Effect of chemical treatments on properties of injection molded *Nypa fruticans* fiber reinforced polypropylene composite

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**ABSTRACT**

The rise in environmental awareness prompted consideration of environment friendly materials. Natural fiber, on the contrary, has a structure that allows it to absorb moisture attributable to its hydrophilicity, which hinders its wide application and leads to poor interfacial bonding with the polymer matrix. Therefore, fiber surface modification is inevitable, which is usually based on using the functional group of some chemicals to replace the hydrophilic hydroxyl group to make it more moisture resistant and ameliorate the bonding between fiber and polymer matrix. In this study, injection molded *Nypa* fiber reinforced polypropylene composites were fabricated. Three different chemical modification i.e., mercerization, *H*₂*O*₂ treatment, maleic anhydride polypropylene (MAPP) compatibilizer, were employed. Other parameters on which the properties of the composite depend, i.e., fiber volume (30%), manufacturing process, etc. were kept the same. Field emission scanning electron microscopic (FE-SEM) images were also investigated to verify the result of experiments. Moisture resistance of the composite was also evaluated. The tensile and flexural properties of treated composite were significantly enhanced than the untreated one. The maximum strength was obtained for MAPP treated composite. The chemical treatment has a less impact on the impact strength of the composite. Better moisture resistance was observed for treated fiber composites. This study provides the insight of using chemical treatment for better adhesion between the fiber and the polymer.

**1. Introduction**

Recent technologies are progressing by taking environmental concerns into account. Anything that is harmful to the environment is now strictly outlawed by any country's legislation. Biodegradable materials are currently one of the most explored areas since they have no or minimal negative influence on the environment. Researchers are working to solve the drawbacks of natural fiber composites (NFC) so that synthetic fibers, which may be hazardous to the environment, can be replaced. As a result, the number of natural fiber composite applications is expanding gradually. In the automotive sector, construction, and packaging industries, jute, hemp, coir, and bamboo fibers have all been used [1]. Sports, aircraft, electrical and electronic equipment, and other sectors are gradually moving towards the adoption of use natural fibers composite as well [2, 3].

NFCs have the qualities to substitute traditional synthetic fiber-based products. After its service life has expired, the material should be degraded in such a way that it has no adverse impact on the environment. However, a composite made of synthetic fibers is not biodegradable, which has a negative impact on our environment, as well as our future generations. If the flaws associated with NFC can be eradicated or mitigated, it could be a feasible solution to this problem. Biopolymers are now approaching the mainstream, with a sales boost of over 20%–30% per year [4]. NFCs are becoming more popular as people become more concerned about the environment. Synthetic fiber is produced at a rate of 1.5 × 10⁸ tons per year, whereas lignocellulosic fiber is produced at a rate of 2.1 × 10¹¹ tons per year [5]. As a result, natural fiber could be a viable alternative to synthetic fiber, lowering the end product's cost while simultaneously reducing the negative impact on the environment. It's crucial to pick the right natural fiber. The utilization of plant-based resources will expand by up to 50% by 2050, according to the Technology Road Map for Plant/crop based Renewable Resource 2020 [6]. In the last ten years, natural fiber adoption has increased by 13% in the commercial and industrial sectors [5]. The per capita consumption of plastics in Bangladesh...
is still much less than the neighboring countries. This can be further reduced by incorporating natural fibers into the plastics.

*Nypa fruticans* (NF) belongs to family Palmae or Arecales is a monoeccious palm with special characteristics. Nypa consists of frond, husk, shell, leaf. Chemical analysis revealed the presence of cellulose (28.9–45.6 wt.%), hemicellulose (21.6–26.4 wt.%), lignin (19.4–33.8 wt.%), starch, protein, and other inorganic elements in each section. Frond of the nypa fiber can be a great source of fiber to use as reinforcement in NFC. The mechanical properties of the fiber largely depend on the constituents of the fiber. Proper selection of fiber as a reinforcing material largely depends on the constituents of fiber.

The properties of composites largely contingent upon the extraction process employed. Among various extraction processes such as dry extraction, wet extraction, mechanical decortication etc., the wet extraction process yields a large number of fibers than others keeping fibers in good shape. Usually fibers need to be submerged under static water for 8–12 weeks for easy extraction of fibers from the frond [7].

