



Received: 03-09-2026

Accepted: 13-10-2026

International Journal of Advanced Multidisciplinary Research and Studies

ISSN: 2583-049X

Hybrid Organic–Mineral Fillers in Polyurethane Foam Composites for Sustainable Nursery-Farming Materials: A Review

¹Okeke Onyedikachi Jude, ²Nneji Eleanor Chidera, ³Prince Ndubuisi Uzoma, ⁴Asogwa Chisom Vincent

¹Department of Pure and Industrial Chemistry, Nnamdi Azikiwe University Awka, Anambra State, Nigeria

²Department of Chemistry, Federal University of Technology Owerri, Imo State, Nigeria

³Maritime Management Technology [Maritime Technology], Federal University of Technology Owerri (FUTO), Imo State, Nigeria

⁴Science, Government Technical College, Nsukka, Enugu State, Nigeria

DOI: <https://doi.org/10.62225/2583049X.2026.6.5.7056>

Corresponding Author: Okeke Onyedikachi Jude

Abstract

Biodegradable polyurethane (PU) foams reinforced with hybrid organic–mineral fillers are increasingly explored as sustainable alternatives to conventional nursery-farming materials, combining functional performance with controlled end-of-life degradation. This review synthesizes current literature on the incorporation of lignocellulosic agro-wastes—corn husk, guinea corn husk, millet bran, and wheat husk—alongside calcium carbonate-rich snail-shell powder into PU foam matrices. The molecular chemistry of PU formation, including toluene diisocyanate synthesis and polyol–isocyanate reactions, is examined alongside the roles of catalysts, blowing agents, and surfactants in governing foam morphology. Emphasis is placed on how hybrid organic–mineral fillers influence rise time, cure time, density, tensile and compressive strength, flexural

performance, hardness, and thermal stability, with the mineral fraction providing rigidity and nucleation sites while the lignocellulosic fraction promotes biodegradability. Environmental and green-chemistry perspectives, including life-cycle considerations and soil-burial degradation mechanisms, are discussed to highlight the ecological benefits of agro-waste valorization. Despite extensive research on single-filler PU systems, this review identifies a significant gap in hybrid filler systems specifically designed for nursery applications requiring seedling support, water retention, and controlled biodegradability. The findings underscore the potential of hybrid agro-waste/snail-shell PU foams as innovative, low-cost, and environmentally sustainable materials for agricultural applications.

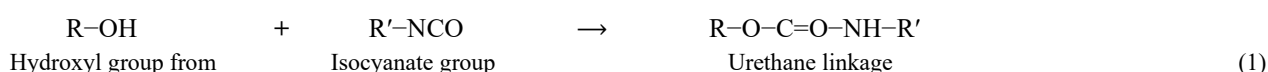
Keywords: Polyurethane Foam, Biodegradability, Agro-waste Fillers, Snail-shell Powder, Nursery Farming

Introduction

The imperative to develop materials that fulfill functional demands in nursery farming such as support for seedlings, aeration, water retention and yet degrade harmlessly in soil or compost has inspired current research in biodegradable polyurethane foams. PU foams can be engineered to meet this dual objective by carefully designing the polymer structure and by incorporating agro-waste fillers to modulate both mechanical properties and degradability^[1, 2].

The molecular architecture, comprising soft and hard segments, ester or ether polyol types, crosslink density, and the ratio of isocyanate to polyol, determines key properties: Mechanical strength, thermal stability, cell morphology (cell size, open vs closed cell), hydrophilicity, and the susceptibility of ester bonds to hydrolytic or microbial attack. Recent studies demonstrate that replacing part of petrochemical polyols with bio-polyols or introducing biomass-derived fillers accelerates biodegradation insofar as ester functionalities are exposed and accessible to water and soil microbes without severely compromising compressive strength and dimensional stability^[1, 2, 11, 15-17].

Agro-waste fillers bring multifaceted contributions. The lignocellulosic fraction (cellulose, hemicellulose, lignin) in corn husk, guinea corn husk, millet bran, and wheat husk provides abundant hydroxyl groups which can form hydrogen bonds with urethane or urea N–H groups, potentially fostering interfacial adhesion and influencing local chain mobility^[1, 3, 19, 20].



The snail-shell powder is rich in calcium carbonate (CaCO_3), imparting rigidity, acting as a nucleation site during cell growth, and potentially influencing thermal stability. The hybrid 50:50 agro-waste: Snail shell blend is conceived to balance organic filler functionality with inorganic reinforcement, hydrophilicity with structural stiffness. The particle size distribution and filler loading are crucial in that, too high filler load or large particles may lead to cell collapse, reduced foam expansion, increased density, or brittleness and too little, may produce no significant impact on the mechanical and morphological properties of the foam^[1, 4].

Functionally, foam properties required for nursery farming applications include: Moderate to high compressive strength to support growth media and water weight; controlled density and porosity to allow gas exchange; water retention without excessive water uptake that could degrade prematurely; a balanced life cycle so the foam maintains integrity during use, then degrades via environmental mechanisms such as; hydrolysis, microbial action, soil moisture, etc. A study of PU foams incorporating rice straw show that biomass fillers can be used to produce foams for soil erosion control, suggesting that such materials can survive functional demands before degrading^[1, 2].

Production Chemistry of Toluene Diisocyanate (TDI)

Toluene diisocyanate (TDI) is one of the most widely used aromatic diisocyanates in the polyurethane industry, primarily employed in the production of flexible foams due to its high reactivity, moderate volatility, and ability to form soft, resilient polymer networks. Commercial TDI is a mixture of two structural isomers—2,4-toluene diisocyanate and 2,6-toluene diisocyanate—typically in an 80:20 or 65:35 ratio, depending on the intended foam application^[1].

