Review

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Biobased Filler Materials in Polymeric Composites: A Comprehensive Review of Epoxy and Polyurethane Systems

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Abstract: Polymeric composites, particularly epoxy and polyurethane systems, have gained significant attention due to their excellent mechanical, thermal, and chemical properties. However, the environmental concerns associated with petroleum-based polymers have driven research towards biobased alternatives. This review explores the integration of biobased filler materials derived from agricultural and marine waste into epoxy and polyurethane matrices to enhance their performance while promoting sustainability. The empirical review of epoxy and polyurethane resins reinforced with natural fillers highlights the significant role of bio-based additives in enhancing mechanical properties while promoting sustainability. Findings from reviewed studies demonstrate that natural fillers such as jute, sisal, lignin, and rice husk fish scales improve tensile strength, flexural strength, and wear resistance of polymer composites. However, excessive filler content can lead to agglomeration, reducing mechanical integrity. Optimal filler content varies depending on polymer type, with moderate concentrations yielding the best mechanical performance. Additionally, chemical modifications, such as silane treatment and alkalization, enhance filler-polymer adhesion, further improving material properties. Despite their advantages, challenges such as moisture sensitivity and long-term durability require further investigation.

Keywords: Biobased fillers; polymeric composites; epoxy resin; polyurethane foam; sustainability; natural reinforcements; mechanical properties; thermal stability; eco-friendly materials; waste valorization

1. Introduction

Polymeric composites are materials composed of a polymer matrix reinforced with fillers or fibers to improve their mechanical, thermal, and chemical properties. These composites are extensively used in industries such as aerospace, automotive, and construction due to their customizable properties, lightweight nature, and high strength-to-weight ratios [1,2]. Among commonly used polymer matrices, epoxy resins and polyurethane foams (PUF) stand out due to their versatility and superior performance. Epoxy resins are renowned for their excellent chemical resistance, mechanical strength, and thermal stability, but their intrinsic brittleness limits their impact resistance [3,4]. Similarly, PUF materials are prized for their flexibility, biocompatibility, and tunable mechanical properties, making them suitable for applications ranging from insulation to automotive interiors [5].

Despite their widespread applications, traditional polymer production heavily relies on petrochemical derivatives, raising significant environmental concerns [6,7]. Furthermore, the mechanical properties of bio-based alternatives, such as soy-based PU, often lag behind their petroleum-based counterparts [5]. To mitigate these challenges, researchers have increasingly explored the incorporation of natural fillers and reinforcements to enhance the mechanical and

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thermal properties of polymeric composites while advancing sustainable materials development [8]. Biobased fillers derived from agricultural and marine waste are gaining attention for their renewability, cost-effectiveness, and environmental benefits [9]. Previous studies have shown that natural fibers such as wood fiber [10], sawdust [11], eggshells [12], and coconut husks [13] among others can significantly enhance the mechanical properties of polymer composites.

In the polymer industry, the growth in bio-based, biodegradable, and recycled materials has a huge positive impact on the environmental research and development field [14]. With a massive growth in the development of science especially in polymer fields, it is of good concern to develop and synthesize new and improved methods and materials used in our daily lives for cost-effectiveness, reducing toxic pollutants such as emissions and using up waste products of everyday human lifestyle to develop newer biomaterials [14]. As many of the polymers currently used in different industrial applications are harmful to the environment [15,16], it is necessary to incorporate eco-friendly and recycled ways to manufacture polymeric materials to improve the quality (strengthening) of the product and reduce the build-up of food product waste causing numerous environmental factors.

Besides, the versatility of polymer composites comes from the ability to tailor their properties by selecting appropriate matrix materials and reinforcements [17]. The main function of these reinforcements is to enhance the mechanical properties of the composite, including strength, stiffness, and durability, without adding significant weight [18–21]. Reinforcements work by distributing loads more efficiently throughout the composite [22,23]. Nilagiri Balasubramanian and Ramesh [24] note that better improvement in mechanical, thermal, and electrical properties could be attained along the filler-aligned direction. Fibers, for instance, align along the direction of applied stress, allowing the composite to bear heavier loads and resist deformation. The inclusion of powders or particulate fillers, such as silica or calcium carbonate, can also improve the hardness and wear resistance of the composite, contributing to its longevity in demanding applications [25,26].

Given the beneficial properties of reinforcement in enhancing the properties of polymeric materials, this review highlights the role of biobased reinforcement materials in enhancing the mechanical, thermal, and chemical performance of polymer composites. By summarizing current developments and research trends, the paper aims to provide a foundation for further studies, particularly the potential of incorporating recycled biobased materials, as fillers to reinforce epoxy and polyurethane polymers. This approach aligns with the broader goal of advancing eco-friendly and high-performance composite materials.

2. Epoxy Resin and Polyurethane as Matrix Materials

Two of the most widely used matrix materials in polymer composites are epoxy resin and polyurethane, both of which provide a range of desirable properties for industrial applications.

