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**Research Paper / Makale**

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**Seawater Durability of Nano-Montmorillonite Modified Single-Lap Joining Epoxy Composite Laminates**

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**Abstract:** The objective of this study was to investigate of nano-montmorillonite modified epoxy composite single-lap bonded joints, after being exposed to seawater immersion in order to understand the effect of seawater environment on their performance. To prepare the nano adhesives, nano montmorillonite (2 wt %) was incorporated into epoxy resin. Composite bonded specimens which manufactured with VARIM (Vacuum Assisted Resin Infusion Method) were prepared accordance with ASTM D5868-01 and immersed in seawater for 6 months. As a result of seawater immersion, considerable reductions were observed in the adhesives performance. However, the properties of 2 wt% nano montmorillonite/epoxy adhesives were observed that the performance changed less after exposing to seawater. Scanning electron microscope (SEM) and optical microscope were used to investigate the microstructures of the damage surfaces.

**Keywords:** Seawater, nano-montmorillonite, nano adhesives, epoxy, composite

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**Nano-Montmorillonit Modifiyeli Tek Taraflı Bindirme Bağlantılısıyla Birleştirilmiş Tabakalı Kompozitlerin Deniz Suyuna Dayanıklılığı**

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**Özet:** Bu çalışmanın amacı, deniz suyunun nano-montmorillonit modifiyeli epoksi yapıştırıcı ile birleştirilmiş kompozit tek taraflı bindirme bağlantılarının performansına etkisinin incelenmesidir. Nano yapıştırıcıları hazırlamak için epoksi reçinesine ağırlıkça % 2 nano montmorillonit ilave edilmiştir. VARIM (Vakumlu Destekli Reçine İnfüzyon Metodu) ile üretilen kompozit numuneler ASTM D5868-01 standartına göre yapıştırılmış ve 6 ay süreyle deniz suyuna daldırılmıştır. Deniz suyuna daldırmanın sonucunda yapıştırma bağlantılarının performansında önemli ölçüde bir azalma gözlenmiştir. Bununla birlikte, ağırlıkça % 2 nano montmorillonit / epoksi yapıştırıcıların özellikleri, deniz suyuna daldırmadan sonrada daha iyi geldiği gözlenmiştir. Hasar yüzeylerinin mikroyapılarını incelemek için taramalı elektron mikroskopu (SEM) ve optik mikroskop kullanılmıştır.

**Anahtar kelimeler:** Deniz suyu; nano-montmorillonite; nano yapıştırıcı; epoksi; kompozit

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## 1. Introduction

Nowadays polymer composites have been traditionally employed for marine applications due to its superior specific properties. The rapidly increasing uses of composites in marine environment lead a need for enhanced composite adherents. Adhesive joints offer advantages such as reduction of corrosion, more uniform stress distribution cheap, fast and robust joining [1, 2]. However, its use is limited restriction for many applications due to the resist under aggressive environments. Adhesive joints' may weaken both the physical or chemical

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properties and the interface between the adhesive under moisture presence [2]. Considering the strength of adhesive joints in these conditions, studies show that the joint strength can considerably be decreased as a function of exposed time [3]. At room temperature nearly no effect was seen up to 15 days. However, after this duration, the adhesive strength decreased about 30% up to 45 days [4]. Therefore, this work intends to enhance the durability of adhesive joints under seawater environments during short-term immersion.

## 2. Experimental

Epoxy resin and curing agent (MGS® L 160 and MGS® H 160) were supplied by Momentive Hexion Inc. A commercial grade of nano- montmorillonite (nano-MMT) was provided by ESAN Eczacibasi. Carbon fiber fabric and the all other vacuum infusion equipments were provided by Dost Kimya Inc. The area density of carbon fiber was  $300 \text{ g/m}^2$  and each bundle consisted of 12K filament. Carbon fiber reinforced epoxy matrix laminated composite panel was prepared by means of VARTM [5, 6]. The laminated composites were cut according to recommended dimension ( $100 \text{ mm} \times 25 \text{ mm} \times 3 \text{ mm}$ ) as indicated Standard Test Method for Lap Shear Adhesion for Fiber Reinforced Plastic Bonding (ASTM D5868-01) standards to prepare adherent materials.