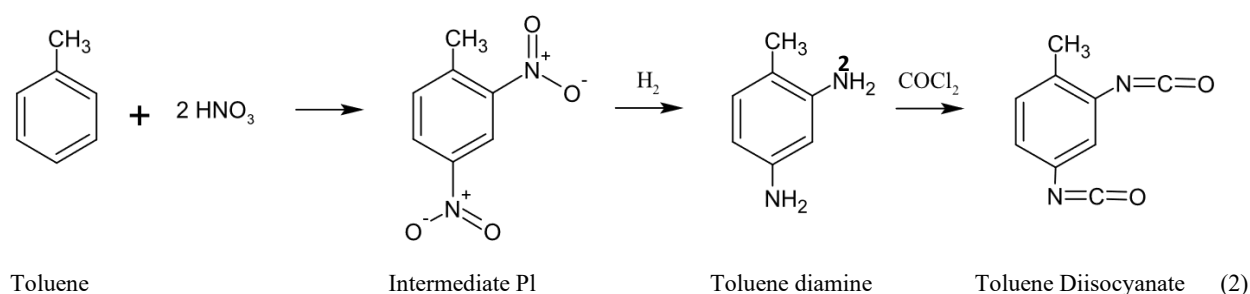
The industrial production of TDI proceeds through three main stages: Nitration, hydrogenation, and phosgenation. The process begins with the *nitration of toluene* using a mixed acid system of nitric and sulfuric acids to produce dinitrotoluene (DNT). This reaction introduces nitro groups at the 2,4- and 2,6-positions of the aromatic ring. The DNT is then subjected to *catalytic hydrogenation*, typically over nickel or palladium catalysts, converting the nitro groups ($-\text{NO}_2$) to amino groups ($-\text{NH}_2$) and yielding toluene diamine (TDA)^[1].

In the final stage, TDA undergoes *phosgenation*, where it reacts with phosgene (COCl_2) to form toluene diisocyanate. The reaction proceeds via the formation of an unstable carbamoyl chloride intermediate ($\text{R}-\text{NH}-\text{COCl}$), which subsequently eliminates hydrogen chloride to generate the isocyanate functional group ($-\text{NCO}$). Two moles of phosgene are consumed for every mole of diamine. The overall reaction is highly exothermic and is carried out in a controlled, two-step process—first in a cold reactor ($0-10^\circ\text{C}$) to limit side reactions, followed by a hot stage for complete conversion^[1].

After phosgenation, fractional distillation separates the 2,4- and 2,6-isomers to achieve the desired commercial blend ratios. The resulting TDI is a colourless to pale yellow liquid with low viscosity, making it particularly suitable for flexible polyurethane foam formulations. During foam production, the $-\text{NCO}$ groups of TDI react with the hydroxyl groups of polyols to form urethane linkages, while side reactions with water release carbon dioxide (CO_2) that acts as an in situ blowing agent, contributing to the foam's cellular structure^[1].

Due to the toxicity of phosgene and the sensitizing nature of isocyanates, TDI production requires stringent safety measures, including closed-system reactors, phosgene recovery units, and continuous environmental monitoring. Modern research is actively exploring phosgene-free synthesis routes, such as urea-decomposition and carbonylation pathways, to improve environmental sustainability^[1, 10].

The chemistry of TDI thus defines the reactive foundation of flexible polyurethane foams, its molecular architecture, isomer ratio, and purity directly influence foam rise time, density, and elasticity. The simplified reaction pathway for the industrial synthesis of toluene diisocyanate is illustrated in equation 2.2^[1].

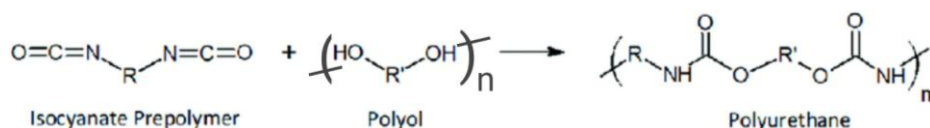


Synthesis of TDI

Chemistry of Polyurethane Foams

Polyurethane (PU) foams are synthesized through a step-growth polymerization process in which multifunctional isocyanates react with polyols to form a three-dimensional network of urethane and, to a lesser extent, urea linkages. Their versatility, ranging from flexible cushioning foams to rigid structural materials, stems from the wide variety of monomers, catalysts, and additives that can be employed, as well as the ability to control crosslink density and cell morphology^[1].

At a molecular level, PU is formed via step-growth polymerization in which diisocyanates ($-\text{NCO}$ groups) react with polyols ($-\text{OH}$ groups) to yield urethane linkages ($-\text{NH}-\text{COO}-$). The fundamental reaction may be expressed as shown in equation 2.3^[1].



(3)

The Chemistry of Polyurethane

Where;

R = Toluene

R' = alkyl, ether, or ester-containing backbone of the polyol

Polyurethane Foam Formulation

The successful preparation of biodegradable PU foams depends not only on the primary reactant polyols and diisocyanates, but also on a carefully balanced suite of auxiliary ingredients. Catalysts, blowing agents, surfactants, and post-treatment additives collectively determine the kinetics of urethane formation, the morphology of the cellular network, and the ultimate mechanical and biodegradation profiles of the foam ^[1, 2].

Classes of Polyurethane Foams

PU foams are distinguished primarily by the architecture of their cellular network, which dictates performance in applications from cushioning to structural reinforcement. Flexible foams possess an open-cell matrix where gas pockets interconnect, creating exceptional compressibility and rapid recovery. These qualities suit bedding, automotive seating, and acoustic insulation. Rigid foams, by contrast, contain predominantly closed cells that trap blowing-agent gases, giving high dimensional stability and very low thermal conductivity properties indispensable for building insulation and refrigerated transport. Semi-rigid foams occupy a middle ground, combining moderate elasticity with higher load-bearing capacity, while high-resilience foams provide enhanced impact absorption for dynamic applications. Precise control of isocyanate index, blowing-agent composition, and catalyst activity allows chemists to tailor these classes for specialized industrial demands ^[1].

