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Pre-Treatments of Natural Fibers, Particulate Reinforcement for Polymer Composites – A Review

Nirmal Prasad Sahu*, Mukesh Kumar Singh**
*(Department of Mechanical Engineering, RSR Rungta College of Engineering and Technology, Kohka-KurudRoad, Bhilai, Chhattisgarh, India. Email: nirmalsahu038@gmail.com)
** (Assistant Professor, Department of Mechanical Engineering, RSR Rungta College of Engineering and Technology, Kohka-Kurud Road, Bhilai, Chhattisgarh, India. Email :mks20387@gmail.com)

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Abstract:

Natural fibre reinforced composites have attracted a lot of interest recently due to its lightweight, nonabrasive, flammable, nontoxic, affordable, and biodegradable characteristics. Flax, bamboo, sisal, hemp, ramie, jute, and wood fibres are among the many natural fibres that are of interest. The use of natural fibres as a reinforcing material for the creation of various types of composites has been the subject of extensive research worldwide. However, the usage of natural fibre reinforced composites is less appealing due to poor interfacial adhesion, low melting point, and weak moisture resistance.

The inclusions' size, shape, and distribution have an impact on the particulate composites' macroscopic behaviour. Another crucial factor is the matrix-inclusion interface adhesion. Carbon materials, particularly in the form of glittering diamonds, have mesmerised mankind for centuries. In addition, carbon materials in other forms, such as coal and coke, continue to serve mankind as a fuel material, and in other applications, carbon black, carbon fibres, carbon nanofibers, and carbon nanotubes meet the requirements for reinforcing filler. The tensile strengths of natural fibre reinforced polymer composites typically rise with fibre content up to a maximum or optimum value, after which the value starts to fall.

However, when fibre loading increases, the Young's modulus of natural fibre reinforced polymer composites rises. The surface incompatibility between hydrophilic natural fibres and non-polar polymers (thermoplastics and thermosets), however, may adversely affect the physical and mechanical properties of the resulting composites.

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I. INTRODUCTION

In numerous applications during the last few decades, polymers have largely taken the role of traditional metals and minerals. Due of the benefits polymers have over traditional materials, this is conceivable. The simplicity of processing, increased productivity, and lower costs are the three most significant benefits of employing polymers. For most of these applications, fillers and fibres are used to alter the characteristics of polymers to meet the demands for high strength and high modulus. When comparing certain qualities, fibre-reinforced

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polymers have an edge over other traditional materials.

These composite materials are being used for everything from aerospace to appliances. Due to the benefits that natural fibres offer over conventional reinforcement materials, scientists and technologists have recently become interested in them, and the creation of natural fibre composites has garnered interest in recent years [1-4]. These natural fibres are inexpensive, have a low density, and have several unique qualities. These differ from conventional reinforcing fibres in that they are biodegradable and nonabrasive. Their specific qualities are equivalent to those of other fibres used as reinforcements, and they are also easily accessible. The potential of natural fibres, however, is significantly diminished by limitations such incompatibility with the hydrophobic polymer matrix, a propensity to form aggregates during processing, and weak moisture resistance.

A fibre reinforced polymer (FRP) is a composite material made of high-strength fibres like glass, aramid, and carbon embedded in a polymer matrix [8]. In general, thermoplastics and thermo-settings are the two kinds of polymers. As matrices for biofibers, thermoplastic materials currently predominate; the most popular thermoplastics used for this purpose are polypropylene (PP), polyethylene, and poly vinyl chloride (PVC); the most popular thermosetting matrices are phenolic, epoxy, and polyester resins; and natural fibres include flax, hemp, jute, sisal, kenaf, coir, banana, henequen, and many others [8]. Natural fibres have several benefits over synthetic glass and carbon fibres, including lower cost, lower density, comparable specific tensile qualities, lack of abrasiveness on equipment, lack of skin irritation, lower energy consumption, and lower health risks renewability, recyclability, and biodegradability.

[5-7].

Natural fibres offer several benefits over conventional inorganic fillers like glass fibre and carbon fibre, including: (1) abundance, which makes them inexpensive; (2) biodegradability; (3) flexibility during processing and less machine wear; (4) minimal health hazards; (6) a desirable fibre aspect ratio; and (7) relatively high tensile and flexural modulus. Composites with a high specific stiffness and strength are produced when strong and lightweight natural fibres are incorporated into polymer (thermoplastic and thermoset) matrix. [8-14].