The SEM image of the nano-MMT which used in this study is shown in Fig. 1. Nano-MMT was incorporated at concentrations 2 wt% relatively to the epoxy resin according to the identified optimal particle ratio in previous studies [7]. Prepared mixture was mixed via ultrasonicator for 30 min and degassed in a vacuum oven  $25 \text{ }^\circ\text{C}/0.6 \text{ bar}$  for 20 min.

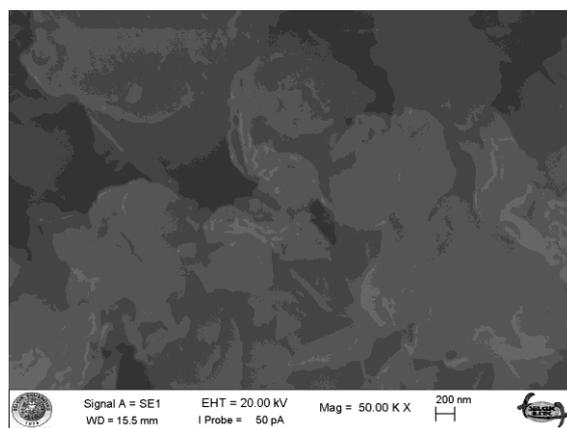


Figure. 1. SEM image of the nano-MMT

Firstly adhesive areas were signed as  $25 \text{ mm} \times 25 \text{ mm}$  and abraded with silicon carbide paper to roughen the adhesive surfaces. The image of the sanded samples was given in Fig. 2.a. Then specimens immersed in acetone to remove any dust and dry at  $35 \text{ }^\circ\text{C}$  for 10 min.

Then the hardening agent was added into the mixture according to supplier instructions. The prepared adhesives were glair on the sanded surface and then it was kept until become gelate form.

Drying these adherents and after prepared adhesives become gelate form, laminated composite specimens were joined. Alignment tabs, which were made of the laminated composite, were also bonded to the heading parts of adherents with epoxy adhesive. Pressed down via clamp after assembly, the specimens were cured in the vacuum oven  $100 \text{ }^\circ\text{C}$  for 3 h.

The composite panels were immersed in a large tank room temperature for 6 months. The tank was containing natural seawater with a salinity content of about 2.2%. The seawater in the tank was renewed about every month. All specimens were tested using an Instron 8801 testing machine at room temperature. The crosshead-loading rate was adjusted as 1 mm/min.

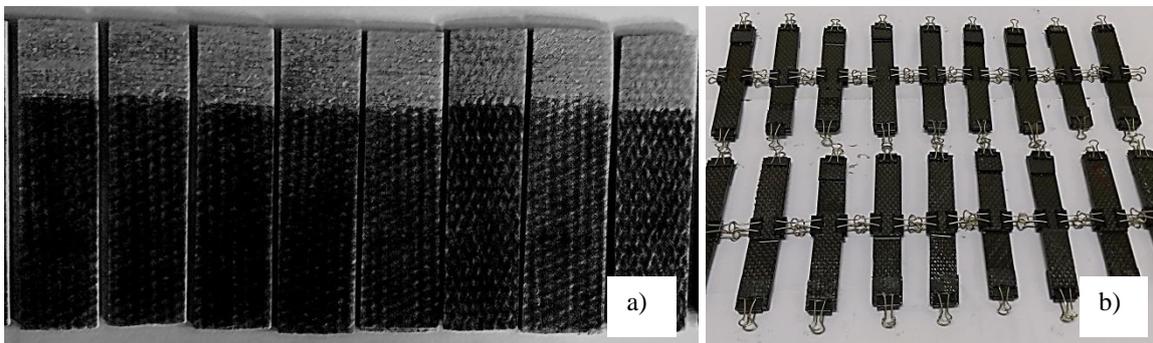


Figure. 2. (a) Image of sanded laminated samples, (b) Single lap joining of composite laminates

### 3. Results and Discussion

Figure 3 shows that load and strain curves of single lap specimens in both dry and wet conditions. In general, it can be seen that seawater absorption has a negative effect on adhesive performance. Shear load of unmodified epoxy and nano-MMT modified epoxy based adhesives decreases after subjecting to seawater compared to dry specimens. This degradation in adhesives strength can be attributed to the plasticization effect of seawater absorption in epoxy adhesives. This can cause drop in the interfacial strength between the adhesive and resulting in performance reduction of adhesives.