Catalysts and Kinetic Control

Polyurethane foaming is governed by the competing reactions of isocyanate groups with polyols (urethane formation) and with water (urea formation accompanied by CO₂ evolution). Organometallic catalysts such as stannous octoate or dibutyltin dilaurate accelerate the gelling reaction, while tertiary amines including triethylenediamine (TEDA) and N,N-dimethylcyclohexylamine—promote the water–isocyanate blowing reaction. The delicate ratio of these catalysts dictates the rise time, cell density, and the balance between flexible and rigid domains. For bio-filled systems, slightly higher amine levels have been reported to offset the hydroxyl-rich nature of lignocellulosic fillers, which can otherwise slow gelation ^[1].

Blowing Agents and Cell Morphology

Gas generation within the reacting mixture creates the characteristic foam structure. Water remains the most widely employed chemical blowing agent, reacting with isocyanate to release CO₂. Physical blowing agents such as pentane or hydrofluoroolefins are occasionally added to fine-tune density or thermal conductivity. For environmentally benign nursery foams, purely water-blown formulations are preferred, minimizing volatile organic emissions and ensuring rapid biodegradation. The presence of finely milled agro-waste/snail-shell fillers influences nucleation, often producing smaller and more uniformly distributed cells ^[1, 2].

Surfactants and Stabilizers

Silicone-based surfactants are indispensable for maintaining cell stability during foam rise. They lower surface tension, prevent cell coalescence, and improve filler dispersion. Research shows that in natural-filler PU systems, optimized surfactant dosage counteracts the hydrophilic character of lignocellulose and yields open-cell structures conducive to water retention and seedling growth ^[1].

Structural Properties of Polyurethane Foams

The versatility of PU foams arises from the interplay between molecular composition and microstructure. Hard-segment content, derived from diisocyanate domains, governs modulus and compressive strength; soft polyol segments determine elasticity and glass-transition behaviour. Cell size and distribution controlled by nucleation and gas expansion during foaming affect density, thermal conductivity, and acoustic damping. Cross-link density provides a final tuning mechanism, where slight increases can transform a cushioning foam into a load-bearing structural material. Mastery of these relationships enables accurate prediction of end-use performance and streamlines product development across markets such as construction, packaging, and automotive components ^[1].

Polyols

Polyols supply the hydroxyl groups that determine the “soft segment” of the polymer network. They may be petroleum-derived polyether polyols or bio-based polyester polyols. Polyester polyols, containing ester linkages, promote biodegradability by hydrolytic cleavage, while polyether polyols enhance hydrolytic stability but reduce degradation rates ^[2, 3, 6].

Recent studies show that incorporating bio-polyols derived from lignocellulosic biomass such as liquefied corn stover or palm kernel shells produces foams with improved environmental profiles and tunable mechanical properties.

In the present study, partially bio-based polyols are selected to complement the agro-waste/snail-shell fillers and to facilitate eventual soil degradation^[15-17].

Catalysts

Catalysts accelerate the isocyanate–hydroxyl reaction and the water–isocyanate blowing reaction. Tertiary amines such as triethylenediamine (TEDA) are effective gelling catalysts, while organotin compounds (e.g., stannous octoate) promote urethane formation. The balance between gelling and blowing catalysts is critical: Excessive gelling leads to high viscosity before full expansion, whereas excessive blowing produces coarse or collapsed cells^[1].

Blowing Agents and Foam Formation

Cellular structure arises from the generation of gas during polymerization. Traditionally, physical blowing agents such as pentane or hydrofluorocarbons were used, but environmental concerns have shifted attention to water as a chemical blowing agent^[1].

Water reacts with isocyanate to produce unstable carbamic acid, which decomposes to carbon dioxide and a primary amine. The amine can further react with another isocyanate to form a urea linkage. These side reactions contribute to the hard-segment content, increasing rigidity and compressive strength of the foam^[2].

Crosslinking and Morphology

Crosslink density is governed by the functionality of the polyol and isocyanate, as well as the presence of chain extenders or crosslinkers such as glycerol or trimethylolpropane. Higher crosslinking reduces cell size, enhances dimensional stability, and improves compressive modulus, but excessive crosslinking may lower elongation at break and increase brittleness. The addition of finely divided agro-waste/snail-shell filler particles provides heterogeneous nucleation sites, promoting uniform bubble formation and smaller average cell diameters, which in turn raise compressive strength and lower foam density. Mineral components from snail shells (CaCO_3) may also act as mild reinforcing agents and as pH buffers during degradation^[1].

Role of Agro-Waste/Snail-Shell Blends

The unique hybrid fillers corn husk/snail powder, guinea corn husk/snail powder, millet bran/snail powder, and wheat husk/snail powder introduce both lignocellulosic hydroxyl groups and calcium carbonate surfaces. The lignocellulose enhances hydrogen bonding and potential chemical interaction with the polyurethane matrix, while the mineral fraction improves stiffness and acts as a thermal stabilizer^[1, 3, 4].

These fillers also serve as sites for microbial colonization during soil burial, accelerating degradation through enzymatic attack on the polymer network and gradual dissolution of the CaCO_3 phase, which increases local porosity and water uptake^[19, 20].

The chemistry of PU foam formation thus, involves a delicate interplay between monomer selection (MDI/TDI ratios), polyol structure, catalyst balance, blowing agent chemistry, and crosslinking density. The incorporation of agro-waste/snail-shell hybrid fillers adds another layer of complexity, simultaneously influencing nucleation, mechanical properties, and biodegradation. The next chapter will describe the materials and experimental methods used to optimize these parameters for biodegradable nursery-farming foams^[1, 2].

