



**NAZARBAYEV
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**School of Engineering and Digital Sciences
Department of Mechanical and Aerospace Engineering**

MSc Thesis

**DEVELOPMENT OF SUSTAINABLE HIGH PERFORMANCE
COMPOSITE MATERIAL**

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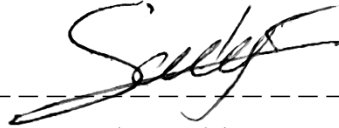
**This MSc thesis submitted to Nazarbayev University in partial fulfillment of the
requirements for the degree of Master of Science in Mechanical and Aerospace
Engineering**

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DECLARATION

I hereby, declare that this manuscript, entitled “*Development of sustainable high performance composite materials*”, is the result of my own work except for quotations and citations, which have been duly acknowledged.

I also declare that, to the best of my knowledge and belief, it has not been previously or concurrently submitted, in whole or in part, for any other degree or diploma at Nazarbayev University or any other national or international institution.

A handwritten signature in black ink, appearing to read 'Sadyr', is written over a horizontal dashed line.

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Abstract

The growing demand for lightweight and sustainable engineering materials has increased interest in natural fiber-reinforced and hybrid laminated composites. However, their wider structural application remains limited due to weak interfacial bonding, moisture sensitivity, and compatibility issues. This thesis investigates two related approaches for improving their performance: optimization of alkali treatment for flax fiber-reinforced epoxy composites, and development of flax-based natural fiber metal laminates (NFMLs) using aluminum treated by an environmentally friendly potassium chloride (KCl) anodizing.

In the first part of the study, flax/epoxy composites were fabricated using flax fibers subjected to alkali treatment (NaOH). The effect of concentration, treatment duration, and temperature on tensile and flexural performance was studied. The results showed that aggressive treatment conditions resulted in low mechanical performance, while moderate treatment conditions led to improvement. Optimal treatment conditions to enhance fiber-matrix adhesion without damaging the fiber structure were: 2 wt% NaOH, 40 min, and 40 °C. Tensile and flexural strength were improved by 28.9% and 21.2%, respectively, compared with the untreated composites.

In the second part of the study, NFMLs with aluminum (6061-T4, 0.5 mm) and flax/epoxy composite layers were prepared. The metal-composite interface was improved by Al electrochemical treatment with KCl. The effect of anodizing concentration, duration, and voltage on laminate tensile and flexural properties was investigated. Optimal anodizing conditions were: 0.1 M, 20 min, and 16 V. KCl-treated NFMLs showed increase of 11.3% in tensile strength and 15.5% in flexural strength over the untreated laminate.

The thesis shows the importance of interface engineering in the development of sustainable high-performance composites. On the fiber-matrix level, alkali treatment enhanced the effectiveness of flax reinforcement in epoxy composites, while on the metal-composite level, KCl anodizing enhanced the mechanical performance of flax-based NFMLs. Through the combination of optimized flax fiber treatment and environmentally friendly aluminum anodizing, this study demonstrates a practical way to advance natural fiber composites both as environmentally attractive materials and mechanically competitive systems for structural applications.

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List of Abbreviations & Symbols

FRP	Fiber-reinforced polymer
NFRP	Natural fiber-reinforced polymer
FML	Fiber-metal laminate
NFML	Natural fiber-metal laminate
ANF	Aramid nanofiber
CNT	Carbon nanotube
CNF	Cellulose nanofiber
GNP	Graphene nanoplatelet
CAA	Chromic acid anodizing
PAA	Phosphoric acid anodizing
SAA	Sulfuric acid anodizing

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Chapter 1 – Introduction

1.1. Background

The increasing demand for lightweight construction materials is closely linked to the need to improve energy efficiency, reduce emissions, and enhance resource utilization. Structural weight directly impacts fuel consumption, operational efficiency, and overall carbon footprint in transportation, aerospace, and shipbuilding sectors [1–3]. This has resulted in extensive use of polymer composites, which offer low density, high specific strength and stiffness, corrosion resistance, and considerable design flexibility. Thus, fiber-reinforced polymers (FRPs) started being widely used in applications where conventional metallic structures are considered heavy or inefficient.

Despite their advantages, high-performance FRPs are based on synthetic fibers such as glass and carbon. Their production is energy-intensive and depends on non-renewable resources, which raises concerns regarding sustainability and end-of-life management [1–3]. This has resulted in an increasing interest towards more sustainable natural fiber-reinforced polymers (NFRPs). Among natural fibers, flax stands out with its relatively low density, high specific mechanical properties, and availability in textile forms suitable for composite manufacturing [1–3]. This means that flax NFRPs have potential to replace synthetic FRPs in modern structural applications where a balance between performance and sustainability is required.

At the same time, the properties of NFRPs may be insufficient in applications where high structural reliability, impact resistance, or hybrid load-bearing behavior is needed. In such cases, fiber metal laminates (FMLs) can be considered as an alternative. FMLs are composed of thin metal and synthetic FRP layers. This structure unites the ductility and surface durability of metals with the low density and high specific strength of composites [1,4,5]. This concept can be extended to flax fibers to develop flax-based natural fiber metal laminates (NFMLs), which are FMLs composed of aluminum and flax NFRPs layers for improved sustainability. However, the potential of flax-based composites is strongly influenced by various factors. For NFRPs, these factors are fiber-matrix adhesion, fiber variability, and moisture sensitivity. While for FMLs the main issue is the matrix/metal interface.

1.2. Problem statement

Drawbacks of NFRPs such as intrinsic variability of natural fibers, hydrophilic nature, and relatively low compatibility with polymer matrices, limit their use. These issues are observed most clearly at the fiber-matrix interface: weak bonding reduces stress transfer efficiency and makes the composite more vulnerable to mechanical degradation and moisture. For this reason, surface treatment of flax fibers is crucial to improve NFRPs performance [6–8]. Alkali treatment is among the most widely used methods because it can remove non-cellulosic surface constituents and improve interfacial interaction. Nevertheless, treatment effectiveness depends strongly on treatment conditions like concentration, duration, and temperature that control its harshness. Insufficient treatment may have an insignificant effect on NFRPs properties while excessive treatment may damage the fiber and reduce NFRPs performance. Moreover, high variability of natural fibers hinders the development of universal treatment conditions. This creates a need for optimization of alkali treatment parameters for each case instead of using general treatment conditions reported in the literature.

At the same time, the development of natural fiber metal laminates remains at a relatively early stage compared with conventional FMLs. NFMLs offer an attractive route towards more sustainable hybrid structures, but their performance depends critically on reliable metal-composite bonding. In aluminum-based NFMLs, weak interfacial bonding can lead to weak load transfer and premature delamination, limiting the structural usefulness of the laminate. Conventionally, anodizing is considered an effective approach to improve aluminum/matrix bonding because it develops an oxide layer that enhances wettability and promotes mechanical interlocking with the matrix [9]. However, conventional anodizing routes rely on chemically aggressive and environmentally hazardous electrolytes like sulfuric acid, phosphoric acid, and chromic acid, which significantly reduces sustainability of this laminate development approach [9]. Alternative methods of interface strengthening are also available; however, they either are less efficient or have not been extensively integrated for FMLs.

The central problem addressed by this thesis therefore consists of two parts: first, flax/epoxy composites require better-controlled surface treatment to improve interface quality and mechanical performance; second, flax-based NFMLs require an effective and more

environmentally friendly aluminum surface treatment to achieve reliable hybrid bonding. These challenges are linked, because both concern the design of sustainable composite systems whose performance is governed by interfacial behavior.

1.3. Research Objectives

The aim of this thesis is to develop procedures to manufacture sustainable high-performance composite materials based on flax fiber-reinforced epoxy systems and flax-based natural fiber metal laminates, with particular emphasis on interfacial improvement through flax alkali treatment and eco-friendly KCl anodizing of aluminum.

The specific objectives of this study are:

- To investigate the effect of alkali treatment on flax fiber surface for flax/epoxy composite applications.
- To optimize the selected alkali treatment conditions to improve fiber-matrix adhesion and the resulting mechanical performance of flax/epoxy composites
- To develop flax-based natural fiber metal laminates using aluminum and flax/epoxy composite layers.
- To apply KCl-based anodizing as an environmentally friendlier aluminum surface treatment for improved metal-composite bonding.

Chapter 2 – Literature Review

2.1. Natural fiber-reinforced polymer composites

2.1.1. Natural fibers: types, composition and properties

Natural fibers are commonly classified according to their origin into three main groups: plant, animal and mineral fibers [2,3,10–12]. Plant fibers are cellulose-based, animal fibers are protein-based, and mineral fibers are naturally occurring inorganic fibers such as asbestos [2,3,11]. Although this broad classification is useful, plant fibers are considered the most relevant group for polymer composite applications because they are cheaper, more widely available and more suitable for structural and semi-structural engineering use than animal fibers, while also avoiding the health concerns associated with mineral fibers [3,11]. Consequently, most research on natural fiber-reinforced polymer composites, as well as the present study, focuses on plant-based fibers [10,11].

Plant fibers are classified further according to the part of the plant from which they are extracted. The main types are bast fibers, leaf fibers, seed fibers, fruit fibers, straw or stalk fibers, grass or reed fibers, and wood fibers [2,3,10–12]. Bast fibers include flax, hemp, jute, kenaf and ramie; leaf fibers include sisal, abaca and pineapple leaf fiber; seed and fruit fibers include cotton, kapok and coir; while bamboo, bagasse and wheat straw are typical examples of grass, stalk or related lignocellulosic resources [3,10,11]. Among these groups, bast fibers are generally regarded as the most attractive non-wood natural fibers for composite reinforcement because they usually provide the best balance of tensile strength, stiffness and low density [3,12]. These properties are mainly defined by the structural composition of fibers.

From a structural point of view, plant fibers are composed mainly of cellulose, hemicellulose and lignin [2,3,10]. Cellulose is the principal load-bearing constituent and is primarily responsible for fiber strength and stiffness. Hemicellulose is less ordered and more hydrophilic and therefore contributes strongly to moisture absorption. Lignin is an amorphous binding component that surrounds the cellulose-rich structure and contributes to rigidity and resistance to biological attack [2,10]. A review by Nurazzi et al. reports that, in a typical lignocellulosic material, cellulose, hemicellulose and lignin may fall broadly within the ranges of 30–60%, 20–40% and 15–25%, respectively, although specific fibers can differ markedly from these general values [10].

The variation in chemical composition among natural fibers is reflected directly in their physical and mechanical behavior. For example, flax, similarly to other bast fibers, is reported to contain about 60–81% cellulose, 14–20.6% hemicellulose and 2.2–5% lignin as shown on Table 1. In contrast, coir contains considerably lower cellulose, around 32–43%, but very high lignin, around 40–45%, which explains its greater toughness and lower stiffness compared to bast fibers [10]. These compositional differences largely determine fiber stiffness, strength, and moisture sensitivity. In terms of mechanical performance, flax is frequently identified as one of the strongest plant fibers, with reported tensile strength in range of 345–1035 MPa in the review by Peças et al. [2]; hemp is reported at around 690 MPa tensile strength; jute in the range of 393–773 MPa, kenaf around 215–930 MPa, and sisal around 511–535 MPa. Coir, in contrast, has much lower strength and modulus but a much higher elongation at break, indicating more ductile behavior [2,10]. Natural fibers also show substantial variation in density. Reported density values are typically much lower than those of glass fibers and often fall in the range of about 1.2–1.6 g/cm³, which is one of the main reasons natural fibers are attractive for lightweight composites [11]. However, natural fibers should not be regarded as a uniform material class. Their properties are strongly influenced by plant species, fiber diameter, microfibril angle, crystallinity, defects, maturity, extraction method, and the conditions under which the plant was grown and harvested [2,3,10]. As a result, even fibers of the same nominal type may show considerable scatter in both chemical composition and mechanical performance. This variability is one of the principal challenges in the design of natural fiber composites, since it makes standardization and property prediction more difficult than in conventional synthetic-fiber systems [3,12].

Overall, natural fibers are a diverse group of reinforcement materials whose properties and suitability for polymer composites depends on their origin, structure, and composition. Among the different groups, bast plant fibers generally provide the most favorable balance of low density, relatively high strength and good stiffness. For this reason, the following section focuses specifically on flax fiber, which is one of the most promising bast fibers for structural polymer composite applications [2,3,10,12].

Table 1. Typical mechanical properties of natural fibers

Fiber type	Fiber class	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Density (g/cm³)	Tensile strength (MPa)	Tensile modulus (GPa)
Flax	Bast	60–81	14–20.6	2.2–5	0.6–1.1	345–1035	27.6
Hemp	Bast	70–92	18–22	3–5	1.48	690	70
Jute	Bast	51–84	12–20	5–13	1.3	393–773	26.5
Kenaf	Bast	44–87	22	15–19	1.45	215.4	53
Sisal	Leaf	65.8	12	9.9	1.5	511–535	9.4–22
PALF	Leaf	66.2	19.5	4.2	0.8–1.6	400–627	1.44
Ramie	Bast	68–76	13–15	0.6–1	1.5	560	24.5
Coir	Fruit	32–43	0.15–0.25	40–45	1.2	138.7	4–6
Bamboo	Grass	73.83	12.49	10.15	1.25	140–230	11–17

2.1.2. Flax fiber and flax fiber reinforced polymers

The suitability of flax for polymer reinforcement is strongly linked to its structure and composition. Flax fibers have a hierarchical architecture extending from the stem to fiber bundles, elementary fibers, cell walls and cellulose microfibrils as shown of Figure 1 [2,13–15]. The secondary cell wall, especially the G layer, contains highly oriented cellulose microfibrils and is largely responsible for the fiber's stiffness and strength [16,17]. Reported cellulose contents are typically around 60–75%, with relatively low microfibril angle, often below 10°, which distinguishes flax from many other natural fibers and helps explain its superior mechanical performance [16]. Reviews also note that flax fibers have low density, typically around 1.4–1.5 g/cm³, together with tensile strength in the range of about 345–1035 MPa and modulus values that can approach those of glass fiber on a specific basis. For this reason, flax is frequently identified as one of the strongest and stiffest plant fibers for composite reinforcement.

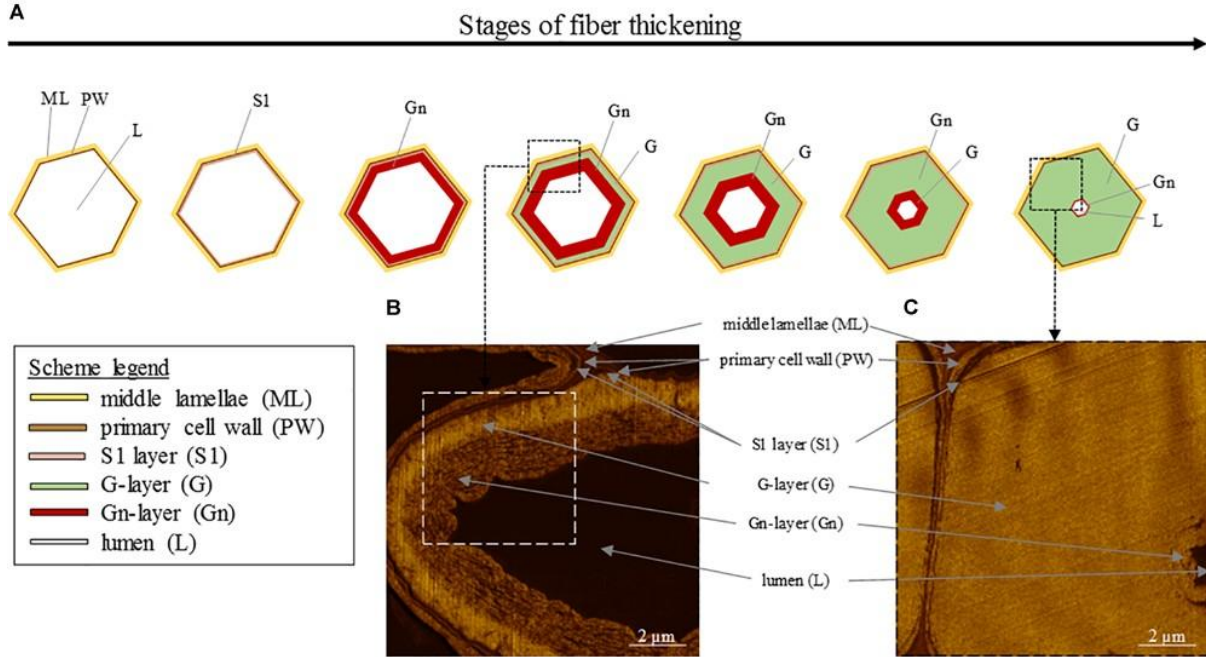


Figure 1. (a) Different stages of the fiber thickening (b) AFM image of an intermediate stage of cell thickening (c) AFM image of final stage of cell thickening [16]

Flax fiber has been combined with both thermoplastic and thermoset matrices, including polypropylene, polyethylene, polylactic acid, polyester, vinyl ester and epoxy. However, epoxy-based systems are especially important in the context of structural applications because epoxy generally provides better mechanical performance and stronger fiber-matrix bonding than many other common polymer matrices. Reviews note that epoxy is widely favored in thermoset flax composites because of its excellent mechanical and interfacial properties, even though it is more expensive than polyester systems [18,19]. In addition, the processing route has a strong influence on final performance, with resin transfer molding, vacuum infusion, prepreg and autoclave-based routes generally producing higher-quality composites than simpler hand lay-up methods when fiber alignment and void control are improved [18].