2.2.1. Epoxy

Epoxy resin is a thermosetting polymer known for its excellent mechanical strength, chemical resistance, and adhesive properties [27]. It forms a highly cross-linked structure when cured, making it highly resistant to environmental factors such as moisture, heat, and chemicals. Because of its strength and durability, epoxy resin is commonly used as a matrix material in high-performance composites, especially in the aerospace, automotive, and construction industries. Epoxy polymers stand out as popular polymer matrices for composite applications owing to their exceptional mechanical properties, chemical resistance, and thermal stability [1,28]. Despite these strengths, epoxy polymers exhibit limitations such as low impact resistance, poor toughness, and susceptibility to crack propagation [3]. To improve the physical and mechanical properties of this polymer, several current reinforcing materials such as natural fibers, glass, and graphite have been added to epoxy to such an extent that epoxies can be used in many structural applications [29].

Epoxy resins are widely used in composites reinforced with glass or carbon fibers, where they enhance the material's tensile and flexural strength. In aerospace and automotive applications, epoxy-

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based composites provide a lightweight yet strong alternative to traditional metals, contributing to fuel efficiency and improved performance. Additionally, the biocompatibility of epoxy resins makes them suitable for use in biomedical devices such as prosthetics, implants, and medical adhesives. According to Fink [30], epoxy resins are favoured in composite manufacturing because of their low shrinkage upon curing, excellent adhesion to a wide variety of substrates, and superior mechanical performance under a broad range of conditions. From a chemistry perspective, epoxy resins represent a crucial and highly adaptable category of cross-linkable polymers, derived from monomers containing at least two oxirane groups [31]. These strained-ring structures, composed of one oxygen and two carbon atoms, are attached to a diverse array of aliphatic or aromatic organic molecules [31]. The majority of commercially significant epoxy resins are synthesized through the reaction of polyphenolic compounds or other active hydrogen-containing molecules (such as amines or aliphatic alcohols) with epichlorohydrin in basic conditions. Among these, bisphenol A (diphenylolpropane) is one of the most widely used phenolic compounds, forming the foundation for an entire family of epoxy resins with a characteristic general structure (Figure 1).

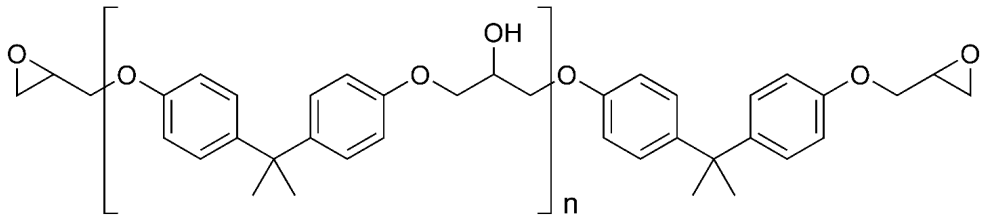

Figure 1. Structure of epoxy resins.

2.2.2. Polyurethane

Polyurethane (PUF) is another versatile polymer matrix widely used in composites. Unlike epoxy resin, which is primarily a thermosetting polymer, polyurethane can be either thermosetting or thermoplastic, depending on its formulation. Polyurethane composites are known for their flexibility, abrasion resistance, and impact strength, making them useful in both structural and non-structural applications. Polyurethane foams (PUF), widely used in various industries, are versatile materials known for their lightweight nature, insulation properties, and affordability [32,33]. In engineering, for example, PUF is widely used due to its tunable mechanical and biocompatible properties which can be tailored by the type and composition of their components [5]. In the construction industry, polyurethane-based composites are used for insulating panels and coatings due to their thermal insulation properties. In the automotive and transportation sectors, polyurethane composites provide shock-absorbing components such as bumpers and seat cushions. The biocompatibility of polyurethane also allows it to be used in medical devices such as catheters and artificial organs, where flexibility and durability are essential.

Polyurethane (PUF) polymers are synthesized through a reaction between diisocyanates and polyester diols[6,33], a fundamental process in the polyurethane industry. The PUF macromolecule consists of alternating non-polar segments: the hard segment (HS), derived from aliphatic or aromatic isocyanates, and the soft segment (SS), typically derived from macrodiols such as polyester, polyether, or polycarbonate-based compounds (Figure 2). Each segment contributes distinct properties to the polymer. The HS imparts stiffness, abrasion resistance, and film-forming capabilities, while the SS enhances elastomeric properties [34]. The chemical composition of these segments significantly influences the overall characteristics of PUF materials [35]. For instance, aliphatic isocyanates in the HS improve environmental stability compared to their aromatic counterparts [36]. Similarly, polyester-based polyols in the SS provide high tensile strength and excellent resistance to light and aging, while polyether-based polyols enhance chain flexibility and elasticity but are more susceptible to degradation by heat, light, and oxygen. Polycarbonate-based

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polyols, on the other hand, offer superior hydrolysis and aging resistance, along with good mechanical strength [37].

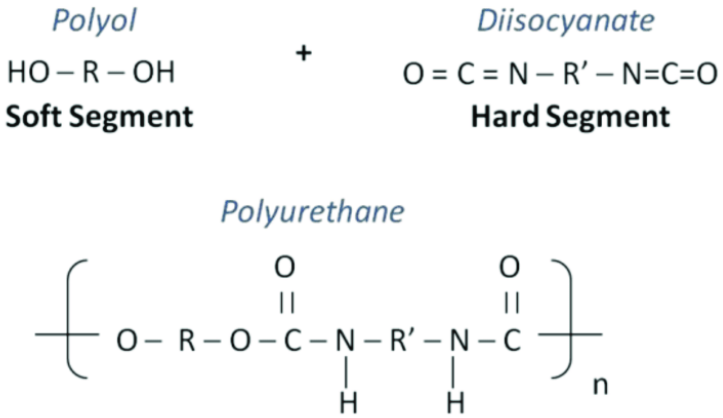

Figure 2. Polyurethane chemical structure (source: Patti, Costa, Perrotti, Barbarino and Acierno [35].

