

Review Article

A Review on Surface Modification of Bast Fibre as Reinforcement in Polymer Composites

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Abstract: In the past few decades, natural fibres have shown remarkable achievements in the field of reinforced polymer composites because of environmental issues and petroleum crises. Biodegradable fibres (bast, animals hair, stalk, seed etc.) has been used by researchers because of its low cost, low density, abundant in nature, high stiffness etc. over other man-made fibers. The majority of plant fibers which are being considered as reinforcement materials for polymer composites are bast fibers (the outer cell layers of various plants) such as hemp, jute, kenaf, grewia optiva etc. Among these fibers Grewia optiva is recently explored fiber and is presently being assessed as reinforcement in polymeric composites. In this paper, we have discussed and reviewed the extraction process of Grewia optiva fibers and various surface treatments such as graft copolymerization, mercerization, Benzoylation and silane methods for enhancement of the surface adhesion properties of Grewia optiva fibres with their matrice and the effects of these surface treatments on mechanical properties of such fabricated composites.

Keywords: Natural Fiber, Grewia Optiva, Fiber Extraction, Surface Modification

1. Introduction

During last few years many conventional materials are replaced by composite materials in various applications. The most advantageously used composites in today's are polymer composites, Polymer composite is defined as type of composite in which matrix materials are polymer. There are two types of polymers: thermoset and thermoplastic. Thermoset is a hard stiff cross-linked material that doesn't soften or become mouldable when heated. Thermosets are stiff and do not stretch the way that elastomers and thermoplastics do. Unsaturated polyester, Vinyl Ester, Phenolic Epoxy, Novolac, Polyamide, and Epoxy are thermoset polymer is used a matrix in fibre reinforced polymer composites [1-3]. Thermoplastics are polymer that

requires heat to make them process able. After cooling such material retain their shape. These polymers may be reheated and reformed, often without significant changes in their properties. High density polyethylene, low density polyethylene, polypropylene, poly vinyl chloride etc. are thermoplastics polymer is used as a matrix in fibre reinforced polymer composites [4].

Natural fiber based thermoplastic composites play a major role in material science because of their several advantages over other inorganic materials like glass, carbon and Kevlar fibers such as: abundant in nature, low cost, low density, minimal health hazard, relatively high tensile and flexural modulus incorporating the tough and light-weight natural fibers into polymer matrices produces with a high specific stiffness and strength. The properties and performance of

composite materials depend upon the properties of the individual components and their interfacial compatibility. Now a day's natural plant fibers are used as reinforcement in polymer composites for making low cost engineering materials. Also, the use of natural fibers reinforcement with polymer matrix has grown rapidly because of their good process ability to be recycled. Natural fibers are broadly classified in to two categories namely plant based and animal based. Seed hair (cotton), leaf fiber (sisal and abaca), stalk fibers (straws of wheat), and skin fibers (banana) and bast fibers (ramie, jute, grewia optiva and flax) are the main categories of the plant natural fibers while wool, hair and silk (animal proteins) are used by researchers for synthesizing fibers from animal.

1.1. Bast Fiber

Bast fibres are defined as the outer cell layer of various plants and also have majority in plant fibre categories which are being considered as reinforcement for polymeric materials [5]. There are various bast fibers as reinforcement is used by various researchers for making polymer composites like jute, kenaf, hemp, grewia optiva etc [6-9]. The polymer composites reinforced with bast fibres are reasonable strong, economical, light in weight, less hazardous and have a potential to be used as structural materials. Bast fibres like jute, hemp, flax, kenaf and grewia optiva fiber are becoming increasingly important in composite production due to its better strength and stiffness as compared to other natural fibres. Among these fibers Grewia optiva are recently exposed fiber and are presently being assessed as reinforcement in polymeric composites. Despite of the above advantages, they have some limitation also, such as high water uptake capability, and low strength when compared to inorganic fibres such as aramid, glass, carbon. These limitations of bast fibre based composites can be improved by various chemical treatments method.