Functional Additives in Polyurethane Foams

PU foams are versatile polymeric materials whose properties can be precisely tailored through the incorporation of functional additives. In polymer chemistry, additives are introduced to modify mechanical performance, thermal stability, processability, and environmental behaviour. Common classes include plasticizers, stabilizers, flame retardants, and fillers, each serving distinct but sometimes overlapping roles. Plasticizers, for instance, reduce intermolecular forces within the polymer network, enhancing flexibility and elongation, while stabilizers help preserve material integrity during thermal or oxidative aging^[1].

Among additives, fillers are particularly significant due to their ability to simultaneously influence mechanical properties, dimensional stability, and degradation behaviour. Fillers can be organic, inorganic, or hybrid, and are selected based on factors such as particle size, surface chemistry, and interaction with the polymer matrix. Organic fillers often derive from natural sources, including cellulose fibers, lignocellulosic residues, or plant-derived powders. These materials can impart reinforcement while maintaining biodegradability, and they frequently contain surface functional groups that promote adhesion with PU chains^[11, 17, 19].

Inorganic fillers, by contrast, typically provide structural reinforcement, thermal resistance, and nucleation sites for foam cell formation. Common examples include calcium carbonate, silica, and alumina. These minerals are valued for their rigidity, high thermal stability, and relatively inert behaviour, which allow them to enhance stiffness without significantly compromising polymer flexibility. Hybrid fillers combine both organic and inorganic characteristics, aiming to balance mechanical performance with functional degradability^[1, 4].

Performance of fillers is highly dependent on particle size, morphology, surface treatment, and dispersion within the polymer matrix. Fine particles, often below 100 μm , improve stress transfer and reduce defects, while chemical or physical surface modifications can enhance interfacial adhesion and compatibility with the polymer. By carefully selecting and optimizing these parameters, fillers can be tailored to act as reinforcing agents, degradation modulators, or both, without adversely affecting foam processing or dimensional stability^[19, 20].

Of particular interest in biodegradable PU foams are organic fillers, which offer the dual advantage of reinforcing the polymer matrix while providing sites for controlled biodegradation^[12, 19].

Wheat Husk



Plate 1: Wheat Husk

Wheat husk is one of the most abundant lignocellulosic agro-residues generated during cereal processing. It is composed primarily of cellulose, hemicellulose, lignin, and minor amounts of extractives, which makes it a valuable natural filler for polymer composites. When incorporated into polymer matrices such as polypropylene (PP) and PU, wheat husk has been shown to improve the stiffness and dimensional stability of the final material while simultaneously reducing production costs due to its low price and wide availability^[3]. The fibrous nature of wheat husk provides a reinforcing effect by promoting stress transfer between the polymer and the filler, while the silica content present in its structure contributes to abrasion resistance. Importantly, studies reveal that even with higher filler loading, the mechanical strength of wheat husk composites remains within acceptable limits for practical applications. Furthermore, its natural biodegradability enhances the eco-friendliness of the material, making it attractive for packaging, furniture, and lightweight construction applications^[5].

Millet Bran



Plate 2: Millet Bran

Millet bran, a by-product of millet grain milling, remains relatively underutilized compared to other cereal brans. Chemically, millet bran is rich in cellulose, hemicellulose, lignin, and proteins, which makes it a promising filler for biodegradable polymer composites. The cellulosic fraction contributes to reinforcement by providing rigidity, while the protein content may enhance interfacial adhesion with polyurethane matrices^[3]. Research suggests that millet bran incorporation not only improves the mechanical properties of polymers but also accelerates biodegradation, since microorganisms readily attack the polysaccharide and protein fractions of the filler. This makes millet bran an appealing candidate for applications where environmental sustainability is a priority, such as in biodegradable packaging films and agricultural mulch composites. Its relatively small particle size also ensures better dispersion within polymer systems, thereby reducing defects and improving impact resistance^[5].

Corn husk



Plate 3: Corn Husk

Corn husk is an abundant lignocellulosic residue whose chemical and physical attributes make it highly suitable as a functional bio-filler for biodegradable PU foams. Chemically, corn husk is composed predominantly of cellulose ($\approx 35\text{--}42\%$), hemicellulose ($\approx 28\text{--}32\%$) and lignin ($\approx 14\text{--}18\%$), together with minor extractives and ash; this composition supplies a high density of surface hydroxyl groups that can engage in hydrogen bonding with urethane N–H groups and, under certain conditions, react with residual isocyanate to form covalent linkages. Physically, husk particles are fibrous and porous; when milled to a controlled particle size (commonly D50 in the $20\text{--}100\ \mu\text{m}$ range) they act as effective heterogeneous nucleation sites for CO_2 bubbles during foaming, which tends to refine cell size and produce a more uniform microcellular structure^[3, 5]. Prior studies specifically assessing corn-husk fillers in polymer systems report that moderate loadings ($10\text{--}20\ \text{wt}\%$) increase tensile and compressive properties while slightly raising apparent density, provided the particles are well dispersed and pre-treated to remove surface oils and sugars^[3, 5]. Typical pretreatment regimes include oven drying to $<0.5\%$ moisture, mild alkali washing to remove hemicellulosic extractives and increase surface roughness, and optional silane sizing when improved covalent coupling to organic matrices is desired; these steps reduce variability in rise and cure times and improve interfacial adhesion. Unmodified husk can retain bound water and soluble organics that interfere with isocyanate stoichiometry and catalyst activity, so controlled drying and extraction are recommended prior to compounding^[8]. Functionally in PU foams, corn-husk inclusion is expected to increase compressive modulus and energy absorption through reinforcement of cell walls, to reduce average cell diameter via heterogeneous nucleation, and to accelerate environmental degradation by supplying enzymatically labile carbohydrate domains that facilitate microbial colonization once the foam is buried in soil^[3, 7]. Thermally, the presence of lignocellulose may lower onset decomposition temperature slightly but contributes to char formation that can enhance residual thermal stability at higher temperatures. For these reasons, corn husk is well suited to the application aims of this thesis: At controlled particle size and $5\text{--}25\ \text{wt}\%$ loadings it provides a renewable, low-cost route to mechanical reinforcement while promoting end-of-life biodegradability in nursery-farming foams^[19, 20].