The literature shows that the mechanical performance of flax fiber reinforced polymers depends strongly on fiber architecture, fiber volume fraction, matrix type and manufacturing method. Reported values for flax/epoxy composites cover a relatively broad range. Reviews summarizing unidirectional and fabric-based epoxy laminates report tensile strength values from around 160 MPa for some knitted unidirectional flax/epoxy composites up to about 280 MPa for high-quality Arctic flax/epoxy laminates. Their tensile modulus is ranging from about 15 GPa to

roughly 40 GPa [14]. Their flexural properties are also notable, with reported flexural strength around 190 MPa for some unidirectional knitted flax/epoxy laminates and higher values in more optimized systems. Another review reports that 50% flax reinforcement in epoxy can raise stiffness to about 40 GPa and tensile strength to about 280 MPa, compared with much lower values for neat epoxy [19]. These findings show clearly that flax can provide substantial structural reinforcement when fiber quality and laminate architecture are well controlled.

A further point repeatedly highlighted in the literature is the importance of fiber arrangement. Long, aligned flax reinforcements produce much better performance than random mats or poorly aligned non-wovens because the load can be transferred more efficiently along the fiber direction [15,17,18]. Reviews state that long flax fiber composites may exhibit mechanical properties three to four times higher than non-woven flax mat composites [16,17]. This is consistent with the broader understanding that unidirectional and highly aligned flax architectures are most suitable where tensile and flexural properties are critical. Recent experimental work on unidirectional flax/epoxy prepreg laminates also confirms that flax/epoxy systems exhibit relatively high axial stiffness, with tensile moduli of 35.9 GPa and 26.3 GPa before and after yield, respectively, together with a clearly non-linear, time-dependent response associated with the fiber-matrix system [14,17,19].

Overall, the literature supports the selection of flax as a reinforcement for polymer composites on both mechanical and sustainability grounds. Flax combines low density with comparatively high specific strength and stiffness, can be processed into a variety of useful textile architectures, and has already demonstrated promising performance in both thermoplastic and thermoset systems. Among these, flax/epoxy composites are especially relevant for semi-structural and structural applications because they offer some of the best mechanical properties reported for natural fiber reinforced polymer systems. For this reason, flax provides a well-justified basis for further investigation in the present work.

2.1.3. Interfacial bonding and environmental degradation

The performance of natural fiber-reinforced polymer composites is primarily governed by the fiber-matrix interface. This interfacial region is responsible for transferring stress from the polymer matrix to the reinforcing fiber, and therefore strongly influences the tensile, flexural, thermal and durability behavior of the composite [20,21]. Because plant fibers are inherently

hydrophilic whereas most polymer matrices are relatively hydrophobic, untreated systems generally exhibit poor compatibility, inadequate wetting and weak adhesion at the interface [21,22]. This incompatibility leads to inefficient stress transfer, premature debonding and inferior overall composite performance [20,22].

Interfacial bonding in plant fiber composites is commonly explained through several complementary mechanisms, including interdiffusion, chemical adhesion and mechanical interlocking [21]. Among these, mechanical interlocking is particularly important in natural fiber systems, since surface roughness and fiber morphology strongly affect polymer penetration into surface irregularities. A rougher and cleaner fiber surface provides more anchoring sites for the matrix, whereas the removal of non-cellulosic constituents such as waxes, hemicellulose and portions of lignin can improve both wettability and interfacial contact [6,21]. For this reason, surface treatment is widely used to engineer the interface and improve load transfer efficiency [6,21].

The importance of the interface is especially evident in flexural loading. Unlike simple tensile loading, flexural deformation imposes combined tensile, compressive and interfacial shear stresses, making bending performance particularly sensitive to adhesion quality. It has therefore been reported that flexural strength is often more dependent on interfacial bonding than tensile strength [21]. When adhesion is poor, failure is commonly associated with fiber pull-out, interfacial debonding and void-assisted crack propagation. By contrast, stronger interfaces promote more effective stress transfer and can improve tensile and flexural properties, although excessively strong bonding may reduce energy dissipation during impact because fiber pull-out is suppressed [20,21].

Another major issue is associated with susceptibility of natural fibers to moisture absorption. Cellulose- and hemicellulose-rich fiber surfaces contain hydroxyl groups that readily form hydrogen bonds with water molecules. As moisture diffuses into the composite, the fibers swell, the interface becomes stressed and local microcracks begin to form in the surrounding matrix [20,23]. Continued exposure can then cause fiber-matrix debonding, plasticization of the matrix, hydrolysis and gradual deterioration of mechanical properties [23,24]. Thus, the interfacial region is not only the key pathway for stress transfer, but also one of the most vulnerable regions under environmental exposure [20,23].

Moisture-related degradation may occur under ambient humidity, water immersion, hygrothermal ageing and weathering conditions. In such cases, the absorbed moisture can initially soften the composite, but prolonged exposure often leads to irreversible changes such as swelling, microcracking, leaching of low-molecular-weight species, polymer relaxation and interface damage [23]. High temperature can accelerate these processes since it increases diffusion rate and causes chemical degradation. Therefore, NFRPs intended for structural or semi-structural applications must be evaluated not only for their dry mechanical properties, but also for performance after moisture and thermal exposure [23,25].

2.1.4. Alkali treatment of natural fibers

These issues can be mitigated via the application of chemical treatments to natural fibers before composite fabrication. Among them, alkali treatment is the most widely used because of its simplicity, low cost and effectiveness [6,21]. In this treatment, sodium hydroxide reacts with accessible hydroxyl groups and removes part of the non-cellulosic surface layer, including hemicellulose, lignin, pectin, waxes, and oils. As a result, the fiber surface becomes cleaner and more reactive, which facilitates improved adhesion with the surrounding matrix [7,8,26].

From a structural point of view, alkali treatment changes both fiber morphology and fine structure. The partial removal of constituents reduces fiber diameter, increases aspect ratio, and produces a rougher topography that promotes mechanical interlocking at the interface [7,8,26]. In many cases, fibrillation also occurs, meaning that fiber bundles split into finer elements, increasing the effective contact area between fiber and matrix [8,26]. Depending on treatment severity, changes in cellulose organization may also occur. Mild alkalization can preserve the native cellulose structure while increasing crystallinity, whereas more severe treatment may damage the fiber cell wall [26,27].

These microstructural changes are important because the main purpose of alkali treatment is not to clean the fiber, but to improve stress transfer across the interface. A rougher and less contaminated fiber surface usually leads to stronger interfacial bonding, reduced debonding, and better tensile and flexural behavior of the resulting composite [7,28,29]. A classic example is provided by Yan et al., who showed that treatment with 5 wt.% NaOH for 30 min reduced the tensile strength and modulus of flax yarns themselves, yet increased the tensile and flexural strengths of flax/epoxy composites by 21.9% and 16.1%, respectively, due to improved fiber-

epoxy adhesion [30]. This distinction is important: alkali treatment may weaken an individual fiber or yarn while still enhancing the performance of the composite through better interfacial efficiency [30]. For flax in particular, the literature shows that treatment severity must be carefully controlled. Bahrami et al. compared treatments of flax fibers with different concentrations of NaOH and found that treatment in 5% NaOH preserved tensile properties, reduced moisture absorption by 18%, and increased the thermal decomposition temperature from 198 °C to 254 °C [27]. In contrast, treatment in 20% NaOH produced more extensive structural changes, reduced fiber rigidity, and yielded only a limited further reduction in moisture uptake [27]. This shows that more aggressive treatment does not necessarily produce better reinforcement. Rather, once removal of non-cellulosic material becomes excessive, the gain in cleanliness and roughness may be outweighed by damage to the fiber framework itself [26,27]. Recent studies on flax composites support the same conclusion. Rothenhäusler et al. compared sodium hydroxide, silane, and siloxane treatments for flax prepreg composites and found that NaOH was the only modification that improved Young's modulus and tensile strength in both unconditioned and humidity-conditioned states [29]. They attributed this to changes in fiber composition, increased cellulose crystallinity, and a rougher surface that enhanced fiber–matrix adhesion [29]. However, the same study also noted that the rougher NaOH-treated surface increased water uptake, most likely because of increased pore volume and exposed fibrillar structure [29]. Therefore, alkali treatment can improve mechanical retention in humid environments, but it does not automatically minimize moisture absorption [29].

The optimal treatment window also varies with fiber type and composite system. Kabir et al. reported that in hemp/polyester composites produced by VARTM, 4% NaOH reduced interfacial bonding and lowered composite properties, whereas higher concentrations of 6–10% improved mechanical behavior because of stronger fiber–matrix interaction [28]. By contrast, Frącz et al. showed that in PHBV biocomposites reinforced with short fibers, increasing NaOH concentration was beneficial for hemp but harmful for flax; flax treated with 10% NaOH exhibited significant geometry and its tensile properties decreased [31]. These findings confirm that alkali treatment is highly system-dependent. The optimal concentration depends on the source of the fiber, its initial lignin and hemicellulose content, the fiber form, and the specific matrix and processing route used [28,31].

Overall, alkali treatment remains one of the most effective routes for improving the interfacial performance of natural fiber composites. It removes hemicellulose, lignin, waxes, and pectin; increases roughness; improves fibrillation; and in some cases improves crystallinity [7,8,26,27]. Nevertheless, the process must be optimized for each fiber-matrix system. For flax NFRPs especially, moderate NaOH treatment is generally more beneficial than severe mercerization, since it offers improved adhesion and reduced moisture sensitivity without severe fiber damage [27,29,31].

2.1.5. Optimization of alkali treatment using Taguchi design

The effect of alkali treatment depends on several variables, therefore optimization of the design of experiments is necessary. The effectiveness of treatments depends on NaOH concentration, treatment time, temperature, fiber geometry, and in some cases fiber-to-solution ratio or extraction route [32,33]. Testing targeting one factor at a time can identify general trends, but it is inefficient and interactions between parameters are not accounted. For this reason, design-of-experiments approaches, particularly the Taguchi method, are often used for alkali-treatment studies [32,33]. The Taguchi method uses orthogonal arrays to evaluate the effect of several control factors with a limited number of experiments and quantifies the contribution of each factor to the measured response via analysis of variance (ANOVA).

For alkali etching the treatment variables are assigned to levels and arranged in an orthogonal array such as L9 or L16, based on the number of factors and levels. The resulting responses are converted into signal-to-noise (S/N) ratios, which are used to identify the most robust combination of parameters. For properties that are intended to be maximized, such as tensile strength, flexural strength, or modulus, the “larger-the-better” criterion is normally used. Then ANOVA is applied to evaluate the effect of each parameter on the performance in comparison to other parameters [33,34].

This approach is especially useful for the optimization of treatment conditions and, therefore, often used in other studies. Benamrane et al. used a Taguchi L9 design to optimize the tensile properties of alfa fibers. They used gauge length, NaOH concentration, and treatment duration as variables with levels of 20, 40, and 60 mm, 0.5, 2, and 5% of NaOH, and 48, 24, and 12 h respectively. The optimum combination was 60 mm gauge length, 5% NaOH, and 24 h treatment, giving the best balance of tensile stress, strain, and Young’s modulus. This study is

particularly useful because it shows that a favorable treatment conditions can be identified without a full-factorial set of experiments. A similar approach was used with kenaf fibers by Sathish Kumar et al., who optimized four treatment variables: NaOH concentration, reaction temperature, reaction time, and fiber-to-solution weight ratio [35]. They found that 6% NaOH, 30 °C, 8 h, and a 1:15 fiber-to-solution ratio produced the highest tensile strength of 58.16 MPa. Moreover, ANOVA showed that NaOH concentration was the most influential factor, contributing 28.66%, followed by reaction time and reaction temperature, while fiber-to-solution ratio had the smallest contribution among the selected variables. This illustrates the practical value of Taguchi analysis: it can be used to identify an optimum condition in a quicker way and indicate which parameters are structurally important and which are secondary [34]. This makes it highly attractive for composite research, where evaluation of each treatment condition consists of drying, laminate manufacture, curing, and testing. Thus, the Taguchi approach is not only statistically rigorous but also economical, which explains its growing use in the optimization of alkali-treated natural fibers and their composites [36–38].

2.2. Fiber Metal Laminates

2.2.1. Introduction to FMLs

Fiber metal laminates (FMLs) are hybrid structural materials composed of alternating thin metal sheets and fiber-reinforced polymer composite layers bonded into an integral laminate [4,39,40]. This concept was developed to combine the ductility, impact resistance and manufacturability of metals with the high specific strength, stiffness and fatigue advantages of continuous-fiber composites [39,40]. In this way, FMLs occupy an intermediate position between monolithic metallic structures and conventional polymer composites, while overcoming some of the main limitations of each material class when used alone. Their most widely recognized advantage is exceptional fatigue resistance, which arises from the crack-bridging effect of the fiber layers between cracked metal sheets [26,39].

The historical development of FMLs can be traced to bonded sheet structures used by Fokker, where layered aluminum assemblies were found to show improved fatigue behavior compared with monolithic sheets [39,40]. During the late 1970s, research at Delft University of Technology advanced this concept by introducing fiber reinforcement into the bond layers and reducing metal sheet thickness, which led to a major improvement in fatigue performance [39,40].

The first prototype tested in 1979 became known as ARALL, an aramid-reinforced aluminum laminate [40]. In the 1980s and 1990s the concept expanded further with the development of GLARE, in which glass fibers replaced aramid fibers to overcome limitations in compressive performance and fiber stability, and later CARALL, where carbon fibers were introduced to increase stiffness and strength [4,39,40]. This development path reflects a continuous attempt to tailor the hybrid laminate architecture to specific structural requirements.

Conventional FML families are therefore commonly classified according to the reinforcing fiber used, namely ARALL, GLARE and CARALL [4,26,39,40]. Early ARALL systems were applied in structures such as the Fokker F-27 and the Boeing C-17 cargo door, while GLARE became the best-known commercial FML because of its subsequent large-scale aerospace application [4,26,39,40]. Sinke notes that after more than twenty years of research and development, GLARE was adopted for significant sections of the Airbus A380 fuselage as well as local doublers and leading-edge components [40]. More recent reviews also show that the original aluminum-based concept has expanded to titanium-, magnesium- and steel-based laminates, and that thermoplastic matrices are increasingly being explored in addition to conventional epoxy systems [4] [26]. This broadening of constituent options shows that FMLs are not a single material, but a family of laminates whose performance depends on constituent selection and lay-up design.

From a mechanical point of view, the behavior of FMLs is governed by hybrid interaction between the metal layers, the fiber-reinforced plies and the interface between them. The layered structure modifies tensile, flexural, fatigue and impact response through combined mechanisms such as metal plasticity, crack bridging, matrix cracking, fiber fracture and delamination [4,40,41]. Under cyclic loading, cracks may initiate in the outer metal sheets, but their propagation is slowed markedly because the intact fiber layers bridge the crack and reduce the stress intensity at the crack tip [40]. Sinke emphasizes that this fatigue-retarding mechanism depends on a balance between crack growth in the metal and local delamination at the interface, since some delamination is required to provide the fibers with sufficient free length to elongate and bridge the crack effectively [40]. This mechanism is one of the main reasons why fatigue resistance has historically been the defining property of FMLs.