Natural fibres can be eventually disposed of through composting or cremation more easily than most manufactured fibres can because of these qualities. The fibres always have lower embodied energy than glass fibres manufactured industrially and contain atmospheric carbon dioxide trapped in their structure. The matrix phase is essential to the functionality of polymer composites. Thermosets and thermoplastics are both desirable choices for composite matrix materials. The formulation of thermoset composites is complicated due to the numerous components used, including base resin, curing agents, catalysts, flowing agents, and hardeners.

These composite materials undergo chemical curing to form a three-dimensional network structure that is heavily cross-linked. Strong, hard, and creep-resistant cross-linked structures with good solvent resistance. Up to 80% of the fibres can be loaded, and the characteristics are noticeably improved due to the alignment of the fibres. Compared to thermoset polymers, thermoplastics have several advantages. The reduced processing costs of thermoplastic matrix composites are one of their benefits. Flexibility in design and simplicity in

moulding complex pieces are two more. These composites are processed using straightforward techniques like extrusion and injection moulding.

Most of the thermoplastics research that has been published to far involves polymers including polyethylene, polypropylene, polystyrene, and poly (vinyl chloride). This is mostly because, to prevent heat destruction of the natural fibres, the processing temperature is limited to temperatures below 200°C. The dispersion of the fibres within thermoplastic composites is a crucial factor in achieving consistency in the final product. Thermo-plastic composites havegood mechanical qualities, are robust and flexible. The composite's processing capacity, however, imposes a limit on the loading percentage.

The random fibre orientation in composites results in a lower level of property alteration than that seen in thermoset composites. The fibres' characteristics, their aspect ratio, and the fiber-matrix interaction control the composites' characteristics. The performance of the composite is influenced by the surface adhesion between the fibre and the polymer, which is crucial in the transmission of stress from matrix to fibre. The heat stability of these fibres is a further crucial feature. These fibres are lignocellulosic and mostly made of cellulose, lignin, and hemicellulose.

As processing temperature rises, the fibres' cell walls undergo pyrolysis and aid in the creation of char. The lignocellulosic is protected from additional heat deterioration by these charred layers. The thermal resilience of the fibres at processing temperatures is significant because most thermoplastics are treated at high temperatures. Thus, the thermal stability of the fibres, surface adhesion qualities, and, in the case of thermoplastic composites, fibre dispersion, are the three main

problems in the creation of natural reinforced composites.

The tensile strength of 20-mesh and 40-mesh hardwood, reinforced HDPE composites, and fibres from rice and flax hulls. According to Li et al. [8], bio-composites were created by extruding and injecting high-density polyethylene (HDPE) with flax fibre contents ranging from 10% to 30% by mass. The findings demonstrated that raising the fibre content initially increased the tensile characteristics. It fell after reaching a volume peak of 20%. The tensile strengths of HDPE composites supplemented with 40-mesh hardwood fibres grew progressively and peaked at 25% fibre loading by volume before declining.

On the other hand, when the fibre loading increased, the tensile strength of HDPE composites reinforced with 20-mesh hardwood fibres decreased [9]. This is completely different from the hardwood fibres made of a 40-mesh gauge. Tensile strengths of rice husk fiber-reinforced HDPE composites [10]; curve behaviour was essentially identical to that of 20-mesh hardwood, with maximum tensile strength occurring at 5% by volume of fibre content [10]. With increased particle loading, the tensile strengths somewhat declined [10]. The Young's modulus of HDPE composites reinforced with 20-mesh hardwood, 40-mesh hardwood, flax, and rice hull fibres with different percentages by volume of fibre loading. The Young's modulus of reinforced HDPE composites with 20-mesh and 40-mesh hardwood fibres can be obtained with fiber loading of 0–40 wt.% [11].

The Young's moduli of 20-mesh hardwood fibre composites were lower than those of their counterparts, while the value increased with increasing fibre loading, reaching up to 30% volume fraction of hardwood. The Young's moduli

of 20-mesh hardwood fibre composites were higher than those of their counterparts after 35% volume fraction of hardwood.

