Effect of Sea Water on Mechanical Properties of Composite Adhesive Joints Under Different Temperature Environments

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Abstract: - Glass fiber reinforced polymers (GFRP) are widely used in various industrial and structural applications because of their high strength-to-weight ratio, design flexibility, and better insulating properties. Adhesive bonding has emerged as a popular joining process for GFRP structures, offering advantages such as economical fabrication cost, reduced structural weight, and enhanced damage resistance. However, the long-term performance and durability of adhesive bonded joints under static and cyclic loads remain a concern. This study aims to investigate the effect of sea water exposure on the mechanical properties of adhesive joints in glass fiber reinforced polymer structures. The degradation of adhesive joints over time and under different environmental conditions, particularly temperature variations, is also examined. The study focuses on epoxy and polyester adhesives, which are commonly used in GFRP applications. Glass fiber reinforced polymer specimens are prepared using the hand layup method, with glass fibers as reinforcement and epoxy or polyester as the resin. The adhesive materials are blended with the appropriate ratios of resin and hardener, and the curing process is carried out under specific loading conditions at room temperature. Unidirectional glass fiber sheets are used to prepare laminates, and a lower viscosity epoxy curing agent is employed. The mechanical properties of the adhesive joints are evaluated and compared over time and under different temperature environments. The study aims to contribute to a better understanding of the degradation mechanisms and long-term behavior of adhesive joints in GFRP structures exposed to sea water.

Keywords: *composites; GFRP; mechanical properties; adhesives; polymers.*

1. Introduction

The Glass fiber reinforced polymers (GFRP) are used in many industrial and strutural applications because of its high strength to weight ratio. Many other advantages are avoiding of welding, design flexibility, and better insulating properties [1]. Adhesive bonding is a joining process in which two surfaces are joined using an adherent. These joints are becoming great alternatives for mechanical joints concerned with engineering applications [2]. Many other advantages of using adhesive joints are economical fabrication cost, lower structural weight and enhanced damage resistance. The application of such adhesive joints has increased drastically in engineering structures and industries recently [3]. Traditional methods like fasteners and all use to cut the fibers and induce stress concentration in the GFRP structures leading to reduced structural integrity for these reasons adhesively bonded joints have taken over many applications in the field of aeronautics, industries, automotive, electronics, sports and packaging [4].

These adhesive bonded joints must uphold the strength when exposed more to static and cyclic loads for considerable duration of time, without affecting the load carrying capacity of the structures. Still because of deficiency of relevant material model and analysis, composite structures are over-designed [5]. Adhesive bonded structures mainly at primary load bearing applications are mechanically fastened as an enhanced safety precaution. This type of design increase manufacturing costs. The development of still more refined design and predictive methodologies are required for better usage of composites in engineering structures [6, 7].