Depending on the manufacturing process, various thermoplastics such as polypropylene, PVC, HDPE, LDPE etc., and different thermostets such as epoxy resin, phenol-formaldehyde, unsaturated resin etc. are available. By processing temperature range, the choice of matrices is limited because of the instability of natural fiber at a high temperature. There are many ways available for natural fiber composite manufacturing, such as compression molding, hand lay-ups, resin transfer mold, vacuum assisted resin transfer mold, injection molding, etc [8]. The method which is chosen for fabrication of NFCs contingent upon the type of matrix used and the condition for processing NFCs depends on the type of fiber used. The long processing time, post processing and high cost associated with the thermosetting resin have drawn the interest of the researchers towards thermoplastic resins as polymer matrix. Conversely, thermoplastic matrix composite can be produced at a much shorter processing time (in a minute or less) since it only melts the materials to become formable and solidifies it with cooling. In addition, the tensile and flexural properties of polypropylene are much better than polyethylene [9].

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Natural fiber composites have the disadvantage of not being easily compatible with the polymer matrix. The hydrophobic polymer matrix contrasts with the hydrophilic fibers. Therefore, a poor interfacial attachment between fiber and matrix usually formed which leads to reduced mechanical properties than the continuous phase since fibers acts as a stress riser or act as a void space within the matrix rather than reinforcing it. Thus, it is one of the main reasons for not getting wide application despite having a large production rate than the synthetic fibers. Therefore, proper treatment of natural fibers is inevitable before incorporating them into a matrix as a reinforcing medium. There are many chemical treatments available for augmenting the interfacial bonding of NFCs as an instance- mercerization, MAPP treatment, silane treatment, H2O2 treatment, acetylation, etc. Among these, not all chemicals are readily available at the local market.

Hydrogen peroxide (H2O2), which is commonly used in the textile industry, can be utilized to modify natural fiber [10]. H2O2 produces fiber discoloration as an oxidative bleaching agent. The composite’s physical appearance can be improved by incorporating bleached fiber. Besides improving the cosmetic appearance of polymeric composites, fiber surface treatment can improve their mechanical performance. Razzaz et al. [11] employed H2O2 to treat kenaf fiber, results in improved crystallinity index. Fiber-matrix mechanical interlocking was ameliorated which is attributable to the increased surface roughness, resulting in improved mechanical properties. Innocent et al. [12] constructed a composite with Pineapple Leaf fiber (PALF) fiber treated with H2O2 and compared the mechanical properties to the untreated one, finding that the treated fiber composite outperforms the untreated one.

**Table 1. Chemical Constituents of Nypa fiber frond [29].**

| Constituents  | Percentage (%) |
|--------------|----------------|
| Cellulose    | 35.1           |
| Hemicellulose| 26.4           |
| Lignin       | 19.7           |

**Table 2. Mechanical and thermal properties of polypropylene.**

| Properties                  | Value                      |
|-----------------------------|----------------------------|
| Molecular weight of repeat unit | 42.08 g/mol               |
| Density                     | 0.90 g/mL at 25 °C        |
| Melting point               | 165 °C                    |
| Hardness                    | 100 (Rockwell R, ASTM D 785-A) |
| Melt flow index             | 1.2 g/min at 230 °C       |

**Table 3. Properties of MAPP.**

| Properties | Value                   |
|------------|-------------------------|
| Composition | Maleic anhydride, 8–10 wt.% |
| Viscosity  | Average Mn –3,900 by GPC  |
|           | Average Mw –9,100 by GPC  |
| Density    | 0.934 g/mL at 25 °C      |
| Molecular weight | 4.0 P at 190 °C           |
| Melting point | 156 °C                   |

Figure 1. SEM image of nypa fiber.
Graft co-polymerization affects the fiber's chemical, thermal, and physical properties. In this approach, a functional group MA (maleic anhydride) that can combine with the cellulose or other natural fiber constituents is grafted to a base polymer that is either the same as or comparable in polarity to the supplied matrix. The grafted system then serves as a bridge, altering both the fiber surface and the polymer to produce a strong attachment between the fiber and the continuous matrix. By activating the copolymer at 170 °C, maleic anhydride interacts with PP and fiber, causing the fiber's surface energy to match that of the matrix, then fiber treatment, and ultimately cellulose fiber esterification [13]. The MA portion of MAPP combines with the OH group of cellulosic fiber, while the PP portion is allowed to co-crystallize with polypropylene that hasn't changed. No specific operation is required for manufacture since malleated coupling agent can be effortlessly coupled with raw materials and extruded while composite fabrication [14]. Mohanty et al. [15] impregnated jute fiber with 0.5% MAPP in toluene, 30% fiber loading, and observed 72.3%, 30% and 24.2% enhancement in flexural, tensile, and interfacial shear strength, respectively.