The tensile and flexural behavior of FMLs is highly sensitive to laminate architecture. Hu et al. showed that, in Ti/CF/PMR polyimide laminates, tensile strength and elastic modulus were

determined by interfacial adhesion, fiber volume fraction and lay-up direction, while flexural loading produced a combination of tensile stress on one surface and compressive stress on the other, with delamination and local buckling as dominant failure modes [41]. Similarly, Wang et al. reported that in titanium-based carbon/basalt FMLs the principal damage mechanisms under tensile and flexural loading included fiber/matrix debonding, matrix microcracking, fiber pull-out and delamination, and that both hybridization ratio and stacking sequence affected strength significantly [5]. These findings confirm that FML behavior cannot be predicted from constituent properties alone, since it depends strongly on the way the constituents are arranged through the thickness.

Flexural performance is strongly controlled by stacking configuration and fiber orientation. In CARALL laminates, Hu et al. reported that a 3/2 configuration achieved flexural stiffness of 109.70 GPa and flexural strength of 1673 MPa, and that bending performance decreased when metal volume fraction increased excessively, showing that the composite plies remain essential load-bearing components in bending [42]. In thermoplastic-based FMLs, Rajabi et al. likewise emphasized that FMLs combine metal ductility, impact tolerance and surface quality with the high specific strength and stiffness of fiber composites, and their results showed good correlation between flexural experiments and finite element simulations [43]. Frankiewicz et al. further observed that, in three-point flexural fatigue, laminates with predominantly longitudinal reinforcement had the best fatigue resistance and survived beyond 10^6 cycles at stress levels below 30% of static bending strength [44]. Together, these studies show that the relative position, orientation and volume fraction of metal and fiber layers govern whether the laminate behaves in a stiff and brittle manner, or in a more ductile and energy-absorbing one.

Impact behavior is another central reason for the continuing interest in FMLs. Reviews consistently state that FMLs offer superior damage tolerance and energy absorption compared with monolithic composites because the metal sheets can undergo plastic deformation while the composite plies distribute damage through matrix cracking, fiber fracture and delamination [4,26,45]. At the same time, the interface between metal and composite is structurally critical. Poor interfacial adhesion leads to premature debonding and delamination, whereas appropriate pretreatment and interface control improve stress transfer, interlaminar shear strength and overall mechanical reliability [4,41]. This means that the mechanical behavior of FMLs is inseparable

from interface quality, which explains why surface treatment and bonding technology remain central themes in FML research.

Overall, FMLs were originally developed as fatigue-resistant lightweight laminates for aerospace structures, but their importance has since expanded because the same hybrid concept can be applied using different metals, fibres, matrices, and lay-up configurations. Their mechanical behaviour depends on the combined effect of metal plasticity, fibre reinforcement, and interface quality, which together control tensile and flexural performance, crack growth, impact resistance, and failure mode. This makes FMLs a flexible structural concept rather than a single material system, and it also provides the foundation for later developments such as NFMLs and more sustainable surface-treatment approaches.

2.2.2. Natural fiber metal laminates

Natural fiber metal laminates (NFMLs) are an emerging extension of conventional fiber metal laminates. In NFMLs the matrix layers are reinforced with plant fibers rather than synthetic fibers. The purpose of the use of natural fibers in FMLs is to preserve the benefits of hybrid metal-composite structure while reducing density, cost, production energy and environmental burden. Natural fibers are attractive because they are renewable, less energy-intensive to produce, and in some cases they offering competitive specific properties which can be sufficient for a wide range of applications [46–48]. Although NFMLs are promising, they are still less developed than conventional FMLs such as GLARE and CARALL. Their main limitations are lower strength, higher variability, moisture sensitivity, weaker thermal stability, and difficulty in achieving strong and durable metal-composite bonding. Therefore, interfacial debonding and delamination remain the main challenges in NFMLs. For this reason, most current studies focus on fibre and metal surface treatment or on hybridisation with synthetic fibres to improve structural reliability.[47,49,50].

NFML research can be divided into two main approaches. The first uses NFRPs that consist of only natural fibers, such as flax/polypropylene, jute/epoxy, or coir/polymer, combined with aluminium skins [46]. The second uses hybrid natural/synthetic reinforcement, which combine natural fibres glass or carbon to improve stiffness, strength, interlaminar behaviour, and impact resistance while still reducing environmental impact compared to fully synthetic laminates [46]. Xiao et al. developed aluminium laminates reinforced with pineapple leaf fibre (PALF) and carbon

fibre using VARTM and showed that hybridisation significantly improved performance. The ACPCA laminate had 86.50% higher interlaminar shear strength and 59.59% higher impact strength than the non-hybrid APPPA laminate, while all hybrid laminates were stiffer than the fully PALF-based version. These results suggest that hybrid NFMLs may offer a practical balance between sustainability and mechanical performance, especially for automotive and transport applications where fully natural-fibre systems may not meet the required strength levels [51]. However, the focus of this research is on NFMLs that do not contain synthetic fibers.

Flax has received particular attention in NFMLs, like in NFRPs, because it offers low density, relatively high specific stiffness, good damping, and lower environmental impact than glass fibre. Alcaraz et al. showed that flax-based metal laminates should not be viewed as direct substitutes for GLARE, but as materials with a different property balance. In their FLARE system, aluminium reduced the loss factor by about 80% compared with neat flax composite, while the specific energy absorption under low-velocity impact was about 25% lower than in a glass-based laminate. This reflects a typical NFML trade-off: aluminium improves impact behaviour and recyclability, but the lower intrinsic strength of natural fibres still limits direct replacement of high-performance glass-based FMLs in strength-critical aerospace applications [48].

Flax-based NFMLs have also been studied from a structural mechanics perspective. Song et al. showed that lay-up sequence strongly affects the tensile behaviour of aluminium/flax/polypropylene laminates. Compared with the unidirectional laminate, the [0/90] and [± 45] lay-ups reduced ultimate tensile strength by 41.9% and 30%, respectively. Their study also showed that interface behaviour and delamination play a major role in tensile failure. This means that, even before surface treatment or process optimisation is considered, fibre orientation alone can significantly change load transfer and failure behaviour in NFMLs. [51].

Jute-based NFMLs provide another useful example, especially because jute is low-cost and widely available. Haq et al. developed jute/aluminium laminates using plain and twill woven jute and found that twill architecture performed better than plain weave. They also showed that chemical treatment of both jute and aluminium significantly improved the interface. The treated twill laminate reached a flexural strength of 151 MPa and a flexural modulus of 21.3 GPa, which were 186.5% and 722.7% higher than those of the untreated laminate. These results clearly show

that interface optimisation is one of the main factors controlling mechanical performance in NFMLs. [52].

A related direction is the use of three-dimensional natural-fibre reinforcements. Hussain et al. developed 3D jute-reinforced aluminium laminates using four-layer 3D woven jute preforms and phosphoric-acid-anodized aluminium skins. Their results showed that 3D woven reinforcement can improve mechanical performance and may also be more economical than some conventional preforms. They also found that adhesion depended strongly on both the reinforcement system and the aluminium surface treatment, showing that NFML performance is controlled not only by fibre type, but by the combined effect of laminate architecture and interface quality [48].

A similar direction can be seen in coir-based NFMLs. Santos et al. studied random short-coir laminates with aluminium skins and different matrices, including epoxy, polyester, and castor-oil-based resin. They reported flexural strengths of 89.47–103.07 MPa and flexural moduli of 24.19–29.05 GPa, while NaOH-treated epoxy laminates showed about 15% higher flexural strength than the polyester-based ones. This study is important because it shows that NFML development depends not only on strength improvement, but also on finding the best balance between performance and sustainability through proper selection of fibre, matrix, and surface treatment [52].

Overall, the available studies show that NFMLs are no longer only a conceptual green alternative to conventional FMLs. They now represent a growing research area with clear material systems, performance trends, and design challenges. Their main advantages are lower environmental impact, low density, good damping potential, and promising impact or formability behaviour in selected applications. However, they still remain limited by lower absolute strength, weaker durability, higher variability, and unreliable interfaces. As a result, current research is still focused mainly on coupon-scale studies, hybridisation, textile architecture, and surface treatment rather than on design allowables or primary structural applications. This is why NFMLs are currently more suitable for automotive, transport, and secondary structural uses than for direct replacement of aerospace-grade conventional FMLs. [1].

2.2.3. Aluminum surface treatment

Metal surface treatment is a key factor in fibre metal laminates because the metal–composite interface governs load transfer, delamination resistance, damage tolerance, and long-term durability. In aluminium-based laminates, the natural oxide layer is too thin and unstable to ensure reliable bonding, so surface pre-treatment is required to remove contaminants and weak oxide layers and to create a more active and wettable surface. Among the available methods, anodizing remains the most established conventional treatment because it forms a porous oxide layer that improves both corrosion resistance and adhesion.

Anodizing is an electrochemical treatment in which aluminium acts as the anode and an artificial oxide layer is formed on its surface [53]. Unlike the natural oxide, this anodic film is much thicker and, in acidic electrolytes, usually consists of a thin barrier layer and a porous outer layer. This porous structure is important in FMLs because it increases surface area, improves wettability, and allows resin or primer to penetrate the oxide, which improves mechanical interlocking and interfacial bonding [54]. However, the final oxide structure depends strongly on the electrolyte, voltage, current density, and temperature.

Among conventional anodizing methods, the most common are chromic acid anodizing (CAA), phosphoric acid anodizing (PAA), and sulfuric acid anodizing (SAA) [55]. Historically, CAA became the aerospace benchmark because it offered a particularly favorable balance between adhesion, corrosion protection and fatigue performance in bonded aluminum structures. Abrahami et al. describe CAA as the central pre-treatment for structural adhesive bonding for more than six decades [53], while Martínez-Viademonte et al. note that aerospace corrosion protection traditionally relied on Cr(VI)-containing anodic systems because of their effectiveness and versatility [54].

From the bonding point of view, the main benefit of conventional anodizing is the surface it produces. Wu et al. showed that anodized aluminium developed a porous oxide layer with better wettability than sanded aluminium, and that phosphoric acid anodizing gave the highest shear strength among the surface treatments they studied for FML interfaces. The anodized surfaces also had lower contact angles and higher surface energy, which indicates better adhesive spreading and penetration. Similarly, Drożdziel-Jurkiewicz and Bieniaś reported that electrochemical treatments

produce thin porous oxide layers with higher surface area and polar functionality, making them more suitable for metal–composite bonding than untreated surfaces [56].

The positive effect of anodizing is also reflected in the mechanical performance of FMLs. Aghamohammadi et al. showed that abrasion and alkaline treatment resulted in weak interfacial bonding and mainly adhesive failure, whereas FPL etching and anodizing produced oxide surfaces with microscale pits that promoted resin penetration and stronger mechanical interlocking. Under the best anodizing condition, the flexural strength reached about 623 MPa, which was roughly 55% higher than that of the mechanically abraded laminate. This shows that anodizing is not only a corrosion-protection treatment, but also a method that directly affects failure mode and structural efficiency in FMLs [57].

However, conventional anodizing is not an ideal solution in all cases. Its main limitation is that the required functions are partly conflicting. In high-performance laminates, the anodic film is expected to provide corrosion resistance, strong adhesion to resin or primer, and minimal reduction in fatigue performance at the same time. In practice, these requirements often do not align. A thick and dense oxide layer usually improves corrosion protection, but may reduce adhesion or fatigue resistance, whereas a more open porous structure may enhance bonding while providing weaker barrier protection. For this reason, no single conventional anodizing system is universally optimal for all aluminium–polymer laminate applications [54].

A second limitation is that each conventional anodizing method has its own weaknesses. PAA is usually preferred for bonding because it creates a more open porous oxide, but its corrosion resistance is generally lower than that of CAA and it often requires additional primer systems to achieve sufficient durability. In contrast, SAA tends to produce a thicker and denser oxide, which is better for corrosion and wear resistance, but less suitable for adhesive bonding and potentially less favorable for fatigue-sensitive structures. For this reason, PAA is generally considered more adhesion-oriented, while SAA is more corrosion-oriented, and neither fully reproduces the balanced performance historically associated with CAA. This difference is reflected in oxide morphology. Drożdżiel-Jurkiewicz and Bieniaś reported that CAA produced pores of about 20–32 nm with an average thickness of $4 \pm 0.3 \mu\text{m}$, whereas SAA produced smaller pores of about 8–12 nm and a thicker oxide of $6 \pm 0.2 \mu\text{m}$ [56]. They also observed that primer filling was more effective in the CAA-generated pores than in the SAA-generated ones [56]. These findings help

explain why CAA historically performed so well for structural bonding, while SAA often requires modification or combination with other steps to reach similar interface quality.

A third and now major limitation is environmental and regulatory. CAA, which has long been the main benchmark for aluminium bonding, is based on hexavalent chromium, a toxic and carcinogenic substance. Recent reviews show that Cr(VI)-based systems are under increasing health and environmental restrictions and are gradually being replaced. Therefore, although CAA is still often used as the reference treatment, it is no longer a suitable long-term solution from a sustainability perspective. In the context of sustainable NFMLs, this provides a clear reason to investigate greener anodizing routes instead of relying on conventional chromate-based processes.

Finally, conventional anodizing is strongly process-sensitive. Oxide morphology changes with voltage, temperature, dwell time and electrolyte composition. Higher temperatures and more aggressive electrolytes can widen pores, roughen the oxide/resin interface and in some cases improve wet durability, but excessive dissolution can also damage the oxide structure and promote degradation. Abrahami et al. showed that durable bonding depends not only on having pores, but on having the right pore size and surface roughness [58]; too little roughness gives weak wet performance, while too much dissolution can make bonds prone to corrosion-related degradation [58]. Thus, conventional anodizing should not be treated as a simple “on/off” surface treatment, but as a tightly controlled process window in which small parameter changes can shift the balance between adhesion improvement and interface instability.

Overall, conventional anodizing remains one of the most effective aluminum surface treatments for fiber metal laminates because it creates a porous oxide capable of increasing wettability, interfacial area and resin anchoring. However, its use is limited by three persistent problems: the trade-off between adhesion and corrosion protection, the incomplete suitability of individual conventional anodizing systems such as PAA and SAA, and the environmental unsustainability of chromate-based benchmark processes such as CAA. These limitations explain why current research is moving toward modified or Cr(VI)-free anodizing systems, which are discussed in the next section.

2.2.4. Sustainable KCl anodizing

The development of sustainable fiber metal laminates requires not only the replacement of synthetic fibers with more environmentally favorable alternatives, but also reconsideration of the metallic surface treatment used to promote metal–composite bonding. Conventional anodizing methods, especially those based on strong acids and chromate-containing chemistries, remain effective but raise significant environmental, safety, and cost concerns. For this reason, recent research has increasingly focused on greener electrochemical treatments capable of producing bond-promoting oxide layers without relying on hazardous acidic systems [53,59].

A particularly relevant recent development is the KCl-based anodizing route proposed by Bakhbergen et al. for aluminum–polyurethane adhesive joints. In that study, a KCl/DMF-based anodizing process was introduced as a green, cost-effective and acid-free alternative to conventional aluminum anodizing for interfacial strengthening [60]. The authors explicitly position the process as a response to the limitations of conventional anodizing, noting that acid-based treatments improve adhesion but introduce handling risk, environmental burden and additional cost. By contrast, the KCl-based system was designed to produce a porous oxide layer using a less hazardous electrolyte while remaining compatible with industrial processing requirements [60,61].

From a mechanistic point of view, the process remains fundamentally anodic oxidation of aluminum. During treatment, aluminum at the anode is oxidized and forms a porous alumina-based surface layer. At the cathode, water reduction generates hydroxide ions, while the anodized surface develops a textured oxide morphology that increases surface roughness and surface free energy. According to the schematic and microstructural interpretation presented by Bakhbergen et al., the resulting surface is governed primarily by the formation of a porous alumina layer, while aluminum hydroxide precipitates may also appear under some processing conditions as a secondary effect [60]. This distinction is important: precipitation is not the main adhesion-promoting feature, whereas the porous oxide morphology is. The authors further show through SEM, EDS and FTIR that the treatment produces a rough, porous and chemically activated aluminum surface, which is highly favorable for adhesive wetting and mechanical interlocking [60,62].

The relevance of this mechanism to FML-type bonding lies in the way the oxide morphology modifies the interface. A sufficiently rough and porous anodized surface can increase real contact area, promote resin or adhesive infiltration into pores, and enhance mechanical interlocking between aluminum and the polymer phase. At the same time, increased surface free energy improves wettability and encourages stronger interfacial interaction. Bakhbergen et al. showed that, after KCl/DMF anodizing, the aluminum surface became much more hydrophilic and exhibited a major increase in surface free energy, especially in its polar component, which played an important role in improving adhesion [60]. Their structure–property analysis indicates that the best bonding performance was achieved not with the most extreme roughness, but with a balanced surface state, where roughness and pore morphology were sufficient to promote interlocking without creating excessive defects or unstable wetting conditions [60].

