

Citric Acid Treatment of Natural Fibers for Enhanced Strength in Polymer Composites: A Critical Review

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Abstract—Natural fiber reinforced polymer composites (NFRPC) offer sustainable alternate to synthetic composites, yet their industrial applications are often hindered by inherent hydrophilicity of natural fibers. Hydrophilicity of natural fibers results in meager interfacial adhesion with hydrophobic polymer matrices like polyester. This review critically examines the effectiveness of citric acid (CA), a non-toxic and biodegradable organic acid, as a surface modifier to address these compatibility challenges. The primary mechanism of CA treatment involves esterification, where carboxyl group of CA react with hydroxyl groups of fibers to form ester linkages, significantly reducing water absorption and increasing surface roughness for improved mechanical strength with better interlocking. Evidence from various polymer systems (Polylactic acid PLA, Polycaprolactone PCL and Epoxy) indicates that CA treatment consistently improves tensile strength, yield strength and modulus. However, crosslinking induced by CA can increase fiber brittleness, leading to the reduction of impact strength. Furthermore, a significant research gap has been identified regarding a specific application of CA treated fibers in unsaturated polyester laminates, as most of the current data is derived from other matrices or CA used as a binder. The paper concludes that the CA is viable, ecofriendly alternative to toxic alkaline treatments and the future research can focus on optimising treatment parameters to balance tensile strength with toughness in polyester systems.

Index Terms—Natural fibers, Citric acid, Surface modification, Polyester composites, Interfacial adhesion

I. INTRODUCTION

Natural fiber reinforced polymer composites (NFRPC) have gathered substantial attention over the traditional synthetic fiber reinforced composites offering sustainable alternative. Natural fibers are advantageous with respect to their availability, cost

effectiveness, low density, and biodegradability making themselves as an ecofriendly and sustainable choice in composite applications(1). However, several factors such as fiber diameter, pore size, pore distribution, methods of extraction of fibers, fiber origin etc. affect the mechanical properties of the fibers restricting the widespread use in composite applications (2)

Further, a fundamental challenge is observed because of hydrophilic nature of natural fiber. Poor fiber-matrix interfacial adhesion is observed due to incompatibility of functional groups present on the surface of natural fibers with that of hydrophobic functional groups of polymer resins used in making laminates. Such inadequate adhesion is responsible for affecting mechanical performance of the composite formed. The trade-off between environmental advantages and its hydrophilicity underlines the need of effective surface modifications of the natural fibers (3) Without effective surface modification, it will be difficult to realise full potential of natural fibers for composite applications(4)

Polyester resins, as a matrix, are widely used in composite materials because of their unique properties. Polyester resins show good mechanical strength suitable for load bearing applications. They show resistance to chemicals, moisture and temperature variations, thus making them suitable for widespread applications. Polyester resins are cheaper compared to other resins such as epoxy and vinyl esters. Because of the lightweight nature, polyester resin composites find applications in automobile parts. Water and corrosion resistance makes it suitable for making parts of yotch, ships and boats and other marine applications. Light weight, durable and corrosion resistance of polyester composites make it suitable for construction industry in making panels,

pipes, building facades etc. Environment resistance and high strength to weight ratio finds applications in renewable energy such as solar panel components, wind turbine blades. High tensile and compression strength makes them suitable for construction and automotive applications. Polyester resins are generally linear polymers with ester bonds and unsaturated double bonds, formed by polycondensation of diol and diacid. During formation, polyester linkages undergo cross linkages to form solid material.

In comparison to epoxy resins, polyurethane resins, vinyl ester resins, polyester resins are cost effective and easy to use as it can cure at room temperature. Although epoxy resins and vinyl ester resins show better adhesion and strength, polyester resins are preferred for its low cost and processability where moderate mechanical strength is expected (5).