**Table 4. Material content of discontinuous fiber.**

| % of fiber (V/V) | % of fiber mass (m/m) | % of Polypropylene | % of Chemicals used |
|-----------------|----------------------|--------------------|---------------------|
| 0               | 0                    | 100                | 0                   |
| 30              | 30                   | 70                 | 5% (NaOH)           |
| 30              | 30                   | 70                 | 5% (H₂O₂)           |
| 30              | 30                   | 65                 | 5% (MAPP)           |

**Figure 2.** Relation between tensile strength and cellulose content [35, 36, 37, 38, 39, 40].

**Figure 3.** Relation between Interfacial shear strength and lignin content [41, 42, 43, 44, 45, 46, 47].

\[
y = -0.0001x^3 + 0.016x^2 - 0.5703x^2 + 10.324x - 0.0469
\]

\[
y = -0.0659x^2 + 2.6422x - 0.4163
\]
tensile and impact strength respectively, on the contrary a 61% reduction in moisture absorption. Increasing the concentration from 0.5 to 1% has a negative impact on the composite's mechanical characteristics. For jute and flax fiber, Keener et al. [16] discovered that a concentration of 3 percent MAPP was optimal. When MAPP is used, the mechanical characteristics of the material improve. Han et al. [17] added 1.7% maleic anhydride polyethylene (MAPE) to a bamboo reinforced high density polyethylene (HDPE) composite and saw an enhancement in the tensile strength tensile modulus. Sisal fiber treated with 1% MAPP showed an enhancement in tensile, flexural and impact strength respectively [18]. Lu et al. [19] used 3% MAPE to treat thermomechanical pulp reinforced HDPE and found a 58% rise in tensile strength and an 11% rise in tensile modulus.

By creating a rough surface and lowering the fiber's hydrophilicity, alkali treatment improves fiber matrix adherence. By eliminating lignin, hemicellulose, and other impurities, it also enhances interlocking. Researchers are always attempting to determine the optimal concentration, treatment time, and temperature, as these factors have a significant

Figure 4. Stress vs. Strain curve for nypa fiber reinforced polypropylene composite.

Figure 5. Comparison of Tensile strength of treated and untreated fiber composites.
impact on the treatment. The concentration of NaOH is a critical variable. Sreekala et al. [20] found that the optimal concentrations for mercerization were 5%, 18%, and 10%. Higher concentrations might sometimes lead to a loss of some characteristics. Mishra et al. [21] discovered that sisal fiber-reinforced polyester treated with 5% NaOH had greater tensile properties than sisal fiber-reinforced polyester treated with 10% NaOH. Tensile strength can rapidly fall after a specific concentration due to extreme delignification, resulting in fiber that has been deteriorated. When oil palm fiber was treated with 5%, 10%, and 15% NaOH and used those treated with oil palm fiber to reinforce natural rubber composite. As the concentration of the composite increased, the characteristics of the composite deteriorated [22]. Hassan et al. [23] determine the appropriate mercerization parameter (NaOH concentration, treatment duration, drying time, among others) for bamboo fiber reinforced epoxy composite using the Box-Behnken design. They discovered that 5.81wt% NaOH is the best concentration for mercerization, with a soaking period of 3.99 h and a drying duration of 72 h. The composite has improved tensile characteristics and specific energy absorption capability in this optimum condition. Surface roughness is increased via mercerization, which improves interlocking. Ahad et al. [24], used NaOH concentrations of 5%, 10%, and 15% to treat coconut husk and banana fiber and found that surface impurities and waxes were properly removed and surface unevenness was augmented, which was confirmed using FE-SEM inspection. The fiber’s tensile strength was dramatically lowered when it was wet. Because of the high moisture level, intermolecular hydrogen bonding is weakened. Zikri et al. [25] reported a 50% or more attrition in tensile strength due to the presence of high moisture content, which impairs intermolecular hydrogen bonding. Natural fibers’ mechanical characteristics were also improved via mercerization. Rokbi et al. [26] used NaOH at 1, 5, and 10% concentrations on alfa fibers for 0, 24, and

![Figure 6. Comparison of Young Modulus of treated and untreated fiber composites.](image)

![Figure 7. Elongation at failure of untreated and treated nypa fiber composites.](image)
48 h at 28 °C. When contrasted with fiber composites that have not been treated, mercerized fiber composites have better bending properties. The flexural properties of Alfa fiber treated with 10% NaOH for 24 h improved from 23 MPa to 57 MPa and from 1.16 to 3.04 GPa, respectively. The tensile and flexural properties of flax/epoxy composites were enhanced by 30% and 27%, respectively, after treatment with NaOH [27]. Mechanical properties, rupture modulus, and interfacial bonding were all augmented for mercerized coir fibers [28].