This makes parameter optimization essential. In the KCl-based study, a full factorial design of experiments was used to evaluate the effects of electrolyte concentration, anodizing voltage, and treatment time, each at three levels [60]. Statistical analysis showed that the surface characteristics and joint performance were not controlled equally by all parameters. For average surface roughness and maximum valley depth, anodizing time emerged as the dominant factor, while for lap shear strength the most influential effects were concentration and time, together with their interaction [60]. The study reported that the optimum condition was 0.1 M KCl, 12 V, and 5 min, under which lap shear strength increased from 1.09 MPa for the untreated joint to 3.51 MPa, while fracture energy increased from 2.41 mJ/mm³ to 115.32 mJ/mm³ [60]. This corresponded to an improvement of approximately 218% in lap shear strength and 67-fold in fracture energy relative to the untreated condition [60,63].

An important outcome of the same study is that the optimum did not correspond to the most aggressive treatment. Very long treatment times and excessively developed topography could produce over-roughened surfaces with large pores and less favorable wetting states, which in turn reduced bonding efficiency [60]. This is highly relevant for the present thesis because it supports the broader principle that anodizing should not be maximized indiscriminately. Instead, the process should be tuned to obtain an oxide layer with an appropriate balance of compactness, porosity and surface activity. In other words, the best aluminum treatment is one that creates sufficient

anchorage and wettability without causing excessive defect formation or unstable interface morphology [60,64].

The fracture analysis in that work also provides strong support for the role of KCl-based anodizing in improving interface integrity. Untreated joints showed predominantly adhesive failure, whereas the optimized anodized joints displayed almost fully cohesive failure, indicating that the aluminum–polymer interface had become stronger than the bulk adhesive itself [3]. This transition in failure mode is particularly important in the context of fiber metal laminates, where interfacial debonding is often one of the earliest damage mechanisms under tensile, flexural or fatigue loading. Therefore, although the study was conducted on aluminum–polyurethane joints rather than full FMLs, its conclusions are directly relevant to FML and NFML interface design [3][65].

The same paper is also highly useful because it places the KCl-based route in direct comparison with conventional anodizing methods. Under the selected optimum condition, the proposed KCl/DMF process outperformed sulphuric-acid and phosphoric-acid anodizing conditions tested in the same study, while also being cheaper and less hazardous [3]. The cost analysis reported by the authors showed that the KCl/DMF route was substantially less expensive than conventional sulphuric- and phosphoric-acid anodizing, while still providing higher or comparable adhesion performance [60,65]. Thus, KCl-based anodizing is not only environmentally attractive in principle, but also technically and economically competitive [60,65].

Overall, the recent literature now provides direct support for the use of KCl-based anodizing as a sustainable aluminum surface treatment. The mechanism involves the electrochemical formation of a porous alumina-rich surface with increased roughness and surface free energy, thereby improving wettability and mechanical interlocking at the metal–polymer interface. At the same time, the treatment response is strongly dependent on concentration, voltage and time, making optimization essential. These findings provide a strong foundation for the use of KCl anodizing in the present work, where it is explored as an environmentally friendlier route for improving aluminum bonding in natural fiber metal laminates.

Chapter 3 – Methodology

3.1. Materials

Fiber etching was performed using NaOH pellets (purified, 97%, SRL) and DI water. Random orientation flax fiber mats sourced locally were used for all experiments. KER 828 DGEBA epoxy resin (Kumho P&B Chemicals, Inc.) with Jeffamine® D-230 Polyetheramine hardener (Huntsman Co., USA) were used as matrix.

Aluminum alloy 6061-T4 with a thickness of 0.5 mm was selected as the metallic substrate for the fabrication of FMLs. The chemical composition and mechanical properties of the Al6061-T4 metal sheets are given in Table 2.

Table 2. Chemical composition and mechanical properties of Al6061-T4

Chemical composition									
Element	Al	Si	Fe	Cu	Cr	Mg	Mn	Ti	Zn
Percentage (%)	Bal.	0.4-0.8	0.7	0.15-0.40	0.04-0.35	0.8-1.2	0.15	0.15	0.25
Mechanical properties									
Young's modulus	Tensile strength		Elongation at break			Shear strength		Hardness	
68.9 GPa	205 MPa		16-25 %			140 MPa		65 HB	

Acetone, sourced locally, was utilized for degreasing the Al surface. Electrochemical surface treatment was performed using potassium chloride (KCl, ACS reagent, 99–100%, Sigma-Aldrich). NaOH pellets (purified, 97%, SRL), and HCl (ACS reagent, 37%, Honeywell) were used during the pre-treatment stage. Deionized (DI) water was used for solution preparation, ultrasonic cleaning, and as a polar solvent for contact angle measurements, in addition to dimethyl sulfoxide (DMSO, ACS reagent, $\geq 99.9\%$) from Sigma-Aldrich. For the salt spray test, NaCl (chemically pure grade, Russia) was utilized.

3.2. Sample preparation

3.2.1. Flax fiber etching

NaOH etching of flax fibers was performed under varying solution temperature, concentration and treatment duration to achieve optimal lignin removal without damaging fibers' structure. Optimal etching conditions are not defined conventionally because flax fibers' properties range significantly depending on the plant's growing conditions and manufacturing methods used during production. However, based on available literature efficient etching duration, concentration, and temperature are in range of 20-60 min, 1-5wt% of NaOH, and 20-60°C respectively [35,66]. To find optimal conditions in given ranges, 9 experiments were designed following Taguchi L9 design of experiments as shown in Table 3. This method allowed the evaluation of the effect of each etching parameter on the flexural and tensile strength using minimal number of experiments. Owing to this approach number of experiments required to identify optimal etching parameters reduced from 27 to 9.

Flax fiber mats were cut into 22 x 16 cm sheets and stacked on the bottom of the container. Container with fibers was placed in oven and heated to the required temperature to avoid the temperature fluctuations. The NaOH solution was prepared by adding 1, 2 or 5 wt% of NaOH pellets into the beaker with 500 ml of DI water. Solution was constantly stirred at 500 rpm and heated by a hotplate. The temperature of the solution was measured by thermometer. This process continued until the temperature reached required level. Then container was taken out of the oven, solution was poured in, fibers were pressed and released using a roll to make sure that the solution is absorbed. The volume of the solution was sufficient to fully submerge the fibers. Then the container was placed back in the oven and timer was set. After half of the required duration passed, container was taken out, fibers were flipped upside down to ensure uniform etching, and container was placed back into the oven for the remaining duration of etching. By the end of the etching process samples were taken out of the container and washed. Washing was conducted by submerging fibers into the container filled with DI water, pressing and releasing to facilitate water absorption, and replacing the water with clean DI water. This process was repeated several times until the pH level became neutral. Then fibers were placed into the oven and heated to 105°C for 3 h to dry. The mass of fibers was monitored to ensure complete moisture evaporation.

Table 3. Taguchi L9 alkali etching condition parameters

Time, min	Concentration, wt%	Temperature, °C	Sample ID
20	2	40	20min-2%-40deg
20	5	60	20min-5%-60deg
20	1	20	20min-1%-20deg
40	2	60	40min-2%-60deg
40	5	20	40min-5%-20deg
40	1	40	40min-1%-40deg
60	2	20	60min-2%-20deg
60	5	40	60min-5%-40deg
60	1	60	60min-1%-60deg

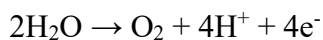
3.2.2. Fundamentals of Al surface anodizing

Electrochemical surface treatment is one of the effective methods to enhance the interfacial strength between metal and polymer layer in composite materials. Controlling the oxidation process leads to the formation of highly ordered porous oxide layer on the metal surface, improving mechanical interlocking of the polymer with the metal, as illustrated in Figure 2.

The overall anodizing mechanism is governed by two fundamental stages: metal oxidation and oxide layer formation. Metal substrates such as aluminum act as the anode and will be submerged in an electrochemical cell under an applied external potential [11].



In the first stage, the metal undergoes the oxidation process, they lose electrons forming metal cations, which are dissolved in the electrolyte and can react with the oxygen containing species, such as hydroxide or oxide. These oxygen species are mainly formed on the surface via decomposition of water.



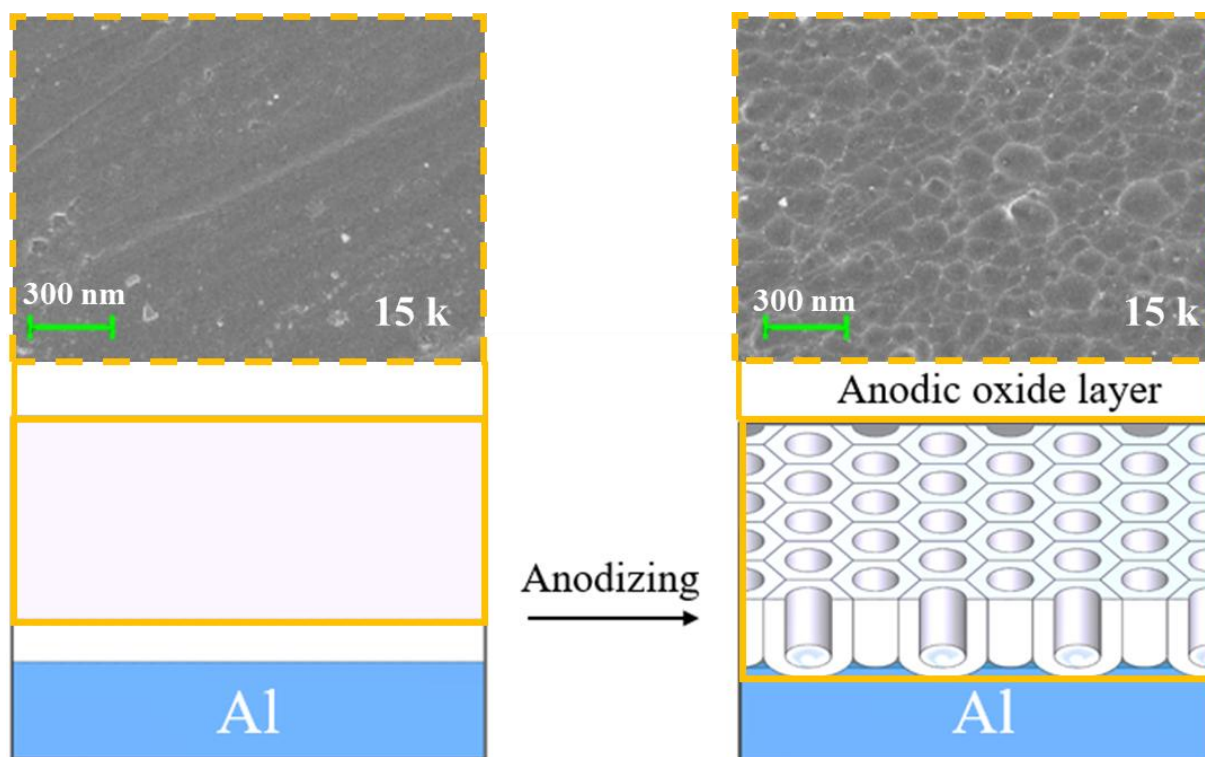


Figure 2. SEM characterization and schematic illustration of nanoporous oxide formation on Al surface

Most research has used the field-assisted dissolution model to explain the pore initiation and growth during the anodizing [12]. Based on this approach, a homogeneous oxide layer develops under constant electric field strength. Oxide growth occurs at the metal-oxide interface, while dissolution is active at the oxide-electrolyte interface. This leads to the formation of a steady-state condition, where the formation and dissolution of the oxide take place simultaneously, but in two distinct interfaces. The short path that the oxygen ion must diffuse and the high electric field at the pore bottom also contribute to the growth of the porous structure.

Conventional electrochemical surface treatment methods involve acid-based electrolytes – hazardous chemicals, such as sulfuric [13, 14], phosphoric [15, 16] and tartaric [17]. Therefore, green and cost-effective alternative of electrochemical surface treatment method – KCl based anodizing [8] was used to modify the surface topography for FML production. At the aluminum surface, the metal is oxidized to Al^{3+} ions and then form aluminum oxide.



The growing oxide layer will act as dielectric barrier preventing further ionic transport and decreasing the current density until chemical dissolution or formation of pore occurs. However, continuous oxide layer development is maintained through a dynamic balance between oxide layer formation at the metal-oxide interface and dissolution at the oxide-electrolyte interface. In conventional acid-based anodizing, aggressive anions enhance localized dissolution, hence promoting ordered pore formation. In KCl-based systems, chloride ions play a similar role, facilitating localized chemical dissolution and thus affecting pore formation. However, this effect is less aggressive than acid based anodizing methods. The interplay between electrochemical oxidation, ion migration, and chloride-assisted dissolution in KCl anodizing governs the change of surface morphology and the formation of porous oxide layers, which improves the interfacial bonding between metal and fiber reinforced polymer layers.

3.2.3. Electrochemical surface treatment

Prior to lamination, a green anodizing approach based on KCl solution that was discovered by Bakhbergen et al. [8] was applied to enhance the interfacial bonding between Al and natural fibers/epoxy layers. Initially, Al6061-T4 sheets were cleaned with acetone to remove surface contaminants, such as dirt and grease. Then, a pre-treatment process was carried out to remove the native oxide layer and activate Al surface. Metal sheets were first soaked in 5wt% NaOH solution and rinsed in 11wt% HCl solution, as shown in Figure 3 (a). For the anodizing process, the required quantity of KCl was dissolved in water and stirred at room temperature during the process, as illustrated in Figure 3 (b). After anodizing, samples were gently wiped with ethanol to remove residual electrolyte and dried in a vacuum oven at 60°C.

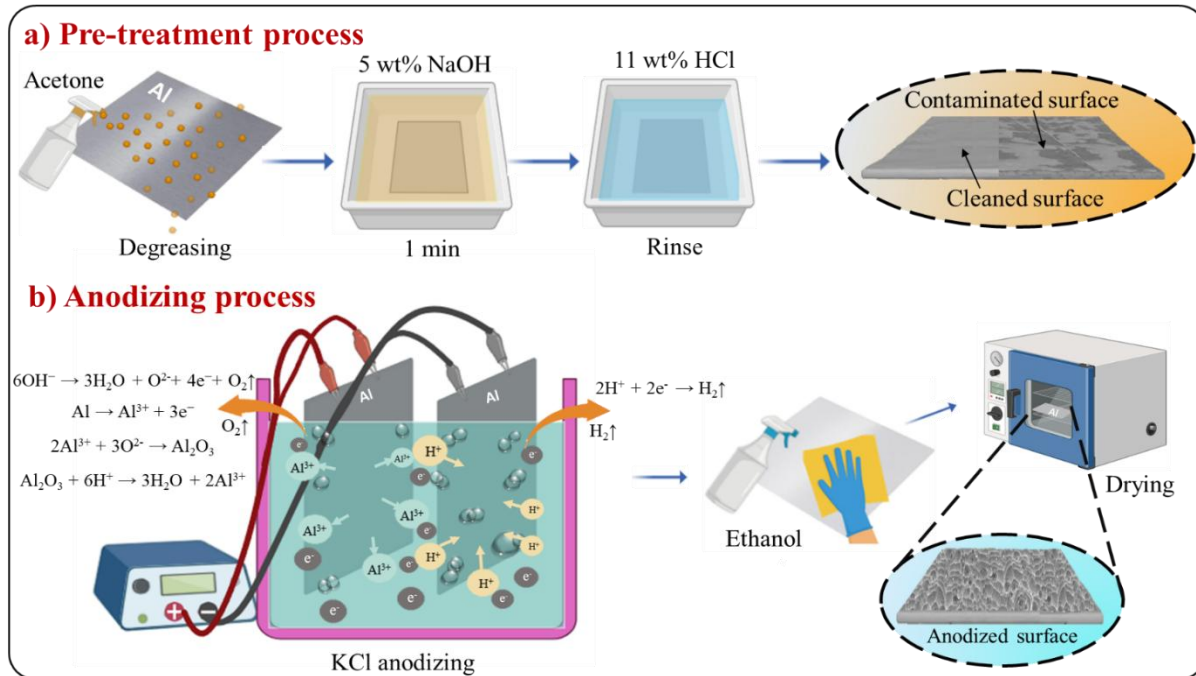


Figure 3. The schematic illustration of anodizing Al6061-T4 surface

Taguchi design of experiments was utilized to optimize the KCl anodizing conditions. Three process parameters were considered: electrolyte concentration, anodizing duration and applied voltage. The selected levels and combination of these parameters are given in Table 4.