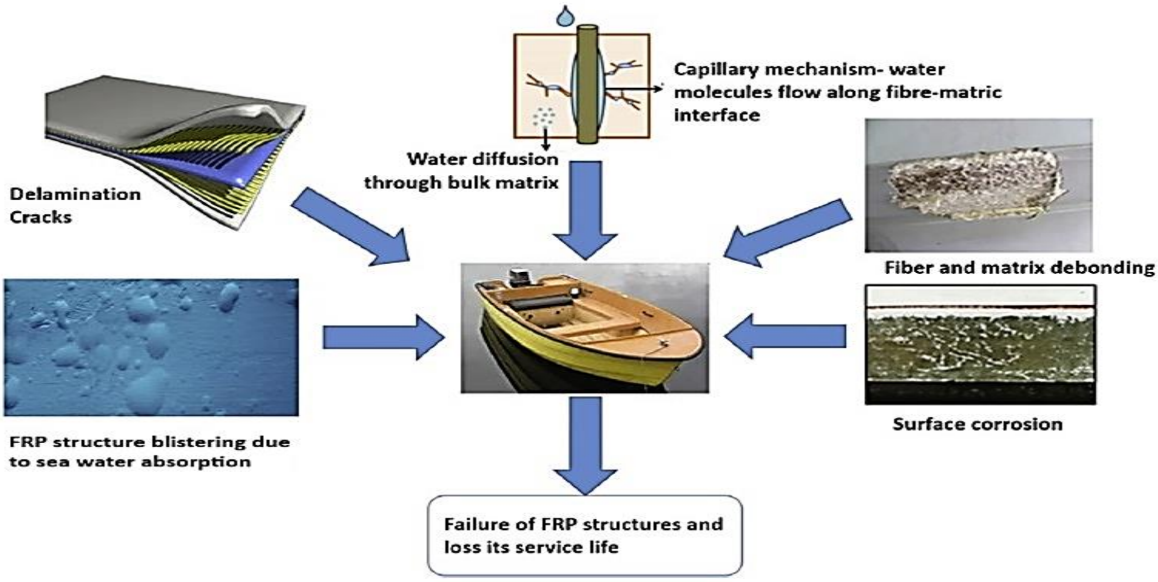

Figure 1. Effect of sea water on marine structures [8]

The structural composites material made up of adhesive joints are widely used in marine environments. These marine applications include pipelines, underwater structures, offshore structures, concrete structure coatings, ship body structures etc. [9]. In these conditions degradation is major problem of adhesives and adherents in composite material structures [10]. This degradation of composite adhesive joints leads to deterioration of mechanical properties of structures and leading to failure [11]. Even water and vapor are the most common influencing agents for the deterioration of mechanical strength among structures. [12].

Many composite adhesive joints are exposed to sea water with relatively high humid atmosphere. The mechanical behavior of adhesives is completely influenced by the surrounding temperature and humidity [13]. These properties also change with respect to time mainly when exposed to changing environments in a larger period of time [14]. These in-turn makes need for study of degradation effecting mechanical properties under different environmental conditions [15]. Many researchers have studied the degradation of structural adhesives in air and conclude that photo-oxidation influences degradation [16]. Studies also carried out on degradation with epoxy resin [17] and polyurethane [18]. Many studies are being carried out on durability of polymeric adhesives influenced by various processes in sea water atmosphere [19]. Among these, swelling, hydrolysis and plasticization are considered which in-turn reduces the joint strength [20]. Bulk modulus of natural elastomers, polyurethanes after aging for around 2 years is also studied [21, 22]. Polymeric adhesive joints degradation with respect to time (viscoelastic behavior) and different environmental conditions is needed for better prediction of life of composite structures [23, 24].

Operating temperature plays a vital role in the adhesive joint, because each and every component used in joints gets affected by temperature. Study shows that joints strength depends on co-efficient of thermal expansion, cure shrinkage of adhesive and properties of the adhesive & adherend [25]. Another study also shows that the viscosity of adhesive also depends on operating temperature. [26]. It is also revealed that adhesive material shows brittle behaviour at lower temperature and ductile at higher temperature [27]. Always for polymeric adhesives, using them at higher temperatures reduces strength because of increase in molecular mobility [28].

Hence it all depends on glass transition temperature (Tg) of a given adhesive. Above this temperature, there will be an irregular response of viscoelastic property & difficult to predict the material behaviour [29].

The structures present in marine atmosphere face high humidity, salt water & variation in temperature which hampers their performance. In adhesive bonded joints, the mechanical properties are mainly affecting by degradation of adhesives, adherends & interface of them [30]. Besides moisture, salinity also has a major effect on adhesive joints. Several authors have shown that prediction of aging of adhesive joints because of the effect if saline water is very helpful to schedule regular repair and maintenance of the structures.

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2. Objectives

The objectives of the present research are as follows,

- To study the effect of sea water on glass fiber reinforced polymer adhesive joints.
- To study the mechanical properties of adhesive joints with respect to time period of degradation.
- To study the effect of different temperature environments on mechanical properties of composite adhesive joints.

3. Materials and Methods

The unidirectional glass fabric with 360 g/m2 was used as the reinforcement, which was supplied by Mark-Tech Private limited, Bangalore. The epoxy resin (Lepox-12) and hardener (K-6) were supplied by Supplied by Atul in-dustries Ltd, Gujarat, India. The polyester resin and catalyst were supplied by ARP composites, Karnataka, India. The physical and mechanical properties of the fiber and matrix are listed in Table 1. In this study, composite laminates are prepared using a hand layup technique with a stacking sequence of 0^0. Further, the manufactured laminates are cured at room temperature for an about 48 hours. The tensile, flexural, and shear test samples were cut from base laminate according to the dimensions given in ASTM standards [31] using a diamond saw cutter.

