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Original Article

Bio-based Composites from Agricultural Wastes for Structural Applications

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Abstract

Agricultural wastes such as rice husk, wheat straw, sugarcane bagasse, banana pseudostem, coconut coir residues, and pineapple leaf fiber (PALF) are increasingly recognized as valuable lignocellulosic resources for the development of sustainable bio-based composites (Faruk et al., 2017; Sanjay et al., 2021). From a chemistry perspective, these materials offer cellulose-rich microfibrils, hemicellulose–lignin matrices, surface hydroxyl functionality, and-in the case of rice husk-silica-rich inorganic phases that strongly influence interfacial adhesion, curing behavior, moisture sensitivity, and durability (Xie et al., 2020; Thakur et al., 2022. This paper provides a comprehensive chemistry-oriented review of agricultural-waste-derived composites for structural and semi-structural applications. Chemical composition, surface modification routes (alkali treatment, silane coupling, acetylation, grafting), and interphase formation are discussed in relation to polymer matrices including bio-based epoxies, bio-polyesters, recycled thermoplastics, and mineral matrices such as rice-husk-ash-modified cement and geopolymer systems. Advanced characterization techniques (FTIR, XPS, solid-state NMR, TGA/DSC, DMA, SEM–EDS) are correlated with mechanical performance and durability. This paper presents a chemistry-focused review of agro-waste-derived composites for structural applications, integrating reaction mechanisms, interphase chemistry, and durability considerations.

Keywords: *Agricultural wastes, Lignocellulosic fibers, Interfacial chemistry, Silane coupling, Alkali treatment, Acetylation, Bio-based epoxy, Eugenol, PLA, Recycled polypropylene, Rice husk ash, Geopolymer chemistry, FTIR, XPS.*

Introduction

Decarbonizing construction and structural products increasingly requires materials that can reduce embodied emissions while maintaining engineering reliability. Biocomposites and natural-fiber composites have been widely proposed for building products such as panels, profiles, decking, and sandwich structures, with recent construction-focused reviews emphasizing both the opportunity and the performance barriers that still limit broad structural adoption (Ahmad et al., 2025; Olanrewaju et al., 2025). From a chemistry viewpoint, the key bottleneck is not simply the intrinsic strength of lignocellulosic fibers, but the stability and efficiency of the fiber–matrix interphase under moisture, heat, and chemical exposure. Agricultural residues are chemically heterogeneous: cellulose microfibrils provide stiffness; hemicellulose contributes polarity and moisture uptake; lignin offers hydrophobic aromatic domains; and surface layers contain waxes/pectin and low-molecular extractives that inhibit wetting. Consequently, many agro-waste composites fail by interfacial debonding and fiber pull-out, particularly after hygrothermal aging.

The chemistry of the fiber surface strongly dictates adhesion to common matrices. Hydrophilic –OH groups on cellulose/hemicellulose drive high surface energy and water sorption, while many polymers (polyolefins, some bio-polyesters) are comparatively hydrophobic.

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Interface engineering therefore relies on chemical treatments (e.g., alkali) and coupling/compatibilization to increase effective wetting, create covalent/ionic bridging, and reduce moisture pathways. Recent reviews on sugarcane bagasse treatment and natural fiber composite aging highlight that optimized chemical modification can raise mechanical properties and significantly improve property retention during accelerated aging (Chougala et al., 2025; Das et al., 2025). Another chemistry-driven pathway is the development of bio-based thermosets-particularly epoxies derived from plant phenolics such as eugenol-which can improve sustainability while maintaining desirable thermoset network properties (Matykiewicz, 2025; Li et al., 2025).