Table 4. Combination of the anodizing conditions

Concentration, M	Time, min	Voltage, V	Sample ID
0.05	10	8	0.05M-10min-8V
0.05	10	12	0.05M-10min-12V
0.05	10	16	0.05M-10min-16V
0.1	20	12	0.1M-20min-12V
0.1	20	16	0.1M-20min-16V
0.1	20	8	0.1M-20min-8V
0.15	30	16	0.15M-30min-16V
0.15	30	8	0.15M-30min-8V
0.15	30	12	0.15M-30min-12V

3.2.4. Composite preparation using VARTM

NFRPs and FMLs were prepared using XM-5104 electronically heated resin transfer mold (RTM). First, RTM was prepared. The mold consisted of a bottom part, a top part, a touchscreen used to control the heating elements, a resin inlet and outlet, a vacuum pump connected to the resin outlet through a resin trap and other parts as shown on Figure 4. For NFRPs 4 layers of flax fiber mats were stacked inside the mold. Similarly, for FMLs 1 layer of anodized aluminum followed by 2 layers of flax fiber mats and 1 layer of aluminum were stacked. A 2.5 mm thick shim was then placed around the stack to ensure uniform thickness of the final laminate. After that, the top part of the mold was closed and tightened to ensure vacuum sealing. The mold was switched on and preheated to 60°C. The vacuum pump was then turned on to create negative pressure inside the mold. Once the pressure stabilized, the resin was allowed to infiltrate the composite stack. After complete impregnation of the fabric layers, the resin inlet and outlet were sealed, and the mold was kept closed under vacuum and cured at 60°C for 24 h. After curing, the laminate was removed from the mold and left to cool to room temperature.

VACUUM-ASSISTED RESIN TRANSFER MOLDING TOOL (VARTM)

VARTM tool transfers resin between the layers of fibers using negative vacuum pump



Figure 4. Vacuum assisted resin transfer mold

3.3. Testing and characterization

3.3.1. Mechanical properties of composite materials (NFRP, FML)

The mechanical performance of the fabricated NFRPs and FMLs were determined using tensile and flexural tests at ambient temperature as shown on Figure 5. All tests were performed using a microcomputer controlled electronic universal testing machine (UTM) (CMT5105, China) with a maximum load capacity of 100 kN. Radial extensometer shown on Figure 5 (a) was used to measure strain (CMT5105, China). For each test condition, three specimens were tested to ensure reproducibility.

The tensile properties of the composite materials were measured following ASTM D3039 standard [1, 2]. Waterjet cutting was employed to obtain specimens with precise dimensions. The specimens had dimensions of 160 mm in length and 25 mm in width. The specimens were attached to the UTM using grips and the extensometer was attached to them as shown on Figure 5 (b). The grip distance of 30 mm on each side was maintained for all tests. The test was conducted at a crosshead speed of 2 mm/min. Both load and displacement were recorded to get the stress-strain behavior. The ultimate tensile strength and Young's modulus were subsequently calculated. The ultimate tensile strength was determined using equation (1).

$$\sigma = \frac{F}{b \cdot h} \quad (1)$$

Where σ is the ultimate tensile strength (MPa), F is the maximum applied load (N), b and h are the width and height of the specimens, respectively.

Three point bending test was conducted to evaluate the flexural properties of composite materials according to the ASTM D790 standard [3], with the same specimen size as for the tensile test. The specimen was located with its center in the middle of the supports as shown on Figure 5 (c). The distance between supports was 105.6 mm. The test was determined at a crosshead speed of 13.7 mm/min. The flexural strength and flexural modulus values of specimens were calculated using equations (2) and (3), respectively.

$$\sigma_f = \frac{3FL^2}{bh^2} \quad (2)$$

and

$$E_b = \frac{L^3 m}{4bh^3} \quad (3)$$

Where E_b is the modulus of elasticity in bending (MPa), L is the support span. The interface and fracture analysis of NFRP and FML were characterized by scanning electron microscopy (SEM, Helios 5 CX DualBeam, Thermo Scientific).

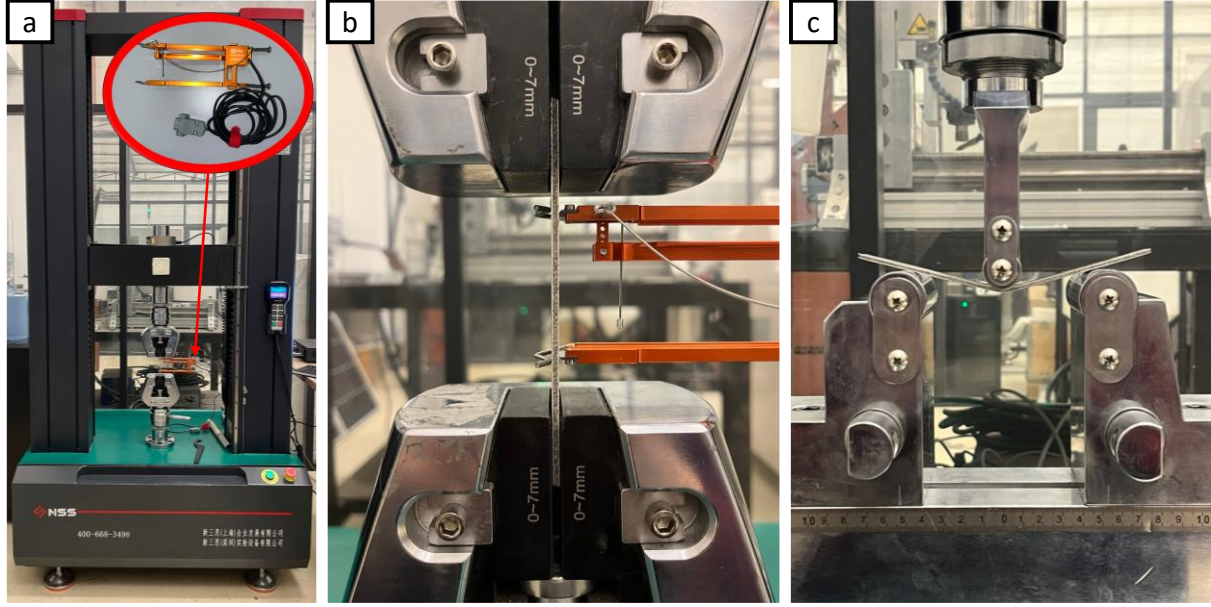


Figure 5. (a) Universal testing machine; (b) Tansile test setup; (c) 3-point bending test setup

3.3.2. Anodized surface characterization

The surface characteristics of the anodized Al were assessed through roughness measurements using a contact profilometer (Dektak XT Stylus Profiler, Bruker). The arithmetic mean roughness (R_a) and the maximum valley depth (P_v) were evaluated from surface roughness analysis in accordance with JIS B 0601 standard [4]. Measurements were carried out along four randomly distributed 800 μm lines scattered across the sample. Contact angle values were used to determine the surface wettability by OCA 25 by DataPhysics. Distilled water and DMSO with a droplet volume of 1 μL were used as the test droplets, and surface energy was calculated according to Owens and Wendt equation [5]. The values for dispersive and polar components of surface tension for the solvent are given in Table 2. Atomic force microscopy (AFM, SmartSPM 1000, Horiba Scientific) and SEM were used for topographical and morphological analysis of the anodized surface.

Table 5. Dispersive and polar components and liquid surface tension [6]

Surface tension, mJ/m²	Dispersive	Polar	Total
Water	27.19	45.61	72.8
DMSO	36	8	44

3.3.3. Salt spray test

The durability of NFRPs was evaluated using a salt spray chamber test (S-750, China) through simulating the harsh environment in accordance with ASTM B117 standard [7]. Specimens were subjected with an inclination of 20° to the vertical direction and exposed to a continuous fog of 5wt% NaCl solution at constant temperature of 35°C. At different ageing durations (72h and 168h), three specimens were removed from the chamber for further analysis. After exposure to environmental conditions, mechanical characterization was conducted through tensile and flexural tests. Prior to testing, samples were rinsed with DI water and dried at room temperature for 24h. The interfacial characteristics and microstructural changes were examined through SEM. The obtained results were compared with unexposed specimen (0h) to assess the effects of salt spray aging.

Chapter 4 – Results and Discussion

4.1. NFRPs

4.1.1. Effect of NaOH etching on mechanical properties

The mechanical results showed that alkali treatment affected the flax/epoxy laminates in a non-monotonic manner, indicating that composite performance depended strongly on the balance between interfacial improvement and fiber damage. As shown in Figure 6 (a, c), the untreated reference laminate exhibited the lowest tensile strength, 64.4 MPa, while one of the weakest treated conditions was 20 min, 5 wt.% NaOH, 60 °C, which gave 66.0 MPa. Another low tensile result was obtained for 60 min, 1 wt.% NaOH, 60 °C (67.1 MPa). In contrast, the best tensile responses were recorded for 40 min, 1 wt.% NaOH, 40 °C (73.8 MPa), 40 min, 2 wt.% NaOH, 60 °C (77.4 MPa), and 60 min, 2 wt.% NaOH, 25 °C (79.9 MPa). Young's modulus generally followed the same trend, indicating that the treatment conditions that enhanced tensile strength also tended to improve the stiffness of the composite.

A similar tendency was observed in flexural tests as shown on Figure 6 (b, d). The weakest flexural performance was again associated with the untreated laminate and the most severe treatment conditions, with flexural strengths of about 129 MPa for reference and 125 MPa for 20 min, 5 wt.% NaOH, 60 °C. The best flexural result among the Taguchi runs was obtained for 40 min, 1 wt.% NaOH, 40 °C, which reached 143.7 MPa, while flexural modulus showed a similar ranking. These results indicate that moderate treatment conditions were generally more beneficial than untreated or overly aggressive conditions. This interpretation is consistent with the literature, which shows that alkali treatment improves composite performance by removing waxes, lignin and other surface impurities, increasing fiber roughness, and enhancing fiber-matrix adhesion, whereas excessive treatment can weaken the fiber itself [11,29,35].

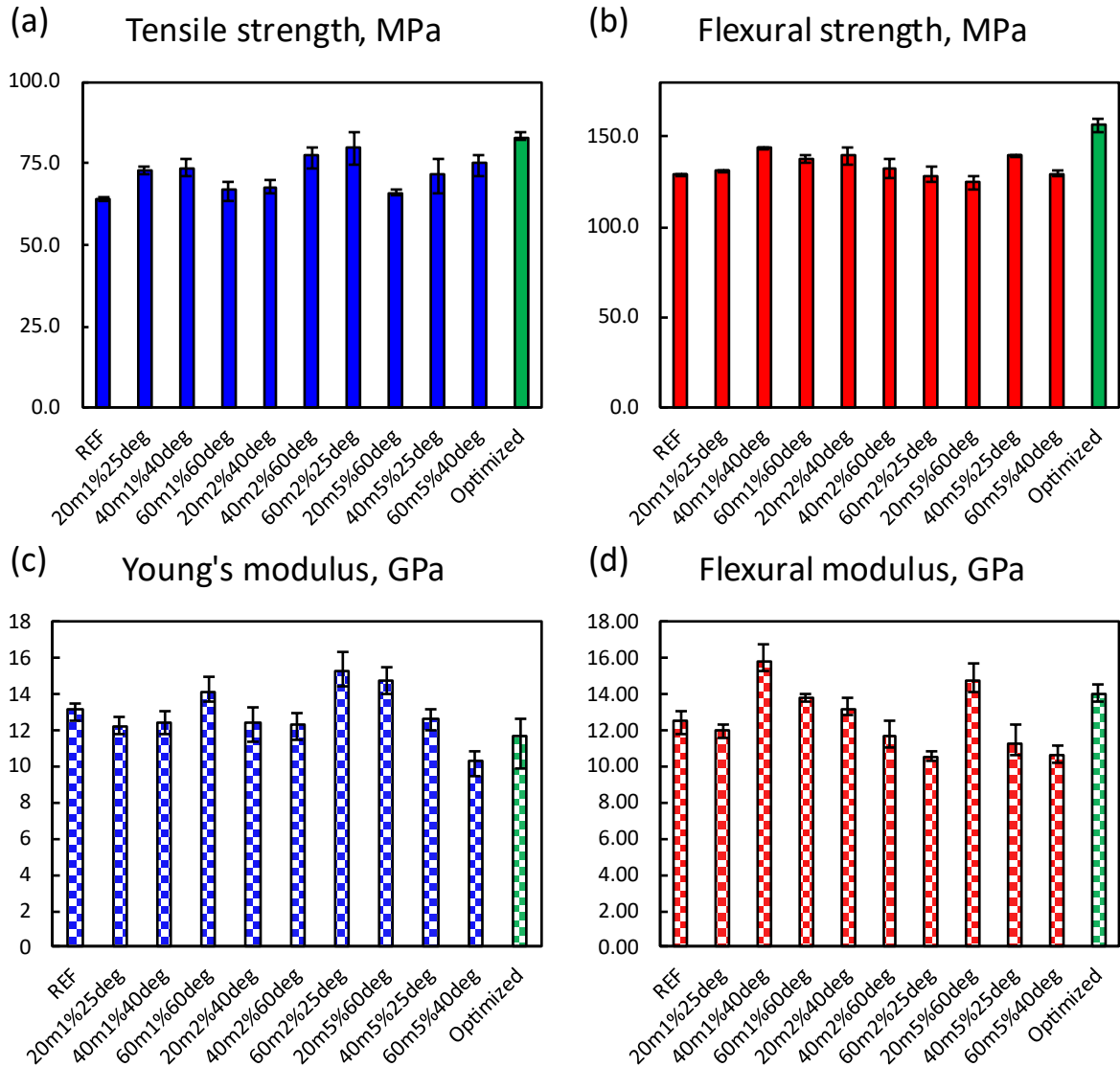


Figure 6. (a) Tensile strength, (b) Flexural strength, (c) Young's modulus, and (d) Flexural modulus values of NFRPs under different etching conditions

The comparatively low strength of the untreated laminate can be attributed to the relatively weak flax–epoxy interface. Without surface modification, non-cellulosic constituents on the fiber surface hinder effective wetting and reduce stress transfer from matrix to fiber [11,29,35]. By contrast, moderate alkali treatment can expose a cleaner and rougher surface, thereby improving mechanical interlocking and interfacial bonding. Yan et al. reported that although alkali treatment reduced the tensile properties of the flax yarn itself, the tensile and flexural strengths of the flax/epoxy composite increased by 21.9% and 16.1%, respectively, due to better fiber/epoxy adhesion and improved fracture-surface characteristics [11,29,35]. The same mechanism explains

the present improvement under the more favorable treatment conditions. At the same time, the low mechanical values obtained under 5 wt.% NaOH and 60 °C suggest that treatment severity became excessive when high concentration and high temperature were combined. This is also supported by literature. Bahrami et al. showed that mild alkalization of flax fibers in 5% NaOH preserved tensile behavior and reduced moisture uptake, whereas severe mercerization in 20% NaOH reduced fiber rigidity because of excessive elimination of non-cellulosic constituents and structural transformation in cellulose [27]. In this research work, concentration was the same as the optimal etching concentration used by Bahrami, however high temperature made the reaction more aggressive. Similarly, Chandrasekar et al. noted that there is an optimum treatment window, beyond which over-treatment leads to fiber cracking and deterioration of mechanical properties. Therefore, the weak performance of the most aggressive conditions in the present study is most reasonably attributed to fiber damage outweighing the benefit of surface cleaning.

The Taguchi analysis, presented in Figure 7, helped interpret these trends at the factor level. For tensile strength, the main effects plot suggested the highest response at 2 wt.% NaOH, 40 min, and 20 °C, while the Pareto chart indicated that treatment duration and temperature had the largest relative effects, with duration being slightly more influential. For flexural strength, the main effects plot indicated an optimum at 1 wt.% NaOH, 40 min, and 40 °C, and the Pareto chart ranked NaOH concentration as the most influential factor. However, none of the effects crossed the reference line in either case. This means that, within the investigated parameter ranges, the effects of concentration, duration and temperature were not statistically significant at the selected confidence level. Therefore, the Taguchi analysis should be interpreted as indicating relative trends rather than definitive factor significance. This is not unusual for natural-fiber composites, where material variability and fabrication scatter can reduce the statistical separation between treatment levels.