Citric acid is a nontoxic, biodegradable natural organic acid which can be obtained from renewable sources like the citrus fruits like lime and lemon or by fermentation (6). These characteristics offer an attractive and ecofriendly alternative to many conventional treatments of natural fibers. It has been studied as a surface modifier for various polysaccharide-based fibers aiming to improve compatibility and interactions with biopolymer matrices (7). Beyond its role as a surface modifier, citric acid is also studied and applied as a green modifying agent and a primary binder for wood and other lignocellulosic composite materials. In this capacity, it forms ester linkages by reacting with hydroxyl groups present in lignocellulosic molecules, thereby contributing to the adhesive properties (8). The dual functionality of citric acid, as a surface modifier for natural fibers and as a binder for composite boards, introduces a critical nuance for this review. While the focus is on treatment of natural fibers for increasing strength in laminates, a significant portion of the available literature discuss citric acid as a binder. Although the underlying mechanism (esterification and crosslinking) is similar in both applications, the context and the implications for composite performance differ. This necessitates careful differentiation and a critical assessment of how findings of citric acid as a binder might, or might not, directly inform its efficacy as a surface modifier for natural fibers in polyester laminates composites.

II. MECHANISM OF CITRIC ACID TREATMENT ON NATURAL FIBERS

2.1 Esterification and hydroxyl group reduction:

Citric acid is organic acid with the formula $C_6H_8O_7$. It is tricarboxylic hydroxy acid and is slightly stronger as compared to other carboxylic acids (6). The fundamental mechanism underlying citric acid treatment of natural fibers involves chemical reaction between carboxyl groups ($-COOH$) of citric acid with the hydroxyl groups ($-OH$) inherently present on the surface of the natural fiber. This reaction results in the formation of ester bonds ($-COO-$) and the release of water as a byproduct (8). This esterification process is consistently demonstrated by Fourier Transform Infrared (FTIR) spectroscopy. CA treated fibers show characteristic absorption peaks corresponding to ester linkages, such as 1720 cm^{-1} for citric acid treated wood fibers (7), 1731 cm^{-1} for *Ampelodesma mauritanica* fibers (9), or 1736.8 cm^{-1} for starch modified with citric acid. (10) Simultaneously, a reduction in the intensity of broad O-H stretching peak (typically around 3300 cm^{-1}) is observed, indicating the consumption of hydroxyl group during esterification reaction (11)(12). The reduction in the number of available hydroxyl groups on the fiber surface is critical as it renders the fibers more hydrophobic nature. This increased hydrophobicity is crucial for improving compatibility and interaction between inherently hydrophilic natural fibers and hydrophobic polymer matrices such as polyesters (13).

The esterification reaction, while primarily serving to reduce fiber hydrophilicity, also actively creates new functional groups ($-COO-$) on the fiber surface. This suggests a dual mechanism for improved fiber-matrix compatibility. Due to decrease in hydrophilicity, the repulsive forces due to water affinity decreases. Additionally, there is also stronger interfacial interaction through introduction of new reactive functional group which facilitates covalent bonding or stronger intermolecular forces with polymer matrix. This may lead to the formation of numerous cross linkages across the interfaces (14).

2.2 Surface morphology alterations (fibrillation and roughness):

Citric acid treatments have shown to modify the surface topology of natural fibers, by increasing their surface roughness(12). Scanning Electron Microscopy

(SEM) analyses provide visual evidence of these changes. For example, citric acid treated wood fibers exhibited a slight roughness at lower concentrations of citric acid. At higher concentrations, more visible etched regions, fibrillation and fragmentation is observed resulting into rough and fragmented surface morphology(11) This enhanced surface roughness and increased fibrillation are widely believed to improve the mechanical interlocking between the treated fibers and polymer matrix. This physical interlocking mechanism is a critical factor in enhancing interfacial adhesion within the composite structure(15)The relationship between citric acid treatment temperatures, concentrations and resulting fiber morphology is complex and critical for optimum performance. While increased surface roughness is generally beneficial for mechanical interlocking, excessive treatments (e.g. temperature above 80°C for wood fibers) can lead to the embrittlement of the fibers(11)This indicates the existence of optimal treatment window where the benefits of surface modification like improved roughness and adhesion outweigh the potential for fiber degradation that may lead to loss of intrinsic strength of composite.