Agricultural wastes also contribute inorganic chemistry advantages. Rice husk ash (RHA) contains high silica content and can act as a reactive supplementary cementitious material or as a reactive/pozzolanic component in geopolymer systems; reviews and recent studies report that modest RHA addition can enhance strength and durability when properly integrated with metakaolin or fly ash and controlled alkaline activation (Hamada et al., 2025; Mulapeer et al., 2025). In polymer composites, micronized rice husk provides silica-rich reinforcement but requires compatibilizers (e.g., maleic anhydride-grafted PP) and particle-size control to achieve useful mechanical performance, including in extrusion-based manufacturing (Wiley/SPE,2025).

This chapter therefore centers on the chemistry that connects agricultural residues to structural composite performance: (i) feedstock chemical composition and variability, (ii) modification/coupling chemistries and interphase formation, (iii) matrix chemistry (bio-based epoxies, bio-polyesters, recycled thermoplastics), (iv) mineral-matrix systems involving RHA and alkali activation, (v) chemical and physicochemical characterization linking interphase chemistry to mechanical/durability outcomes, and (vi) chemistry-informed design guidelines for construction.

Agricultural Waste Feed stocks: Composition and Surface Chemistry

Agricultural residues are predominantly lignocellulosic, consisting of cellulose, hemicellulose, and lignin. Cellulose crystallinity governs stiffness, hemicellulose contributes polarity and moisture uptake, and lignin provides aromatic rigidity and thermal stability (Faruk et al., 2017; Thakur et al., 2022).

1. **Lignocellulosic Composition and Variability**

Most agricultural residues used in composites are lignocellulosic materials composed primarily of cellulose, hemicellulose, and lignin, with minor fractions of pectin, waxes, ash, and extractives. Cellulose crystallinity and microfibril angle influence stiffness and tensile strength; hemicellulose introduces amorphous polarity and contributes strongly to moisture uptake; lignin provides aromatic hydrophobicity and contributes to thermal stability but may hinder fiber fibrillation. Variability arises from cultivar, harvest season, retting/extraction route, and storage. For example, PALF reviews emphasize that isolation technique and pretreatment significantly affect cellulose content, surface functionality, and thus fiber-matrix adhesion (Yadav et al., 2025; Sethupathi et al., 2024; Liao et al., 2025).

2. **Rice Husk and Rice Husk Ash (RHA): Silica-Rich Chemistry**

Rice husk is distinctive because it contains substantial silica in addition to lignocellulosic components. Controlled combustion yields rice husk ash (RHA), which can be amorphous and reactive when processed appropriately. In geopolymer and cementitious systems, RHA participates in silicate network formation and can densify microstructure, improving durability metrics such as permeability and chemical resistance. A recent comprehensive review of RHA in geopolymer concrete reports strength improvements at optimized replacement levels, especially with metakaolin-based blends (Mulapeer et al., 2024; Hamada et al., 2025).

Interfacial Chemistry: Surface Modification, Coupling, and Compatibilization

1. **Alkali Treatment (Mercerization) Chemistry**

Chemical modification is required to improve compatibility between hydrophilic fibers and polymer matrices. Alkali treatment (commonly NaOH) partially removes surface waxes, pectin, and hemicellulose, increases surface roughness, and exposes cellulose microfibrils. Chemically, hydroxide ions can cleave ester linkages in hemicellulose/pectin and disrupt hydrogen-bonded networks, leading to fibrillation. Moderate treatment often improves interfacial shear strength and flexural performance; over-treatment can reduce degree of polymerization and damage cellulose, lowering intrinsic fiber strength. Reviews on bagasse treatments and recent experimental work continue to show treatment-dependent trends in tensile/flexural properties via improved wetting and reduced interfacial defects (Chougala et al., 2025; Samanth et al., 2025).

Figure 1: Schematic Representation of Alkali Treatment (Mercerization) of Lignocellulosic Fibers

This reaction illustrates removal of surface waxes and hemicellulose, increasing surface roughness and reactivity and thereby enhancing fiber-matrix interfacial adhesion (Chougala et al., 2025).