Most of the regular plastic commodities and toys in Bangladesh are prepared using the injection molding process. Fibers are usually flung as a wastage before reaching their end of life. Therefore, some utilities of the fiber still remain unutilized. Incorporation of this fiber may be increasing the properties of the commodities as well as helps to reduce the cost of production which in turn reduce the price of final product. But inclusion of fiber is not an easy task. There are several chemical treatments available. Not all the treatments produce similar results. Some produce some promising results than the others. The main objective of this study is to chemically treat the fibers with locally available chemicals and fabricate composite with different chemically treated fiber. Finally, study the effect of chemical treatment on the mechanical and thermal properties of the nypa fiber composite and proposing the best chemical treatment which will improve the properties with reduced cost from the existing. Therefore, the research gap is mechanical properties of injection molded nypa fiber reinforced polypropylene (PP) and comparison of different chemical modification.

**Figure 8.** Flexural properties for both untreated and treated nypa fiber composites.

**Figure 9.** Impact strength of unnotched samples of both untreated and treated nypa fiber composites.
2. Experimental methods

2.1. Materials

Nypa fronds were collected from Mongla and Khulna district of Bangladesh. Almost 50-piece of 8 m long fronds were collected for fiber extraction. Then they were cut into pieces of suitable sizes. The overall yield of nypa fiber is around 2%. The fiber is tubular in shape. Fiber has a large hollow at the center, as shown in Figure 1. The outer layer consist of three prime constituents of the fiber cell wall. Each cell wall consists of primary and secondary layers of cellulose microfibrils. The outer layer of the fiber consists of some debris and particles. The constituents of nypa fiber (NF) are shown Table 1.

Polypropylene was used as a matrix material, supplied by the Advanced Petrochemical Company. Polypropylene was used as a granule. The granule size was 4–5mm. The properties of the polypropylene are tabulated in Table 2.

2.2. Fiber surface treatment

The structure of natural fiber such that it allows the absorption of moisture which is attributable to its hydrophilic nature. It causes poor

![Rockwell hardness number of both untreated and treated nypa fiber composites.](image1)

![Thermogravimetric analysis (TGA) of both untreated and treated nypa fiber composites.](image2)
interfacial bonding with the polymer matrix and making it difficult to develop strong attachment between constituents of NFC. As a result, fiber surface modification is unavoidable, which usually entails replacing the hydrophilic hydroxyl group with the functional group of certain reagents to improve moisture resistance and bonding between fiber and polymer matrix. Chemicals that are used to alter the surface of fibers have varying degrees of impact on the increase of properties. In this study, three different chemical treatments and their impact on different mechanical and physical characteristics are evaluated.

2.2.1. Mercerization

Mercerization is usually done using NaOH. However, it can also be done with KOH or LiOH. It results in the staving of fiber bundles through fibrillation. Thus, aspect ratio of fiber increases and exposes more reaction sites in cellulose for forming a strong bond with the continuous phase through increased fiber surface wetting and it also removes impurities and non-cellulosic constituents, i.e., potentially reducing the fiber’s hydrophilic nature. Thus, enhance the interlocking with the matrix.

NaOH Pellets were collected from Taj scientific store, Chittagong, Bangladesh. 5% w/v NaOH solution was prepared. At first, 5 g of NaOH pellets were taken in the jar, then a little amount of distilled water was added to the pellets, so that all the pallets remain submerged in the water. NaOH pellets are soluble in water. When all pellets are dissolved in water, then extra water is added in the solution to the total volume of solution 100 ml.

Figure 12. Thermogravimetric analysis DTG of both untreated and treated nypa fiber composites.

Figure 13. Differential Scanning Calorimetry curve (DTG) both untreated and treated nypa fiber composite.
After preparing the solution, the fibers were fully submerged in solution for 4 h. The elimination of impurities and lignin from the fibers resulted in the solution taking on a dark brownish color when the treatment was completed. The fibers were extensively rinsed with distilled water after the treatment four times until the residue NaOH is eliminated from the fiber surface and pH was continuously monitored with pH strip until pH 7 was achieved. The treated fiber was again oven dried for 48 h so that no moisture remains in the fiber.

### 2.2.2. MAPP coupling agent

As a coupling agent, Sigma-Aldrich’s MAPP was used. MA reacts with cellulose or other fiber components grafted onto base polymers. By altering both the fiber surface and the polymeric matrix, this treatment increases interfacial adhesion between the fiber and the matrix. 5% MAPP was blended with the fiber and matrix before they were fed onto the hopper for fabrication.