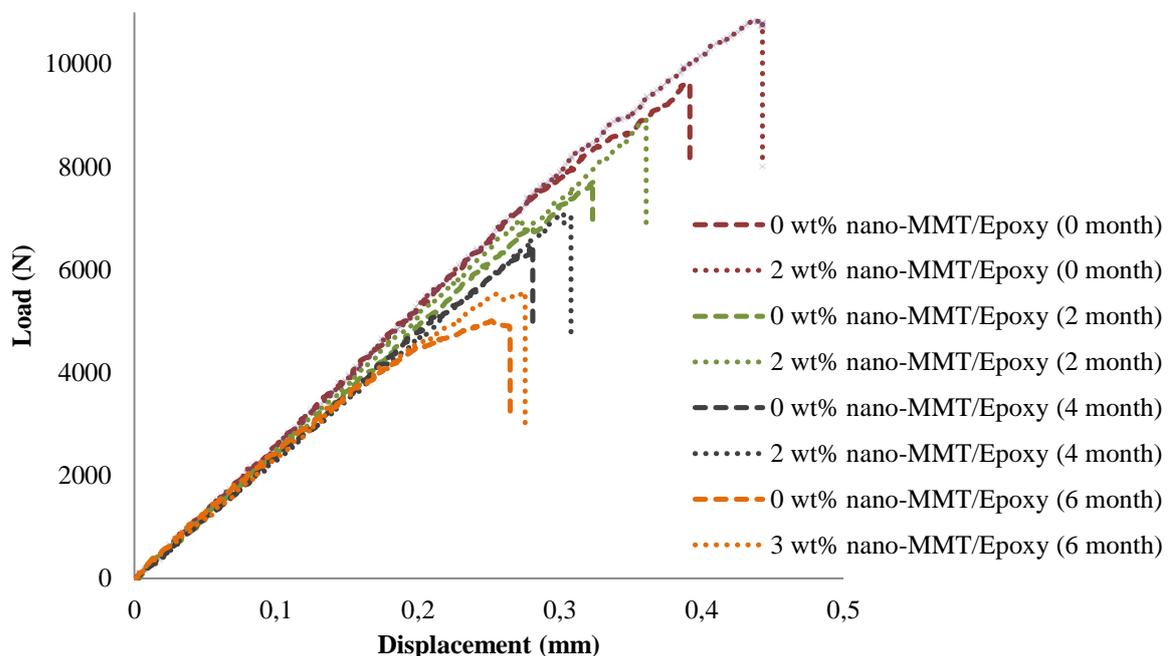


Figure. 3. Load–displacement curves for seawater immersed epoxy joining

The fluctuation in force and displacement values of the specimens as a function of immersion time is illustrated in Fig. 4. Similar to the tendency of load values, there is a degradation in displacement values after the immersion in sea water. It shows in the figure that the load carrying and elongation capability of adhesives decreases with increasing immersion time. In general, considering the effect of water conditioning on the properties of the epoxy, it is known

that the displacements are increased [8, 9]. However, there are studies in which water absorption has a negative effect on elongation [10]. Seawater molecules thought to be act as a canker in composite joining, leading to a decrease in adhesive properties, which results in occurs in lower strain.

