times in length and 8 times in width
Puncture degradation			
Neat	(2 ± 0.96) μm dia	(4 ± 2.8) μm dia	Size of punctures increased by 2 times
Reinforced	(1.5 to 3.5) μm dia	(1 to 4.5) μm dia	Size of punctures remained almost stagnant

With regards to general deterioration, it can be concluded that wider punctures on the neat specimens were not present in the MWCNT-reinforced specimens, due to the crack bridging capabilities of CNTs, as verified in a previous study [35]. Moreover, the authors of [36] explained that the processing of long, aligned CNTs remains the main barrier in bridging to achieve major fracture toughness enhancement. Similarly, the authors of [37] explained that long aligned MWCNTs with small diameters (i.e., a high aspect ratio) are recommended for use in the reinforcement of FRP composites in order to obtain superior fracture resistance toward initiated cracks. All of these claims confirm the results presented in our study. The neat specimens underwent more deterioration due to an acidic environment, as compared to the MWCNT reinforced specimens, where cracks were narrower; this is also verified elsewhere [38]. Hence, CNTs behave differently when an acidic environment is caused by sulfates, which become attached to the polymer chains of epoxy. This is shown by the punctures, which remained stagnant throughout the 30 days from Phase 1 to 2; the width of the cracks increased, but the CNT tried to prevent the crack increment due to its bridging capabilities. The table shows the summary of the specimens and outcomes.

In terms of recommendations for future research, studies could explore the specimens that are reinforced with MWCNTs and examine the effects of these different CNTs, observing the property changes under SEM; this would further extend the applicability of MWCNT in infrastructure rehabilitation. FTIR spectra of both pure MWCNTs-COOH and MWCNT-reinforced epoxy composites will also be included.

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