Snail Shells



Plate 4: Snail Shell

Unlike the plant-based fillers, snail shells are calcium carbonate-rich biowastes obtained as by-products of food consumption and processing. Their primary constituent, CaCO_3 , accounts for over 90% of the shell composition, with trace amounts of chitin and organic^[21]. When processed into fine powders and introduced into polymer matrices such as PU, snail shells significantly enhance rigidity, hardness, and thermal stability of the resulting composites. The mineral nature of snail shells allows them to act as effective organic reinforcements, much like commercial calcium carbonate fillers, but with the added benefit of valorizing agro-waste materials. Their presence reduces the flammability of composites, improves dimensional stability, and lowers production costs compared to virgin fillers. Additionally, snail shell powders can act synergistically with natural fibers to improve overall mechanical performance while promoting partial biodegradability of the composite system^[4].

Guinea Corn



Plate 5: Guinea Corn Husk

Guinea corn husk, a major agricultural by-product from the post-harvest processing of sorghum (*Sorghum bicolor*), represents an abundant and renewable lignocellulosic resource widely available across northern Nigeria, particularly in Yobe State. Traditionally regarded as waste, this material offers significant potential as a sustainable reinforcement additive in polymer composites due to its rich composition of cellulose, hemicellulose, and lignin [3]. These constituents not only contribute to mechanical rigidity but also enhance interfacial compatibility when properly treated and dispersed within polymer matrices [5]. In this study, the guinea corn husk was processed into fine powder form to serve as a bio-based functional filler in PU foam production. Its incorporation was aimed at improving the biodegradability and mechanical integrity of the foam through enhanced filler–matrix interaction. To achieve this, the husk powder was blended with calcined snail shell powder at varying ratios, forming a hybrid filler system that synergistically combines the organic reinforcement of the husk with the mineral reinforcement of the snail shell [1, 4]. This hybridization strategy leverages the complementary properties of both additives, the toughness and flexibility imparted by the plant-derived husk and the rigidity and thermal stability introduced by the shell component, resulting in a more balanced and environmentally sustainable polyurethane composite [3, 4].

Hybrid fillers

Combining bio-based and mineral components, are increasingly explored to achieve synergistic effects such as improved stiffness without excessive brittleness. The agro/snail combination in this study fits into this emerging category of hybrid agro-waste fillers [4, 19].

Types of Fillers and Their Functional Roles

Incorporating particulate fillers extends the functionality of PU foams beyond what polymer chemistry alone can achieve. Mineral fillers such as calcium carbonate, talc, and alumina trihydrate improve dimensional stability, reduce cost, and promote flame retardancy through char formation [1]. Renewable lignocellulosic materials including wood flour, rice husk, and other agricultural residues introduce sustainable content and can lower overall density while enhancing biodegradability [8]. At the nano-scale, layered silicates, nanocellulose, and graphene derivatives dramatically increase modulus and barrier properties at very low loadings due to their high aspect ratio and surface area. Effective surface treatment and homogeneous dispersion are essential to ensure strong filler–matrix adhesion and to prevent stress concentrations that could compromise the foam's cellular structure [4, 8].

Agro-waste fillers such as corn husk, guinea-corn husk, millet bran, and wheat husk are lignocellulosic in nature, rich in cellulose, hemicellulose, and lignin, which furnish hydroxyl groups capable of hydrogen bonding and limited covalent urethane formation with residual isocyanates [1]. Lignin, being more hydrophobic and aromatic, tends to reduce interfacial adhesion but contributes stiffness, while polysaccharides enhance biodegradability [3]. Conversely, snail shell powder is predominantly calcium carbonate, contributing rigid particulate domains that act as heterogeneous nucleation sites for CO₂ bubbles and load-bearing inclusions that increase modulus and thermal stability [5].

Particle morphology and size distribution are decisive factors. Fine, uniformly distributed particles act as efficient nucleation centres, producing a high population of small, closed or semi-closed cells that raise compressive strength and reduce apparent density [1]. Coarse or agglomerated particles, however, create stress concentrators that may induce cell rupture and reduce foam uniformity. Moisture content is equally critical, since water reacts with isocyanates to produce CO₂ and amines, altering rise time, cream time, and cell morphology [7]. Pretreatment strategies such as thermal drying, alkaline activation, or silane coupling are therefore widely employed to improve compatibility and reproducibility [1, 7, 8].

Thermal stability of fillers must exceed the exothermic excursions encountered during foaming. Lignocellulosic fractions typically begin significant mass loss above ~200 °C, which is safely above typical PU exotherms, while calcium carbonate remains inert under normal foaming conditions but decomposes at higher temperatures into CaO, relevant for end-of-life recycling scenarios. Characterization techniques such as FTIR, TGA, XRD, SEM, and particle size analysis are routinely applied to assess filler chemistry, morphology, and dispersion quality, ensuring reproducibility and guiding formulation adjustments [1, 3, 4].

Finally, the physicochemical profile of hybrid fillers influences the foam's environmental end-of-life behaviour. Exposed polysaccharide domains encourage microbial colonization and enzymatic hydrolysis of ester bonds, while the mineral fraction provides a scaffold that slows collapse, allowing the foam to retain functional strength during use and then fragment progressively [1, 10]. Balancing these tendencies is central to sustainable filler design: Providing sufficient reactivity and porosity for biodegradation while preserving mechanical integrity for applications such as seedling support [9, 10].