1.2. Grewia Optiva Fiber

The local name of Grewia optiva is Bhimaal or Bihul, is small to medum size deciduous tree with 9-12 m height and main region of availbality of Grewia optivais hilly area in India like Uttarakhand, Himachal Pradesh Jammu & Kashmir etc. Grewia optiva, a multipurpose tree of the Himalayan region and is found on the boundaries of field up to 2000 m. It provides fodder for animals, fiber, fuel wood, edible fruit, as a shampoo and also used for medicinally. It has so far played a key role in the village economy because this fibrous material has been used by people for making low cost article such as ropes, mats, bags, boots etc. products made from this fiber as shown in Figure1. Other uses of optiva grewia are:

- Domestic fuel wood, the barks of Bhimal are used as superior source of fuel wood because they catch fire very easily without smoke and also burn more time as compared to other fuel wood and also make it possible to burn moist twigs as Indigenous torch. Bhimal fibres are used as a light source by villagers to move from one

hill to another at night.

- Farm implements, *Grewia optiva* woods are semi hard, strong and elastic and its old twigs are used for making light farm implements like handles of spades, axes, pick axes, gluel for bird scaring, wooden oars.
- Small farm implements like kutla are used for weeding, and its branches are also used for making baskets which provide employment to rural poor.
- Frames of cots and the indigenous apparatus for catching fish.
- Indigenous cosmetics, hill women have been using the mucilage found in the bark of Bhimal as indigenous hair shampoo since centuries.
- It is used as reinforcement in polymer composites.

The present paper focuses on the Grewia optiva as reinforcement in polymer composites and improvement of mechanical behavior of Grewia optiva reinforced polymer composites by surface treatment which is used by various researchers. Adhesion characteristics of the fibre have been improved by surface treatment, due to improved work of adhesion because it increases the surface roughness and surface tension. Inter crystalline and other waxy lignin and other waxy substances from the surface of natural fibres have been removed by this treatment, as it increase the possibility of chemical bonding and interlocking.



Figure 1. Products made from grewia optiva fiber.

2. Extraction Process of Fiber from Grewia-Optiva Plant

Grewia optiva is a medium size deciduous tree of 10-12 m height which is grown up to an elevation of 2000 m in India. It sheds its leaves during month of March-April and flowers appear with the new flush of leaves and fruits are formed soon but ripen from October-December depending upon the climate condition of locality. The villagers extract the Grewia Optiva during first week of November, and the branch are chopped and green leaves are used for animals' fodder. The sticks are placed under a tree for shade drying. At spring season, in first week of April, All the dried sticks are collected together and put under the sun for complete drying. After this process is completed, bundles of stick weighing 15-20 kg each are tied and brought to a brook (locally Ghadhera) for retting process. An artificially created water pool called Khall is prepared for stopping the running water by placing stone around, where these bundles of sticks finally kept for retting. A stone is placed over each bundle and submerged it into water for about three months. In the month of June the retting process is completed. The bark of each sticks is pulled out in narrow strips, washed thoroughly in running water, and the outer pulp is cleaned by continuous washing in water to get inner bark and finally the extracted fibers are dried under sun-bath for complete removal of moisture. The whole process of extraction of fibers from Grewia optiva are summarized into four steps of (a) Grewia optiva plant, (b) Preparation of khall, (c) Retting in process in Khall and (d) Separation of bark for fibre extraction and finally Sun drying of extracted fiber as shown in Figure 2.



Figure 2. Extraction of fibers from Grewia optiva (a) Grewia optiva plant (b) preparation of khall (c) retting in-process in Khall (d) Separation of bark for fiber extraction and finally sun drying of extracted fiber [10].

3. General Overview of Surface Modification Method for Natural Fibres

The properties of composite materials depend upon the interfacial behaviour between the fibre and polymer matrices.

Fibre-matrix interfacial phenomena control stress transfer between fibre and matrix, mechanism of damage accumulation and propagation and stress distribution. Generally composite materials with strong interfaces have relatively high strength and stiffness but are somewhat brittle, whereas with weak interface have low strength and stiffness but high resistance to fracture if the crack grow perpendicular to the fibres [11]. By physical surface activations, compatibility or coupling agents which are deposited or reacted on to the fibre is improved the quality of fibre-matrix adhesion. The most serious concern with natural fibre is its hydrophilic nature due to the presence of pendant hydroxyl and polar groups in various constituents, which can lead poor adhesion between fibre and hydrophobic polymers. Treatment of natural fibre in general by Corona discharge is one of the most popular techniques for surface oxidation and activation changing the surface energy of the cellulose fibres. It is most likely that an increase in the polarity subsequent to corona treatment is caused by an increase in the number of hydroxyl and carboxyl group. Surface cross linking could be introduced and surface energy could be increased or decreased with generation of groups and reactive free radicals [12].