2. **Silane Coupling Chemistry**

Silane coupling agents (e.g., amino-, epoxy-, methacryloxy-silanes) hydrolyze to silanols that can condense with fiber surface –OH groups and form siloxane networks. The organofunctional group can co-react with thermoset matrices or interact strongly with polar thermoplastics, improving wetting and creating a more moisture-resistant

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interphase. Silanes are particularly valuable with silica-containing fillers (rice husk/ash), where siloxane bonding can be strong and durable (Xie et al., 2020).

Hydrolysis → condensation → fiber–siloxane bonding

$$R\text{–}Si(OR')_3 \rightarrow \text{Fiber–O–Si–R}$$

Figure 2: Schematic Representation of Silane Ccoupling Mechanism at the fiber-matrix Interface

Hydrolysis of alkoxy silane followed by condensation with fiber –OH groups forms siloxane bridges (Fiber–O–Si–R). The organofunctional group (R) reacts with the polymer matrix, producing a durable interphase (Xie et al., 2020).

3. **Compatibilizers and Grafting for Polyolefins**

In polypropylene and polyethylene matrices, maleic anhydride-grafted compatibilizers (PP-g-MA, MAPP) introduce polar anhydride groups capable of forming ester linkages with fiber –OH groups and increasing interfacial adhesion. A recent Polymer Composites study on recycled PP/rice husk filaments for extrusion/3D printing highlights that compatibilizer level and rice husk particle size jointly govern mechanical performance and processability (Polymer Composites/Wiley, 2025).

$$\text{Fiber–OH} + (CH_3CO)_2O \rightarrow \text{Fiber–OCOCH}_3$$

Figure 3: Schematic Representation of Acetylation Reaction of Cellulose Fibers

Acetylation reduces hydrophilicity and moisture uptake of natural fibers, improving dimensional stability under humid conditions (Sanjay et al., 2021).

Matrix Chemistry for Structural Agro-Waste Composites

1. **Bio-Based Epoxy Thermoset (Eugenol-derived and other routes)**

Epoxy thermosets are widely used for structural laminates because they deliver high modulus, dimensional stability, and strong adhesion when wetting is adequate. Bio-based epoxy development increasingly leverages lignin-derived aromatics and plant phenolics such as eugenol. Matykiewicz (2025) reports that eugenol-derived epoxy resin can be used for impregnation of natural fibers and composite preparation, indicating compatibility with composite manufacturing workflows. Complementary resin chemistry advances include bio-based curing agents and network designs that balance toughness and heat resistance (Li et al., 2025). A chemistry advantage of aromatic bio-epoxies is improved rigidity and potentially higher glass transition temperatures compared with some aliphatic bio-resins, though cure kinetics and viscosity must be tuned for infusion processes.

Epoxide ring opening + R-NH_2 → -CH(OH)-CH_2-NH-R (Crosslinked thermoset epoxy network)

Figure 4: Schematic Representation of Bio-based Epoxy Reaction (Epoxy-Amine Curing Reaction)

Epoxide ring opening by amine curing agents leads to a crosslinked thermoset network. Eugenol-derived epoxy systems retain aromatic rigidity and enhanced sustainability (Matykiewicz, 2025; Li et al., 2025).

2. **Bio-Polyesters (PLA, PBS) and Hydrolysis Considerations**

Bio-polyesters such as PLA and PBS provide bio-based content and thermoplastic recyclability, but they are sensitive to hydrolysis and hygrothermal degradation. For structural parts in humid climates, chemistry-informed stabilization (chain extenders, nucleating agents, coatings) and robust interphase design are required. PLA also has a relatively low heat deflection temperature, necessitating formulation or hybrid design for certain construction environments (La Mantia & Morreale, 2022).

3. **Recycled Thermoplastics for Circular Structural Profile**

Circular-economy composites combine agricultural residues with recycled PP/HDPE to produce durable profiles and boards. The chemistry problem is interfacial incompatibility; compatibilizers and controlled filler moisture are essential to limit voids and interfacial defects. Recent composite-filament and PP composite studies with rice husk emphasize the role of coupling chemistry and particle size to achieve stable extrusion and improved mechanical properties (Polymer Composites/Wiley, 2025; Santos et al., 2025).

