Review Article

Fiber Surface Treatments for Lightweight PA6 Composites

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Abstract
Natural fiber-reinforced composites (NFRC) have gained significant attention due to their eco-friendliness, affordability, and excellent mechanical properties. However, inadequate interfacial bonding between the fiber and the polymer matrix often results in inferior mechanical and thermal properties. Various surface treatments, including alkali, silane, and plasma treatments, have been developed to address this issue by modifying the fiber surface. These treatments have been shown to improve the interfacial bonding, leading to enhanced mechanical strength and thermal stability of natural fiber-reinforced PA6 composites (NFRC-PA6). In this study, we applied these surface treatments and evaluated their impact through mechanical and thermal testing. The results indicate significant improvements in the composites' properties, although challenges such as optimizing treatment parameters and ensuring uniformity persist. Future research should focus on overcoming these challenges and exploring innovative treatments to further advance the application of NFRC-PA6 composites.

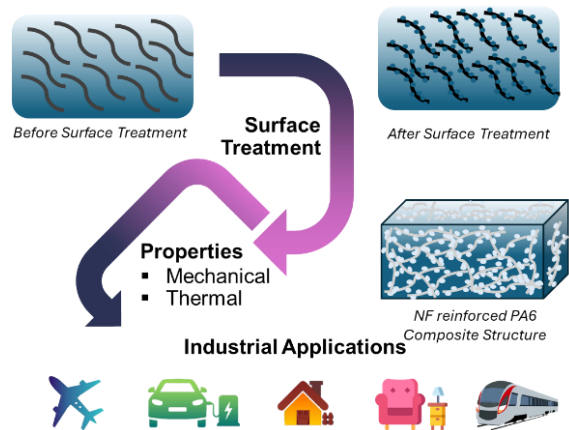**Keywords**: Lightweight transportation, Natural fiber-reinforced composites (NFRC), Polyamide 6, Surface treatment

1 Introduction

Within the next few decades, it is anticipated that the supply of petroleum and natural gas as raw materials for the production of plastics will decrease, resulting in demand for sustainable and environmentally friendly enterprises [1], [2]. Natural materials, such as cellulose fiber, are employed as natural fiber reinforcements in composites to replace petroleum-based polymers partially [3]. Owing to their low cost [4], sustainability, and lightweight qualities, NFRC has become popular in various material fabrications. Some of the most frequently utilized natural fibers for composite fabrications include flax, hemp [5], pineapple leaves [2], carbon fiber [6], banana fiber [7], and jute. Natural fiber reinforcing with polyamide 6 (PA6) has been considered to improve the performance of natural fiber for lightweight transport applications [3]. Polyamide 6 (PA6) is a popular choice for the matrix of natural fiber-reinforced

composites owing to its favorable mechanical properties and processability [8]. Hydrophilic properties arise from hydrogen bonding between the amide groups and polyamide chains. This semi-crystalline engineering thermoplastic is particularly well-suited to applications that require creep resistance, stiffness, and a certain degree of toughness, while also enabling weight and cost savings. PA6 is widely used in under-hood components in the automotive industry. Although PA6 and natural fibers exhibit hydrophilic behavior and good compatibility, researchers are actively investigating methods to enhance interfacial adhesion for lightweight transport applications.

However, numerous kinds of challenges make fiber-reinforced PA6 composites difficult to use in lightweight transportation applications. Elevated temperatures and humidity levels can degrade the mechanical properties of PA6 reinforced with carbon long fiber [9]. Although high-strength glass fiber/polyamide composites are promising, their performance may not be up to par, which prevents widespread adoption [10]. Furthermore, although efforts have been made to improve mechanical performance and fire retardancy using novel fillers like graphene nanoplatelets and aluminum metal-organic frameworks, the cost and multifunctional properties of glass fiber-PA6 composites continue to be difficult [11]. Furthermore, while electrospun nanofibers can enhance bulk matrices' properties, their use in strengthening fiber-reinforced composites is more prevalent, which restricts their potential in lightweight transportation materials [12]. Furthermore, the mechanical properties and wear resistance of the composite are greatly influenced by the orientation of its fibers, as wear rates are affected by the fiber breakage that occurs in particular orientations. For carbon fiber-reinforced PA6 composites to have better mechanical properties, the polymerization conditions must be optimized. This necessitates careful consideration of design variables like injection speed and activator/catalyst rates [13]. Reports have also indicated, however, that adding cellulose pulp fibers to PA6 matrices has improved characteristics like flexural strength and elastic modulus, with fiber orientation being a key factor in determining the composite's tensile qualities [14]. Thus, investigating substitutes such as natural fiber-based bamboo-thermoplastic composites, which provide similar strength and a lower density to conventional materials like Apitong wood, offers a promising way forward for lightweight transportation applications [15].


Figure 1: Schematic diagram of natural fiber.

In recent years, enhancing the mechanical and thermal properties of NFRC-PA6 composites for use in lightweight transportation applications has been the primary focus of research. Many studies focus on improving the interfacial adhesion between carbon fibers and the PA6 matrix by employing novel surface treatments, such as polydopamine/nano-silica interfacial layers. To solve this issue, researchers explored the natural fiber surface treatment techniques to enhance the properties of NFRC-PA6 composites including physical, chemical, and enzymatic treatments to increase their adherence to polymer matrices [5], [16], [17]. Figure 1 depicts the schematic representation of a natural fiber reinforced PA6 composite for industrial applications. The impact of natural fiber surface treatment on the thermal and thermomechanical properties of NFRC-PA6 for lightweight transport applications is the subject of the current research studies. In this chapter, we review recent developments in the field, with a particular focus on how surface treatments on fiber impact the mechanical and thermal properties. This chapter is organized into sections discussing different surface treatments and their effects on interfacial adhesion, mechanical and thermal properties, followed by a summary of challenges and opportunities in the field.