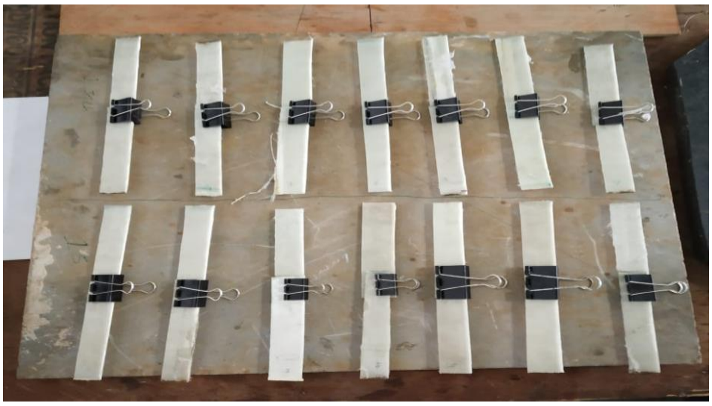

Figure 2. Adhesive joint Specimens.

Table 1. Properties of epoxy and polyester.

Property	Fiber	Epoxy	Polyester
Viscosity at 25°C μ (cP)	--	12000-13000	250-350
Density ρ (g.cm-3)	--	1.16	1.09
Heat distortion tempreture (°C)	---	100	85
Modulus of elasticity E (Gpa)	78	5.0	3.3
Tensile strength (MPa)	2000	73	40
Maximum elongation (%)	4.8	4	1

3.1. Materials and Methods

Glass fiber single lap adhesive joints are prepared by following steps

- Composite laminates are prepared using hand layup method by placing glass fiber sheets resin layer alternatively until required thickness is obtained.
- These laminates are cured in room temperature.
- According to standards these laminates are cut with required size and strips are prepared.
- Taking these laminate strips of 130mm length and 20mm width, single lap joints are prepared with overlap length of 50.8mm.
- Two types of adhesives are used for joints i.e. epoxy and polyester.

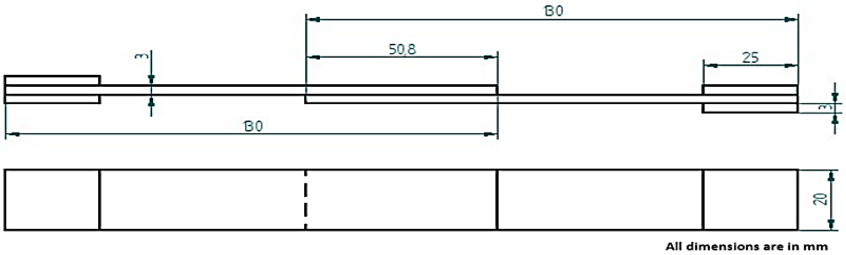

Figure 3. ASTM 5868-01 Bonded joint specimen.

3.2. Water Treatment

In a large glass container natural sea water (sampled from sea shore of panaji, goa) is taken and the specimens are placed inside them. The pH of water measured was 7.6. The periods for the specimens to be placed in container based on literature review are 30 days, 60 days, 90 days and 120 days. Processing of these specimens was carried out at three different temperatures of room temperature i.e. 270 C, below room temperature at 30 to 50 C and above room temperature at 500 to 550C. These temperatures are considered based on global sea water temperature ranges. Temperature of the water is maintained consistently in said range.

Figure 4. Water treatment of adhesive Joints.

3.3. Testing

The adhesive joint specimens prepared by using epoxy and polyester as adhesives are further taken for testing. For tensile, shear, and bending, Universal Testing Machine was used. Uni-axial tensile load was applied till the failure of specimens and the tensile strength of the specimens was obtained. In the same way, using proper jigs and fixtures, shear and bending test were also carried out and shear strength and bending strength was obtained.