Mineral-Matrix Systems: RHA in Cementitious and Geopolymer Chemistry

Beyond polymer matrices, agricultural wastes contribute to structural materials through mineral-matrix composites. RHA contains reactive amorphous silica that can participate in pozzolanic reactions with calcium hydroxide in cement systems and in silicate network formation in alkali-activated geopolymers. Hamada et al. (2025) synthesize literature reporting that optimized RHA content can enhance compressive strength and durability, especially when blended with metakaolin. Recent experimental work further examines RHA as partial replacement in geopolymer mortars and evaluates durability under aggressive chemical exposures (Mulapeer et al., 2025). For alkali activation, the chemistry of activator generation from RHA-derived silicates is also an active area (Das et al., 2024).

SiO_2 + Al_2O_3 + NaOH → Si–O–Al–O– polymeric network

Figure 5: Schematic Representation of Geopolymerization Reaction using

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Rice Husk Ash (RHA)

Amorphous SiO_2 from rice husk ash dissolves under alkaline conditions and participates in –Si–O–Al–O– network formation, resulting in dense and chemically durable geopolymer matrices. RHA participates in silicate network formation improving strength and durability (Hamada et al., 2025).

Table1. Agricultural Residue, Dominant Chemistry, and Composite Relevance

Residue	Dominant chemistry	Typical form	Chemistry issues	Structural relevance
Rice husk/ RHA	Silica-rich + lignocellulose	Micronized filler; ash SCM	Needs coupling; ash reactivity depends on processing	Profiles/boards; geopolymer/cementitious blocks (Hamada et al., 2025)
Wheat straw	Cellulose/hemicellulose + waxy surface	Strands/fibers; densified strands	Waxy cuticle hinders wetting; delignification/densification helps	High-density composites, boards (Neudecker et al., 2025)
Bagasse	Cellulose-rich; extractives	Short fibers/mats/powder	Treatment-sensitive; moisture uptake	Panels/laminates (Chougala et al., 2025)
PALF	High cellulose; low microfibril angle (often)	Long fiber/fabric	Extraction and surface chemistry control critical	Laminates/panels (Yadav et al., 2025)
Banana fiber	Lignocellulosic; variable pectin	Fiber mats	Needs surface modification; drying critical	Panels, laminates

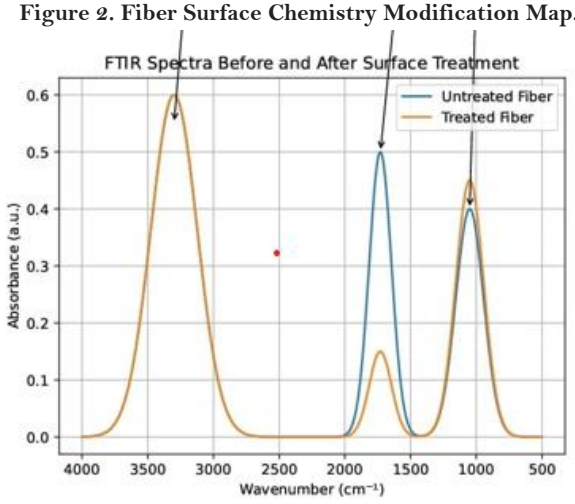
Agro-Residue	Cleaning & Drying	Extraction/ Milling	Chemical Modification (NaOH/ Silane/ Acetylation/ Grafting)	Reinforcement Architecture (Filler/ Short Fiber/ mat/ Strand)	Matrix Chemistry (Bio-epoxy/ PLA/ PBS/ Recycled PP/ Geopolyme)	Processing (Extrusion/ Compression/ Infusion/ Board pressing)	Strctural Products

Figure 1. Schematic Flow Diagram of Chemistry-driven pathway from agro-waste to structural composite.