2 Surface Treatment Methods

Addressing the fundamental immiscibility between the hydrophilic nature of natural fibers and the hydrophobic nature of PA6 is the primary goal of surface treatment. This results in a weak adhesion between the surfaces. 1) Poor stress transfer between fiber and matrix. 2) Reduced mechanical properties of the composite (strength, stiffness). 3) Moisture sensitivity,
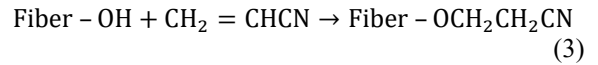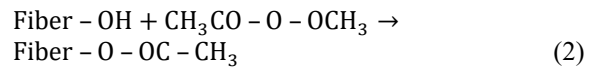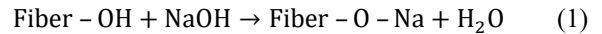
leading to degradation. The natural fiber surface is altered by the surface treatment with the intention of: 1) Increasing its compatibility with PA6. 2) Enhancing the interfacial adhesion. 3) Improving the overall mechanical performance of the composite. Three categories—chemical, physical, and biological treatments—are typically used to classify natural fiber surface treatments (Figure 2) [3], [18].
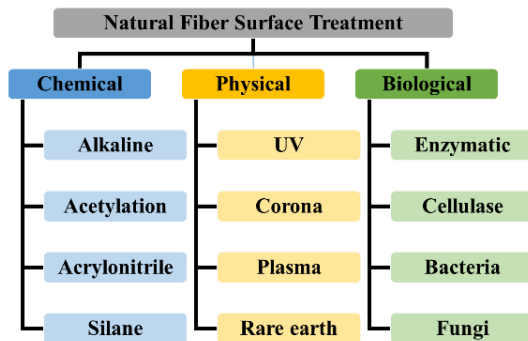
Figure 2: Types of surface treatment methods for natural polymer.
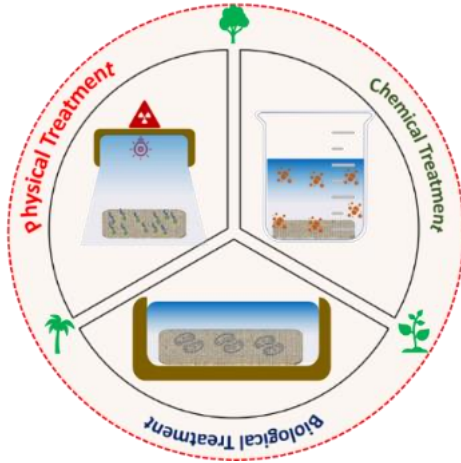
2.1 *Chemical treatment*

Figure 3 shows a schematic representation of the surface treatment method for natural fibers. Chemical treatments, such as alkaline, acetylation, acrylation and acrylonitrile and silane reactions, alter the natural fiber surface to enhance the adhesive properties of polymer matrices in composite materials. Equation (1)–(3) shows the alkaline, acetylation and acrylonitrile treatments of natural fibers for the surface alteration. In contrast, alkaline treatment involves soaking the fibers in an alkaline solution to eliminate non-cellulosic components, enhancing crystallinity, tensile strength, and wettability [19]. The alkaline treatment directly affects the cellulose fibril, degree of polymerization and extraction of lignin and hemicellulose compounds [19]. The acetylation involves adding acetyl groups to the fiber surface, increasing their hydrophobicity and thermal stability, and enhancing their bonding with polymer matrices [20]. Acrylation and acrylonitrile ($CH_2 = CHCN$) free radicals of the cellulose molecules initiate the reaction, whereas the cellulose molecules can be treated with high-energy radiation to generate radicals together with chain sessions. Silane treatment modifies the fiber surface using a coupling agent, which creates a covalent at the interface between the fiber surface and matrix, resulting in improved interfacial adhesion and mechanical properties [21].

$$Fiber - OH + NaOH \rightarrow Fiber - O - Na + H_2O \quad (1)$$

$$Fiber - OH + CH_3CO - O - OCH_3 \rightarrow$$
$$Fiber - O - OC - CH_3 \quad (2)$$

$$Fiber - OH + CH_2 = CHCN \rightarrow Fiber - OCH_2CH_2CN \quad (3)$$

These treatments enhance the physical and mechanical properties of natural fiber-reinforced composites, making them stronger, stiffer, more durable, and less prone to water absorption while improving their dimensional stability [20].

2.2 *Physical treatment*

Physical treatments comprising of high radiation beams such as $\gamma -$ radiation, e-beam, X-ray corona, UV, plasma and ion beams have been used to surface treat natural fibers to enhance compatibility with the polymer matrix [18]. These high-energy radiation beams form highly reactive intermediatory species that can react instantly with natural fibers. Plasma treatment replaces the polymer functional groups with different atoms from the ions to increase the surface energy. Exposure of polymer surface to energetic radiation beams or ions, results in degradation of polymer surface through formation of free radicals. Plasma ions contain high amounts of UV radiation, causing more free radicals over the natural fiber surface. Because they are very unstable in nature, thus react with materials immediately [18], allowing them to form stable covalent bonds capable of printing. The rare earth treatment process typically involves treating natural carbon fiber with rare earth elements to soak it for several hours in an alcoholic solution of lanthanum chloride (LaCl$_2$). This increases the concentration of reactive functional groups on natural fiber because of the chemical activity of rare-earth elements. The rare-earth nuclei have a strong affinity for the electrons of other atoms around them and strongly attract the C-C bonds of the carbon fiber [22]. Simultaneously, corona discharge treatment occurs between the electrodes with different geometries to generate strong electric fields. When the needle-like electrode is inserted into the natural fiber, discharge occurs at the sharp points and, as a consequence of corona discharge, the polarity of the fiber, and the number of new oxygen functional groups (-OH and -COOH). This behavior suggested that the epoxy-based composite was formed after the surface modification. Natural fibers such as pine, eucalyptus, sugarcane bagasse and flax fiber have been used to improve surface roughness [18], [20].

Figure 3: Schematic representation of natural fiber surface treatment methods.