The Young's modulus of HDPE composites reinforced with flax fibres and fibre loading ranging from 0 to 40% volume [15]. It was discovered that the Young's modulus rose as the fibre content, The Young's modulus of HDPE composites reinforced by rice hull fibres with fibre loadings ranging from 0 to 40% volume [16]. Rice hull fibre reinforced composites saw the least increase with increasing fibre content, whereas flax fibre reinforced composites saw the biggest increase.

Tensile strength values for natural fibre reinforced composites rose as fibre loading climbed to a maximum or optimum value before declining. However, it is generally true that as fibre loading rose, the values of the Young's modulus also increased gradually. On the other hand, some researchers discovered a completely different pattern from the one that links a rise in fibre content with an increase in composite strength. Numerous variables, including incompatibility between the matrix and the fibres, faulty production techniques, fibre degradation, and others, might be blamed for this. Natural fibres' hydrophilic nature is incompatible with hydrophobic polymer matrices and tends to agglomerate.

Because of their poor moisture resistance and significant water absorption, these hydrophilic fibres have poor tensile qualities in natural fibre reinforced composites. Additionally, waxes and other non-cellulosic materials like hemi-cellulose, lignin, and pectin on fibre surfaces lead to poor adhesion between the matrix and fibres. Therefore, it is required to raise fibres hyphobicity by subjecting the natural fibres to surface chemical modification (surface treatment) in order to improve and develop natural fibre reinforced

polymer composites with higher tensile qualities.Natural fibres, which are typically polar, have a poor level of compatibility with non-polar polymer matrices, particularly hydrocarbon matrices like polypropylene (PP) and polyethylene (PE), even though the resulting composites can benefit greatly from their use [17-22].

Problems with the production and material qualities of the composite could result from the incompatibility. During compounding processing, hydrogen connections between the hydrophilic fibres may form, causing the fibres to aggregate into bundles and distribute unevenly throughout the non-polar polymer matrix [23-30]. Additionally, the non-polar polymer matrices do not adequately moisten the fibres, which causes weak interfacial adhesion. As a result, the matrix's ability to transfer stress to the reinforcing fibres is less effective.

1.1 PRETREATMENTS OF NATURALFIBERS
Numerous researchers modified the natural fibres' surfaces chemically, including through chemical treatments, coupling agents, and graft co-polymerization, with the goal of enhancing the composites' tensile capabilities. One of the most common chemical processes used to treat natural fibres is alkali treatment, commonly known as mercerization. In this process, sodium hydroxide (NaOH) is utilised to break up the hydrogen bonds in the cellulose fibres' network structure, increasing the surface roughness of the fibres [31]. The original cellulose structure is depolymerated by this process, which also eliminates some of the lignin, wax, and oils coating the fibres' outer surface, exposing the short-length crystallites [32].

The surface of natural fibres was also said to be modified by acrylic acid treatment. According to Li et al.'s investigation into flax fiber-reinforced

polyethylene bio-composites, such a treatment was more effective than alkali and silane treatment. [33-34].

1.1.1 ACETYLATION OF NATURAL FIBERS

Acetylation of natural fibres is a well-known esterification technique for plasticizing cellulosic fibres [35-40]. Initially, wood cellulose was acetylated to protect the cell walls from moisture, improve dimensional stability, and reduce environmental deterioration [41-45]. When fibres are pretreated with acetic anhydride, the cell wall's polymer hydroxyl groups are replaced with acetylgroups, changing the characteristics of these polymers to make them hydrophobic. The process of acetylation involves heating lignocellulosic materials' cell wall hydroxyl groups in the presence of acetic or propionic anhydride. The hydroxyl groups of cellulose (crystalline material) are tightly packed with hydrogen bonds, preventing the diffusion of reagent, in contrast to the hydroxyl groups of lignin and hemicelluloses (amorphous material), which react with the reagent and thus result in very low extents of reaction [46].

1.1.2 ETHERIFICATION OF NATURAL FIBERS

When cellulosic fibres are modified by etherification, new ranges of properties are enhanced, increasing their usefulness and acceptability in a variety of applications [47]. The formation of a charged intermediate species by sodium hydroxide and the fibre (Schemes 3 and 4) enables the nucleophilic addition of epoxides, alkyl halides, benzyl chloride, acrylonitrile, and formaldehyde to occur more quickly [48]. Epoxides, like epichlorohydrin, have an oxygen-containing ring that is stretched (3, 4-members), which causes electron removal from nearby carbons.