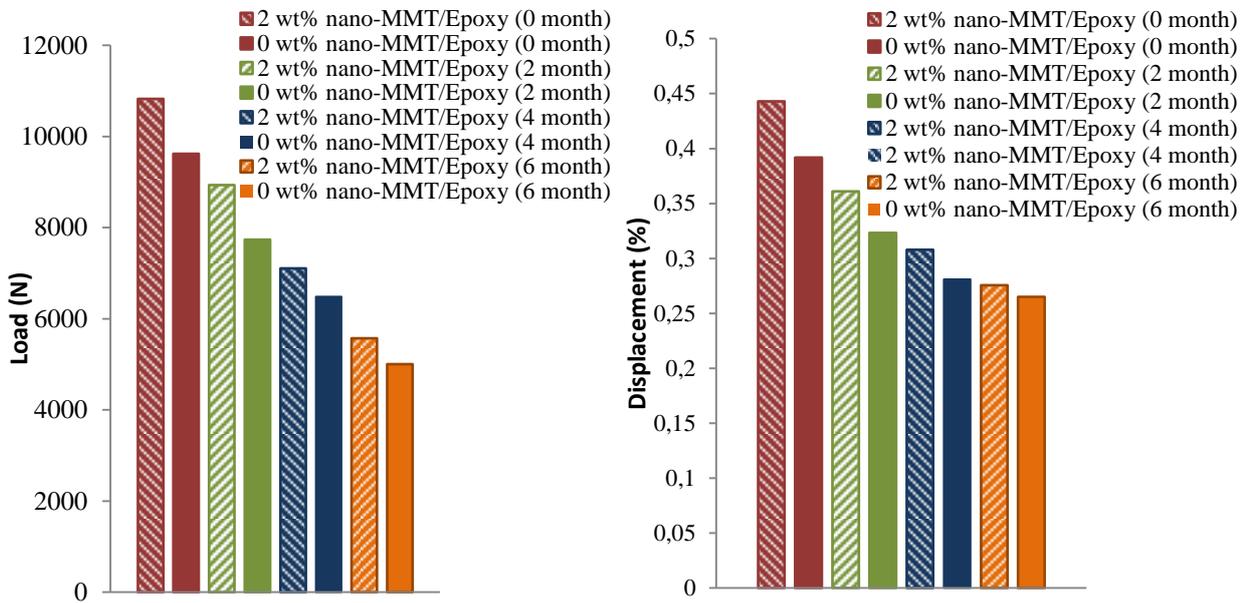


Figure. 4. Single lap joint test results of seawater-treated samples;  
 a) Load variation graphs, b) Displacement variation graphs

Fracture surfaces of seawater exposed neat and modified epoxy adhesives are given in Fig.5. It is seen that in Fig 5.a, there is more micro-void formation due to seawater absorption. This is a directly effect on the load carrying capacity of adhesives. During seawater immersion, some ions can penetrate into the epoxy through voids and react with the resin and/or fiber. As a result, the microstructure is changed and the cracks are consequently formed. This implies that the bonding effect of the epoxy on the fibers has been greatly reduced [11]. It can be seen in these figures, it is thought the improvement in water barrier properties enhanced owing to presence of the nano MMT particles. It is believed that nano-MMT reduces the water absorption in epoxy.

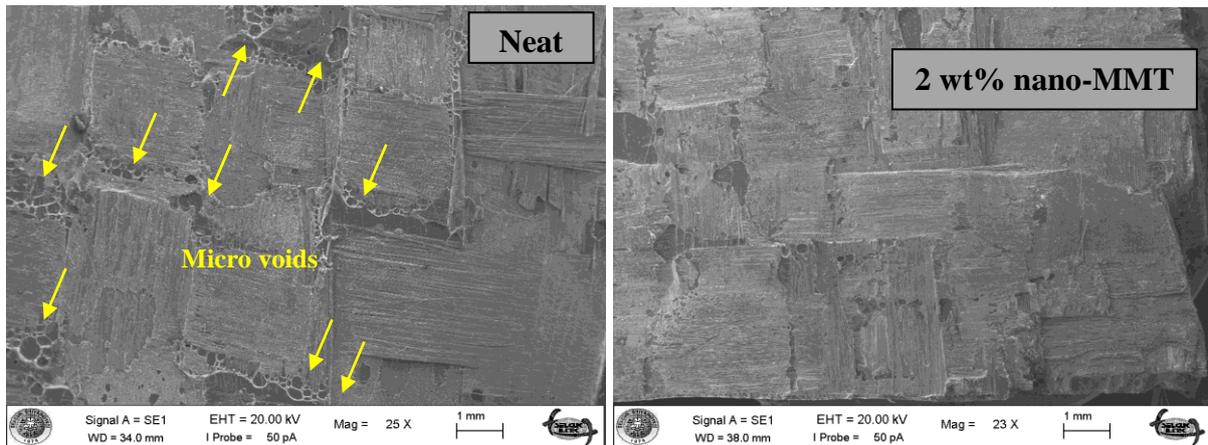


Figure.5. Fracture surface SEM images of epoxy adhesives after 6 months seawater immersed