2.3 *Biological treatments*

Natural fibers are surface-treated biologically by using microbes, such as fungi and bacteria [23]. Although biological treatment is often less expensive, it can be labor-intensive and pollute water. The biological treatment utilizes naturally occurring microorganisms, namely bacteria and fungi, to surface natural fibers [23]. Biological treatment is relatively cheap but tends to be time-consuming and water-polluting. Natural fiber is degraded during biological treatment to free the bast from the bundle and separate the woody core and epidermis. The *Clostridia* species of bacteria and fungi primarily release enzymes to degrade pectic and hemicellulose compounds in the middle of the lamella between individual fiber cells [19]. Enzymatic treatments use enzymes to modify the surfaces of natural fibers in composite materials [24]. Cellulase treatment removes amorphous cellulose, increasing surface roughness and area, whereas laccase treatment introduces phenolic compounds onto the fiber surface, improving adhesion with polymer matrices. Both treatments enhance the thermal stability of natural fibers, and improve the thermal properties of composites [23], [24].

3 Effects of Surface Treatments on Mechanical and Thermal Properties

Gao *et al*., synthesized hyperbranched polyurethane to improve the interfacial adhesion of carbon fiber reinforced composites [6]. Effect of different sizing agent concentrations on the wetting ability of carbon fibers and interfacial properties of the composites.

Compared to unsized carbon fiber/PA6 composites, the interlaminar shear strength and flexural strength of carbon fiber/polyamide 6 composites with a 1.5 wt% sizing agent were improved by 50.3% and 27.7%, respectively, with a maximum value of 60.3 MPa and 508.4 MPa [6]. Weak interfacial adhesion between carbon fiber (CF)/polyamide (PA6) composites leads to poor mechanical performance [25]. To address this, a study developed an effective method to improve the fiber-matrix interfacial adhesion of CF/PA6 composites by introducing interfacial layers of PA6. The CFs were activated at 400 °C in nitrogen for 4 h to remove surface sizing agents and immersed in a formic acid solution of PA6 [25]. The modified CF/PA6 composite exhibited significant improvements in mechanical properties, with a 24.75% increase in tensile strength, a 33.25% increase in flexural strength, a 38% increase in impact strength, and a 72% increase in interlaminar shear strength (ILSS) [25]. Sang and group performed hydrothermal aging on the moisture absorption and property prediction of carbon fiber reinforced PA6 composites [26]. The CF/PA6 composite was immersed in water at 20, 40 and 60 °C. The mechanical properties of CF/PA6 demonstrated a linear reduction in tensile strength and an increase in elastic modulus and impact strength [26]. Compared to composites made without a sizing agent, adding 1.5 wt% of the synthesized hyperbranched polyurethane sizing agent led to significant improvements in the interlaminar shear strength and flexural strength of carbon fiber/polyamide 6 composites. Researchers observed that interlaminar shear and flexural strength had been increased from 27.7% to 50.3%, with a maximum value of interlaminar sheet and flexural strength are 60.3 MPa and 508.4 MPa [6]. Badin *et. al.,* categorically evaluated the effect of ultraviolet (UV-C) irradiation on as-prepared PA6/carbon-fiber (PA6/CF) NFRC-PA6 composites [27]. The as-prepared PA6 and PA6/CF samples were kept under UV-irradiation for 7 days, and several tests were recorded during that period. The results showed that the PA6 sample was more prone to photo-oxidative deterioration than the PA6/CF sample. The emission spectra and 3D fluorescence pictures supported their photooxidative deterioration. The tensile strength of PA6 is significantly decreased but not in PA6/CF, suggesting that carbon fiber provides protection from UV with reinforcement [27]. Thus, the tensile strength of any composite material is directly linked with the amount of fibers present in NRFC-PA6. As the volume fraction of the fiber increased, the tensile strength also increased. This strengthening effect is due to the

improved adhesive bonding between the blend material and the carbon fibers. Adhesion measurements revealed a potential acid/base interaction between the -COOH groups at the end of the polyamide backbone and the -OH groups on the carbon fibers treated with HNO_3. This interaction contributes to enhanced component bonding, increases tensile strength [28]. The mechanical characteristics and interfacial adhesion of carbon fiber/polyamide 6 (PA6) composites were greatly enhanced by the addition of a hyperbranched polyurethane sizing agent. The interlaminar shear strength and flexural strength increased by 50.3% and 27.7%, with maximum values of 60.3 MPa and 508.4 MPa, respectively, when a 1.5-weight percent sizing agent was added. Additionally, PA6 composites were protected from UV rays by carbon fibers, which preserved their tensile strength and stopped photo-oxidative deterioration.

Similarly, the surface presence of oxygenous moieties including -C=O was markedly enhanced by the polyurethane dispersion treatment. These functional groups significantly improved the interfacial interactions between carbon fibers (CF) and the PA6 matrix. This treatment enhances the properties and functionality of the composite material by strengthening the bond between CF and PA6 [29]. Satheesh and his colleagues used an injection molding machine to create composites of PA6 and graphite, then tested the materials using a variety of techniques to examine the mechanical and tribological behaviors of the materials [30]. The study found that incorporating graphite significantly improved the mechanical behavior, wear resistance, and the reduced friction coefficient of the composite, with the uniform distribution and incorporation of graphite particles being the primary factor responsible for the enhancement. This study provides practical recommendations for the preparation of PA6 polymer composites in engineering. Composites containing 20 wt% graphite demonstrated the best performance [30]. A recent study by Florent *et al.*, found that severe thermo-oxidative aging can affect the mechanical behavior and fatigue durability of short glass fiber reinforced PA6/6.6 [8]. However, adding fibers as reinforcements can help mitigate the overall effect of aging on polyamides, leading to an increase in fatigue life and partial preservation of mechanical properties. The most accurate indicator of fatigue lifetime in both aged and unaged materials is cyclic creep energy. [8]. In 2014, Panyasart *et al.*, carried out research to investigate the effects of various surface treatments on the characteristics of PA6 composites reinforced with

pineapple leaf fiber (PALF) [2]. It was discovered that, no matter which kind of PALF was utilized, an increase in the thermal stability of the composites while leaving the thermal properties unchanged. Although the elongation decreased after receiving alkaline (Na-PALF) and silane (Si-PALF) surface treatments, the composites appeared less flexible and more rigid as evidenced by the increases in Young's modulus and tensile strength. After determining that alkali treatment alone was sufficient to improve PALF/PA6 compatibility and properties at a fiber loading of 30%, the researchers concluded [2]. The thermal, mechanical, and morphological characteristics of ABS and banana fiber reinforced PA6 composites were investigated by Rupinder *et al.* [7].