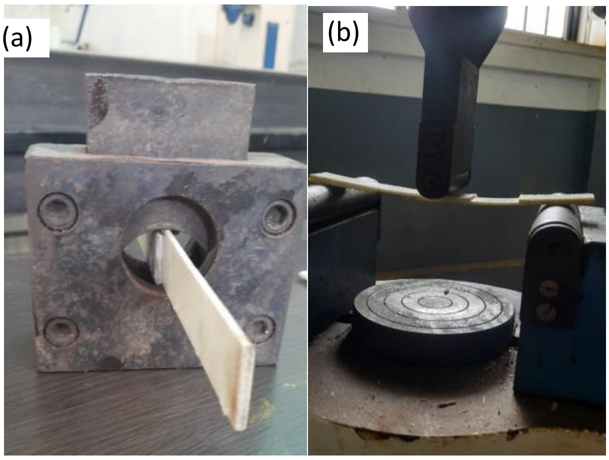

Figure 5. (a) Shear strength testing, (b) Bending strength testing.

4. Results & Discussion

4.1 Epoxy Adhesive joints

Shear, tensile and three point bending strength tests was carried out for Epoxy adhesive joints strips immersed in saline water for different time period of exposures.

Figure, 6 ,7 & 8 shows the effect of saline water on Epoxy adhesive joints tests of glass fiber strips are carried for different time period of exposure and at different temperature conditions. The time period of exposure considered for the tests were 0 days, 30 days, 60 days, 120 & 150 days. The different temperature ranges were at room temperature, below room temperature and above room temperature.

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From the graphs in figures it can be observed that as time period of exposure increases shear, tensile and bending strength of epoxy adhesive joints are decreased. Epoxy adhesives are generally designed to provide strong bonds in dry conditions. When exposed to saline water, the adhesive's properties may deteriorate over time. The water can penetrate the adhesive layer, causing swelling or softening of the adhesive, leading to a decrease in bond strength. Saline water contains dissolved salts that can act as electrolytes, promoting corrosion of metallic substrates. Epoxy resins can undergo hydrolysis, a chemical reaction in the presence of water, which can cause a loss of adhesion. Saline water, with its ionic composition, can facilitate the hydrolysis process and decrease the strength of joints.

Epoxy adhesives and composite materials have different coefficients of thermal expansion. When exposed to higher temperature, the materials expand or contract at different rates. This thermal expansion mismatch can create stress within the joint, potentially leading to debonding or cracking. Elevated temperatures, combined with the presence of saline water, can accelerate the degradation of epoxy adhesives. The heat can increase the rate of chemical reactions, such as hydrolysis or oxidation, leading to a reduction in the adhesive's strength and durability. Epoxy adhesives can soften or lose their structural integrity at elevated temperatures. The increased temperature can cause the adhesive to become more pliable, leading to a decrease in its load-bearing capacity and bond strength. Saline water can act as an electrolyte, facilitating chemical reactions between the adhesive, composite materials, and salts present in the water. Elevated temperatures can accelerate these chemical reactions, potentially leading to the breakdown of the adhesive and weakening of the joint.

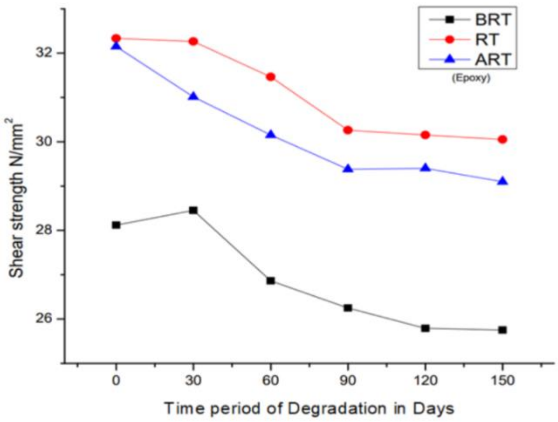

Figure 6. Graphical representation of shear strength of Epoxy adhesive joint w.r.t time period of exposure.