Hydrophilic nature of the fibres and hydrophobic nature of matrix are the main problem in natural fibre composite. As a result, there is an inherent compatibility between fibre and matrix. Hydrophilic tendency of natural fibres can be improved by chemical treatment. Various researches have been conducted to improve fibre properties by different chemical treatment such as acetylation, alkalization, graft copolymerization, permanganate, peroxide, silane etc [13-16].

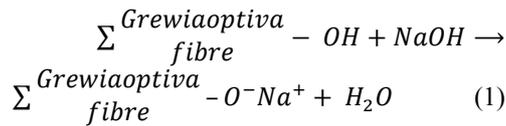
4. Surface Modification Techniques of Grewia Optiva

The fibres obtained from Grewia optiva plant are cellulosic in nature, generally it contains (58-75% cellulose), (10-12% hemicelluloses) and (7-12% lignin) respectively [17]. If, we use raw fibre directly without any chemical treatment, major problem has been seen. The sample made up by this untreated fibre has greater water absorption capacity which affects to a major extent the mechanical properties of composites. Here we discuss some chemical treatments which are used by various researchers.

4.1. Mercerization

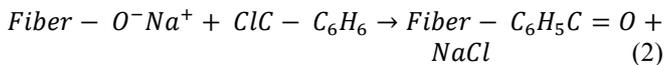
The treatment of natural fibres by NaOH is widely used for both thermoset and thermoplastic composites. Natural fibres have an external surface which is coated with waxy substances. This surface is not suitable for creating strong bond with a polymer matrix and also has a low surface tension. Bond strength can be improved by reacting the fibres with reagent that would make it hydrophobic. Alkali treatment of natural fibres is also called mercerization. It is a common method to produce high-quality fibres.

Mercerization is the term used to explain the conversion of native cellulose or cellulose one in to cellulose two that occurs when native cellulose fibres are swelled in caustic soda followed by removal of the alkali by washing. Alkali treatment is recognized to hydrolyse the amorphous part of cellulose present in fibres so that after treatment the material contains more crystalline cellulose. In case of mercerization of raw *Grewia optiva* fibre, it was soaked in 10 % (w/v) NaOH solution at room temperature for 4hour [18]. Scheme of the reaction is represented by Reaction (1):



4.2. Benzoylation

The hydrophilic nature of pre-treated fibre by NaOH can be minimized by Benzoylation chemical treatment method. In this method, Benzoyl ($C_6H_5C=O$) group react with cellulosic OH group of fibre after 30 minute pre-soaking with NaOH which activate the hydroxyl group of the cellulose and lignin in the fibre [19]. The isolated fibres are then soaked in ethanol for 1 hour to remove the benzoyl chloride and finally washed with water and dried in the oven. This results in more hydrophobic nature of the fibres which improves the surface adhesion with the matrix. The possible reaction between cellulosic-OH and benzoyl chloride is given by Reaction (2).



4.3. Silane Treatment

Silane is used as coupling agent to modify fibre surface. This treatment is based on the use of reactant that bear reactive end groups which at one end can react with hydroxyl groups of cellulose fibre and at other end can react with the matrix. Silane chemical coupling presents three main advantages as follows.

- Alkoxysilane groups bear at one end which are capable of reacting with hydroxyl group of natural fibres
- They are commercially available in large scale
- They have a large number of functional groups at second end which can be tailored as a function of the matrix to be used.

Silanol is formed in the presence of moisture and hydrolysable alkoxy groups. It reacts with cellulose hydroxyl group of the fibre and improves fibre matrix adhesion to stabilize composite properties [20]. Due to this, a more reactive site can be generated by silane reaction. The efficiency of silane treatment has been found higher for alkaline treatment as compared to untreated fibre.