The results demonstrated that adding bamboo fiber (BF) as reinforcement to the ABS polymer increased its load-resistive capacity but reduced its elongation and Young's modulus. Using a 5% BF reinforcement, the peak load and strength increased by 16.27% and 10.99%, respectively, but the elongation and Young's modulus decreased by 13.24% and 52.22%, respectively. However, all mechanical properties improved when BF was added as a reinforcement to the recycled PA6 polymer. With 5% BF reinforcement, the peak load and strength increased by 29.07% and 37.52%, respectively, and the elongation at peak, Young's modulus increased by 91.73% and 258.8%, respectively [7]. Elsabbagh and their group demonstrated the flame-retardancy properties of natural fiber/PA composite [31]. Researchers have observed the feasibility of producing stable PA6 composites with natural flax and kenaf fibers. Figure 4(a-d) compares the mechanical results of PA6 composites with PA6 and equivalent PA6/GF using flax and kenaf fibers. It was concluded that a maximum fiber content of 22.5% was optimal. Although the mechanical properties of the composites improved compared to those of polymer matrix, they still fell short of those of glass fiber composites. The researchers also examined flame retardant combinations and determined that a composition with a 1.67:1 ratio of mineral to halogen-free FR was still effective. However, an increase in fiber content decreased the degradation temperature, limiting the possible fiber content. Overall, this study provides insights into the production and properties of PA6 composites with natural fibers and flame retardants [31]. The bonding and general performance of the composite material were improved by the polyurethane dispersion treatment, which also markedly increased the interfacial interactions between carbon fibers (CF) and the PA6 matrix. The

best results were obtained with 20 wt.% graphite reinforcement in PA6 composites, which significantly enhanced mechanical behavior, wear resistance, and decreased friction coefficient. Numerous studies have shown that various surface treatments and fiber reinforcements, like glass, bamboo, and pineapple leaf fibers, improve particular mechanical properties and thermal stability of PA6 composites. However, these reinforcements may also come with trade-offs, like lower degradation temperatures or reduced flexibility.

Zainab *et al.*, investigated the creep behavior of a PA6/flax fiber composite through longitudinal tensile tests at different stress levels, showing stationary creep behavior [32]. Schapery's integral relation was highly effective in predicting the creep behavior, with good agreement between the numerical and experimental data at lower stress levels and slightly higher error at higher stress values. However, it was difficult to experimentally observe the tertiary creep zone because of the abrupt rupture of the material. It was discovered that, under static strain, the composite ultimate tensile strength was 100 MPa [32]. The mechanical characteristics and crystallization behavior of rice, wheat, and maize straw-reinforced PA6 composite were examined by Huang *et al.* [33]. The three straw fibers shown in the SEM images have their morphology shown in Figure 4(e)–(g). The surfaces of the fibers made of maize and wheat straw changed after being treated with alkali. They developed noticeable grooves and became rather smooth. The fibers of rice straw, on the other hand, developed rough surfaces. This suggests that the alkali treatment of the wheat straw and maize straw fibers was successful in removing contaminants like lignin and pectin.

After treating the straw fibers with NaOH solution, a coupling agent known as KH-550 was used [33]. As shown in Figure 4(h), the researchers found that the tensile strength of all fiber types peaked at a fiber content of 6wt%. Among the composites, the wheat straw fiber composite exhibited the highest tensile strength, with a 56.9% improvement compared with that of pure PA6. The rice fiber composite showed a 42.8% increase, whereas the maize straw fiber composite showed a 40.4% enhancement. According to the authors, this outcome can be attributed to the favorable interfacial adhesion resulting from the alkali treatment of the fibers. The impact strength of the wheat and rice fiber composites initially decreased but later increased with the fiber content, as depicted in Figure 4(i). At the maximum fiber content of 10% weight, the impact strength peaked. Comparing the impact strength to pure PA6,