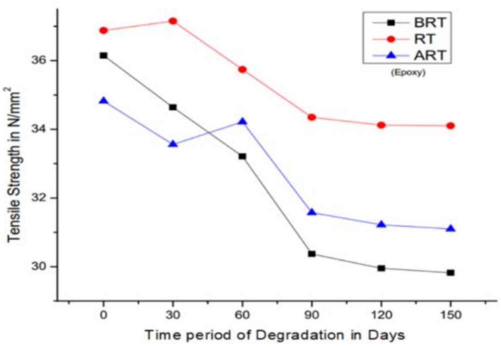

Figure 7. Graphical representation of tensile strength of Epoxy adhesive joint w.r.t time period of exposure.

Cryogenic temperatures can reduce the ductility and toughness of epoxy adhesives. The low temperatures make the adhesive more prone to cracking or fracturing when subjected to mechanical loads or stresses. The low temperatures can cause the adhesive to become more porous, allowing water molecules to penetrate the adhesive more easily. The absorbed water can lead to swelling, softening, and degradation of the adhesive, further weakening the joint.

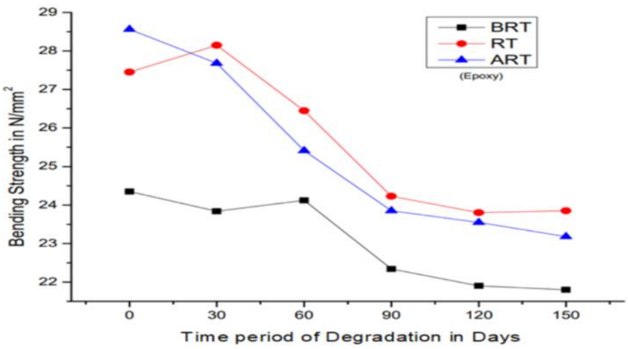

Figure 8. Graphical representation of bending strength of Epoxy adhesive joint w.r.t time period of exposure.

4.2 Ployester Adhesive joints

The graphs in figure 9, 10 & 11 revel that as time period of exposure to saline water environment increases, mechanical strength of polyester adhesive joints will decrease. This may be because of the presence of salts in the water which can interfere with the adhesive's ability to form a strong bond, leading to reduced adhesion strength between the bonded surfaces. These joints can also be susceptible to hydrolysis, which is a chemical reaction with water that can cause a breakdown of the adhesive over time. Saline water, with its ionic composition, can accelerate the hydrolysis process and weaken the adhesive joint. These joints also absorb water from saline environments, causing swelling and softening of the adhesive. This can lead to a decrease in the adhesive's mechanical properties and compromise the overall strength and integrity of the joint. Saline water contains salts that can act as electrolytes, promoting corrosion of metallic substrates.

Elevated temperatures in a saline water environment can lead to a reduction in the bond strength of polyester adhesive joints. The presence of salts in the water can interfere with the adhesive's ability to form a strong bond between the substrates. Additionally, increased temperature can soften the adhesive, further compromising its load-bearing capacity and bond strength. The high temperature can accelerate chemical reactions within the adhesive, leading to a breakdown of its molecular structure and reduced adhesive properties. Saline water can act as an electrolyte, promoting corrosion and chemical reactions that can further degrade the adhesive.

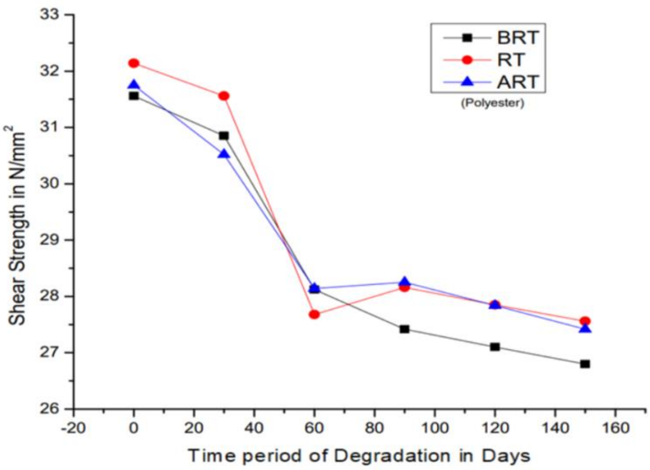

Figure 9. Graphical representation of shear strength of polyester adhesive joint w.r.t time period of exposure.