2.3 Impact on fiber chemical composition and crystallinity:

Citric acid treatment improves the crystallinity of natural fibers like *Ampelodesma mauritanica* or wood by selectively removing non cellulosic and amorphous components like hemicellulose, lignin, wax etc. leading to better alignment of cellulose chains increasing tensile strength of the fiber and improving overall mechanical strength of the composite (9,11) By removing less ordered, more hydrophilic amorphous material, the treatment not only reduces water affinity but also exposes a higher proportion of inherently stronger and more stable crystalline cellulose. This dual effect helps the fiber structure to be equipped to transfer stress from matrix and moisture degradation thereby enhancing the intrinsic properties of fibers and interfacial bonding within the

composites. Citric acid treatment parameters and effect on the natural fibers are as given in Table 1.

III. IMPACT ON MECHANICAL PROPERTIES OF NATURAL FIBER COMPOSITES

3.1 Tensile strength and modulus:

Citric acid (CA) treatments have exhibited consistent enhancement in tensile strength of natural fiber composites. CA treated wood fibers incorporated in polycaprolactone showed significant increase in yield strength of about 30% with 10% wood fiber content at 0°C(11)This enhancement is attributed to the improved interfacial adhesion due to esterification reactions on the surface of wood fibers(11)

Ramie fibers showed improvement in the tensile strength from 62.33 MPa of untreated fibers to 124-172.86 MPa of citric acid treated fibers with CA concentration 0.75-1.875%w/w. A noteworthy increase was observed when ramie fibers were treated with Sodium Hypophosphite (SHP) used as a catalyst. Tensile strength was observed to increase up to 1290.63 MPa at 110°C with 1% CA/SHP. This increase in tensile strength over 19 percent signifies the strong synergetic effect of CA when used with appropriate catalyst(12) The remarkable increase in tensile strength indicates that while CA facilitates benefits of esterification, the catalyst significantly increases the cross linking that leads to superior chemical modification resulting in improved mechanical performance. This suggests that future research and development efforts should priorities optimizing catalyst systems for CA treatments, rather than solely focusing on CA concentration to fully unlock potential of eco-friendly modifications of natural fibers for composites (12)

Citric acid treatment also showed an impact on modulus of elasticity of natural fibers. Citric acid (5%) treated *Ampelodesma mauritanica* fibers integrated with Poly lactic acid (PLA) showed increase in modulus of elasticity to 4.680 GPa along with increase in tensile strength to 48.90 MPa. It also showed 2.52% elongation at rupture (9)

Table 1: Citric acid treatment parameters and effect on the natural fibers

Fiber Type	Citric Acid Concentration	Treatment Duration	Treatment Temperature	Post-treatment	Observed Effects on Fiber Properties	Reference
Wood Fibers	0.05 M, 0.25 M, 1.00 M	1 h	60, 80, 120, 160 °C	Washing to neutral pH,	Esterification confirmed (FTIR 1720 cm ⁻¹), reduced O-	(11)