2.3. Natural Fillers in Polymer Chemistry

Natural fiber-reinforced polymer composites have a long history of use in civil engineering construction due to their advantageous properties and suitability for various applications [38]. Ancient civilizations used natural materials like mud and straw in construction, and early composite products such as pottery and boats utilized straw for reinforcement. The modern development of composite materials began during the chemical revolution of the late 19th century, with the creation of synthetic resins and the introduction of fiberglass in the early 20th century marking significant advancements [38]. Synthetic materials like vinyl, polystyrene, phenolic, and polyester offered improved performance compared to their predecessors. Natural fiber composites have since gained prominence as eco-friendly alternatives to synthetic materials, offering benefits like low density, cost-effectiveness, and renewability, despite challenges such as high moisture absorption requiring chemical treatments [38,39].

Table 1 provides a comprehensive overview of the application of natural filers in polymers. Natural fibers, such as plant fibers (e.g., jute, hemp) and animal fibers (e.g., wool, silk), have been extensively studied as reinforcements in polymer composites due to their renewability, low cost, and biodegradability [39,40]. These natural fibers offer advantages such as high specific strength and stiffness, good thermal insulation properties, and reduced environmental impact compared to synthetic fibers [39,40]. Natural fibers play a critical role in polymer chemistry, offering numerous advantages and applications [41].Sourced from renewable materials like plants and animals, these fibers are valued for their renewability, biodegradability, and enhanced mechanical properties [40]. Incorporating natural fibers into polymer matrices improves composite materials' overall performance by enhancing strength, stiffness, and toughness [42].

Table 1. Comprehensive Overview of Research Papers on Natural Fibers/Fillers in Polymer Composites.

Research paper title	Reference	Type of natural fibers/fillers	Application of fiber/filler	Historical dates found and used
From natural to synthetic fibers	[43–45]	Cotton, wool, silk, jute, flax, wood fibers or straw	Textiles, clothing, construction materials	Pre-20th century to present
Plastics materials: introduction and historical development	[46,47]	Cellulose, wood fibers	Early plastics formulations or their contemporary	1930s-1940s

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			applications in biocomposites	
Plant-based natural fiber reinforced composites: a review on fabrication, properties, and applications	[48]	Fibers like jute, hemp, flax, bamboo	Automotive, construction, packaging	1950s
Natural fiber-reinforced composites for bioengineering and environmental engineering applications" by Hoi-yan Cheung.	[49]	Jute, coir, sisal, bamboo,	Bioengineering and environmental engineering soil erosion control, biodegradable materials, wastewater treatment	1960s
Natural fiber-reinforced polymer composites"	[39]	Fibers like jute, kenaf, hemp, flax, sisal	Automotive parts, construction materials, packaging	1970s
Recent advances of natural fibers based green rubber composites: properties, current status, and future perspectives	[50]	Cellulose, hemicellulose, and lignin. Ute, ramie, hemp, kenaf, silk, wool, angora, mohair	Structural components, consumer products, building, construction, packing, and automotive industries	Late 20th century to present
A review: nanomaterials as a filler in natural fiber-reinforced composites	[51]	Carbon nanotubes, graphene	Aerospace, electronics, automotive	21st century
Influence of filler material on properties of fiber-reinforced polymer composites: a review	[52]	Epoxy, polyurethane	Marine, automotive, civil engineering	Present
Recent progress on natural fiber hybrid composites for advanced applications: a review	[53]	Hybrid composites	Tailored performance requirements	Present and future

Previous research has focused on optimizing processing techniques, surface modification of fibers, and compatibility with polymer matrices to maximize the mechanical performance of natural fiber-reinforced composites [39,40]. The dispersion and alignment of these fibers within the polymer matrix significantly influence the mechanical properties, underscoring the importance of optimizing filler dispersion for maximum performance [41]. Additionally, natural fibers contribute to lightweight and cost-effective composite materials, making them suitable for various industrial and consumer applications [54]. With their biocompatibility and thermal insulation properties, natural fibers are also utilized in medical devices and building materials [14]. In addition, the applications of natural fiber-reinforced polymer composites span various industries, including aerospace, automotive, construction, and packaging [55]. These composites find utility in manufacturing household furniture, fencing, windows, decking, flooring, sports equipment, and lightweight automobile components, among others [56,57]. Overall, the utilization of natural fibers in polymer composites aligns with sustainable practices and offers versatile solutions for addressing environmental and performance challenges [58].

2.4. Mechanical and Physical Properties of Composites with Bio-Based Reinforcements

The mechanical properties of polymer composites are significantly influenced by the incorporation of bio-based reinforcements, such as natural fibers, and biopolymers. These materials

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offer sustainability, biodegradability, and favourable mechanical performance, making them attractive for various industrial applications. This section examines empirical studies focusing on tensile strength, flexural strength, impact strength, hardness, and other relevant mechanical attributes.