Native Cellulose Fiber Surface -OH rich Cellulose (Waxes, hemicellulose, Lignin present)	Alkali Treatment (NaOH) Removal of Waxes & Hemicellulose, Surface Roughening	Silane Coupling Treatment Formation of Silaxone bridge (Fiber-Si-O-Si-Matrix)	Compatibilizer/ Grafting Ester linkages formation Improved Interfacial Bonding	Nano-coating/ Nano mechanical interlocking Barrier layer

Outcome of Surface Modification
↑ Fiber Wetting
↑ Interlaminar Shear strength (ILSS)
↓ Water Uptake & Moisture Sensitivity
↑ Fiber-Matrix Adhesion & Durability

Figure 2. Fiber Surface Chemistry Modification Map.



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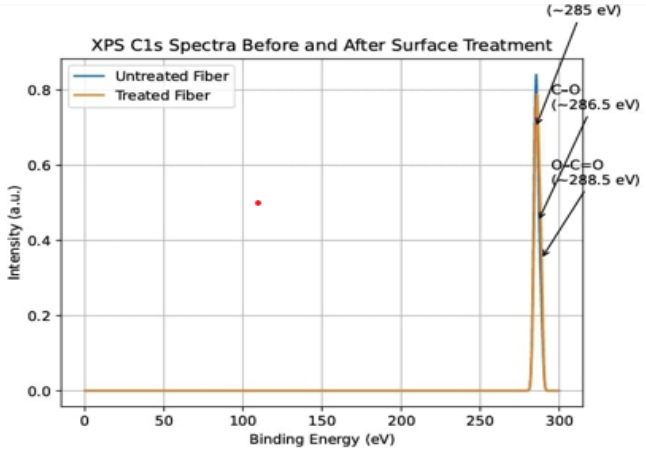

FTIR: Reduction of Hemicellulose Carbonyl Band; XPS: Increased O/C Ratio Changes; Relate to Improved Adhesion and Reduced Extractives.

Figure 3. Schematic FTIR and XPS Signatures Before/After Treatment.

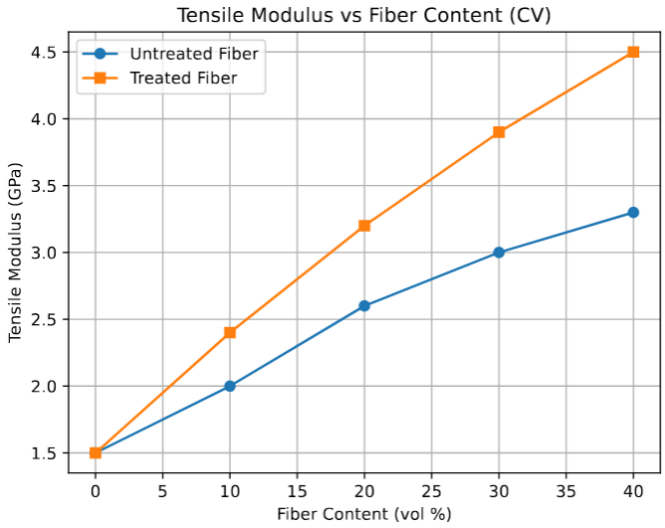

Figure 4. (a) Tensile modulus vs fiber content showing treated > untreated.