The low temperatures cause the adhesive to become rigid and brittle, reducing its ability to maintain strong adhesion between the bonded surfaces. Additionally, the presence of saline water can further compromise the bond strength due to the interference of salts with the adhesive's performance. Polyester adhesives and the materials being bonded may have different coefficients of thermal contraction. Low temperatures cause the materials to contract, potentially leading to significant stress concentrations within the joint. This thermal contraction mismatch can result in joint failure, including debonding, cracking, or delamination. These adhesives can become more brittle at lower temperatures. The low temperatures make the adhesive less flexible and more susceptible to brittle fracture. Under stress or impact, the adhesive joint will experience brittle failure, leading to complete separation of the bonded surfaces.

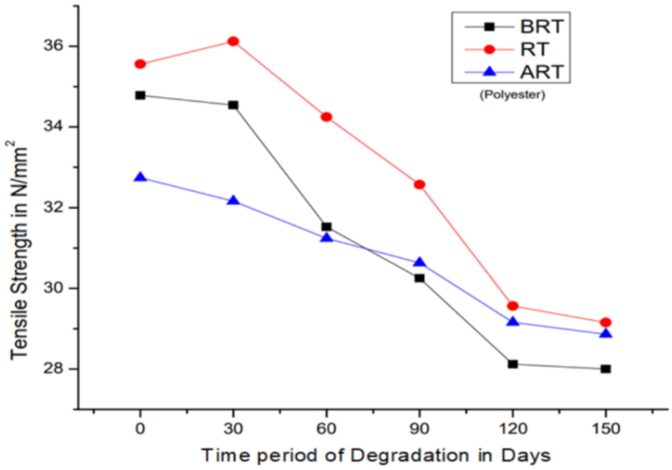

Figure 11. Graphical representation of bending strength of polyester adhesive joint w.r.t time period of exposure.

4.3 Comparison between Epoxy and Polyester Adhesive joints

Figure 12, 13 & 14 shows the comparison of shear strength, tensile strength and bending strength of epoxy and polyester adhesive joints. The graphs show that in all three strengths, epoxy at room temperature gives better strength compared to all other conditions. Epoxy adhesive joints below room temperature gives lower shear strength, polyester adhesive joint with above room temperature condition gives lower tensile strength, and polyester adhesive joint with below room temperature conditions gives lower bending strength.

Epoxy adhesives generally exhibit higher bond strength compared to polyester adhesives. Epoxy adhesives form strong and durable bonds, offering excellent adhesion to a wide range of substrates. Polyester adhesives, on the other hand, may have lower bond strength, especially in the presence of saline water, which can interfere with the adhesive's performance. Epoxy adhesives are more resistant to degradation from exposure to saline water and other chemicals. Polyester adhesives may be susceptible to hydrolysis in the presence of water, including saline water, which can lead to a reduction in their performance over time. Epoxy adhesives generally have higher temperature resistance compared to polyester adhesives. They can withstand higher temperatures without significant degradation, maintaining their strength and integrity. Polyester adhesives may experience softening and loss of mechanical properties at elevated temperatures, compromising the adhesive joint's performance. Polyester adhesives have a higher tendency to absorb water compared to epoxy adhesives. In a saline water environment, polyester adhesives can absorb water, leading to swelling, softening, and potential degradation of the adhesive. Epoxy adhesives, with their lower water absorption, may exhibit better performance and durability in saline water environments.

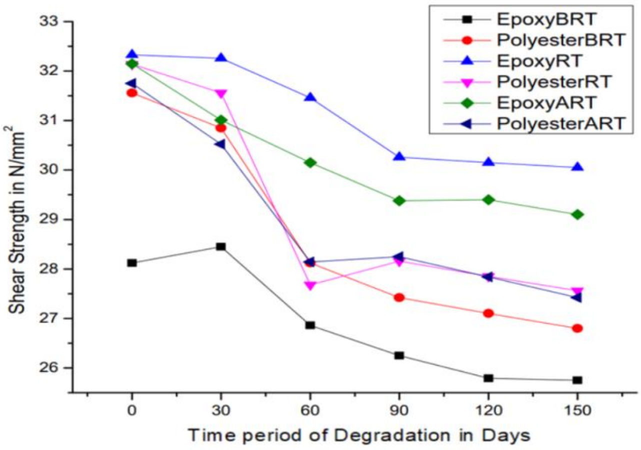

Figure 12. Comparison of epoxy and polyester adhesive joint shear strength w.r.t time period of exposure.