The properties of MAPP as given by the supplier are shown in Table 3.

### 2.2.3. Hydrogen peroxide treatment

50% hydrogen peroxide solution was collected from Taj scientific, Chittagong, Bangladesh. Fibers were treated with 5% hydrogen peroxide solution in an alkaline medium at 80 °C for 1 h. First of all, 5% NaOH solution was prepared using NaOH pellets. After that, 5% NaOH solution was added to the 20% solution of hydrogen peroxide until pH of 11 is achieved. Fibers were submerged in hydrogen peroxide solution for 1 h. The fibers were then dried in the oven at 60 °C for 48 h.

H₂O₂ causes fiber discoloration since it is an oxidizing agent and it also improves the composite's physical appearance. The dissociation of the perhydroxyl ion, which occurs most frequently under alkaline conditions, is what causes H₂O₂ to bleach.

### 2.3. Fabrication

In a composite fabrication, the critical length of the fiber plays an important role. In order for ultimate stress to build in the fibers of a well-oriented short fiber composite, a critical length of fiber (l_c) is required. Otherwise, failure will occur at the interface of constituents rather than in the fiber.

A linear stress transfer from the tip of the fiber to maximum value was proposed by Kelly and Tyson when the fiber strain is equal to the strain of the matrix [30]. The critical length of the fiber can be derived from Eq. (1), considering constant IFSS and by balancing the shear and tensile stress of the fiber and composite:

\[ l_c = \frac{\sigma_{fu}}{2\tau} \]  

(1)

Where \( l_c \) is the critical length, \( d_f \) is the fiber diameter, \( \sigma_{fu} \) is the fiber ultimate strength and \( \tau \) is the interfacial shear stress (IFSS).

Therefore, the critical fiber length largely depends on the fiber ultimate strength, IFSS and fiber diameter. Critical length of the fiber is not often equal to the length of the fiber. It can be seen from the equation that \( l_c \) can be reduced by ameliorated IFSS, by reducing the fiber strength or by implementing smaller diameter fiber.

Ultimate strength of the fiber was determined by some relation from literature. Since tensile strength of the fiber depends on the

| Composite      | Onset temperature (°C) | Endset Temperature (°C) | Melting Temperature (°C) | Enthalpy (J/kg·K) |
|----------------|------------------------|-------------------------|--------------------------|-------------------|
| Polypropylene  | 159                    | 185                     | 175                      | 102.15            |
| Untreated      | 148                    | 176                     | 165                      | 79.75             |
| NaOH treated   | 149                    | 178                     | 170                      | 96.52             |
| H₂O₂ treated   | 153                    | 186                     | 165                      | 82.64             |
| MAPP treated   | 154                    | 188                     | 170                      | 96.88             |

| Composites     | N          | k          |
|----------------|------------|------------|
| Untreated fiber| 0.207      | 0.356      |
| NaOH treated   | 0.197      | 0.386      |
| H₂O₂ treated   | 0.201      | 0.368      |
| MAPP treated   | 0.213      | 0.348      |
cellulose, higher the cellulose content higher the tensile strength. Figure 2. In addition, IFSS depends on the amount of lignin contents, depicted in Figure 3. Using these two relations, the IFSS and tensile strength was determined for calculation of critical fiber length.

The cellulose content of nypa fiber frond is 35.1% [29]. Using the equation mentioned in Figure 2, it is found that the tensile strength of nypa fiber is 200 MPa (approximately). Nypa fiber contains 19.7 wt% lignin [29]. The value of interfacial strength is obtained 26.05 MPa. The average diameter of the fiber extracted from nypa frond is approximately 590–600 μm. With the tensile strength, interfacial strength and diameter of the NF the critical length is found 2.26 mm. Therefore, the fiber length in the NF composite should be greater than or equal to 2.26 mm for efficient transfer of stress from continuous phase to reinforcement. In this experiment, fiber length was kept between 3mm to 5 mm.

To assess the effects of different chemical treatments on fiber, all samples must have a fixed fiber volume. 30% fiber volume was selected for nypa fibers as it gives better properties from other fiber volume. The density of nypa fiber is 1 g/cc [7]. The density of polypropylene is 0.92 g/cc. The percentage of chemicals used is shown in Table 4. The mass of the fiber was determined from Eq. (2),

Figure 15. Water absorption curve for untreated and treated nypa fiber composites.

Figure 16. Theoretical and experimental water absorption of untreated fiber composite.
% of $m = \frac{\rho_f V_f}{\rho_m (1 - V_f) + \rho_f V_f} \times 100 \quad (2)$

The Kawaguchi brand model of KX 140 injection molding machine was used to prepare the specimen. The composites were expelled and suitably cooled when the injection molding process was completed. The items are then cut into specimens for the testing. The thickness of the specimens is flexible under the ASTM standard.