2.4.1. Tensile Strength

Tensile strength is a critical mechanical property that determines how a composite material can withstand pulling forces without failure [59]. It is typically defined as the maximum force that can be applied in this manner before the material fractures [60]. Saba, *et al.* [61] note that tensile strength evaluates the force needed to fracture a composite or plastic specimen and determines how much the specimen stretches or elongates before reaching the breaking point. According to Ismail, Khulbe and Matsuura [60], a tensile test is conducted using standard testing equipment following the ASTM D638-10 method for measuring the tensile properties of plastics. Saba, Jawaid and Sultan [61] clarified that tensile testing of composites typically involves basic tension or flat-sandwich tension testing, following standards such as ISO 527-4, ISO 527-5, ASTM D638, ASTM D3039, and ASTM C297. These tests generate stress-strain diagrams that are used to calculate the tensile modulus. An example of tensile testing is illustrated in Figure 3.

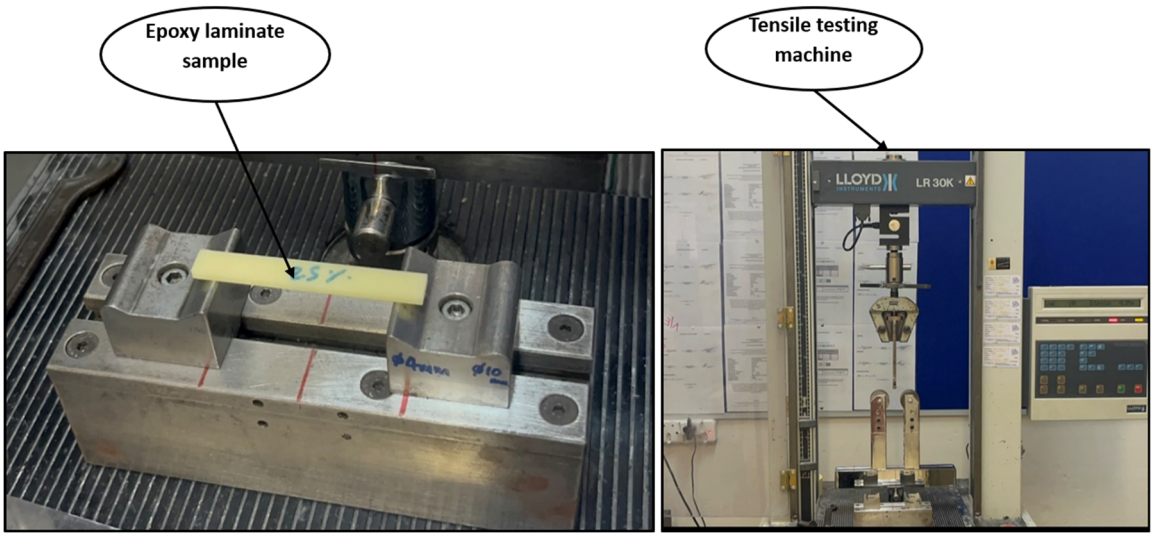

Figure 3. Tensile testing machine.

When a material is exposed to a tensile pulling force, it stretches until it fractures. The results are displayed as a curve illustrating the material's response to the applied forces [60]. Tensile testing also measures properties such as tensile strength (both at yield and break), tensile modulus, tensile strain, elongation, and percent elongation at yield, as well as percent elongation and elongation at break [61]. These parameters help evaluate a material's appropriateness for specific applications [62]. Numerous empirical studies have shown that bio-based reinforcements, particularly natural fibers can enhance the tensile strength of polymer composites [59,62]. For instance, Khan et al. (2020) investigated the tensile properties of epoxy composites reinforced with jute fibers. The results demonstrated a significant improvement in tensile strength and modulus compared to pure epoxy. The tensile strength increased by 25% with the inclusion of 20% jute fiber, attributed to the effective load transfer from the matrix to the fibers due to good interfacial adhesion. Jute fibers in epoxy matrices demonstrated a 10.06% increase in tensile strength, showcasing the reinforcement's effectiveness (Shah *et al.* 2023)

Mohammed et al. (2021) assessed the tensile behavior of composites reinforced with sisal fibers. The tensile strength increased by 30% with 15% fiber addition, although the performance was highly dependent on fiber-matrix bonding quality. Sisal fiber-reinforced epoxy composites achieved a

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tensile strength of 69.1 MPa, significantly outperforming neat epoxy (Huzaifa *et al.* 2024). Sisal fiber reinforced with polyurethane composites enhanced tensile strength by up to sevenfold (17.0 MPa) compared to neat polyurethane resin, with dry fibers improving fiber-matrix adhesion while humid fibers offered higher elongation (11.3%) (Milanese, Cioffi and Voorwald 2011).

Kenaf/Epoxy composites exhibited the highest tensile strength, 3.1 times greater than the neat resin, and achieved the highest Young's modulus at 50% fiber volume fraction (Hafizah *et al.* 2014). Hybrid composites of bi-directional glass fiber and rice husk (RH) fiber in epoxy matrices achieved the highest tensile strength (215.42 MPa) and modulus (1.8 GPa) with 25 wt.% glass fiber and 5 wt.% RH fiber. Increasing RH content to 15 wt.% weakened interfacial bonding, reducing tensile properties by 25% (Ismail *et al.* 2020). A more recent study by Onwubu et al. (2024) analyzed collagen-extracted fish scale-reinforced epoxy composites. The addition of 5-10% fish scale collagen improved tensile strength by 18% compared to the neat epoxy. The improvement was largely attributed to efficient load transfer between the particulates and the polymer matrix.