wheat fiber raised it by 39.2%, whereas rice fiber increased it by 19.2%. On the other hand, as the concentration of maize fiber rose, the impact strength decreased due to its addition. The observation was explained by the authors as a result of the poor compatibility of maize fibers with the matrix, while rice and wheat fibers showed good compatibility [33]. Micromechanics analysis assesses the interface's strength. The interfacial strength of the cellulosic/PA6 reinforcement is 32–40 MPa, greater than that of the polyolefin-based composites. Moreover, the contribution indicates a strong interphase between hemp and PA6 [34]. Various compositions of kenaf/PA6, the dispersion of kenaf in unoccupied areas of blending [35]. For the 10 wt.% of kenaf some of the voids in the composite remains unoccupied. These voids were absorbing moisture from kenaf and were trapped in the polymer. The best Young's and flexural modulus were obtained for the 30 wt.% of kenaf fibers in rPP/rPA6 [35]. The best flexural strength was observed at 20 wt.% of kenaf in the blend. Similarly, the storage modulus E' of the NFC/PA6 composite increased as the natural fiber content (Flax/Kenaf/Hemp) increased up to 20 wt.% in the blend [36]. By analyzing the response surfaces obtained from a Design of Experiments (DOE) study, the mechanical characteristics of flax/PA6 composites were shown to deteriorate with increasing consolidation temperature and time, as reported by Liang *et al.* [37]. When the temperature was raised from 230 to 250 °C and the duration was extended from 2 to 5 min, the tensile strength significantly decreased for flax/PA6 composite, falling from 90.2 to 32.2 MPa, or a 64% loss. It is significant to observe that there is a complicated and nonlinear dependency on these parameters, as evidenced by the nonlinear relationship between mechanical properties and processing parameters [37]. Schapery's integral relation correctly predicts the creep behavior of PA6/flax fiber composites, which exhibit stationary behavior at lower stress levels. However, tertiary creep zone observation is challenging because of abrupt material rupture. The tensile and impact strengths of PA6 composites are greatly increased by alkali-treated wheat and maize straw fibers, with wheat straw exhibiting the greatest overall enhancement because of improved interfacial adhesion. However, as consolidation temperature and time increase, the mechanical properties of flax/PA6 composites deteriorate significantly, underscoring the significance of processing parameter optimization for maintaining composite performance.
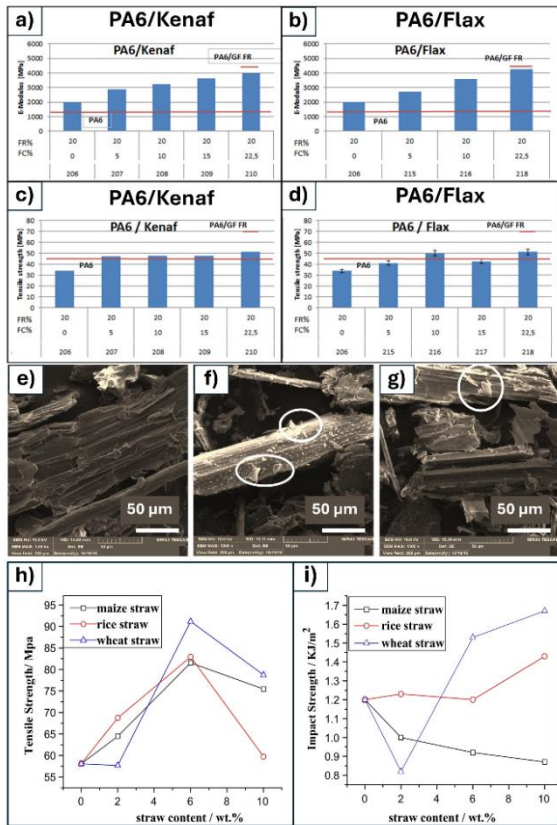
Figure 4: Mechanical results: (a)–(d) PA6 composites compared to PA6 and equivalent PA6/GF (lines) (Reprint with permission from reference no. [31], License No. 5573590001695), SEM images of three alkali-treated straw fibers; (e) wheat straw, (f) rice straw; (g) maize straw (Reprinted with permission from reference no. [33], License No. 5573590446355), Mechanical property curves of PA6 and three straw/PA6 composites; (h) tensile strength; (i) impact strength (Reprinted with permission from reference no. [33], License No. 5573590446355).

Patricia and her group proposed that incorporating 30% fiber content in the composite decreased the amount of polymer used in the formulations [38]. Additionally, this composition led to a substantial increase in the tensile modulus by 119% and a flexural modulus of 133%. In summary, increasing the fiber content positively affects the mechanical properties, significantly improving both the tensile and flexural modulus [38].

After alkaline treatment, the Curaua fiber PA6 composite demonstrated an enhancement in tensile stress [39]. Specifically, the tensile stress increased from 74 to 90 MPa when the fiber content was increased from 20 to 30 wt.%. Increasing the fiber content in the composite and alkaline treatment led to an improvement in the tensile stress, resulting in improved mechanical properties [39]. The curative concentration shows that flexible epoxy coating on the NF/PA6 composite enhances thermal stability with 5 wt.% of epoxy [40].

Bending tests on FLA-EP-PA6 composite-coated fabrics demonstrated higher flexural strength and flexural modulus than those made from uncoated fabrics [41]. Specifically, the coated fabric composites had a flexural strength of approximately 108 MPa, whereas the uncoated fabric composites had an average flexural strength of 59 MPa [41]. Katsuyuki *et al.* observed that Young's modulus and tensile strength significantly improved for flax fabrics/PA6, with increases of 230% and 40%, respectively [42]. As the fiber composition increased from 5% to 25%, the elastic modulus and flexural properties increased linearly. The highest tensile strength of 66.17 MPa was achieved with 20% cellulose content [14]. Although PA6 composites show improvements compared to the polymer matrix, they still have a lower E-modulus (up to 10%) and strength (up to 30%) than GF composites [43].

Due to their superior mechanical properties, natural fiber-reinforced polymer composites are being explored as alternatives to metals or carbon materials. However, these composites generally have lower thermal properties than metals, making heat dissipation more challenging, especially in applications involving proximity to electronic components. To address this issue, a desirable solution involves combining high thermal conductivity reinforcements with a low thermal conductivity resin matrix. The mechanical properties of short fiber-reinforced composites are greatly influenced by factors such as fiber length distribution and orientation [41]. The thermal conductivity of such composites has been predicted analytically by equating it with the elasticity of fiber composites and thermal conduction. Studies have looked at the thermal stability of natural fibers, which is important since reinforcing fibers heat up quickly when processed in composites, especially when thermosetting resins are used. Researchers have also investigated the thermophysical properties of polyester composites reinforced with banana/sisal fibers, observing a decrease in thermal conductivity with the incorporation of the fibers. However, chemical treatments of the fibers can enhance the thermal contact between the components and increase the thermal conductivity and density of the composites [36], [44]. Fabric composites that have been coated exhibit notably greater flexural strength and modulus

than those that have not; coated composites can reach 108 MPa, while uncoated can only reach 59 MPa. The tensile strength and Young's modulus of flax fabric/PA6 composites exhibit significant improvements, reaching up to 40% and 230% increases, respectively, with the best tensile strength at 20% cellulose content. Although natural fiber-reinforced polymer composites have better mechanical qualities than metals, they typically have poorer thermal properties. To improve heat dissipation, high thermal conductivity reinforcements must be combined with low thermal conductivity resin matrices.