The injection parameters used for the production of the samples are given below:

- Injection Pressure (maximum): 100 Bar
- Injection time: 8 s
- Mold Pressure: 70 bar
- Injection Temperature: 180 °C
- Back Pressure: 25 Bar
- Screw Rotation: 185 rpm

Higher injection time is required because a higher volume of fiber creates obstruction of flow of metal from barrel to mold cavity through sprue.

3. Mechanical, thermal and water absorption properties characterization

3.1. Tensile test

The tensile test of the four NaOH treated fiber composite, $H_2O_2$ treated composite, MAPP treated composite, Untreated fiber composite and PP was performed in Shimadzu Tensile tester. The capacity of the
In this uniaxial test, the jaw speed was $50 \text{ mm/min}$ which gives strain rate of $0.0106 \text{s}^{-1}$.

### 3.2. Flexural test

In this experiment, a three-point bending tester was utilized to assess the composite’s flexural strength. The ASTM standard ASTM D790 was implemented to prepare the specimen. In the experiment, the specimen was treated like a beam. The test was performed in a Shimadzu tensile tester of 500 kgf capacity. The jaw speed was 75 mm/min and the distance between the two supports was 65 mm. The specimen was supported at two points and the force was exerted the mid-point. Then, using the necessary equations, flexural properties were computed from the exerted force and geometric characteristic.

### 3.3. Impact toughness

The impact test was performed in this experiment using a simple pendulum hammer impact tester in accordance with ASTM D256. The mass of the hammer is 2.5 kg and the radius is 0.345 m.

### 3.4. Hardness

In this study, Rockwell hardness test was done as it is more accurate than the others. The test was done with L scale where a major load of 60 kg was applied. The test was done according to the ASTM standards (ASTM D785). The major load was applied for 30 s to each sample.

### 3.5. Thermogravimetric analysis

A NETZSCH STA 449 F3 thermal analyzer was used to conduct the test in a N2 environment. TGA was carried out at a heat rate of $0.189 \text{ C/s}$ or $11 \text{ C/min}$, with each step increasing the temperature by $5 \text{ C}$ from ambient to $600 \text{ C}$. At each phase, the remaining mass was measured.

### 3.6. Differential Scanning Calorimetry

DSC is a thermo-analytical technique for determining physical or chemical changes in a substance with temperature. The NETZSCH STA 449 F3 thermal analyzer was used and the endothermic peak of DSC was analyzed with each step increasing the temperature by $5 \text{ C}$ from $30 \text{ C}$ to $300 \text{ C}$ with a heat rate of $0.184 \text{ C/s}$ or $11 \text{ C/min}$ in N2/N2 atmosphere.

### 3.7. Water absorption test

Water absorption test is usually performed by submerging the sample in water until saturation is not reached. For water absorption test, the samples were first dried at $60 \text{ C}$ for 6 h. After that, the samples are brought at room temperature until they achieve a steady-state temperature. The samples are immediately immersed in room-temperature clean water. The dry weights were recorded for calculations. The samples were taken from the water at regular intervals and cleaned with a towel. The weight gained because of moisture absorption at regular interval is recorded. It usually takes some time to reach the saturation.

### 3.8. Field emission scanning electron microscope images of samples

The SEM images of different samples are taken using ZEISS SIGMA 300 Field emission scanning electron microscope. The images are taken at different magnification for observing the effects of chemical treatment on fiber clearly and verify the properties obtained for different treatments.

### 4. Results and discussion

#### 4.1. Tensile properties

The stress-strain diagram for nypa fiber composite with different chemical treatment and polypropylene is depicted in Figure 4. Polypropylene shows greater ductility than all other composites, which verifies that fiber enhanced the stiffness of the composites. The untreated fiber composite has a lower ultimate strength and young modulus than other composites, which could be because of inadequate fiber-to-matrix bonding. Stress is usually transferred from a continuous phase to the fiber. The composite’s tensile strength is weak because of poor stress transfer from the matrix to the fiber because of improper matrix bonding. Fiber that has not been treated behaves as a void, concentrating stress rather than enhancing tensile properties. The ultimate tensile strength of
the untreated composite is about 11.90% less than the strength of the virgin PP.