Epoxides are moderately reactive with alcohol-containing compounds like cellulose due to this structure. Epichlorohydrin's reactivity with wood preservatives like pentachlorophenol was described by [49] as modifying wood.

Ohkoshi [37-39] used hot pressing to join two surfaces of wood that had been changed by etherification with allyl bromide. The shear strength, according to the results, was comparable to that of unaltered wood. Furthermore, the effects of alkylation on certain wood components were investigated [39], as well as the grafting of styrene onto the alkylated wood surface [38].

1.1.3 PEROXIDE TREATMENT OF NATURAL FIBERS

Because cellulose fibre can be processed easily and has improved mechanical qualities, peroxide treatment has caught the interest of many researchers. Organic peroxides have a propensity to break down quickly into free radicals (RO.), which then interact with the hydrogen group of the matrix and the cellulose fibres. The peroxide treatment response suggested by Sreekala et al. [40] is depicted in Scheme 5. After an alkali pretreatment, fibres are subjected to a peroxide treatment that uses 6% benzoyl peroxide or dicumyl peroxide in an acetone solution for around 30 minutes [40, 42]. Following alkali pretreatments, dicumyl peroxide from an acetone solution was applied to the flax fibres. It was utilised as a saturated solution of peroxide in acetone. The fibres were immersed in the solution for 30 minutes at a temperature of 708C.

For the peroxide-assisted decomposition, high temperatures were preferred. After being chemically treated, the fibres were rinsed in distilled water and baked for 24 hours at 808C [43]. In the Periodic Table of Elements, carbon is the

sixth element. It is genuinely notable for its tremendous capacity for catenation, or joining together with other elements in various ways, serving as the building block of organic chemistry and life. It occurs naturally in large quantities as coal or natural graphite, and less frequently as diamonds. Other types of carbon that man has produced include glassy carbons, diamond-like carbon, synthetic diamonds, synthetic graphite, synthetic diamonds, adsorbent carbon, cokes, carbon black, carbon, and graphitic fibres, etc.

For use as electrodes and electrical contacts, lubricants, shoe polish, gemstones, cutting wheels, gas adsorption, catalytic support, helium gas barrier, tyre and elastomer reinforcement, toner for photocopiers and printing inks, high-performance tennis rackets, composite materials for aircraft and spacecraft, heat sinks for ultrafast semiconductors, etc. [49-55]. The addition of rigid particles to polymers or other matrices can have a variety of beneficial outcomes, including an improvement in creep resistance and fracture toughness as well as an increase in stiffness and a decrease in the coefficient of thermal expansion.
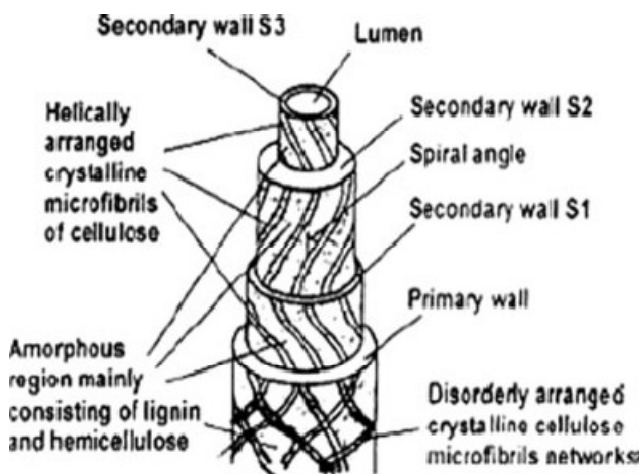

Fig1.1 Structure of natural fiber [26].

The properties of the several constituent phases, including the resin, the filler, and the interfacial region, interact intricately to produce the modulus of a filled resin. A variety of factors, including the size, shape, aspect ratio, and distribution of the reinforcing particles, influence the mechanical properties of the composite.

Rubber compounds were the first materials where the reinforcing action of particles in polymeric polymers was recognised. This resulted from the establishment of a knowledge of the relationship between structure and property for natural rubber filled with carbon black. Because of the viscous nature of the viscoelastic qualities, a rise in modulus was thought to be comparable to an increase in viscosity.

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