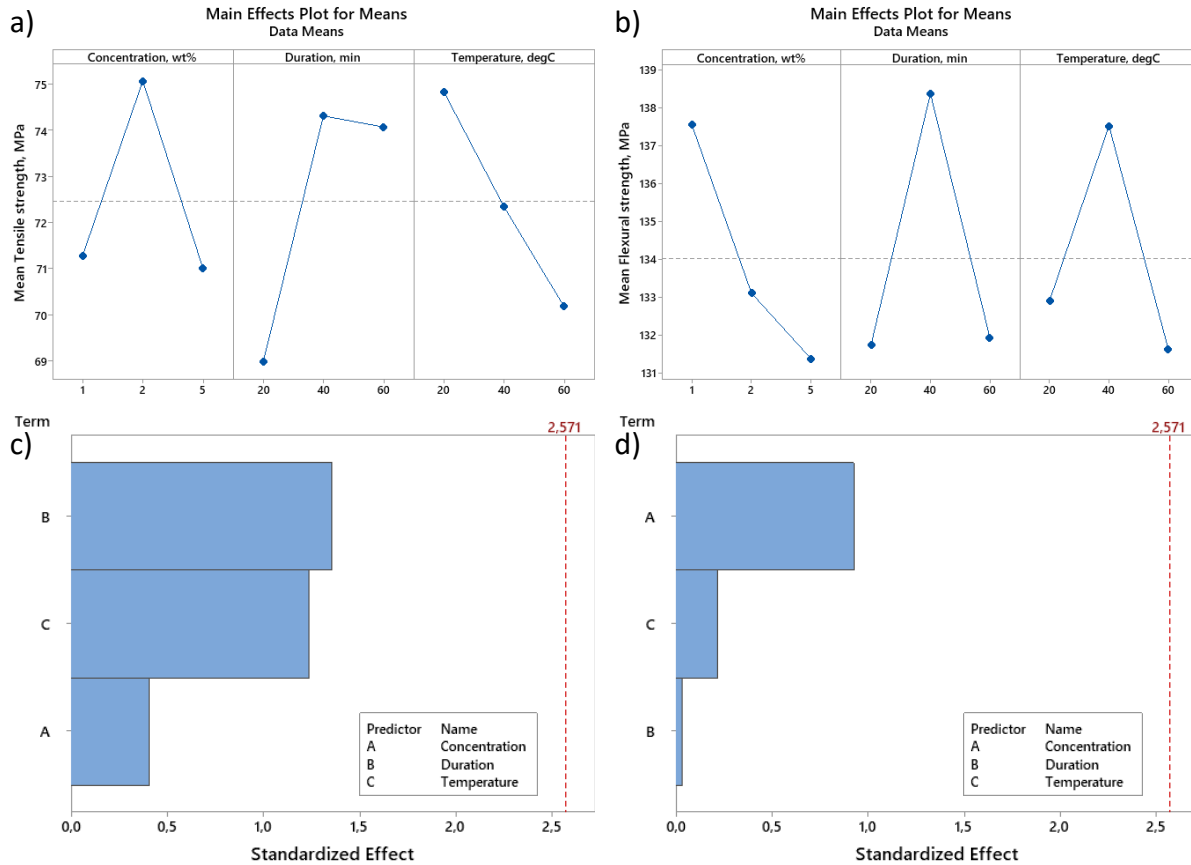


Figure 7. Main effect plots for (a) Tensile strength, (b) Flexural strength, and Pareto charts for (c) Tensile strength, (d) Flexural strength of NFRPs

Based on the combined experimental trends and Taguchi analysis, the condition 40 min, 2 wt.% NaOH, 40 °C was selected as optimal and a confirmation sample was manufactured to confirm the prediction. This specimen gave the best overall mechanical performance, reaching 83 MPa in tensile strength and 156.3 MPa in flexural strength, both higher than any of the original Taguchi runs as shown in green color on Figure 6. This result confirms that the optimization approach was effective even though the individual Pareto effects were not statistically significant. In other words, the selected condition acted as a practical optimum by combining the favorable features identified separately in the tensile and flexural analyses. However, Young's modulus and flexural modulus for this sample remained only at intermediate values. This suggests that the main benefit of the optimum treatment was not an increase in stiffness, but rather a better balance of interfacial bonding, stress transfer, and damage resistance underloading.

Overall, the mechanical results demonstrate that alkali treatment improved flax/epoxy performance only within a controlled treatment window. Both the raw data and the optimization analysis indicate that moderate treatment conditions were beneficial, whereas untreated and overly aggressive conditions were unfavorable. The additional confirmation sample further strengthens this conclusion, showing that a balanced treatment condition of 40 min, 2 wt.% NaOH, and 40 °C provided the highest tensile and flexural properties for this NFRP system.

4.1.2. Effect of salt spray on mechanical properties of NFRPs

The durability of NFRPs was examined utilizing a salt spray test chamber to assess the effect of exposure on their mechanical properties. Among all etching parameters from the previous section, the best condition (40 min, 2 wt.% NaOH, and 40 °C) was selected for salt spray aging. Figure 8 shows the results for unaged sample (0h), representing the mechanical test results of the optimally etched sample, and the aged samples after 72h and 168h samples, which were placed in the salt spray chamber and removed after the required exposure time.

Figure 8 (a, b) presents the mechanical testing results, where both tensile and flexural strengths show marginal changes. The tensile strength decreased by 6.6% after 72h and by 9.3% after 168h, compared to the unexposed (0h) sample. A similar tendency is observed for flexural strength, which decreased by 5.8% after 72h and by 10.9% after 168h, indicating good durability of the material.

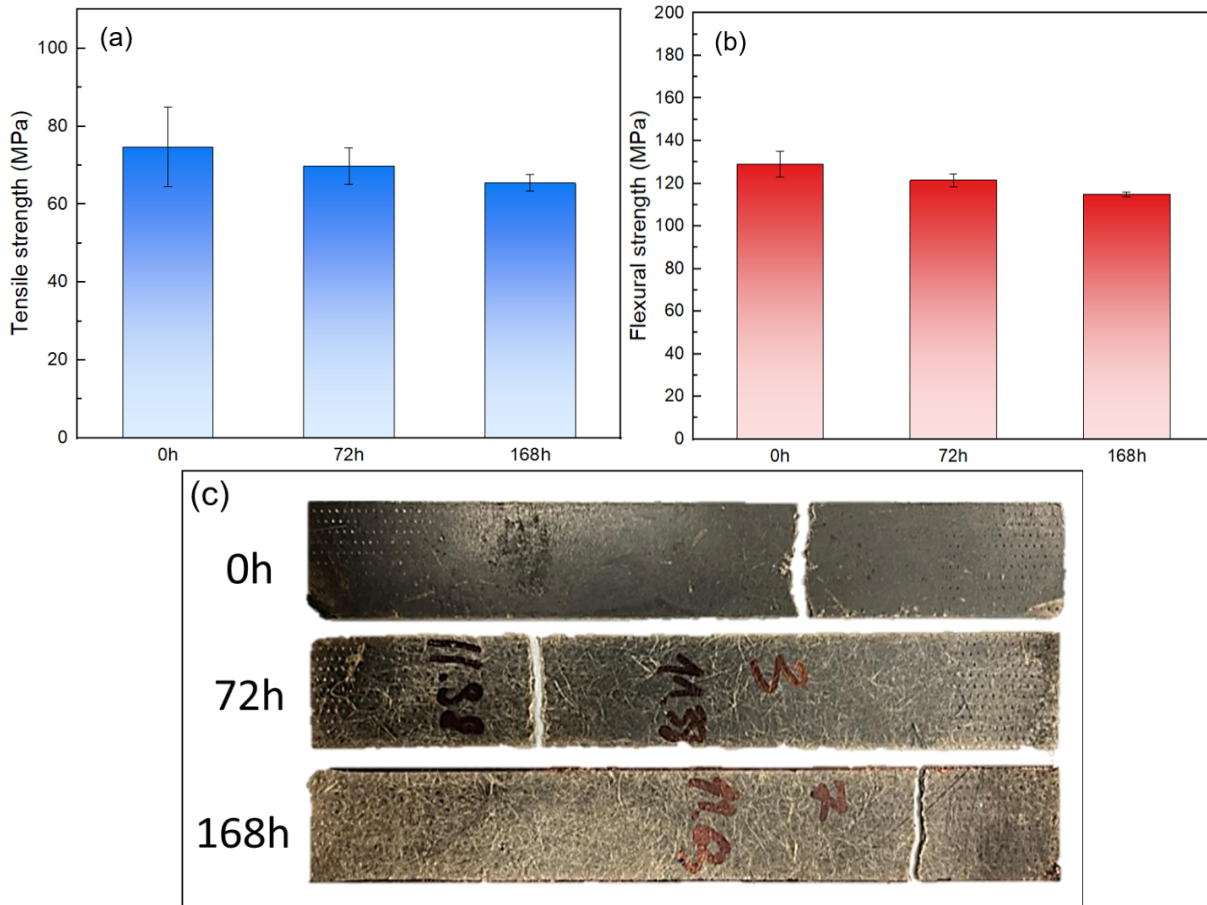


Figure 8. Effect of salt spray aging on NFRPs before exposure (0h) and after 72h, 168h exposure: (a) tensile strength; (b) flexural strength; (c) the failure of NFRPs

Figure 8 (c) demonstrates the failure of NFRPs before and after aging. The shape and tactile characteristics of the aged samples were identical to those of the unaged specimen. However, their visual appearance differed from unexposed samples, as the aged samples appeared brighter and the fibers became more visible.

Figure 9 presents SEM analysis of the unexposed and the sample exposed for 168h in salt spray chamber to determine the presence of corrosion products on NFRP surface. Figure 9 (a) shows the SEM image of the unexposed specimen, clearly exhibiting rough fibers, which indicates successful etching. In contrast, Figure 9 (b) demonstrates the presence of salt products on the fiber surface, highlighted by green circles. It can be explained as a complex degradation mechanism in NFRPs, governed by synergistic effects of ionic diffusion and interfacial deterioration [9].

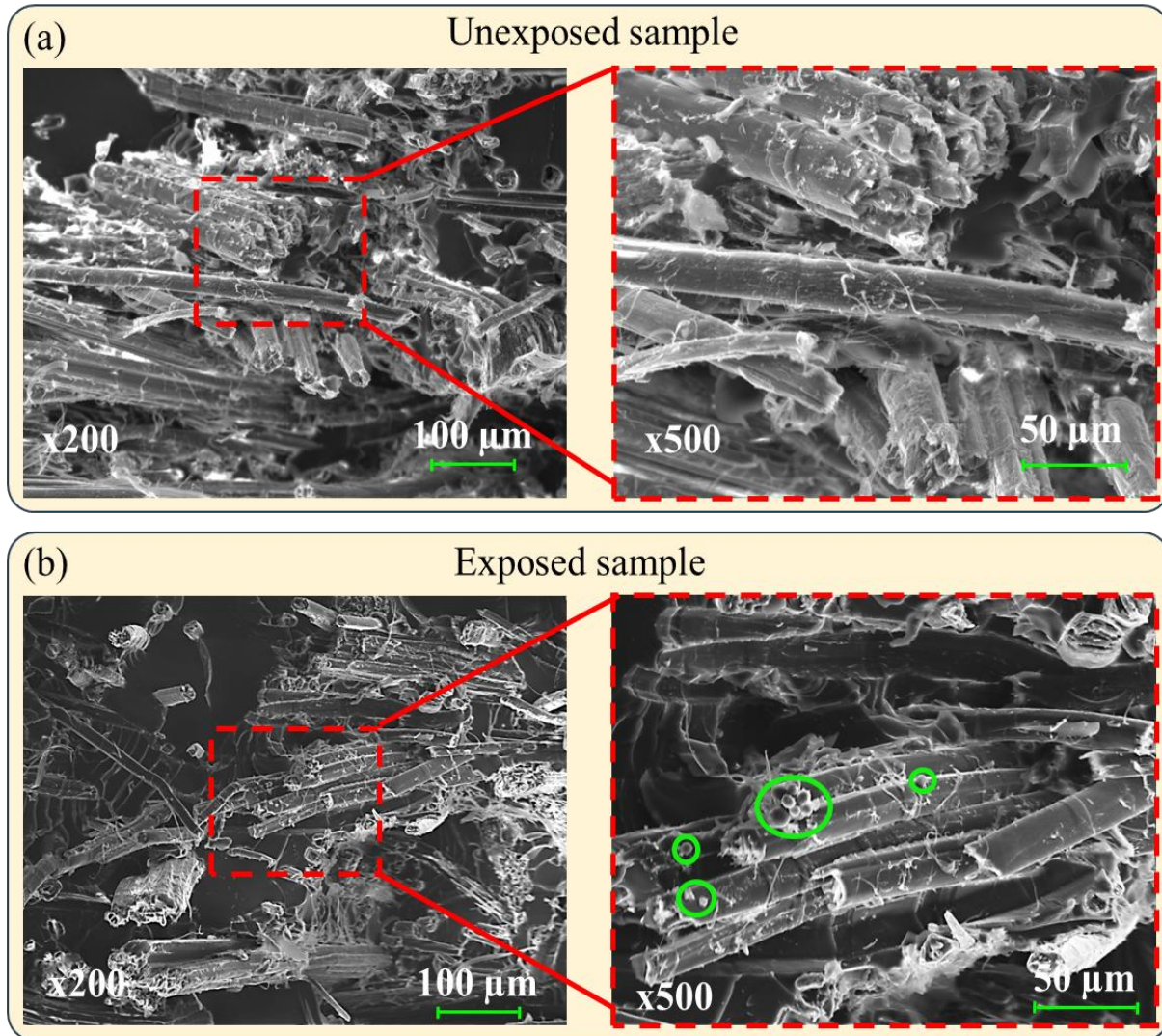


Figure 9. SEM images of NFRPs: (a) unexposed sample; (b) exposed sample after 168h

Figure 10. shows the schematic illustration of degradation processes and their impact on NFRPs. Initially, water molecules and dissolved ions from NaCl solution, such as Na^+ and Cl^- , occur on the material surface. Natural fibers contain abundant hydroxyl groups in their structure, which make them hydrophilic. As a result, microcracks, voids, and defects in fiber-matrix interfaces begin to appear. The fibers then undergo swelling process as water diffuses into the material, promoting debonding and weak interfacial adhesion. Water molecules interact with the polymer matrix and form hydrogen bonds with polymer chains, disrupting intermolecular interactions [10]. Along with physical effects, water also facilitates hydrolytic reactions, contributing to chemical degradation and leading to the formation of low molecular weight

products. Furthermore, ions from the solution can alter the local chemical environment or act as catalysts processes. The salt products shown on the fiber surface appear as agglomerated deposits or crystalline. Such deposits contribute to further degradation, indicating the penetration of saline solution into the NFRP, which can lead to crack propagation.

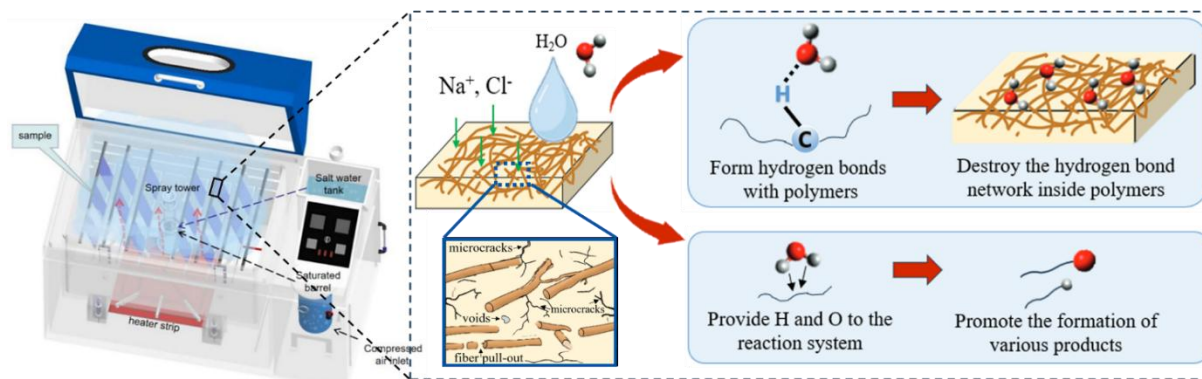


Figure 10. Schematic illustration of salt spray test mechanism and degradation process in NFRPs

4.2. FMLs

4.2.1. Al surface topography

The surface topography of anodized surface was assessed by evaluating the average surface roughness, maximum valley depth and surface free energy, as shown in Figure 11. Anodizing parameters strongly influenced the average surface roughness, as shown in Figure 11 (a). The highest roughness value was 435 nm, obtained at 0.15M-30min-16V, indicating promoted substantial surface texturing, compared to the untreated sample, which exhibited only 105 nm of roughness. At lower anodizing conditions, roughness values decreased, compared to the untreated substrate, producing smoother oxide layers. For instance, at 0.05M-10min the surface roughness measured 60 nm for 8V and 95 nm for 12V, while untreated sample exhibited 105 nm of roughness. Increasing the electrolyte concentration to 0.1M, 0.15M and anodizing duration to 20 min, 30 min at 8V resulted in an increase to 325 nm and 254 nm, for 0.1M-20min and 0.15M-30min, respectively. While at lower concentration the effect of voltage increases linearly with increasing time, at higher concentration it changes non-linearly. For example, at 0.1M-20 min, roughness decreased from 325 nm to 117 nm; at 0.15M-30 min, it increased from 254 nm to 435 nm from 8V to 12V. A reverse trend was observed from 12V to 16V for the same concentration and time

conditions. This may be attributed to competing mechanisms of oxide formation and dissolution, where excessive voltage leads to partial smoothing or restructuring of the surface.