Mechanical and Thermal Performance of Bio-Filled Polyurethane Foams

The incorporation of bio-derived fillers into PU foams introduces complex interactions that strongly influence both mechanical and thermal behaviour. Mechanical strength, stiffness, and resilience are not determined solely by the polymer matrix but emerge from a balance between cell morphology, filler dispersion, and the interfacial bonding between the organic filler surface and the urethane network [7, 8]. Agro-residues such as rice husk, coconut shell powder, and snail-shell ash often possess irregular particle shapes and reactive surface groups. When these particles are well dispersed, they restrict polymer chain mobility, which increases tensile modulus and compressive strength. However, poor interfacial adhesion or agglomeration can act as stress concentrators, leading to premature failure and reduced elongation at break. The density of the foam also plays a crucial role: Higher density systems typically exhibit superior tensile and flexural properties because a thicker strut network supports greater loads, while low-density foams are more susceptible to cell wall rupture under compression [18, 20].

Thermally, bio-fillers impart a dual effect. Many plant-based fillers contain lignocellulosic components that begin to degrade at moderate temperatures, releasing char and volatile gases. This early degradation can lower the initial onset of thermal decomposition. Yet the char layer produced during pyrolysis can act as a physical barrier, slowing heat transfer and enhancing

the residual char yield, which improves flame resistance at elevated temperatures. Fillers rich in minerals, such as calcium carbonate from snail shells or silica from rice husk ash contribute additional thermal stability because the inorganic phase remains intact well beyond the decomposition range of the polymer matrix. The overall thermal conductivity of the foam depends on the interplay between closed-cell content and filler loading: Moderate additions of fine particles can decrease cell size, trap more gas and reduce conductivity, while excessive loading may create solid conduction paths that raise thermal conductivity^[18, 20, 21].

Rise Time

Rise time represents the interval between the start of mixing and the moment the PU foam reaches its maximum height. It reflects the combined kinetics of the urethane-forming reaction between polyol and isocyanate and the concurrent generation of carbon dioxide through the isocyanate–water side reaction. Bio-derived fillers such as finely milled corn husk, guinea-corn husk, millet bran and wheat husk blended with snail-shell powder alter these kinetics in several ways. Conversely, the mineral component of snail-shell powder, dominated by crystalline CaCO_3 , provides numerous nucleation sites that facilitate bubble formation and growth, partially compensating for the retarding effect of the husk fraction^[21]. Achieving the correct filler ratio and particle size therefore allows the formulator to fine-tune rise time, producing a uniform cell structure critical for nursery applications where dimensional stability and water management are essential^[1, 7, 8].

Cure Time

Cure time is the period required for the foam to gel sufficiently to permit demoulding or handling without structural collapse^[22]. It depends on the balance between blowing and gelling reactions and on the exothermic heat that sustains crosslink propagation. Bio-fillers influence cure time primarily through moisture retention and thermal conductivity. Untreated cereal husks carry bound water that generates extra amine intermediates, accelerating urethane crosslinking, whereas the high thermal mass of snail-shell CaCO_3 can dissipate reaction heat and slightly slow network formation^[23]. Surface modification of the husks such as mild alkali washing or salinization, has been shown to stabilize cure time by reducing excessive moisture uptake while maintaining interfacial adhesion.

Density

The apparent density of cured PU foam governs both mechanical and thermal performance. Incorporating agro-waste/mineral blends generally increases density because the solid particles reduce overall expansion and occupy void space. Moderate densification strengthens cell walls and improves water resistance, advantages for seedling trays and root plugs provided cell morphology remains predominantly closed so that thermal insulation is not compromised^[24].

Tensile Properties: Stress–Strain Behaviour and Young’s Modulus

Tensile testing evaluates ultimate tensile strength (UTS), elongation at break and the Young’s modulus, offering a comprehensive picture of the foam’s ability to bear stretching forces. Finely dispersed lignocellulosic particles act as micro-reinforcements, transferring stress to the rigid filler and increasing UTS and modulus by 20–30 %^[25]. Excessive agglomeration, however, produces stress concentrators that lower elongation and can trigger premature failure. The mineral phase of the snail powder contributes additional stiffness but must be uniformly distributed; particle clusters larger than about 50 μm can embrittle the matrix and reduce overall toughness^[8].

Flexural Strength

Flexural strength, determined by three-point bending, measures resistance to simultaneous tensile and compressive stresses. Homogeneous dispersion of the corn-husk/snail blend yields a fine, uniform cell structure that elevates flexural performance^[26]. Strong filler–matrix adhesion ensures that micro-cracks do not propagate along the filler interface during bending.

Compressive Strength

Because nursery substrates are primarily subjected to compressive forces, this parameter is critical. The rigid CaCO_3 skeleton of snail powder markedly increases the compressive modulus, allowing the foam to resist long-term deformation. Calcium carbonate (CaCO_3) has been investigated as a mineral filler for polyurethane (PU) foams, with studies demonstrating that surface modification can improve compressive strength and energy-dissipation-related properties through enhanced interfacial compatibility between the filler and polymer matrix^[27]. Similarly, lignocellulosic reinforcements, including rice husk and sugarcane bagasse, have been explored for improving the mechanical and resilience characteristics of polyurethane-based composites for cushioning and shock-absorption applications^[28]. However, the influence of these fillers depends on their composition, loading, dispersion and interaction with the polyurethane matrix.

Hardness

Surface firmness, measured by indentation force deflection (IFD) or Shore hardness, reflects both foam density and crosslink density. Well-dispersed agro-waste fillers narrow cell-size distribution and stiffen the polymer struts, raising hardness values without sacrificing resilience. However, uneven filler distribution can create localised “hard spots,” a concern in cushioning but advantageous for structural nursery panels that require dimensional integrity^[29].