				vacuum drying (40 °C, 24 h)	H peak (3300 cm ⁻¹), increased surface roughness/ fibrillation, increased hydrophobicity (higher water contact angle), optimal temp 80°C (above 80°C fibers brittle)	
Ramie Fiber	0.5-2.5% (w/w)	3 h	90-110 °C	Rinsing, oven drying (90-110°C, 8-10h), co-treatment with SHP (1-2% w/w) at 90-110°C	Esterification confirmed (FTIR 1710-1780 cm ⁻¹), reduced OH group (3000-3650 cm ⁻¹), surface structure modification (SEM), significant increase in tensile strength (especially with SHP), SHP found to be effective catalyst.	(12)
Ampelodesma mauritanica Fibers	5%	2 h	Room temp, then 60 °C	Rinsing, oven drying (60°C, 24 h), optional bleaching (5% NaClO, 80°C, 2h)	Reduction in hemicellulose, lignin, and wax (attenuation of 1650 & 1731 cm ⁻¹ bands), improved crystallinity, increased tensile strength, modulus of elasticity and elongation at rupture.	(9)
Flax Fibers	5 wt.%	Not specified	Not specified	Not specified	Effective in modifying wettability and surface roughness, 41% decrease in water saturation rate (in cement composites).	(15)
Flax Fibers (Sodium Citrate)	5%, 10%, 20% (w/w)	120 h	25 °C, then 103 °C	Room temp drying (24h), oven drying (103°C, 24h)	Fiber fibrillation, rougher surface, increased reactive sites, removal of cementing substances (similar to mercerization), improved fiber-matrix compatibility, reduced void content (optimal at 10% solution), reduced water absorption.	(16)
Elephant Dung Fibers (CA as binder)	10, 20, 30 wt%	10 min	180, 200 °C	Oven drying (80°C, overnight)	Increased ester linkages (FTIR), improved physical and mechanical properties, reduced thickness swelling and water absorption, reduced surface roughness, optimum properties at 200°C and 20 wt% CA.	(17)
Jute Stick (CA as binder)	10, 20, 30 wt%	Not specified	180, 200 °C	Not specified	Formation of ester linkage (FTIR), improved mechanical properties and dimensional stability, optimum at 20 wt% CA and 200°C.	(18)
Bamboo fibers	5wt%	Not specified	Not specified	Not specified	Increase in tensile strength, lower water absorption, less brittle fibers (SEM) showing effective load sustainability	(19)

Kenaf fibers	0.6 M	30 Minutes	Room Temp.	Oven dried at 50°C for 24 hrs then raised to 120°C for 90 minutes, washed with water	Kenaf/PVA composites showed better elongation modified with 5% CA. rough and uneven surface morphology, better porous structure (SEM), FTIR spectra showed decreased intensity of C-O stretching ($\sim 1251.17 \text{ cm}^{-1}$) of acyl group of hemicellulose, increase in carbonyl group absorption $\sim 1728\text{-}1740 \text{ cm}^{-1}$ for ester linkage by citric acid treatment	(20)
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3.2 Flexural Strength and Modulus:

Direct experimental data specifically on CA treated natural fibers in unsaturated polyester laminates is limited, however, studies involving other polymer matrices offer valuable insights. For example, flax fiber reinforced epoxy composites treated with 10% sodium citrate demonstrated 14.9% increase in flexural strength and 21.1% increase in flexural (16) When citric acid was used as a binder for Salacca frond composite board, the resulting modulus of rupture (MOR) values ranged from 13.4 to 15.6 MPa, and modulus of elasticity (MOE) values between 3.0 and 4.1 GPa, which met the requirement of the JIS A 5908 (2003) standard (21). Similarly, jute stick particle board bonded with CA-glycerol mixture achieved MOR of 19.67 N/mm^2 (18) The consistent positive effects of citric acid or its derivatives like sodium citrate on flexural properties, even when applied as a binder or with different polymer matrices like epoxy, PCL, PLA strongly suggest a generalised mechanism of improved load transfer and enhanced interfacial stiffness. This suggests that if the esterification mechanism facilitated by CA is successfully applied as a surface treatment for natural fibers intended for unsaturated polyester composites, similar improvement of flexural properties could be reasonably anticipated. The current lack of direct studies on the specific system represents a research gap.

3.3 Impact Strength:

Although CA treated wood showed improvement in compression strength and modulus of elasticity as a result of cell wall bulking and crosslinking, it showed reduction in impact strength. CA treatment increased brittleness with the reported losses up to 50% impact

strength. The phenomenon is attributed to the crosslinking within cell wall induced by CA increasing rigidity. However, some studies have shown that combining CA with additives like activated glucose can improve impact strength. Activated glucose consumed CA thereby reducing the crosslinking and extent of embrittlement (22). For flax fiber reinforced epoxy composites treated with sodium citrate, impact strength was observed to decrease significantly ranging from 37.7% to 61.4% lower than the untreated composites with the increasing sodium citrate concentration(16) .