A similar tendency is exhibited for maximum valley depth, as shown in Figure 11 (b). The anodized surface varied from several hundred nanometers (500 nm) to several microns (3600 nm), while the untreated sample showed the valley depth of 700 nm. The surface exhibited a maximum valley depth of 3600 nm, like the surface roughness trend at 0.15M-30min-12V. Higher electrolyte concentration facilitates deeper pore channels and more aggressive oxide dissolution, promoted by localized electric field effects. At moderate voltage (12V) and longer duration deeper valleys were obtained, while at higher voltage (16V) a decrease was observed with increasing concentration. For instance, valley depth increased at 12V from 615 nm to 1044 nm, at 0.05-10min and 0.1M-20min, respectively.

Surface free energy, presented in Figure 11 (c), was calculated, using water and DMSO contact angle measurements according to equation (4),

$$\sigma_L(1 + \cos\theta_L) = 2\sqrt{\sigma_S^d \sigma_L^d} + 2\sqrt{\sigma_S^p \sigma_L^p} \quad (4)$$

It can be observed that KCl anodizing improved the wettability, especially at moderate concentration and anodizing duration, where it reached its maximum. The untreated sample showed only 125 mJ/m² surface free energy, whereas at 0.1M-20min-8V, it approached 970 mJ/m², corresponding to a 676% improvement. At 12V and 16V surface free energy remained high (700-750 mJ/m²) for the same concentration and time, indicating 400-600% enhancement. This suggests the formation of well-developed porous structure, which enhances both surface area and surface energy, indicating optimal surface activation [18]. At higher electrolyte concentration and longer anodizing time the surface free energy decreased, despite the increased roughness and max valley depth. For example, at 0.15M-30min-12V, surface free energy dropped to 280 mJ/m², while at 8V and 16V it remained around 480 mJ/m². The optimal condition for enhancing the interfacial adhesion would be at 0.1M electrolyte concentration, 20 min and at moderate voltage, which consistent with previous KCl anodizing study [8], where optimal performance was also reported at 0.1M concentration.

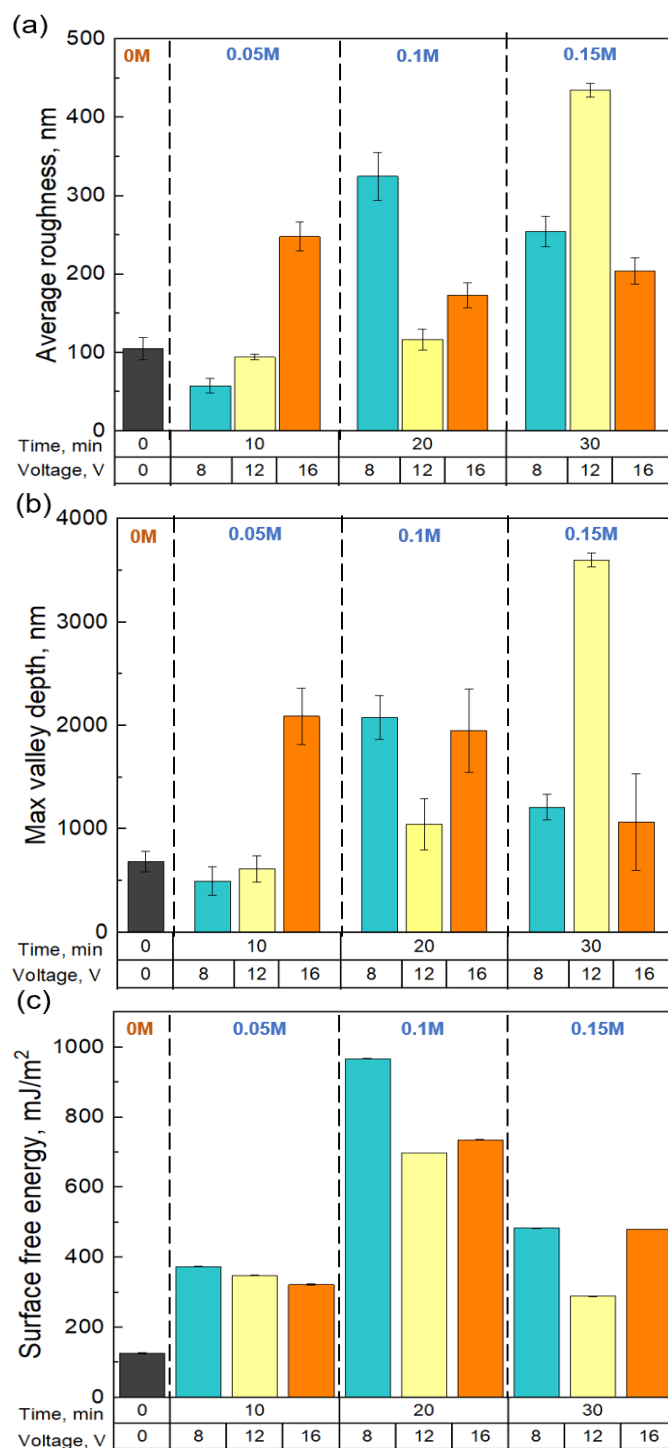


Figure 11. Surface topography: (a) average roughness; (b) maximum valley depth.

The Al surface after KCl anodizing was examined using SEM and AFM images. The results for samples anodized under different conditions are given in Figure 12. The SEM and AFM 3D images presented in Figure 12 (a) depict the untreated sample with a relatively smooth surface.

Figure 12 (b-k) shows the change in surface morphology after KCl anodizing, where a porous structure develops depending on the anodizing conditions. Pore formation is associated with the formation of pits on the barrier layer due to local electric field enhancement. Continued field-assisted dissolution at these regions leads to the progressive deepening of the pits [12, 19]. Increasing electrolyte concentration and anodizing duration led to a noticeable increase in surface roughness and the formation of more continuous porous structure, while the overall depth decreased at lower voltage (8V), as presented in Figure 12 (b, e, h). For example, in Figure 12 b, the AFM image of surface demonstrates a depth of 200 nm with relatively large pores at 0.05M-10min-8V. In contrast, Figure 12 e shows the surface depth of 100 nm with uniformly and densely distributed morphology at 0.1M-20min-8V. Furthermore, Figure 12 (h) SEM image exhibits the abundance of large pores with a decrease in depth to 50 nm at 0.15M-30min-8V.

It is evident from Figure 12 (d, g, k) that at higher voltage the surface becomes more irregular, indicating that under these anodizing conditions there is an excessive dissolution of surface. In this case, high voltage is not sufficient to form a densely porous structure. The surface morphology at moderate voltage (12V) shows more uniform, well-developed pores with increased density. Especially, the 3D AFM topography of the surface anodized at 0.1M-20min-12V presented in Figure 12 (f), demonstrates the interplay between oxide layer growth and field-assisted dissolution. Interestingly, a similar surface roughness is observed at 0.1M-20min-16V (Figure 12 (g)), where highly dense structure is formed, compared to all other surfaces despite the higher applied voltage. Therefore, according to surface morphology of all anodized surfaces it can be concluded that moderate electrolyte concentration and time at high voltages (12V, 16V) formed well-defined porous structure, making them optimal surfaces for enhancing the interfacial adhesion.

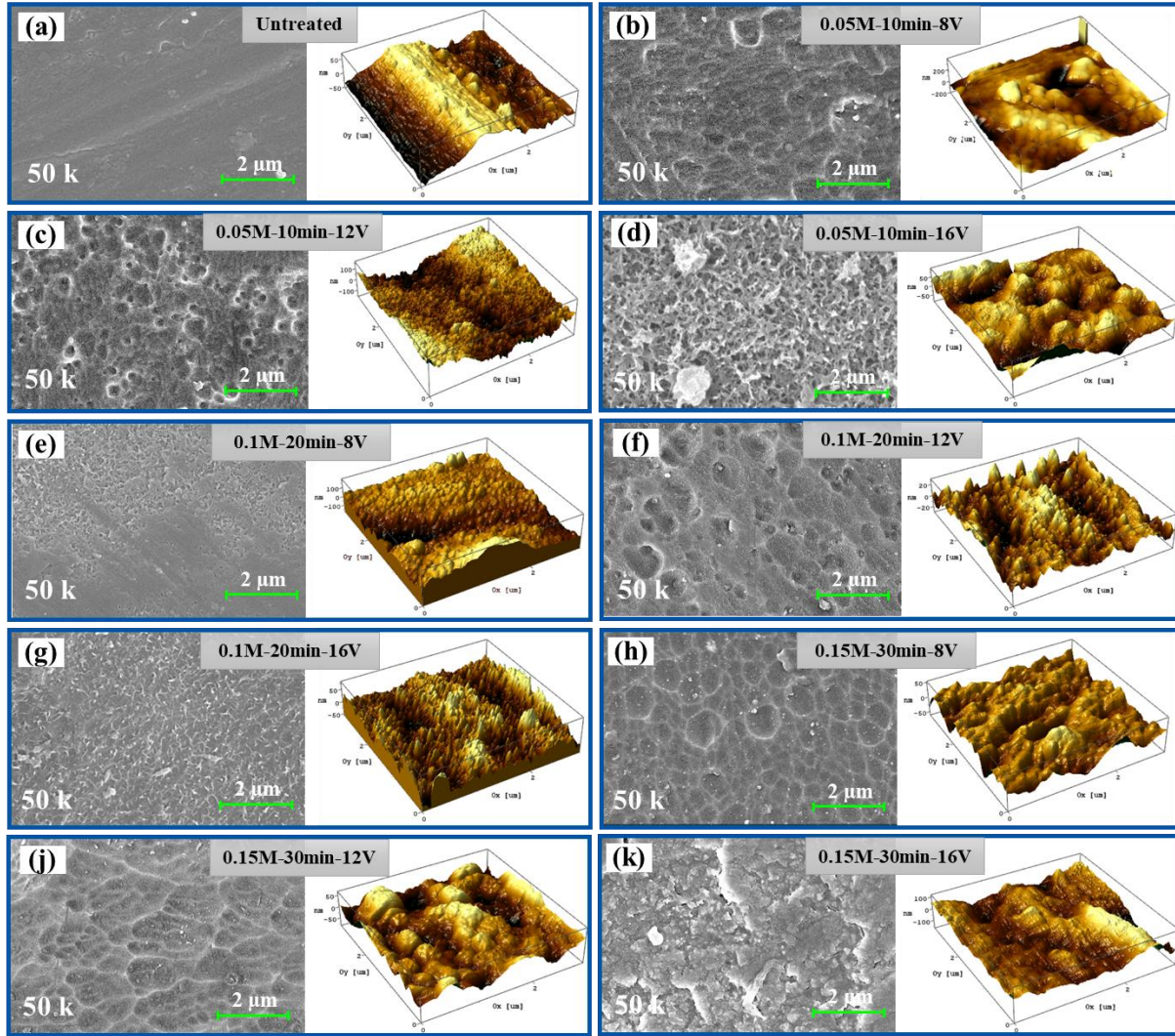


Figure 12. SEM images of anodized surface under different conditions

4.2.2. Effect of anodizing on mechanical properties of NFMLs

The tensile and flexural results showed that the aluminum surface treatment had a clear influence on the mechanical response of the developed NFMLs. As shown in Figure 13, the untreated reference laminate exhibited one of the weakest performances, with a tensile strength of 106 MPa. A similarly low tensile value was obtained for the specimen treated at 0.1 M, 30 min, 8 V, which gave 105.5 MPa. In contrast, the highest tensile strength was recorded for the specimen treated at 0.1 M, 20 min, 16 V, which reached 118 MPa. Tensile modulus followed the same overall tendency, indicating that the treatment conditions that improved load-bearing capacity also improved stiffness.

A similar trend was observed in bending. The untreated reference laminate again showed the lowest flexural strength, 241.3 MPa, while relatively low values were also obtained for 0.15 M, 30 min, 12 V (252 MPa) and 0.1 M, 30 min, 12 V (252 MPa). The highest flexural strength was recorded for the same condition that gave the best tensile performance, namely 0.1 M, 20 min, 16 V, which reached 278.7 MPa. Flexural modulus showed the same ranking trend.

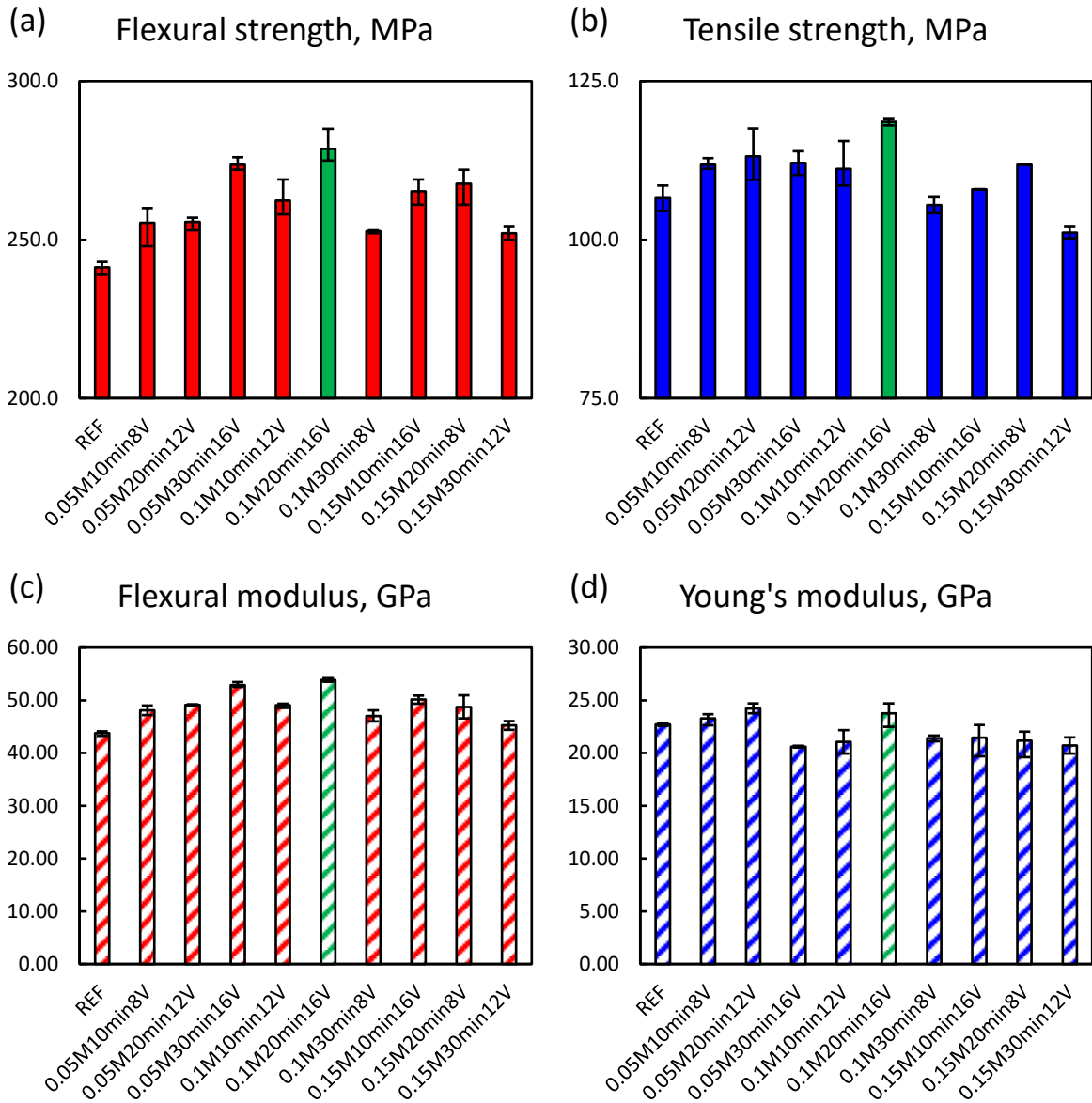


Figure 13. (a) Tensile strength, (b) Flexural strength, (c) Young's modulus, and (d) Flexural modulus values of NFMLs under different anodizing conditions

This consistency between tensile, flexural, and modulus results suggest that the main role of the anodizing treatment was to improve the metal-composite interface rather than to affect only one loading mode. At the same time, the results show that stronger or longer treatment was not always beneficial. For example, the specimen treated at 0.1 M, 30 min, 8 V remained among the weakest in both tests. This confirms that anodizing performance was not directly proportional to treatment severity. Rather, an optimum balance was required between oxide formation, surface roughening, and preservation of a stable interface. Similar trends were observed in literature. Aghamohammadi et al. reported that anodizing and FPL etching significantly improved the flexural behavior of basalt-based FMLs because microscale pits promoted resin penetration and interfacial bonding, whereas less suitable treatments produced weak adhesive interfaces [1,9]. Likewise, the recent KCl/DMF anodizing study by Bakhbergen et al. showed that improved joint performance was associated with a porous oxide layer, increased surface free energy, and stronger mechanical interlocking, but the best performance depended on a balanced treatment condition [9].