Using thermogravimetric analysis (TGA) and differential scanning calorimetric analysis (DSC), the impact of surface treatment on the thermal characteristics of natural fiber reinforced PA6 composites was mainly examined. Natural fiber typically undergoes two stages of thermal degradation, peaking at 290 and 360 °C. The first step is caused by the breakdown of hemicellulose and glucosidic linkage, while the second step is caused by the destruction of lignin and α-cellulose [45]. The addition of clay to resol resin by sonication enhanced the thermal resistance of the jute-reinforced composite at a temperature higher than 300 °C as the lower risk of fire was evolved [45]. Oumayma *et al.*, synthesized the bio-composite using different amounts of olive pomace powder OPP (5% to 20%) [46]. In Figure 5, it can be observed that the initial degradation temperature of PA6 is approximately 180°C, resulting in a minimal mass loss of 13%. This slight loss may be attributed to residual substances such as activators, residual monomers, and catalysts. Due to the hydrophobic nature of PA6, a small amount of water evaporation may also occur during storage. As the temperature increases to 380 °C, a substantial mass loss exceeding 75% is observed. This is primarily caused by the breakage of C-C bonds, leading to depolymerization and decomposition of PA6. The decomposition process involves the formation of hydroperoxide fractions, particularly in the methylene group directly attached to the amide atom. On the other hand, the thermal curves of OPP indicate a significant mass loss of approximately 60% between 180 °C and 360 °C, corresponding to hemicellulose decomposition [47]–[49]. Hemicellulose decomposes through the breakage of glycosidic bonds at approximately 200 °C, while cellulose degrades within the temperature range of 350 °C to 440 °C, and lignin decomposes above 440°C. When incorporating OPP into PA6, the properties remain unchanged until a 20% weight ratio, with similar density and crystallinity to pure PA6. Furthermore, the addition of

20% OPP maintains the same crystallization and melting temperatures as PA6, with a slight increase in decomposition temperature, indicating the potential to enhance OPP value and reduce costs in the final product utilizing PA6 as the base material [46]. Elsabbagh *et al.*, optimized the extrusion process of PA6 thermoplastics by incorporating natural fibers like flax or kenaf and flame retardants (FR) [31]. Figure 5(b) shows that increasing the fiber content, specifically kenaf, decreased the temperature at which degradation began, with a drop from 298 °C for 5% kenaf to 264 °C for 22.5% kenaf. The addition of 20% FR resulted in improved flame retardance, achieving a V-0 rating in UL94 tests and a significant 50% reduction in heat release rate (HRR) according to cone calorimetry, while still allowing for the use of higher proportions of mineral-based FR to maintain the desired flame retardance level [31], [36].

The thermal stability of natural fiber-reinforced PA6 composites is improved by surface treatments through improved fiber-matrix interactions, according to thermogravimetric and differential scanning calorimetric analyses. Clay and olive pomace powder greatly increase the thermal resistance and decomposition temperatures of PA6 composites, respectively. Although treated fibers often exhibit greater thermal stability compared to untreated ones due to improved interfacial bonding, the degradation onset temperature decreases with increasing natural fiber content, such as flax or kenaf.

The alkali treatment of the raw fiber removed some hemicellulose and lignin, resulting in remaining cellulose with a crystalline structure that led to better thermal stability in the Na-PALF than in R-PALF. In comparison to untreated fibers, treated fibers exhibited greater thermal stability, and as the fiber content increased, thermal stability decreased. The Na-PALF hybrid system had the highest thermal stability, which suggested that fiber treatments improved thermal stability by enhancing the fiber-matrix interfacial interaction [2]. The treated fiber-reinforced composites were comparatively similar to neat PA6, according to the DSC values. This could be explained by a high interfacial interaction between the matrix and fibers following surface treatment, which lowers the degree of regularity of the polymer chain and also reduces crystallinity. The natural fiber (Flax/Kenaf/Hemp) content increases in the PA6 composite thermal stability reciprocated inversely [36].

Thermogravimetric analysis (TGA) revealed that the onset temperature of rapid thermal degradation decreased from approximately 440 °C for neat PA6 (Polyamide 6) to 420 °C for a blend containing 20%

natural fibers. This indicates that natural fibers in the blend influence thermal stability, causing a slightly lower onset temperature for thermal degradation compared to the pure PA6 material [36]. Increasing the isothermal testing temperature from 270 °C to 290 °C resulted in a noticeable increase in the degradation rate of treated Curaua fibers [39]. Viscometry analysis showed that Avicel, a composite component, was well-preserved by the polyamide matrix and did not undergo degradation. FTIR measurements revealed a distinctive glucose stretching ring, which suggested that the Curaua fibers in the PA 6 composites underwent little degradation or preservation [39]. Yu *et al.*, categorically studied the effect of fiber surface treatment on the properties of poly(lactic acid)/ramie composite [50]. Using alkali and silane, the researchers produced PLA/ramie composites via a two-roll mill and investigated their thermal properties using DSC (Figure 5(c)). The composites demonstrated a higher glass transition temperature (Tg) compared to neat PLA, consistent with DMA findings. Untreated fiber caused a reduction in crystallization peak, while treated fiber resulted in its disappearance, leading to decreased crystallinity and molecular chain regularity. Surface-treated ramie fiber addition increased the melting temperature (Tm), likely due to strong interactions between the PLA matrix and ramie fiber. These results supported previous research on bamboo fibers' coupling agent effect on PLA crystallization. Enhanced thermal properties were attributed to improved component adhesion, as confirmed by DSC analysis, and surface treatment increased the Vicat softening and degradation temperatures, with improved fiber-matrix adhesion at the interface observed through fracture surface examination [50]. For biomaterials applications, Lim *et al.*, [51] thoroughly investigated the many facets of brass-based natural fiber composites, with an emphasis on enhancing their mechanical and structural qualities for use in biomedicine. The limitations of conventional biomaterials for blunt-force trauma protection demonstrate that low brass fillers greatly improve tensile and flexural strengths [51]. In a different study, Lim *et al.*, [52] show that, in comparison to titanium dioxide fillers, low brass fillers promote cartilage cell growth by providing greater surface membrane

strength and more homogenous pore structures [52]. Another study highlights the possibility of developing materials that can withstand impact better by using finite element meshing to analyze how residual stresses affect fracture mechanisms. This study finds a critical perforation velocity of 382 m/s and a total residual membrane stress of 650 MPa [53]. To improve therapeutic efficacy, the combination of copper and zinc (CuZn) in electrical biosensors for drug delivery systems shows promise in creating on-program triggers and on-demand stimuli within biosensors [54]. CuZn, being a semiconductor, can function as an electrochemical detector to initiate the controlled release of active pharmaceutical ingredients (API). The electrical biosensor drug carrier, which employs CuZn in biosensors, can efficiently administer medications by reacting to particular stimuli, like electrical signals, and releasing the API when required [55]. By addressing the issues of drug clearance, target localization, and therapeutic efficacy in drug delivery systems, this strategy enables precise drug delivery [56]. CuZn in biosensors also provides effective drug delivery and biocompatibility, which raises the possibility of achieving therapeutic efficacy in a variety of medical applications [55].