While the esterification reaction enhances stiffness and strength by increasing crosslinking and reducing hydrophilicity, it can simultaneously lead to increased brittleness. This implies that for optimising CA treatment of natural fibers for polyester laminates, a delicate balance must be struck by maximising tensile and flexural strength reducing potential of reduced toughness. This might necessitate exploring precise control over crosslinking density or incorporating toughening agents in the matrix.

3.4 Interfacial adhesion and stress transfer:

Improved fiber/matrix adhesion is consistent and widely reported outcome of citric acid (CA) treatment. This enhancement is frequently confirmed by Scanning Electron Microscopy (SEM) analysis of composite fracture surfaces, which reveal efficient wetting of fibers by the matrix and significantly limited fiber pull out, for example PCL/wood fiber composite (11) This enhanced interfacial adhesion is important for effective stress transfer from polymer matrix to the reinforced fibers. A strong interface ensures that the applied loads are effectively distributed to the high strength fibers, which directly

translates to improved overall mechanical performance of the composites (4)

Fourier Transform Infrared analysis (FTIR) analysis consistently confirms the formation of ester linkages between the hydroxyl groups of the natural fibers and the carboxyl groups of citric acid, providing chemical evidence of effective bonding mechanism at the interface (23) While direct Interfacial Shear Strength (IFSS) data for CA treated natural fibers in unsaturated polymer matrices is not explicitly provided in the literature, other chemical modifications such as acylation have increased IFSS with unsaturated polyester matrices (24) Similarly acidic modification (using H_2SO_4 and HNO_3) of carbon fibers led to increase IFSS in epoxy composites (25). Despite of the absence of direct Interfacial Shear Strength (IFSS) data for CA treated natural fibers in unsaturated polyester matrices, the consistent evidence of improved adhesion (via SEM images observations of reduced fiber pull out and FTIR confirmation of ester bond formation) and the resulting enhancement in macroscopic mechanical properties across various polymer systems (PCL, PLA, epoxy via sodium citrate) strongly imply that the CA treatment effectively improves fundamental interfacial bond. The underlying mechanism of esterification forming covalent bond linkages is a robust explanation for this improvement. Therefore, lack of IFSS study for CA modified natural fiber/ polyester should be viewed as a significant research gap that need to be addressed.

3.5 Water absorption and Dimensional stability:

A consistent benefit of CA treatment is the reduction in water uptake and a corresponding improvement in the hydrophobicity of both the treated fibers and the resulting composites. This crucial effect is primarily attributed to the reduction of hydrophilic hydroxyl groups on the fiber surface through esterification reaction (11) Specific examples include CA treated wood (where CA acts as a binder), which showed reduction in water absorption with increase in CA content and board density (22) Also flax fibers treated with 5wt% CA solution showed a notable 41% decrease in water saturation rate when incorporated into cement composites (15) Furthermore, enhanced dimensional stability has been reported for composite boards where citric acid functions as a bonding agent (22)

Reduced water absorption is not only an isolated desirable property, for example, for packaging applications (11), but is important to the long-term durability and mechanical stability of natural fiber composites. Water acts as a plasticizer for natural fibers, leading to the swelling and significantly degrades fiber -matrix interface over the time. By effectively reducing water uptake, CA treatment directly addresses composite degradation, thereby indirectly contributing to enhanced long term performance and maintaining mechanical integrity (4) Mechanical property improvement in CA treated natural fiber composites are listed in Table 2.