4.4. Graft Copolymerization

The most important type of chemical modification is the chemical coupling method. This method improves the interfacial adhesion due to formation of chemical bond

between fibre and matrix. Graft copolymerization is the most well-known method regarding non-reactive matrix based composites and the reaction is initiated by free radicals of the cellulose molecule. The cellulose molecule cracks and radicals are formed when cellulose is treated with an aqueous solution with selected ions and is exposed to a high energy radiation. Then the radical sites of the cellulose are treated with a suitable solution, for example polystyrene, acrylonitrile, vinyl monomer, methyl methacrylate [21-22]. The resulting co-polymer possess properties characteristic for both, grafted polymer and fibrous cellulose. For example covalent bond is established when cellulose fibres are treated with hot MAHH-PP (polypropylene-maleic anhydride copolymers) [23]. The mechanism can be divided into two steps i.e. the esterification of cellulose, and the activation of copolymer by heating at temperature of 170°C (before fibre treatment). After this treatment, the surface energy of the fibres is changed to a level much closer to the surface energy of the matrix, which results a higher interfacial and better wettability. The percentage graft yield and efficiency is obtained by using the given relation [24].

$$\% \text{ Grafting}(P_g) = \left(\frac{W_g}{W} - 1 \right) \times 100$$

W_g =weight of grafted fibre, W =weight of ungrafted fibre

$$\% \text{ Percentage}(P_c) = \left(W_g - \frac{W}{W_m} \right) \times 100$$

W_m =weight of monomers

The tensile strength properties of *Grewia optiva* fiber is increased by using grafting. It has been seen that, it is possible to perform potassium per sulphate initiated grafting of methyl methacrylate on to the cellulosic *Grewia optiva* fibers in aqueous medium. The surface morphology of the cellulosic *Grewia optiva* fiber is improved as compared to untreated one. The dielectric and thermal behaviour of *Grewia optiva* based polymer composites is improved by using surface modified methods such as grafting, silanted, mercerized. Among this chemical treatment silane treated fiber shows better properties as compared to other methods. It was demonstrated that the phenol formaldehyde matrix based composites were also prepared by using raw and grafted *Grewia optiva* fiber as reinforcement in polymer composite and was shown that grafted *Grewia optiva* had better mechanical strength as compared to raw fibers [25]. Effects of different *Grewia optiva* fibre loadings on the mechanical properties of the phenolic composites were observed and it was illustrated that, if we increase the fibre loading, the mechanical properties of composite increase [26]. Better interfacial adhesion between fiber and matrix, thus increases the tensile strength. Surface modification of *Grewia optiva* fibre was also done by using graft copolymerization method and it was found that the grafted fibre surface had no artificial and natural impurities having a rough surface topography that resulted in enhanced fibre aspect ratio offering a better surface adhesion between two

constitute of composites.

5. Future Prospects

Due to environment and sustainability issues, this century has witnessed remarkable achievements in green technology in the field of material science through the development of natural fiber polymer composites. The growing use of natural fiber composites is based more on the environmental and low-cost benefits rather than on their strength capabilities. Therefore, more research is needed to obtain better strength and modulus properties including optimizing the interfacial bond between the fiber and resin by means of fiber treatment. Virgin polymeric roof or glass fiber based polymeric roof are already used in world wide. Glass fiber based polymeric roof have definitely long life and high strength as compared to mono polymer roofing system. Natural fibers are widely replaced man-made fibers in various automotive and construction applications because of their low cost, high stiffness and abundantly available in nature, so here we will be able to reinforced the grewia optiva as natural fiber in polymeric roofing system.

6. Conclusion

In this review, the effect of surface treatment of Grewia optiva fibre reinforced polymer composite by various surface treatment methods was investigated. Grewia optiva fibre is gaining interest as reinforcement for polymer composite due to their environmental and economic benefits. However, several limitations must be overcome to exploit the full potential of Grewia optiva fibre for application as reinforcement, but this behaviour can be minimized easily by surface treatment methods like graft copolymerization, mecerization, Silane, Benzoylation etc. These surface treatments result in greater enhancement in the mechanical properties as compared to untreated fibres. So our study shows that Grewia optiva is a promising natural fibre for polymeric composites and various surface treatments can enhance further its mechanical behavior when used as reinforcements.

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