This interpretation is supported by the Taguchi analysis, presented in Figure 14. For both tensile and flexural strength, the main effects plots indicated the same optimal treatment conditions: 0.1 M concentration, 20 min duration, and 16 V voltage. The Pareto charts provided additional information on the relative influence of the parameters. For tensile strength, concentration had the largest effect, followed by duration and then voltage. For flexural strength, voltage had the larger effect, followed by a much smaller contribution from duration, while the effect of concentration was almost negligible. However, in both cases none of the effects crossed the reference line, which means that the factors were not statistically significant at the selected confidence level.

Even so, the practical optimization outcome was clear. The factor combination predicted from the main effects plots, 0.1 M, 20 min, 16 V, had already been tested experimentally and was confirmed to be the strongest condition in both tensile and flexural loading. The agreement between the Taguchi prediction and the raw mechanical data strengthens the reliability of the selected optimal condition. Although the Pareto charts did not show statistically significant effects, the combined experimental and optimization results consistently point to the same conclusion: a moderate KCl anodizing condition was the most effective for improving the mechanical

performance of the NFMLs. The fact that modulus values followed the same overall trend further supports the conclusion that interface strengthening was the dominant mechanism.

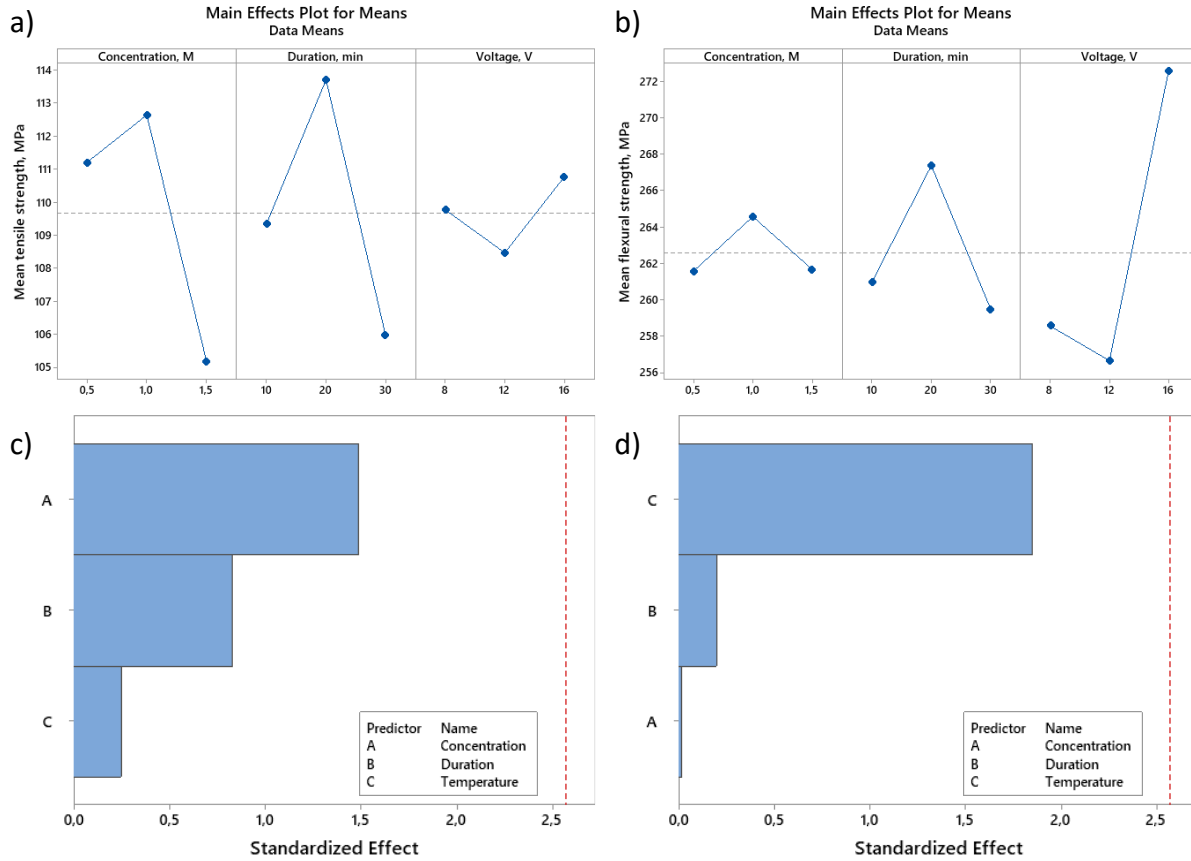


Figure 14. Main effect plots for (a) Tensile strength, (b) Flexural strength, and Pareto charts for (c) Tensile strength, (d) Flexural strength of NFMLs

After establishing optimal anodizing conditions, it is necessary to compare the performance of the obtained NFML with other NFMLs and FMLs based on synthetic materials. FML performance depends strongly on the aluminum alloy and temper, fiber type, stacking sequence, interface treatment, and test configuration therefore a comparison between the present NFMLs and conventional FMLs should be made with caution. The present laminates were based on Al6061-T4 aluminum, whereas many published studies use different alloys [45]. For example, Deng et al. reported that 1060-H112-based GLARE and CARALL reached tensile strengths of 190 MPa and 262.9 MPa, and flexural strengths of 187.3 MPa and 164.7 MPa, respectively [67]. In a separate CARALL study based on Al6061-T6 aluminum, the tensile strength was 321 MPa and flexural strength was 505.7 MPa [41]. It should be noted that the NFMLs are also expected to be lighter

and have higher specific properties because they incorporate NFRP layers. Natural fibers are lighter and more sustainable alternatives to synthetic fibers, and this represents part of the design rationale for NFMLs [11]. However, because most comparison studies do not report specimen mass or laminate density, a specific-property comparison cannot be made. However, comparison with other NFMLs can give more insights into the efficiency of applied treatments. A sustainable jute/aluminum laminate study reported a flexural strength of 151 MPa after chemical treatment [24]. The present optimum flax-based NFML, anodized at 0.1 M, 20 min, and 16 V, achieved 118 MPa tensile strength and 278.7 MPa flexural strength. Although the tensile strength of the present laminate remains below strongest synthetic FMLs, its flexural performance exceeds the values reported for the jute/aluminum laminate and the flexural strengths reported for the 1060-H112 GLARE and CARALL systems. Therefore, the present laminate cannot yet be considered competitive with aerospace-type synthetic FMLs in absolute tensile performance, but it already demonstrates a promising level of flexural behavior for a sustainable NFML.

These findings also show that KCl anodizing is efficient in interface strengthening since the flexural properties of FMLs are highly dependent on the matrix/metal interface strength [1]. The differences between used surface treatment conditions can be observed on Figure 15. The sub-optimal response of the untreated laminate was expected, since the smooth aluminum surface provides limited interfacial anchorage for the polymer composite layer [55]. It resulted in weak interface and, consequently, started a premature delamination as shown on Figure 15 (a). Gap between the metal and matrix started forming prior to the test which resulted in even larger delamination, as shown on Figure 15 (d), after the test and the lowest flexural strength value of 241.3 MPa. In contrast, samples treated under optimal conditions (0.1 M, 20 min, 16 V) demonstrated no signs of delamination prior to the test as shown on Figure 15 (b). Moreover, no signs of delamination were observed after the test. Sample failed due to internal cracks formed inside the NFRP layers as shown on Figure 15 (e). This demonstrates that sufficient bonding strength to prevent the delamination was achieved, and further improvement of composite's strength will be related to the improvement of NFRP layer itself. SEM images also demonstrated the effect of excessive treatment on the samples. As shown on Figure 15 (c), excessively treated sample demonstrated signs of early failure similar to untreated sample which resulted in a delamination. Moreover, for both untreated and excessively treated samples one of the aluminum layers detached completely, which can be observed on Figure 15 (d, f).

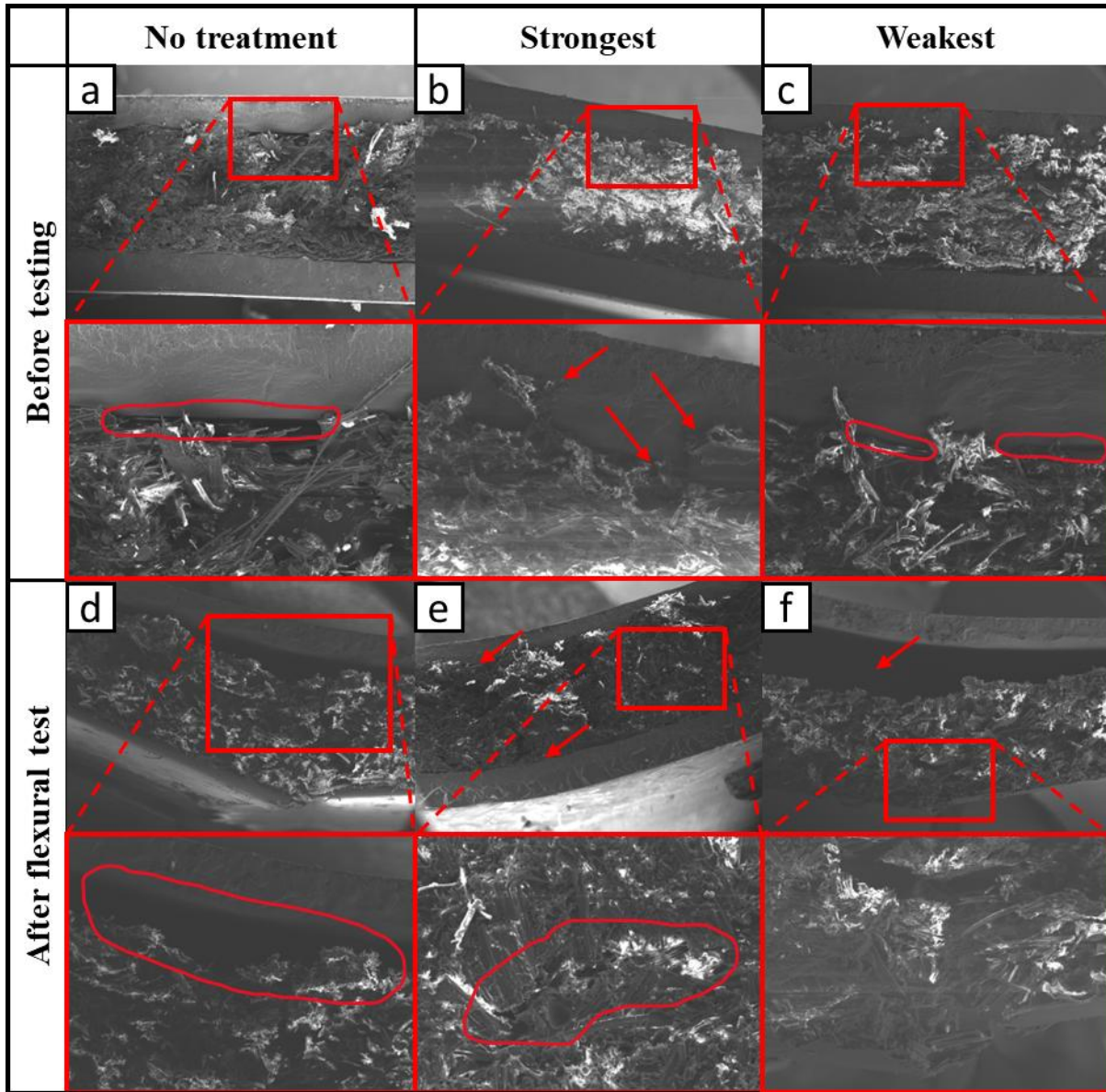


Figure 15. SEM of NFMLs: (a) Untreated, (b) Highest strength, (c) Lowest strength before testing; and (a) Untreated, (b) Highest strength, (c) Lowest strength after flexural testing

In FMLs, adequate surface treatment is required to create a roughened and chemically active oxide layer that improves wetting and promotes stronger adhesion at the metal–composite interface. Previous studies have shown that anodizing and other effective surface treatments enhance FML performance because the resulting oxide morphology contains pores or pits that allow polymer penetration and mechanical interlocking, whereas untreated or inadequately treated surfaces are more prone to adhesive failure and weak interlaminar bonding. In the present case, the improvement from 106 MPa to 118 MPa in tensile strength and from 241.3 MPa to 278.7 MPa

in flexural strength indicates that the selected anodizing conditions enhanced the integrity of the aluminum-composite interface.

Overall, the mechanical results demonstrate that KCl-based anodizing improved the performance of the flax-based NFMLs, but only within a controlled process window. Both tensile and flexural tests showed that the optimum condition was 0.1 M concentration, 20 min treatment time, and 16 V, while untreated or less favorable anodizing conditions resulted in inferior behavior. This indicates that the anodizing process must be optimized carefully, since the mechanical response of NFMLs depends strongly on achieving a sufficiently rough and adherent oxide layer without generating an interface that is either underdeveloped or mechanically inefficient. The agreement between the experimental data and the Taguchi optimum makes this condition a well-justified choice for the present NFML system.

Chapter 5 – Conclusions

This thesis investigated the development of sustainable high-performance composite materials through optimization of alkali-treated flax/epoxy composites and eco-friendly KCl-anodized flax-based natural fiber metal laminates, with particular emphasis on the role of interfacial engineering in improving mechanical performance.

- Moderate alkali treatment improved the mechanical performance of flax/epoxy composites, whereas untreated and overly aggressive conditions were unfavorable, confirming that fiber surface modification must be carefully controlled.
- Based on the combined experimental results and Taguchi analysis, 40 min, 2 wt.% NaOH, and 40 °C was identified as the most practical optimum for the flax/epoxy system.
- The confirmation sample produced the best overall composite performance, reaching 83 MPa in tensile strength and 156.3 MPa in flexural strength, corresponding to improvements of about 28.9% and 21.2%, respectively, compared with untreated references.
- KCl anodizing successfully improved the bonding-related mechanical performance of the flax-based NFMLs, showing that an environmentally friendlier aluminum treatment route can also be mechanically effective.
- The optimum anodizing condition was 0.1 M, 20 min, 16 V, which gave the highest tensile and flexural strengths of 118 MPa and 278.7 MPa, representing improvements of about 11.3% and 15.5% over the untreated laminate.
- In both material systems, the results showed that surface treatment effects were non-linear: moderate conditions were beneficial, while insufficient or excessive treatment reduced performance.

Overall, the thesis demonstrated that interface engineering at both the fiber–matrix and metal-composite scales is essential for developing more sustainable high-performance composite materials.

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