Table 2: Mechanical property improvement in CA treated natural fiber composites

Sr. No.	Fiber Type	Polymer matrix	CA concentration	Co-treatment (if any)	Mechanical property measured	Reported improvement/ Value	Reference
1	Wood fibers	Polycaprolactone (PCL)	1 M CA and 10% wood fibers in PCL	None	Yield strength	~30% increase at 0°C and 25% increase at 25°C	(11)
2	Ramie fibers	NA (only fibers)	0.75–1.875% (w/w)	None	Tensile strength	increased from 62.33 MPa (untreated) to 124–172.86 MPa (CA treated) around 83–155% improvement	(12)

3	Ramie fibers	NA (only fibers)	1.875% (w/w)	Sodium Hypophosphite 1% (w/w) at 110°C	Tensile strength	1290.63 MPa (about 19% improvement over control sample)	(12)
4	Ampelodesma mauritanica Fibers	Polylactic acid (PLA)	5%	Optional bleaching	Modulus of Elasticity	4.680 GPa	(9)
5	Ampelodesma mauritanica Fibers	Polylactic acid (PLA)	5%	Optional bleaching	Tensile strength	48.90 Mpa	(9)
6	Ampelodesma mauritanica Fibers	Polylactic acid (PLA)	5%	Optional bleaching	Elongation at rupture	2.52%	(9)
7	Ramie fibers	Polylactic acid (PLA)	4%	None	Tensile strength	58.06 ± 3.47 MPa	(26)
8	Ramie fibers	Polylactic acid (PLA)	4%	None	Elasticity	413.87 ± 45.82 MPa	(26)
9	Ramie fibers	Polylactic acid (PLA)	4%	None	Elongation at break	15%	(26)
10	Flax fibers	DGEBA epoxy resin	10% Sodium citrate	None	Tensile strength	Increment of 19.5% (81.9 MPa)	(16)
11	Flax fibers	DGEBA epoxy resin	10% Sodium citrate	None	Tensile modulus	Increment of 33.6% (7.35 GPa)	(16)
12	Flax fibers	DGEBA epoxy resin	10% Sodium citrate	None	Flexural strength	Increment of 14.9%	(16)
13	Flax fibers	DGEBA epoxy resin	10% Sodium citrate	None	Flexural modulus	Increment of 21.1%	(16)
14	Flax fibers	DGEBA epoxy resin	5%, 10%, 20% Sodium citrate	None	Impact strength	Reduction of 37.7% to 61.4%	(16)
15	Flax fibers	Cement	5%	None	Flexural strength	Increment of 43.5% (7 days) and 18% (28 days)	(15)
16	Flax fibers	Cement	5%	None	Compressive strength	Increment of 13% (7 days) and 6% (28 days)	(15)

IV. CRITICAL ANALYSIS AND DISCUSSION

4.1 Efficacy and limitations of Citric acid treatment of natural fibers:

Citric acid treatment is established as an effective and eco-friendly approach for modifying the surface of natural fibers. Its key mechanism involves esterification, which effectively reduces hydrophilicity and significantly increases surface roughness. These modifications lead to stronger fiber-

matrix adhesion and result in significant increase in modulus, tensile strength and yield strength in various composites based on biopolymer matrices like Polylactic acid (PLA) (26) and Polycaprolactone (PCL) (11).

However, there are certain noteworthy limitations observed with CA treatment. One of the important drawbacks, when CA acts as a binder or at higher concentrations of CA, is the possible reduction in impact strength and increase in brittleness of the

composite. It is possible due to extensive crosslinking between fiber and matrix as an effect of CA treatment (16) The consistent observations of improved tensile strength and flexural properties alongside a reduction in impact strength suggest that CA treatment, while improving interfacial stiffness and load transfer, may lead to rigid and less ductile composite. Thus, increase in strength does not apply uniformly across all mechanical properties. For practical applications, further research must explore strategies to reduce this induced brittleness, particularly those requiring resistance to sudden loads or impacts. The possibilities could involve incorporating toughening agents into polymer matrix. Other possibilities could be optimising fiber content, orientation and the concentration of CA to control crosslinking to achieve balanced mechanical profile.