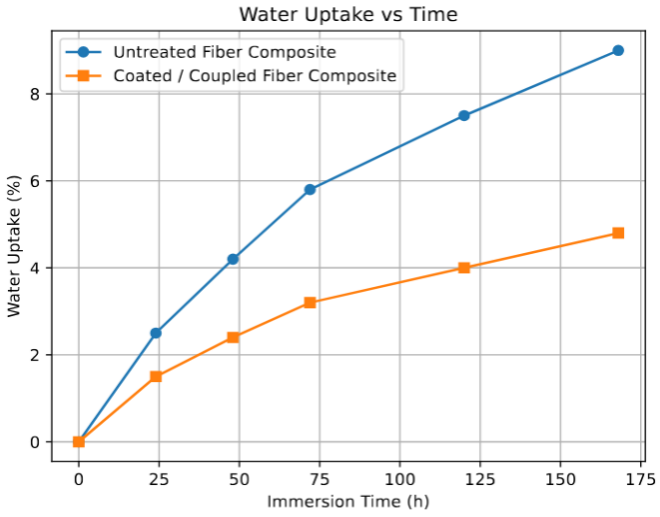

Figure 4. (b) Water uptake vs time showing coated/coupled < untreated.

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Chemistry-Led Characterization Toolkit

Chemistry-led design requires tools that quantify surface functionality, interphase formation, and degradation pathways:

- FTIR/ATR-FTIR: tracks removal of hemicellulose/pectin (carbonyl bands), lignin aromatic signals, and new ester/siloxane signatures after coupling.
- XPS: quantifies surface elemental composition and functional groups (O/C ratio; C1s deconvolution for C–O/C=O), sensitive to treatments and coatings.
- Solid-state NMR (13C CP/MAS): evaluates cellulose crystallinity, lignin/hemicellulose fractions, and chemical changes after delignification.
- TGA/DTG and DSC: assesses thermal stability and transitions; treatment may shift onset temperatures and affect PLA crystallization.
- DMA: tracks storage modulus and glass transition; useful for assessing interphase stiffening and aging effects.
- SEM/EDS: visualizes pull-out, voids, and (for rice husk/ash systems) silica distribution; supports failure analysis.

These methods help translate chemical modification into measurable interfacial improvements that correlate with tensile/flexural and ILSS performance.

Durability and Aging: Chemical Mechanisms

Durability limitations of agro-waste composites are rooted in chemical and physicochemical processes. Water sorption occurs via hydrogen bonding to cellulosic –OH sites and capillary transport along interfaces/voids, leading to swelling, plasticization of the matrix (for polar matrices), and hydrolysis (notably in bio-polyesters). Interphase degradation can be accelerated by cyclic humidity/temperature, producing microcracks and debonding. A recent review on accelerated aging of natural fiber composites summarizes common aging protocols and highlights the importance of coupling agents, coatings, and optimized treatments for property retention (Yan et al., 2019; Das et al., 2025; Shettigar et al., 2025).

Chemistry Focused Design Guidelines for Structural Applications

1. Moisture management is a chemistry problem: reduce accessible –OH groups (acetylation/grafting), increase covalent coupling, and minimize voids.
2. Prefer dual-action interfaces: combine alkali cleaning/fibrillation with silane or compatibilizer coupling to stabilize the interphase.
3. Match resin chemistry to exposure: use tougher/higher-Tg networks for exterior applications; tune cure to reduce residual stresses.
4. For recycled PP/HDPE composites, always include compatibilizer and control filler moisture to avoid steam-voiding during melt processing.
5. In RHA geopolymers, optimize ash fineness and amorphous silica content; control activator concentration and curing to reduce efflorescence and improve durability.
6. Validate with chemistry-aware aging: monitor FTIR/XPS changes alongside mechanical retention to identify dominant degradation modes.

Challenges and Future Research Directions

Key research gaps include (i) standardized chemical grading of agro-waste fibers (extractives, ash, wax fraction) to reduce variability; (ii) scalable, low-toxicity modification routes (water-based silanes, enzymatic or bio-inspired coatings); (iii) fire performance strategies compatible with bio-based matrices; (iv) long-term field exposure datasets to correlate accelerated aging with real service conditions; and (v) end-of-life solutions including thermoplastic recyclability and separable hybrid designs. Chemistry-guided approaches-especially interphase stabilization and bio-based resin chemistry-are likely to provide the largest performance gains for structural deployment.

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Conflicts of interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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