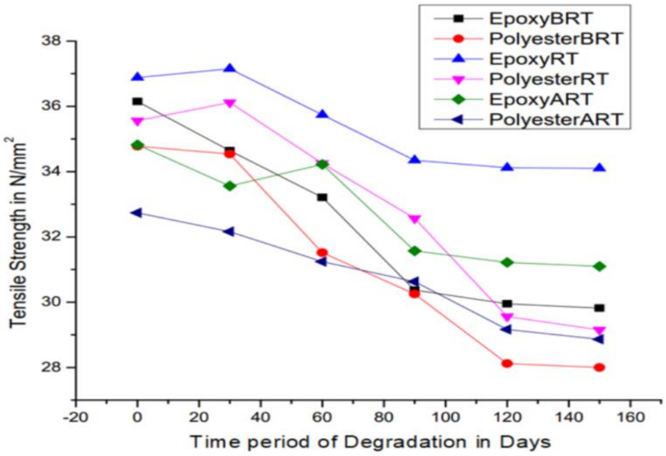

Figure 13. Comparison of epoxy and polyester adhesive joint tensile strength w.r.t time period of exposure.

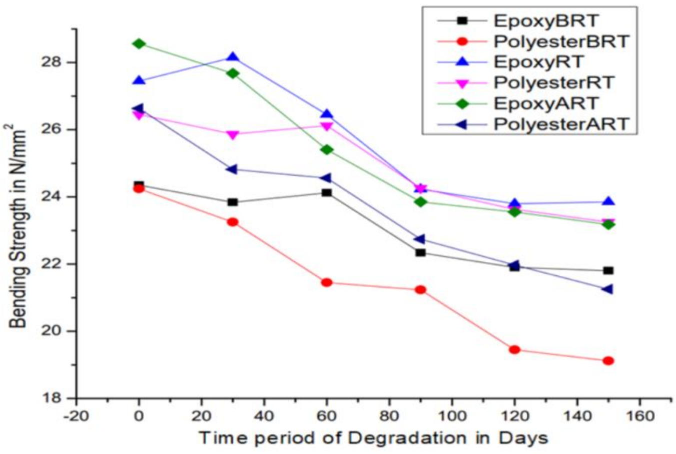

Figure 14. Comparison of Epoxy and Polyester adhesive joint bending strength w.r.t time period of exposure.

5. Conclusion

Epoxy adhesive joints exhibit higher shear strength compared to polyester adhesive joints across all temperature conditions. At room temperature, epoxy adhesive joints demonstrate the best shear strength performance. Epoxy adhesive joints show better tensile strength compared to polyester adhesive joints, particularly when exposed to temperatures below room temperature. Polyester adhesive joints show lower tensile strength when subjected to conditions above room temperature. Epoxy adhesive joints display higher bending strength compared to polyester adhesive joints. Polyester adhesive joints exhibit lower bending strength when exposed to temperatures below room temperature. Overall, epoxy adhesive joints exhibit higher bond strength than polyester adhesive joints. Epoxy adhesives form strong and durable bonds, providing excellent adhesion to various substrates. Polyester adhesives may have lower bond strength, especially in the presence of saline water.

Supplementary Materials

Author Contributions: Conceptualization, M.M. and B.V.H.; methodology, K.L. and V.U; validation, M.M. and KL; formal analysis, M.M. and B.V.H. and V.U; investigation, K.L and B.V.H.; resources, M.M.; data curation, M.M.; writing—original draft preparation, M.M. and KL.; writing—review and editing, B.V.H. and K.L.; visualization, M.M., KL and V.U.

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Conflicts of Interest: The authors declare no conflict of interest.

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