Furthermore, manufacturing of CA-bonded composites often necessitates higher pressing temperatures (exceeding 180°C) and the longer pressing time compared to the composites made with the conventional adhesives. Such conditions can lead to increased energy consumptions during manufacturing. From the economical perspective, the market price of citric acid could be higher than the conventional wood adhesives, hindering the widespread industrial adoption of citric acid replacing the conventional wood adhesives. Some studies have reported that the CA treated wood may exhibit undesirable yellowing which could be a concern for aesthetic applications (22).

4.2 Comparison with alternative chemical treatments: Traditional alkaline treatment, typically using Sodium hydroxide (NaOH), is extensively employed and effective for natural fibers. It operates by removing hemicellulose and lignin, increasing surface roughness, and generally improving fiber-matrix compatibility. However highly alkaline treatments can sometimes lead to reduction in intrinsic mechanical properties of fibers themselves (16) Other chemical treatments such as acylation(24), silane treatment, bleaching and plasma treatment also aim to enhance fiber hydrophobicity and improve interfacial adhesion through various mechanisms (4) Citric acid offers a distinct advantage of environmentally friendly alternative to some of these conventional treatments, particularly compared to highly alkaline treatment that involves toxic chemicals(11) While citric acid offers a “green” advantage, its overall performance relative to the established but less ecofriendly treatments like alkaline modification needs to be evaluated. The selection of fiber treatment method often involves a complex trade-off between cost effectiveness, environmental impact, complexity of processing and precise mechanical properties anticipated for final composite. CA’s unique ability to form ester cross linkage provides a distinct chemical bonding compared to surface roughening or silane coupling. This suggests that the CA treatment might be complementary or superior for specific applications where strong interfacial bonds are critical. Comparison of natural fiber chemical treatments is given in Table 3.

Table 3: Comparison of natural fiber chemical treatments:

Treatment type	Primary mechanism	Typical effect on fiber	Typical effect on composite mechanical properties	Advantages	Disadvantages	Reference
Citric acid	Esterification, reduction of -OH groups, surface roughening, removal of amorphous components	Reduced hydrophilicity, increased roughness/fibrillation, improved crystallinity, potential embrittlement at high temperatures	Increased tensile strength/yield strength/modulus, increased flexural strength, reduced impact strength, increased brittleness, improved interfacial	Ecofriendly, non-toxic, biodegradable, renewable source, strong chemical bonding (ester)	Potential for brittleness, higher processing temperature/time, higher cost than conventional adhesives, yellowing	(23)

			adhesion, reduced water absorption			
Alkaline (NaOH)	Removal of lignin/ hemicellulose, fiber fibrillation, surface roughening, increased reactive sites	Increased surface roughness, improved wettability, increased crystallinity, diameter reduction, increment in aspect ratio	Improved fiber- matrix compatibility, increased tensile/ flexural strength, improved interfacial adhesion	Common, simple, effective, widely studied	Can reduce intrinsic fiber mechanical properties, highly alkaline/ toxic environmental concerns	(23)
Acylation	Esterification of hydroxyls groups with acetic anhydride	Increased hydrophobicity, improved dimensional stability, smoother surface	Increased interfacial shear strength with hydrophobic resin	Effective for hydrophobicity and adhesion	Higher concentration led to poor mechanical properties as the fiber surface gets damaged	(27)
Silane	Coupling agent forms chemical bridge between fiber and matrix	Improved wettability, increased surface roughness	Improved mechanical properties	Enhanced interfacial adhesion, high efficiency and scalability	Higher cost, requires safe handling and moderate environmental impact	(28)
Plasma	Surface etching, introduction of functional groups, surface polymerisation or cross linking	Improved surface roughness, wettability and specific surface area	Improved adhesion and mechanical strength	Environment friendly process, no chemicals, higher precision	High cost, excessive treatment leads to degradation	(29)
Peroxide	Free radical reactions	Removal of impurities, increase surface roughness, crystallinity	Improved tensile, flexural strength and impact strength	Ecofriendly, enhance adhesion	Fiber damage at higher concentration, high cost	(4)