2.4.2. Flexural Strength

Flexural strength indicates a material's ability to resist deformation under bending forces [63], and bio-based reinforcements have shown considerable potential in enhancing this property in polymer composites. The data is frequently utilized to choose materials for components that must bear loads without bending [61]. The most common methods for flexural testing of plastics, polymer composites, and large fiber-reinforced plates are three-point and four-point bend tests, conducted following ISO 14,125, ISO 178, ASTM D790, and ASTM D6272. These tests provide valuable insights into material properties and ensure their suitability for specific applications under various conditions. Flexural properties testing delivers both raw and adjustable data, including flexural stress and strain at yield, flexural stress and strain at break, flexural stress at 3.5% deflection (ISO) or 5.0% deflection (ASTM), flexural modulus, and stress-strain curves. The flexural modulus serves as a measure of a material's stiffness when subjected to bending [61].

An empirical study by El-Shekeil, *et al.* [64] on thermoplastic polyurethane (TPUF) reinforced with 20–50 wt.% kenaf fibers reported increased flexural strength from 6.55 MPa (PUFre TPUF), with higher fiber content improving both strength and modulus. Bamboo fiber-reinforced epoxy composites demonstrated superior flexural strength compared to virgin epoxy and jute fiber composites, with optimal performance at 5% NaOH-treated fibers [65]. Alkali-treated sugar palm fiber-reinforced epoxy composites achieved the highest flexural strength (96.71 MPa, a 24.41% improvement) with 10 wt% reinforcement using 0.25 M NaOH for 1 hour. Flexural modulus reached 6948 MPa (a 148% increase) with 0.5 M NaOH for 4 hours [66]. Bi-directional glass fiber and rice husk (RH) fiber composites showed the best flexural strength (275.51 MPa) and modulus (9.79 GPa) with 25 wt.% glass fiber and 5 wt.% RH fiber, decreasing by 27% and 32%, respectively, at 15 wt.% RH fiber [67].

2.4.3. Impact Strength

Impact strength is the material's ability to absorb energy during a sudden force or impact [61] The impact test is specifically designed to assess the toughness, brittleness, notch sensitivity, and impact strength of engineering materials in their ability to withstand high-rate loading [68,69]. Bio-based reinforcements, including natural fibers and collagen-based materials, have been found to enhance the impact resistance of polymer composites in various studies. In an empirical study by Ribeiro, *et al.* [70], hemp fiber-reinforced epoxy composites showed an increase of 7.5% in impact strength compared to the unreinforced epoxy. This improvement was due to the fibers' ability to dissipate energy during impact, thus enhancing toughness. Similarly, Venkatachalam, *et al.* [71] tested the impact of coir fiber-reinforced epoxy composites. The result reveals the maximum Impact strength (98.35 J/m^2) by combining coir fibre (5 wt.%), and coir fiber powder size (225 μm).

Furthermore, hybrid composites of bi-directional glass fiber and RH fiber achieved peak impact strength (447.19 J/m) with 25 wt.% glass fiber and 5 wt.% RH fiber, outperforming other

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configurations [67]. The impact strength of Moringa oleifera bio-filler-reinforced epoxy composites increased up to 12% v/v bio-filler content but declined beyond 16–24% v/v due to filler agglomeration (Sridevi and Giri 2024). Epoxy-based composites with 3 wt.% Rohu fish scale residue powder achieved an impact strength of 1908.2 J/m², a 54.72% increase over neat epoxy (Kumar, Bansal and Singh 2019). Impact strength peaked at 22.22 kJ/m² with 30 wt.% fiber content in thermoplastic polyurethane composites but decreased beyond this level due to fiber breakage (Radzi *et al.* 2017).

2.4.4. Hardness

Bio-based reinforcements offer other mechanical properties such as hardness, toughness, and wear resistance. Hardness indicates a composite's resistance to surface deformation. The hardness of polymer composites reinforced with bio-based materials was investigated by Martins et al. (2021), where bamboo fiber-reinforced polyester composites showed a 12% increase in hardness compared to pure polyester. The bamboo fibers' inherent stiffness and rigidity contributed to the improved surface hardness, making the composites more resistant to indentation. In addition, an empirical study by Agnihotri et al. (2022) examined the wear of bio-based hybrid composites reinforced with hemp and silk fibers in an epoxy matrix. The wear rate was reduced by 30% compared to the neat epoxy, highlighting the reinforcing effect of the bio-based fibers in reducing material loss under friction.

Sisal-glass fiber-reinforced epoxy composites exhibited the highest hardness value (24.73 RHN) (Huzaifa *et al.* 2024). Bamboo-coir epoxy resin composites achieved the highest Rockwell Hardness Number (38 RHN), outperforming bamboo epoxy (20 RHN) and bamboo-jute epoxy (37 RHN) composites (Bansal, Ramachandran and Raichurkar 2017). WPC with 50% finely ground wood filler achieved the highest indentation hardness (56 MPa, a 125% improvement) and indentation modulus (0.77 GPa, a 201% increase). Coarsely ground wood filler exhibited a hardness of 49 MPa (99% increase), while slate fillers achieved 40 MPa (62% increase). These enhancements highlight the role of filler type and content in improving WPC properties for applications such as tiling and window frames (Dočkal *et al.* 2020).