Thermal Performance

Thermal conductivity and thermo-oxidative stability determine the foam’s suitability for greenhouse environments. Lignocellulosic fractions slightly reduce the onset degradation temperature by about 10°C but increase char yield, improving

flame retardancy^[30]. Calcium-rich snail powder acts as a thermal barrier and refines the closed-cell network, lowering thermal conductivity and enhancing resistance to heat flow^[31]. The synergy between organic char formation and inorganic mineral shielding provides a balanced thermal profile ideal for nursery farming where temperature fluctuations are common^[31].

Morphological and Structural Characterization

Understanding the morphology of bio-filled PU foams is critical because the size, shape, and distribution of cells directly determine density, mechanical strength, water absorption, and thermal insulation. When corn husk, guinea-corn husk, millet bran, or wheat husk is blended with snail-shell powder, the combined organic–mineral filler influences every stage of cell nucleation and growth. Lignocellulosic particles present numerous hydroxyl sites that interact with the reactive isocyanate, while the calcium carbonate crystals of snail powder provide heterogeneous nucleation points. The result, when properly dispersed, is a finer and more uniform cellular network compared with neat polyurethane, a feature repeatedly linked to improved compressive and flexural properties^[25].

Scanning electron microscopy is the principal technique for visualizing these microstructures. SEM images typically reveal closed-cell matrices with well-defined polyhedral walls in optimally formulated bio-filled foams, whereas inadequate dispersion or excessive filler loading leads to irregular, collapsed, or partially open cells. Energy-dispersive X-ray spectroscopy (EDS) coupled to SEM confirms the homogeneous distribution of calcium and other mineral elements derived from snail shells, verifying that the inorganic phase is effectively anchored within the polymer network^[32].

Biodegradability and Environmental Impact of Agro-Waste–Reinforced Polyurethane Foams

The imperative for nursery-farming materials that degrade safely after a single planting cycle drives the scientific rationale for incorporating agro-waste fillers into PU foams. Conventional petrochemical PU is notoriously persistent: The urethane and urea linkages are chemically robust, and the dense crosslinked architecture resists microbial attack. Achieving environmentally acceptable degradation therefore requires a dual strategy, introducing biodegradable domains into the polymer matrix and ensuring that the composite microstructure permits microbial ingress and hydrolytic cleavage. The hybrid fillers used in this research, corn husk/snail-shell, guinea-corn husk/snail-shell, millet bran/snail-shell and wheat husk/snail-shell are central to both strategies^[33].

Lignocellulosic residues from cereal crops supply polysaccharide chains rich in hydroxyl groups and amorphous hemicellulose fractions that are susceptible to enzymatic hydrolysis by cellulases, hemicellulases, and lignin-degrading peroxidases. When these fibers are finely dispersed within the foam, they act as localized nutrient sources, attracting microbial consortia capable of secreting depolymerizing enzymes. Over time, preferential consumption of the plant domains produces microvoids and channels that expose the surrounding polyurethane network to oxygen and moisture. This gradual increase in surface area accelerates abiotic hydrolysis of ester linkages in the polyol segments and fosters further microbial colonization^[34].

The snail-shell component contributes a complementary degradation pathway. Although crystalline calcium carbonate is itself only sparingly soluble, it buffers acidic microenvironments generated during polysaccharide fermentation and provides a stable scaffold that retains porosity as the organic fraction erodes. Soil microflora capable of producing carbonic anhydrase and weak organic acids can slowly solubilize CaCO_3 to Ca^{2+} and bicarbonate ions, releasing trace nutrients that support rhizosphere activity. This mineral phase therefore ensures that as the foam disintegrates, the residual particles pose no toxicological burden and may even enhance soil fertility.

Environmental factors strongly influence the kinetics of these processes. Moisture availability governs both microbial metabolism and the hydrolysis rate of urethane bonds; elevated soil temperature within the range typical of tropical nursery conditions (25–35 °C) further accelerates enzymatic turnover. Aerobic–anaerobic cycles, common in irrigated seedbeds, promote alternating oxidative and reductive reactions that destabilize lignin structures and encourage colonization by diverse microbial communities^[35].

From a mechanistic perspective, the degradation of the polymer matrix proceeds through sequential steps. Initial microbial consumption of exposed agro-waste weakens the mechanical integrity of the composite and generates cracks. These defects admit water that hydrolyzes ester bonds in the soft segments, producing alcohols and carboxylates. Amide linkages in the hard segments are more recalcitrant but can be cleaved slowly under combined enzymatic and oxidative conditions. Ultimately, the polymer reduces to oligomeric fragments small enough to be mineralized to CO_2 , H_2O , and biomass. Because the snail-shell mineral phase remains largely intact until late stages, it serves as a slow-release calcium source long after the organic network has been compromised.

Importantly, the agricultural application of these foams benefits from a controlled degradation profile. Seedling trays or root-ball supports must retain structural integrity during the early growth period, typically eight to twelve weeks, yet disintegrate thereafter to avoid root girdling or the need for manual removal. By judiciously balancing filler loading, particle size, and the isocyanate index of the polyurethane formulation, it is possible to tune the foam so that mechanical strength persists through the nursery phase and then diminishes as microbial and hydrolytic processes dominate.

The environmental fate of degradation products is benign. Cellulose and hemicellulose degrade to glucose and other simple sugars that soil microorganisms metabolize completely, while lignin depolymerization yields phenolic compounds that are further mineralized or incorporated into humic substances. Calcium carbonate either remains as fine particles or dissolves to bicarbonate, buffering soil pH and supplying plant-available calcium. Toxicological assessments of similar biocomposite foams have found no significant accumulation of heavy metals or persistent organic pollutants in the surrounding soil^[36]. Thus, the agro-waste/snail-shell polyurethane system aligns with circular-economy objectives, offering an end-of-life pathway that closes the loop between agricultural residue generation and soil enrichment.