The tensile strength of the NaOH is slightly higher than the virgin polypropylene. It is because NaOH removes the hydroxyl group, thereby reducing hydrophilic nature of the composite. It also creates rough surfaces which help mechanical interlocking of fiber with the matrix, which in turn results in better mechanical properties. NaOH would have improved the properties better than what is achieved. The reason behind not getting the expected result may be because the time of treatment was not optimum. As a result, some damage to the fiber may occur. The NaOH treated composite has a 13.95% higher ultimate tensile strength than the untreated fiber composite, which could be related to the elimination of hemicellulose and lignin, which exposes more reaction sites for matrix in cellulose. Similarly, because of the rough surface created by hydrogen peroxide treatment, better tensile properties were observed. The tensile characteristics of the hydrogen peroxide-treated material are 17% better than the untreated material. The maximum tensile strength was observed in the case of MAPP treated composite, which is about 22.11% greater.

Figure 20. FE-SEM image of Untreated Fiber surface (a) 500X (b) 1000X and (c) 2000X.

Figure 21. FE-SEM image of H$_2$O$_2$ treated Fiber surface (a) 500X (b) 1000X and (c) 2000X.
than the untreated composite. MAPP acts as a bridge between the fiber and the matrix for chemical bonding of the fiber and matrix. One part of MAPP reacts with the hydrophilic fiber and the other parts copolymerize with the polymer. Thereby, a good fiber matrix bonding is established between the fiber and matrix.

The ultimate strength of the samples was observed before 5% elongation. Pure PP has showed the maximum toughness or maximum absorbed energy at a specified volume. These results indicates that treatment of fiber before using in natural fiber composite is vital. Without chemical modification of the fiber surface, it would result in a decrease in mechanical properties rather than increasing. Figures 5, 6, and 7 show the ultimate tensile strength, modulus of elasticity, and elongation at failure calculated from curves.

4.2. Flexural properties

As shown in Figure 8, the flexural properties of the treated fiber are increased in case of treated fiber composite. This is because the fiber and matrix have a stronger interfacial bonding. The MAPP treated composite
has the highest flexural strength of the three. Flexural modulus is also maximum for MAPP treated composite. This could be related to a reduction in the hydroxyl group in the natural fiber, which is responsible for the natural fiber’s hydrophilicity. Since hydroxyl groups of the fiber are reduced, fiber becomes more compatible with the continuous phase. MAPP, NaOH, and H2O2 treated composites had flexural strengths that are 36.73%, 7.66%, and 16% higher than untreated fiber composites, demonstrating the importance of fiber surface modification before use in structural components. Both in the case of tensile and flexural characteristics, the treated fiber showed enhanced properties due to enhanced attraction between fiber and matrix. All samples have shown higher flexural strength than the tensile strength.

4.3. Impact strength

The average of the impact toughness is shown below in Figure 9. In general, the addition of fiber in the polypropylene matrix reduced the impact toughness of the composite. Usually, natural fibers have a higher modulus than the thermoplastic modulus matrix. Because the fibers are
unable to absorb enough energy to promote toughening, it tends to offer a site of stress concentration in the matrix rather than increasing toughness. They lack a large surface area for fracture redirection, and as a result, they tend to behave as crack initiators rather as energy absorption diversions. Because there is no interfacial attraction in untreated fibers, the area occupied by the fiber functions as a void, resulting in low-impact strength. The time of treatment may not be the optimum one, which may be the cause of NaOH having lower strength than that of the untreated. Therefore, damages in the fiber occur which in turn responsible for low-impact strength in the case of mercerized fiber composite. Due to improved interfacial attraction, the other two treatments, H₂O₂ and MAPP showed gradual improvement. Though, they are still below the impact toughness of the virgin PP.

4.4. Hardness

The average hardness number of different composite are depicted in Figure 10. The hardness of the composite decreased when untreated fiber
was added into the composite. Conversely, hardness, though negligible but increased with treated fiber. The maximum hardness was achieved for MAPP treated fiber composite, which may be due to good compatibilization of the fiber with the matrix due to the application of MAPP as an additive to ameliorate fiber matrix adhesion in composite. So, it can be concluded that fiber treatment slightly improves the hardness of the composite and it depends on the proper distribution of fiber. As hardness is a surface property which usually express the resistance to penetration provided by the surface. As volume of the PP is much more than the fibers, the surface of the composite is mostly covered with PP. Therefore, negligible difference in hardness was observed.