4 Advantages and limitations of reinforced composites

Both carbon fiber-reinforced PA6 composites and natural fiber-reinforced composites have benefits and drawbacks. The remarkable mechanical performance of carbon fiber composites can be attributed to their great strength, stiffness, and low weight. They also exhibit excellent electrical conductivity and chemical resistance. However, they are brittle, expensive, and difficult to produce. However, natural fiber composites are typically more affordable and environmentally benign because they use renewable resources. They are biodegradable, have good damping properties, and use less energy in manufacturing. However, they frequently lack the strength and rigidity of carbon fiber composites, have weak moisture resistance, and are susceptible to deterioration over time. The application needs, cost factors, sustainability objectives, and required mechanical qualities influence the choice between various composites.
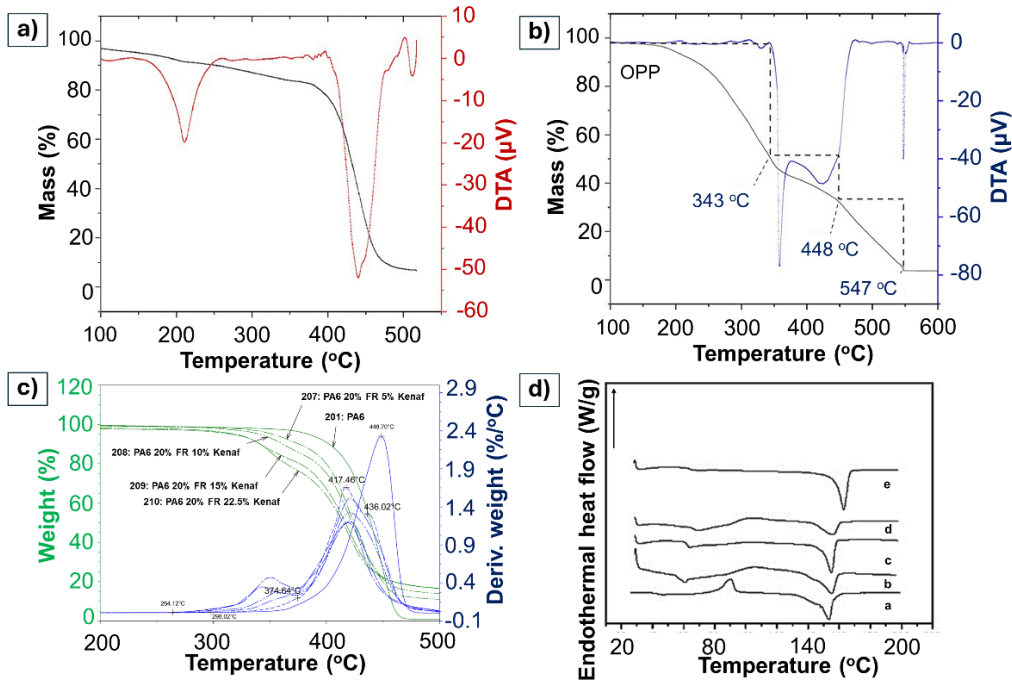
Figure 5: (a), (b) Thermal curve of PA6 and OPP (Reprinted with permission from reference no. [46], License No. 5573591476810), (c) TGA and DTG of PA6, PA6 20% FR and PA6 20% FR reinforced with (5, 10, 15 and 22.5 wt% kenaf) (Reprint with permission with reference [31], License No. 55735900 01695), The DSC curves for neat PLA and PLA-based composites are shown in (d). The composites include 1) neat PLA, 2) untreated PLA, 3) alkali-treated PLA, 4) silane-1-treated PLA, and 5) silane-2-treated PLA. (Reprinted with permission from reference [50], License No. 5573600263320).

Table 1 presents a summary of the different NFRC-PA6 surface treatment techniques along with their associated benefits and drawbacks [18]–[20], [57]. Natural fiber-reinforced PA6 composites face numerous difficulties in the transportation industry. Some of these are poor interfacial adhesion, significant moisture absorption, limited fire resistance, and—weak bonding between the polymer matrix and fiber resulting from incompatible hydrophilic natural fibers and hydrophobic engineered polymers. Because of their high moisture absorption rate, natural fibers cannot be used in maritime shipping. The poor fire resistance of these materials raises questions about their safety in automotive and aerospace applications. Surface treatment methods, including coupling agents, coatings, and fire retardants, are promising for overcoming these difficulties. The characteristics of natural fiber-reinforced PA6 composites and surface treatments to improve their transportation acceptability require additional study and financing. This supports international initiatives to develop lightweight automobiles, increase fuel efficiency and reduce carbon emissions.

The primary advantage of natural fiber-reinforced PA6 composites lies in their sustainability. Natural fibers are renewable and biodegradable, significantly reducing the environmental impact compared to synthetic fibers. This eco-friendly aspect supports sustainable development goals by utilizing renewable resources and lowering carbon footprints. Additionally, the cost-effectiveness of natural fibers is a notable advantage. They are generally less expensive than synthetic fibers and polymers, making natural fiber-reinforced composites (NFRCs) a more affordable option for various applications [18]–[20].

Natural fibers also enhance the mechanical properties of NFRC-PA6 composites, such as stiffness and tensile strength. This improvement in mechanical performance makes NFRCs a potential alternative to synthetic fiber-reinforced composites in several applications, including automotive, construction, packaging, and sports equipment. The versatility of NFRCs is another significant advantage, as they open

opportunities for innovative uses, such as 3D printing and biodegradable packaging.