Principles of Green Chemistry Applied to Polyurethane Foams

The design and manufacture of PU foams have traditionally relied on petroleum-derived polyols, volatile blowing agents, and heavy-metal catalysts. These materials deliver excellent mechanical and thermal performance but raise environmental and health concerns across the product life cycle. The framework of green chemistry, first articulated by Anastas and Warner, provides a scientific and ethical basis for reformulating PU systems so that they meet performance targets while reducing ecological impact^[37]. Applying this framework to biodegradable foams reinforced with agro-waste fillers requires attention to every stage of production, from the choice of raw materials through processing, use, and ultimate degradation.

At the heart of the green approach is feedstock selection. Substituting petrochemical polyols with bio-based alternatives, such as polyols derived from vegetable oils, lignin, or depolymerized agro-residues, directly embodies the principle of using renewable resources. Similarly, incorporating corn husk, millet bran, guinea-corn husk, and wheat husk blended with snail-shell powder exemplifies the valorization of agricultural by-products that would otherwise enter the waste stream. These fillers not only replace a portion of the polymer matrix but also introduce reactive hydroxyl groups that can participate in urethane formation, thereby reducing the need for additional synthetic reagents^[8].

Another central principle is the prevention of waste rather than its remediation. In PU foaming, this involves optimizing the stoichiometry of isocyanates and polyols to minimize unreacted monomers and volatile emissions. The use of water as a co-blowing agent, which reacts with isocyanate to release CO₂, offers a benign alternative to traditional chlorofluorocarbon or hydrochlorofluorocarbon blowing agents, aligning with the goal of safer chemical synthesis^[38].

Energy efficiency is equally significant. The exothermic nature of urethane formation can be harnessed to reduce external heating requirements during curing, while process parameters such as mixing speed, rise time, and cure time can be fine-tuned to limit unnecessary energy input. The inclusion of mineral-rich snail-shell powder, which improves thermal conductivity during foaming, can help maintain uniform temperature profiles, further lowering energy demand^[11].

Designing for degradation and end-of-life is a hallmark of green chemistry. Incorporating lignocellulosic fillers accelerates environmental breakdown through microbial action and moisture absorption, facilitating composting or soil reintegration after the foam's service life in nursery farming. This degradability reduces the burden on landfill and avoids microplastic accumulation.

Finally, attention to catalyst and solvent choice is essential. Research is advancing toward non-toxic, bismuth- or zinc-based catalysts and toward solvent-free or low-VOC formulations. Such changes not only protect workers and end-users but also improve the sustainability profile of the final foam^[1, 10].

Environmental Assessment and End-of-Life Biodegradation of Bio-Filled Polyurethane Foams

Evaluating the sustainability of bio-filled PU foams requires a dual perspective: Life-cycle impacts and end-of-life behaviour. Life-cycle assessment (LCA) quantifies resource use, emissions, and ecological effects across all stages from raw-material acquisition through processing, use, and disposal. For bio-filled foams, the use of agricultural residues such as corn husks or millet bran imposes minimal environmental burden, as these by-products are otherwise discarded. Replacing petroleum-based polyols with renewable alternatives further reduces fossil resource depletion and greenhouse-gas emissions^[11, 12].

During the service life, these foams can offer indirect environmental benefits, such as thermal insulation in nursery or agricultural applications, lowering energy consumption. At end-of-life, organic fillers promote biodegradation, mitigating microplastic pollution and reducing landfill persistence. Lignocellulosic domains in the fillers are susceptible to microbial enzymes cellulases, hemicellulases, and lignin-degrading enzymes which swell and fracture, forming pathways that allow moisture and microbes to penetrate the polyurethane network. Renewable polyols with hydrolytically labile ester or carbonate linkages enable further matrix breakdown into CO₂ and water. Mineral additives such as calcium carbonate can buffer pH and create microenvironments conducive to microbial activity, accelerating decomposition^[39].

Integrating LCA with engineered biodegradation highlights the dual sustainability advantage of bio-filled PU foams: A lowered environmental footprint across their life cycle and controlled, ecologically safe end-of-life disintegration, transforming what would otherwise be persistent plastic into a soil-enriching material^[19].

Environmental Benefit of Agro-Waste Valorization

The conversion of agricultural residues into high-value fillers for PU foams embodies multiple principles of green chemistry and the circular economy. Agro-waste valorization reduces the volume of biomass that would otherwise be openly burned or left to decay, both of which release methane and CO₂^[40].

Using corn husk, millet bran, guinea-corn husk, and wheat husk, combined with mineral-rich snail-shell powder, captures carbon in a durable product during its service life, effectively delaying greenhouse-gas emissions. Local sourcing of these materials reduces transportation distances and supports rural economies. Moreover, valorization provides farmers with an additional revenue stream, incentivizing sustainable agriculture and waste management^[15, 41].

From a materials perspective, these fillers lower the reliance on petrochemical inputs by partially replacing polyol or isocyanate mass. The mechanical reinforcement, they provide enhanced tensile and flexural strength, extends the functional lifetime of foams, reducing the frequency of replacement and further lowering environmental impact.

In sum, agro-waste valorization transforms a disposal challenge into an environmental and economic opportunity, closing the loop between agriculture and advanced materials engineering.

Conclusion

Hybrid organic–mineral fillers offer promising opportunities to enhance the mechanical strength, thermal stability, durability, and functionality of polyurethane foam composites for sustainable nursery-farming materials. Combining renewable organic resources with mineral fillers may reduce production costs, improve environmental performance, and support agricultural

sustainability. However, further research is necessary to optimize filler composition, assess long-term performance, evaluate biodegradability, and establish their practical suitability for diverse nursery-farming applications.

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