2.5. Thermal Properties of Composites Reinforced with Particulate Fillers

According to Haque, *et al.* [72], the mechanical properties of polymers are significantly influenced by temperature. Specifically, as temperature increases, the elastic modulus and tensile strength decrease, while ductility improves [73]. To address these challenges, extensive research has focused on enhancing the thermal properties of various polymers and developing heat-resistant polymers for high-temperature applications requiring reliable performance[72].

Thermo-gravimetric analysis (TGA) is a widely used method to evaluate the thermal stability of materials. TGA measures changes in a material's physical and chemical properties as a function of increasing temperature at a constant heating rate or over time at a constant temperature or mass loss [74]. This technique provides insights into chemical processes such as desolvation (e.g., dehydration), decomposition, and solid-gas reactions like oxidation or reduction. It also identifies physical phenomena, including phase transitions, vaporization, sublimation, absorption, and desorption [75].

Sahu, Mondloe and Upadhyay [75] highlighted that TGA is instrumental in assessing the thermal stability of polymers, ensuring their physical and chemical properties remain unchanged at elevated temperatures. Researchers use TGA to determine the temperature at which a composite begins to degrade, the weight loss with temperature increase, and the residue left behind [74]. Thermal stability within the desired temperature range is characterized by negligible mass loss and minimal slope on the TGA curve. Additionally, TGA determines the upper application temperature beyond which a material starts degrading [75].

Numerous studies have employed TGA to analyze epoxy composites. For instance, Wang, *et al.* [76] investigated the thermal stability of pure epoxy and epoxy composites filled with 4.5 wt.% KH550@EG. They observed initial decomposition temperatures of 318, 329, and 348 °C for untreated and treated samples, respectively, concluding that surface treatment enhances compatibility and

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thermal stability. Similarly, Gu, *et al.* [77] examined graphene nanoplatelets (GNP) and functionalized graphene nanoplatelets (f-GNP) composites. Their findings revealed improved thermal stability with increasing f-GNP content, with heat resistance indices rising from 192 °C for pristine epoxy to 203 °C for composites with 30 wt.% f-GNPs.

Xu and Chung [78] analyzed TGA data for composites filled with boron nitride and aluminum nitride particles, comparing surface-treated samples with those treated using acetone or acids. They reported that silane-treated samples exhibited higher weight loss compared to acid- or acetone-treated samples. Liang and Wong [79] studied nanocomposites with 1 wt.% SiO_2 or Al_2O_3 fillers and hybrid composites containing 1 wt.% nano-fillers and 20 wt.% micro-fillers. Their results showed that both micro- and hybrid composites exhibited significantly lower weight loss compared to neat epoxy, with SiO_2-filled samples displaying similar behaviour to Al_2O_3-filled specimens.

Hani, *et al.* [80] explored the thermal properties of fishbone-based (FBP) epoxy composites using TGA and DSC. Their results demonstrated that incorporating FBPs enhanced thermal stability compared to neat epoxy. The onset decomposition temperature (T_{onset}) increased with FBP content, peaking at 345 °C for composites containing 10 wt.% and 15 wt.% FBPs. Furthermore, composites with thermally treated FBPs (TFBPs) exhibited an additional 21 °C increase in T_{onset} for 10 wt.% TFBPs. Differential scanning calorimetry (DSC) analysis revealed that the glass transition temperature (Tg) of epoxy composites improved with FBP incorporation, rising from 58 °C for neat epoxy to 72 °C for composites with 10 wt.% FBPs.

The above studies collectively highlight the importance of optimizing filler content and surface treatment to enhance the thermal stability and mechanical performance of polymer composites. Cognisance of the effect of filler content is critical for optimum reinforcement.

2.6. Empirical Review of Polyurethane and Epoxy Resins Reinforced with Natural Fillers

The integration of bio-based fillers into polymer matrices has garnered significant attention due to their potential to enhance mechanical properties while promoting sustainability. Table 2 summarises empirical studies investigating the effects of different bio-based fillers on epoxy and polyurethane properties. The narrative is presented as cases.

Case 1: Enhancing mechanical properties of epoxy composites using natural fillers

Shah, *et al.* [81] explored the incorporation of jute fibers at 30% weight in epoxy resin and observed a 10.06% increase in tensile strength and a 4.70% improvement in flexural strength. This enhancement demonstrates better load-bearing capabilities attributed to the strong interfacial bonding between jute fibers and the polymer matrix. Similarly, Huzaifa, *et al.* [82] utilized sisal glass fibers (50%) in epoxy, achieving a tensile strength of 69.1 MPa and a high hardness value of 24.73, indicative of superior resistance to deformation. These results highlight the suitability of natural fibers for structural applications where high strength and durability are critical.

Boopalan, *et al.* [83] studied a hybrid composite of jute and banana fibers (50%) in epoxy, reporting enhanced mechanical and thermal properties, along with reduced moisture absorption. The reduction in moisture uptake is significant as it improves the composites' durability and dimensional stability, making them more viable for applications in humid environments. These findings align with prior studies emphasizing the benefits of hybrid natural fibers for synergistic improvements in polymer performance [84].