However, natural fiber-reinforced PA6 composites are not without their drawbacks. One of the main challenges is moisture absorption. The hydrophilic nature of natural fibers leads to high moisture absorption, which can negatively affect the mechanical properties of composites, especially under humid conditions. To mitigate this issue, moisture barrier coatings and effective treatments are required to enhance the moisture resistance of these composites. Another major disadvantage is the poor fiber-matrix adhesion. Weak interfacial adhesion between natural fibers and the polymer matrix can degrade the mechanical properties of NFRC-PA6 composites. Surface treatments like alkalization, acetylation, and silane treatment are necessary to improve the bonding between fibers and the polymer matrix [18], [20], [57].

Table 1: Methods for surface treatment of PA6 composites with natural fiber reinforcement.

Method	Improvement	Mechanism	Advantages	Disadvantages	References
Alkaline	High	Chemical	Improved fiber-matrix adhesion, increased hydrophilicity, reduced moisture absorption	Harsh processing conditions. Damage fiber surface if not done correctly	[18]–[20], [57]
Silane	High	Chemical	Improved fiber-matrix adhesion, hydrophobicity, and chemical resistance	Relatively expensive. Requires careful application to avoid excess or insufficient treatment	[18], [20], [57]
Plasma treatment	High	Physical	Increased surface roughness, wettability, and fiber-matrix adhesion	Requires specialized equipment. Cause surface damage or degradation	[18], [20], [57]
Acetylation	Moderate	Chemical	Improved hydrophobicity, increased thermal stability	Fiber degradation, Ineffective for all types of natural fibers	[20], [57]
Ultraviolet treatment	Low	Physical	Improved surface roughness, wettability, fiber-matrix adhesion	Limited effectiveness. Cause surface damage or degradation	[18], [20], [57]
Enzymatic	Moderate	Biological	Environmentally friendly. Does not need harsh chemicals.	Longer processing limited effectiveness.	[20], [57]

Table 2: The applications of PA6 Composites [17], [58], [59].

Industries	Parts
Automotive	Lightweight, durable parts of cars, trucks, aeroplanes and other vehicles are used to make dashboards, doors, panels and interior components.
Construction building materials	Mechanically durable construction materials, such as beams, joists and panels are used for roofing, siding and flooring applications.
Transport and packaging	Packaging materials for handling fragile and expensive items are used to make beverage bottles, containers and boxes.
Recreation and Sports	Various sports components include fishing rods, golf clubs, and tennis rackets.
Furniture and other applications	Fire-resistant furniture and electronic, medical, and safety devices, such as helmets and kneecaps are made from nature-reinforced PA6 composites.

Natural fiber variability also poses a challenge. The mechanical properties of composites can vary due to differences in fiber diameters, surface features, and mechanical properties. Standardizing natural fibers and their properties is essential to ensure consistent composite performance. Additionally, the low thermal stability of NFRCs limits their ability to endure high temperatures, restricting their use in applications requiring high thermal resistance. Addressing these disadvantages through various surface treatments and modifications is crucial to expanding the application range and improving the performance of natural fiber-reinforced PA6 composites

NFRC PA6 shows promise, as an alternative to synthetic fiber composites across applications due to its superior mechanical properties and significant advantages in terms of both finances and the environment. However, in order to enhance their performance and uniformity it is crucial to tackle challenges such as stability, weak bonding, between fibers and matrix moisture absorption issues and inconsistent fiber properties through appropriate treatments and optimization techniques [18]–[20], [57].

Application of natural fiber reinforced PA6 composite NFRC-PA6 composites have unique properties that make them suitable for a variety of applications. Jute, hemp, carbon fiber, flax and sisal

are just a few examples of natural fibers commonly used to reinforce the polyamide 6 (PA6) matrix of these composites. They have many advantages over synthetic fibers. The tensile strength, parameters and shock resistance of the composite are all improved by using natural fibers. The automobile, building, and consumer goods industries can use these composites since they also have outstanding thermal and acoustic insulation qualities. They have a lesser carbon footprint and are made from renewable resources, making them environmentally sustainable as well. Automotive parts, packaging, sporting goods, and furniture are just a few of the diverse possible uses for natural fiber reinforced PA6 composites. Expanding ongoing research and development (Table 2) [17], [58].

5 Conclusions

Future research directions and limitations face the development of natural fiber reinforced Polyamide 6 (PA6) composites with improved properties through surface treatment. The PA6 matrix, which prevents effective adhesion and interfacial bonding, and the intrinsic polarity difference between natural fibers, like pineapple leaf fibers (PALF), are the main drawbacks. This leads to low affinity and interaction, which makes it more difficult for a strong interface bond to form. Furthermore, dangerous chemicals and possible process errors are involved in some surface modification techniques due to their high complexity and cost, such as grafting caprolactam-blocked silanes onto fibers. The desired level of improvement in fiber-matrix adhesion has not been significantly achieved with current treatment methods, such as ozone and alkaline treatments. To attain quick kinetics without sacrificing polymerization rates, there are additional difficulties in controlling the salinization, rehydroxylation, and dihydroxylation processes. Complicating matters is the need to handle the high melt viscosities of thermoplastics and the dual-scale permeability effects on resin flow in Liquid Composite Molding (LCM) processes. Another major challenge in manufacturing processes is ensuring part homogeneity and reproducibility because of uncontrollable phenomena that affect shrinkage, crystallization, and polymerization. Future studies should investigate easier and more affordable surface treatment techniques to improve the natural fiber reinforced PA6 composites' interface characteristics. Without going over budget, better interfacial bonding might result from experimenting with different silane agents and maximizing their concentrations. To improve simulation quality, research should also

concentrate on creating numerical benchmarking techniques and incorporating heat transfer and crystallization models into simulation processes.

Author Contributions

R.Y.: Conceptualization, investigation, writing - review & editing, supervision, Funding acquisition; Y.M.: Conceptualization, investigation, writing - review & editing, project administration; W.W.: Writing - original draft; G.Y.: Writing - original draft; B.K.: Writing - review & editing; M.A.: Writing - review & editing; E.H.: Writing - review & editing. All authors have read and agreed to the published version of the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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