4.3 Addressing research gap:

The provided research offers coverage of citric acid treatment for natural fibers integrated into various polymer matrices, including polycaprolactone (PCL) (11) and epoxy resins (often sodium citrate)(16). However, a lack of direct studies for citric acid treatment for natural fibers intended for incorporation into unsaturated polyester resin laminates is observed. It is important to recognise that polyester resins possess distinct chemical compositions, curing mechanisms and overall properties compared to PCL, epoxy resins (30) These differences can significantly influence fiber-matrix interaction and resulting composite performance. The most significant finding in this comprehensive review is the notifiable absence

of direct research of citric acid treatment of natural fibers intended for the unsaturated polyester resin laminates. This represents critical and unaddressed gap in the literature. Although the fundamental principle of citric acid treatment (e.g. esterification and reduced hydrophilicity) is generally applicable across the polymer systems, the specific interfacial chemistry, curing behavior and resulting mechanical performance within unsaturated polyester matrix cannot be extrapolated directly from the studies with PLA, PCL or the applications where citric acid acts as a binder. This highlights a clear need for targeted research to bridge this knowledge gap and fully assess the potential of citric acid treatments in composite systems.

4.4 Long term stability and durability:

While the provided literature does not explicitly detail about the long-term durability of citric acid treated natural fiber polyester laminates, the consistently reported reduction in water absorption achieved through CA treatment is a key factor in enhancing long term stability(11) High water absorption in natural fibers is known to lead to increased biomass weight, promote weathering, cause weakening of fibers, ultimately degrading the composite properties over the time (4) As a result of CA treatment, improved interfacial adhesion contributes significantly to better durability by reducing moisture absorption and maintaining stress transfer at the interface throughout the service life of the composite (4)

However, potential for increased brittleness (as indicated by reduced impact strength) with CA treatment could negatively impact on long term durability on the composite. The relationship between citric acid treatment and the long-term durability of natural fiber composites is largely inferred from observed improvements in hydrophobicity and interfacial adhesion, rather than directly demonstrated through long term aging and environmental exposure study. While the reduced water uptake and stronger adhesion are the positive indicators for the extended service life of the composite, the potential for increased brittleness introduces a counteracting factor that could compromise on durability under certain stress conditions. This highlights that the comprehensive long-term testing including environmental aging, fatigue studies and creep behavior is essential for a complete and accurate understanding of real-world performance and durability of CA treated natural fiber polyester composites.

4.5 Environmental and economical aspect:

Citric acid is non-toxic, natural, biodegradable compound derived from renewable sources making it an attractive ecofriendly option for modification of materials(22). However, higher market price of citric acid compared to conventional, formaldehyde-based adhesives, could potentially hinder the direct replacement for industrial applications when used as a binder. In addition to this, higher pressing temperature required for CA bonded composites attracts higher energy cost and need to be considered for economical aspect of the composite. The “green” advantage of

citric acid is a significant motivating force for its research and development, aligning with the global sustainability goals in material science.

V. CONCLUSION AND FUTURE DIRECTIONS

Citric acid treatment offers an effective and ecofriendly method for modifying natural fiber surfaces. Its main mechanism involves esterification, which reduces fiber hydrophilicity and significantly increases surface roughness. These modifications collectively improve fiber-matrix adhesion and result in notable enhancement in various mechanical properties, particularly tensile strength and modulus. The efficacy of CA treatment can be amplified with the use of catalyst such as Sodium Hypophosphite, dramatically improving tensile strength (22). . However, a critical trade-off exists: while a CA treatment enhances strength, it can concurrently lead to a reduction in impact strength and increased brittleness, especially at higher concentrations or when used as a primary binder. There is a notable lack of direct and comprehensive studies on the application and evaluation of citric acid surface treatment for natural fibers specially intended for unsaturated polyester resin composites. Much of the existing literature focuses on other polymer matrices or utilises CA in its role as a binder for composite boards.

Based on the current critical literature review, the future scope lies in direct studies on surface modification of natural fibers and their subsequent study of polyester composites, optimisation of treatment parameters and co treatments, long term durability studies.

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