Wood, *et al.* [85] investigated the addition of lignin (1–10%) in epoxy, finding the highest tensile and flexural strengths at 2.5 wt.% filler (86.16 MPa). The decline in strength at higher filler content suggests filler agglomeration, leading to stress concentration and matrix disruption. This underscores the importance of optimizing filler content for achieving peak mechanical performance, a recurring observation in polymer-filler studies [86].

Majhi, *et al.* [87] introduced rice husk (5–20%) in epoxy and observed a 10% reduction in abrasive wear loss, with wear resistance maximized at optimal filler content. The use of surface-treated rice husk further amplified these benefits, emphasizing the role of chemical modifications in enhancing

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filler-polymer interactions. Such treatments mitigate filler incompatibility with hydrophobic matrices, improving composite properties [88,89].

Hani, Firouzi, Islam and Sumdani [80] investigated the effect of thermal treatment on the mechanical and thermal properties of fishbone-based epoxy composites (FBPs). The study revealed significant improvements in both tensile and flexural strength, with increases of 30% and 200%, respectively, compared to the neat epoxy (NE). These enhanced properties were attributed to the thermal treatment of the FBPs. The authors observed that when FBPs were embedded in epoxy, they formed mechanical interlocks with the epoxy molecules, resulting in a strong interfacial layer. Additionally, epoxy molecules formed a bonding layer at the interface with the FBPs, further reinforcing the composite structure. This combination of factors contributed to the superior mechanical performance of the thermal-treated FBPs.

Case 2: Enhancing the mechanical properties of Polyurethane Composites using natural fillers

Członka, *et al.* [90] added grounded clove (1–5%) to polyurethane, achieving an 18% increase in compression strength, 11% improvement in flexural strength, and 8% enhancement in impact strength at 1–2 wt.% filler. However, beyond this range, diminishing returns were noted, aligning with findings from Fan, *et al.* [91], who investigated glass microsphere and nanoclay fillers (1–7%) in biobased rigid polyurethane. Although foam volume increased with filler content, compressive strength decreased at 7% filler due to lower density and weaker cell wall structures. The impact of fiber type and content on polymer properties is exemplified by Głowińska, *et al.* [92], who incorporated sisal fibers (5–15%) into polyurethane. While hardness improved at lower filler contents, tensile strength and elongation properties declined at higher percentages, attributed to poor dispersion and matrix weakening. Husainie, *et al.* [93] also reported similar trends with cellulose, chitin, hazelnut, and eggshell fillers (1–5%), where tensile strength peaked at 1 wt.%, but properties such as split tear strength deteriorated significantly at higher concentrations.

Ozgur Seydibeyoglu, *et al.* [94] demonstrated the potential of the olive kernel and nutshell fibers (2.5–7.5%) in polyurethane, with the highest compressive strength recorded at 2.5 wt.% olive kernel filler, enhancing structural performance. This improvement highlights the strategic role of rigid fillers in boosting foam stability and load-bearing capacity, which is critical for lightweight structural applications.

Naidoo, *et al.* [95] investigated the incorporation of fish scale powder (FSP) into polyurethane foam, examining its effect under varying temperature conditions. Their study revealed that at a concentration of 0.5 wt% FSP, there was an 18.8% increase in tensile strength and a 15.7% increase in elongation at break at room temperature. Additionally, the inclusion of FSP significantly enhanced the tear resistance of the foam, with a 22% improvement at 0.5 wt% FSP and a remarkable 37% increase at 1 wt% FSP, particularly under heat aging conditions. These results suggest that FSP can effectively improve the mechanical properties of polyurethane foam, making it a promising reinforcing agent.

Table 2. Summary of empirical work on enhancing mechanical properties of epoxy and polyurethane with natural fillers.

Authors & Year	Type of Bio-based Fillers	Weight %	Polymer Material	Outcome of Mechanical Properties
Shah, Ahmad, Abid, Arif, Khan, Khan and Djavanroodi [81]	Jute fibers	30%	Epoxy	Tensile strength increased by 10.06%, while flexural strength improved by 4.70%, highlighting better load-bearing capabilities.
Huzaifa, Zahoor, Akhtar, Abdullah, Haider, Khan and Alam [82]	Sisal glass fibers	50%	Epoxy	Achieved a tensile strength of 69.1 MPa, demonstrating superior strength, and recorded the highest hardness value of 24.73, indicating excellent resistance to deformation.
Boopalan, Niranjanaa and Umapathy [83]	Jute/banana fiber	50%	Epoxy	Enhanced mechanical and thermal properties with a notable reduction in