Optical images of the tested samples at the end of each period are as shown in Fig. 7. Considerable diversity is observed on fracture surface morphology after seawater immersion. The rich epoxy coatings on the surfaces are an indication that the separation or crack propagation does

not progress in the epoxy adhesive (after 2 months). In addition, at the end of 4 and 6 months, the increase in the surface porosity is also noticeable. The increase in porosity in the adhesive layer also accounts for the decrease in adhesion strength. For the immersed joining, all their fracture surfaces show micro cracks, indicating the degradation of the adhesive surface after short term immersion. Those cracks served as paths for the penetration of seawater into the composite which weaken the adhesive and adherent's interfacial bonding [10].

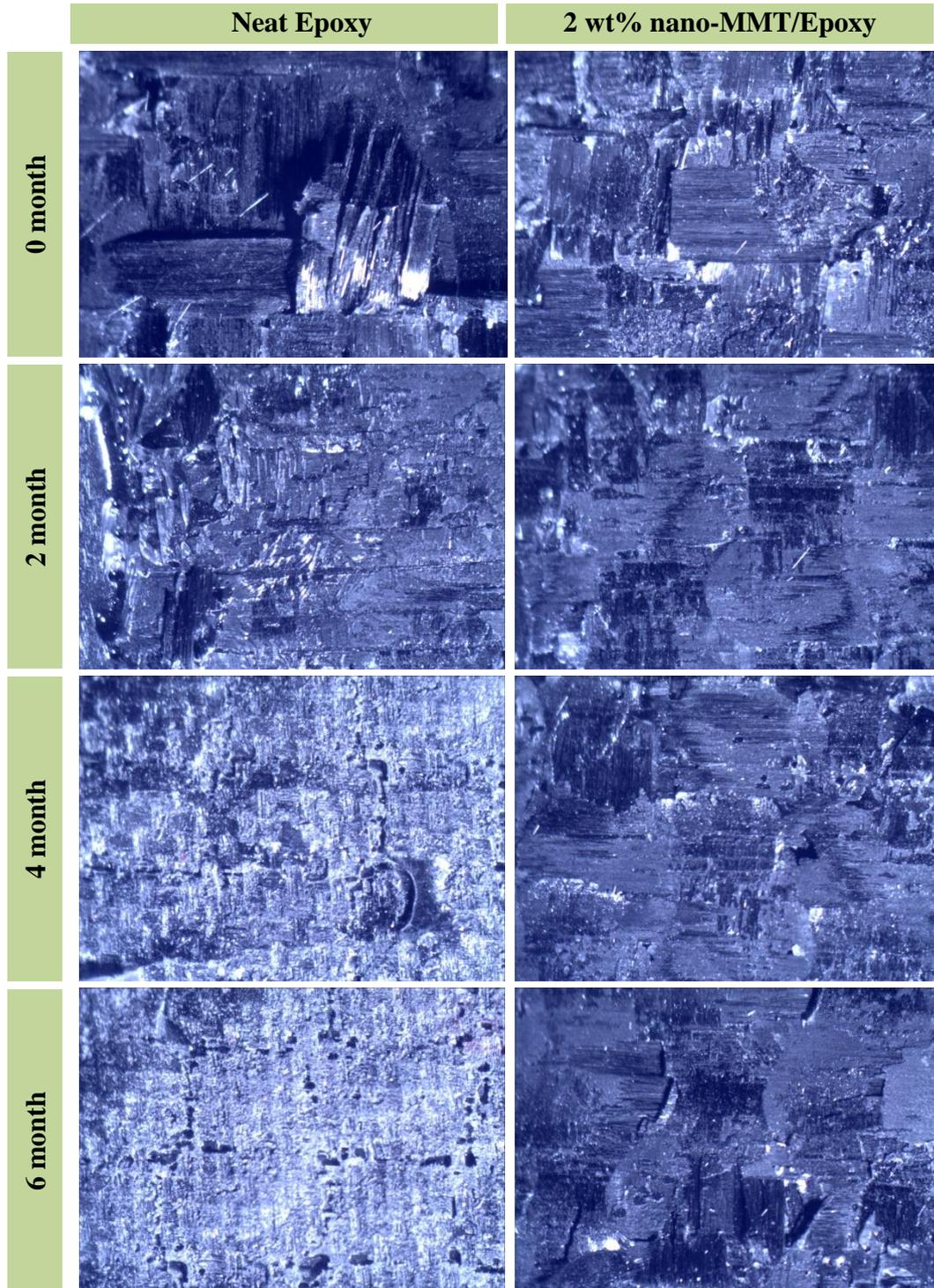


Figure. 6. Optical microscopy images of epoxy adhesives fracture surface

#### 4. Conclusion

In this study, the degradation of adhesive joining of carbon fiber reinforced epoxy composites used for engineering applications was investigated by seawater treated conditions for 6 months. Seawater treatment led to micro void formation of the adhesive surface after the short-term immersion. It was shown that the adhesive performance of carbon fiber reinforced composites shortened dramatically due to seawater exposure. Seawater immersion resulted in severe degradation in the load and elongation properties of the adhesives. It has also been clearly demonstrated that the addition of 2 wt% nano-MMT to epoxy resin, lead to significant increases on the failure load of the adhesive. SEM images clearly show the difference in modified and unmodified epoxy adhesives interfaces. The modified adhesives had good adherents/adhesive interfacial bond while the immersed specimens experienced degradation in interfacial bonding.

#### References

- [1] Pereira, A., et al., Effect of saline environment on mechanical properties of adhesive joints. *International Journal of Adhesion and Adhesives*, 2013. **47**: p. 99-104.
- [2] Banea, M., et al., Effects of temperature and loading rate on the mechanical properties of a high temperature epoxy adhesive. *Journal of Adhesion Science and Technology*, 2011. **25**(18): p. 2461-2474.
- [3] Zhang, F., et al., Durability of adhesively-bonded single lap–shear joints in accelerated hygrothermal exposure for automotive applications. *International Journal of Adhesion and Adhesives*, 2013. **44**: p. 130-137.
- [4] Ashcroft, I., et al., The effect of environment on the fatigue of bonded composite joints. Part 1: testing and fractography. *Composites Part A: Applied Science and Manufacturing*, 2001. **32**(1): p. 45-58.
- [5] Ulus, H., et al., Low-velocity impact behavior of carbon fiber/epoxy multiscale hybrid nanocomposites reinforced with multiwalled carbon nanotubes and boron nitride nanoplates. *Journal of Composite Materials*, 2016. **50**(6): p. 761-770.
- [6] Ulus, H., Ö.S. Şahin, and A. Avci, Enhancement of flexural and shear properties of carbon fiber/epoxy hybrid nanocomposites by boron nitride nano particles and carbon nano tube modification. *Fibers and Polymers*, 2015. **16**(12): p. 2627-2635.
- [7] Ulus, H., Kaybal, K., Demir, O., Tatar A.C., Senyurt, M.A., Avci, A., Improvement in Adhesive Performance of Single-Lap Joining Composite Laminates by Using Nano-Montmorillonite Modified Epoxy. *El-Cezerî Journal of Science and Engineering*.
- [8] Alamri, H. and I.M. Low, Effect of water absorption on the mechanical properties of nano-filler reinforced epoxy nanocomposites. *Materials & Design*, 2012. **42**: p. 214-222.
- [9] Sala, G., Composite degradation due to fluid absorption. *Composites Part B: Engineering*, 2000. **31**(5): p. 357-373.
- [10] Yan, L. and N. Chouw, Effect of water, seawater and alkaline solution ageing on mechanical properties of flax fabric/epoxy composites used for civil engineering applications. *Construction and Building Materials*, 2015. **99**: p. 118-127.
- [11] Wei, B., H. Cao, and S. Song, Degradation of basalt fibre and glass fibre/epoxy resin composites in seawater. *Corrosion Science*, 2011. **53**(1): p. 426-431.