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				moisture absorption, improving durability and stability.
Wood, Coles, Maggs, Meredith and Kirwan [85]	Lignin	1-10%	Epoxy	Tensile and flexural strengths significantly increased at 2.5% w/w filler, reaching 86.16 MPa. Strengths declined at higher filler content.
Majhi, Samantarai and Acharya [87]	Rice husk	5-20%	Epoxy	Abrasive wear loss was reduced by 10% with improved wear resistance at optimal filler content. Surface-treated rice husk enhanced these effects.
Członka, Strąkowska, Strzelec, Kairytė and Kremensas [90]	Grounded clove	1-5%	Polyurethane	Compression strength increased by 18%, flexural strength improved by 11%, and impact strength enhanced by 8% at 1-2 wt.% filler content.
[91]	Glass microsphere and nanoclay fillers	1-7%	Biobased rigid Polyurethane	Foam volume increased with filler content. However, compressive strength decreased at 7% filler due to lower density and weaker cell walls.
Głowińska, Datta and Parcheta [92]	Sisal fibers	5-15%	Polyurethane	Hardness slightly improved at 5% filler content, but tensile strength and elongation decreased with higher filler percentages.
Husainie, Khattak, Robinson and Naguib [93]	cellulose, chitin, hazelnut, and eggshell	1-5%	Polyurethane	At 1 wt.%, tensile strength and elongation improved. However, properties, including split tear strength, decreased significantly at 5 wt.%.
Ozgur Seydibeyoglu, Demiroğlu, Erdoğan, Akın, Ayvalık and Karavana [94]	olive kernel and nutshell fibers	2.5-7.5 %	Polyurethane	The compressive strength of polyurethane foam increased at 2.5 wt.% olive kernel, enhancing structural performance.
Naidoo, Onwubu, Mokhothu, Mdluli and Mishra [95]	Fish scale	0.5-1%	Polyurethane	Tensile strength polyurethane form increases by 18.8% increase and a 15.7% increase in elongation at break at 0.5 wt% (room temperature). Tear resistance exhibited significant improvements under heat aging, with a 22% increase (0.5 wt%MFSP) and a remarkable 37% increase 1 wt%
Hani, Firouzi, Islam and Sumdani [80]	Fish bone	10-15%	Epoxy	The tensile and flexural strength of the composites were improved by 30% and 200%, respectively, compared to the neat epoxy (NE) as an effect of the thermal treatment

3. Discussion

The empirical review of epoxy and polyurethane resins reinforced with natural fillers highlights the significant role of bio-based additives in enhancing mechanical properties while promoting sustainability. The findings from the reviewed studies underscore critical trends and challenges associated with natural filler incorporation.

Mechanical Performance Enhancement

From the review, it was evident that the integration of natural fillers into epoxy and polyurethane matrices improve tensile strength, flexural strength, and wear resistance. Shah, Ahmad, Abid, Arif, Khan, Khan and Djavanroodi [81] and Huzaifa, Zahoor, Akhtar, Abdullah, Haider, Khan and Alam [82] demonstrated that jute and sisal glass fibers significantly enhance tensile and flexural strength, reinforcing their suitability for structural applications. The work of Boopalan, Niranjanaa and Umapathy [83] further supports the advantage of hybrid fiber composites, where combining jute and banana fibers results in superior thermal stability and moisture resistance.

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These results align with previous studies [84,86] that emphasize the importance of fiber-matrix adhesion in determining mechanical performance. However, the findings by Wood, Coles, Maggs, Meredith and Kirwan [85] and Majhi, Samantarai and Acharya [87] highlight a critical limitation: excessive filler content leads to agglomeration, which weakens the composite structure due to stress concentration. This issue suggests that optimization of filler content is crucial to achieving the desired balance between strength and durability, a factor consistently observed in polymer-filler research [88,89].

Role of Filler Content in Property Optimization

The studies reviewed indicate that optimal filler content varies depending on the type of polymer and filler material. In epoxy composites for example, the highest mechanical performance was observed at moderate filler percentages, such as 2.5% for lignin [85] and 10% for rice husk [87]. This suggests that bio-fillers effectively reinforce polymer matrices within a specific concentration range before the drawbacks of excessive filler loading, such as brittleness and reduced tensile strength, outweigh the benefits.

Similarly, in polyurethane composites, Członka, Strąkowska, Strzelec, Kairytė and Kremensas [90] and Fan, Tekeei, Suppes and Hsieh [91] found that filler loadings between 1-2% resulted in maximum compression and flexural strength, while higher concentrations led to diminishing returns. The results obtained by Husainie, Khattak, Robinson and Naguib [93] and Głowińska, Datta and Parcheta [92] further emphasize that while natural fillers can improve rigidity and hardness, they may simultaneously reduce elongation and flexibility at excessive loading levels.

These observations are consistent with broader studies on polymer composites, where optimal filler dispersion is a key determinant of improved mechanical properties [94]. The findings suggest that tailored filler percentages should be adopted for specific engineering applications, ensuring an optimal balance between strength, stiffness, and flexibility.

Chemical Modification and Interfacial Adhesion

A recurring theme in the reviewed literature is the role of chemical modifications in improving filler-polymer compatibility. As seen in the study by Majhi, Samantarai and Acharya [87], surface-treated rice husk resulted in better adhesion, enhancing wear resistance. This is supported by similar findings in the work of [88] and [89], which stress that untreated fillers often exhibit poor dispersion within the polymer matrix, leading to performance degradation.

The studies suggest that chemical modifications, such as silane treatment or alkalization, can mitigate the inherent hydrophilicity of natural fibers, improving adhesion to hydrophobic matrices. This insight has implications for polymer composite manufacturing, where pre-treatment processes can be standardized to optimize mechanical properties across different polymer-filler systems.

4. Conclusions

The empirical review provides compelling evidence that natural fillers enhance the mechanical properties of epoxy and polyurethane composites. However, the effectiveness of these fillers is highly dependent on content optimization, dispersion techniques, and interfacial bonding strategies. The findings have significant industrial and environmental implications, emphasizing the need for further research into sustainable polymer reinforcement technologies. Particularly, more research is needed on the aging behavior of bio-based composites under real-world environmental conditions.

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