4.5. Thermogravimetric analysis (TGA)

The TGA and DTG curves for polypropylene, untreated fiber, untreated fiber composite, NaOH treated composite, H2O2 treated composite, MAPP treated composite are illustrated in Figures 11 and 12. The
temperature increments, it lost around 59% more of its weight when the temperature reaches at 440 °C. At higher temperatures, fiber outperforms composites in terms of thermal stability. All the composites’ losses their weight significantly between temperature range 330 °C–490 °C. This indicates reinforcing PP with natural fibers enhances the thermal stability of the composite. The H₂O₂ treated fiber composite and MAPP treated fiber composite showed better thermal stability than the other two, which may be due to better interaction of fiber with composite. Because of fiber breakdown, the NaOH-treated fiber composite had lower thermal stability than the others.

There were some unusual weight gains in the case of H₂O₂ and MAPP treated samples. Buoyancy effects are created by the surrounding gas's density decreasing as it heats up. In most cases, this results in a weight gain. The measurement curve can also be affected by fluctuations in the purge gas flow rate.

The DTG curves are usually used for a better interpretation of the TGA curve. From TGA curve, it is difficult to measure the precise temperature at which the highest weight loss usually occurs. The picks of DTG indicates the temperature at which maximum rate of weight losses occurs. The untreated fiber was degraded in three stages. The evaporation of water contained in the NF filler contributed to early weight loss, while the temperature ranged from 35 to 115 °C. The decomposition of hemicelluloses in untreated fiber was assigned to the second peak in the temperature range of 205–300 °C, while the decomposition of cellulose and lignin was attributed to the third peak in the temperature range of 320–400 °C. The higher degradation temperature indicates that cellulose has high thermal stability than the other components. The other degradation picks are at 445 °C, 450 °C, 455 °C for NaOH, MAPP, untreated and H₂O₂ treated fiber composites. Because of improved inter-facial bonding and greater dispersion between the natural fiber and polypropylene matrix, treated nypa/PP bio composites had higher thermal stability than untreated nypa/PP bio composites.

4.6. Differential Scanning Calorimetry

The DSC curve and specific heat capacity curve for different samples are shown in Figures 13 and 14. The DSC data of untreated and chemically treated composites are summarized in Table 6. Figure 13 indicates all the composite follow similar trend with single endothermic peak. The peak represents the melting of the composite.

From Table 5, it is evident that the melting peak for polypropylene is higher than other composites. The melting temperature of the composite was not changed significantly due to the addition was natural fiber both treated and untreated. The onset temperature was determined by drawing a tangent to the DSC curve's starting slop that intersected the base line. The end set temperature was derived from the final slope in the same way. The MAPP and NaOH treated fiber composites had the highest heat capacity, which could be attributable to the fibers’ strong interaction with the matrix.

4.7. Water absorption test

The water absorption vs square root of time plot is shown in Figures 15, 16, 17, 18, and 19. The moisture absorption rate is higher at the initial stage of the test, which becomes saturated after a few days of test. Since it absorbs most of the moisture at the early stage, the initial slope is therefore higher in all the samples. To minimize the degree of the curves, the% of water absorption vs. the square root of soak time is shown. Because of its hydrophobic nature, PP had the lowest water absorption of the five samples. Untreated fiber absorbs more water than the other samples, which could be related to the presence of hydroxyl groups in the fiber. All the other samples show almost a similar amount of water absorption. NaOH showed better moisture resistance than the other two due to the removal of the hydroxyl group, which is responsible for the hydrophilicity of natural fibers. All the composites become almost saturated after 10 days of submersion.
Three factors are responsible for transporting water molecules to composites [44].

- Water molecules spread in the microscale space between one polymer chain or fiber.
- Water is transported by the capillary effect at the fiber-matrix contact due to gaps and defects.
- An imperfect compounding process results in cavities and micro-fissures in the matrix, which allow water to diffuse.

Eq. (3) or 4 distinguishes the absorption curve for these three reasons conceptually [44],

\[
\frac{M}{M_\infty} = k t^n \quad (3)
\]

\[
\log \frac{M}{M_\infty} = n \log t + \log k \quad (4)
\]

where,

Figure 31. Comparison of Tensile Strength and Young Modulus of coir and nypa fiber composite.

Figure 32. Comparison of Flexural Strength and Flexural Modulus of coir and nypa fiber composite.
\[ M_t = \text{Mass of moisture absorbed at time } t, \quad M_\infty = \text{Mass of moisture absorbed at saturated condition}, \quad k = \text{Constant}, \quad n = \text{Constant which } < 1, \quad t = \text{submersion time.} \]

These water absorption coefficients are calculated by fitting the experimental results to a curve. The co-efficient \( n \) and \( k \) for different chemically treated sample are listed in Table 6.

The comparison of experimental and theoretical moisture resistance of different sample is shown in Figures 16, 17, 18, and 19. There was slight difference in the experimental and theoretical water absorption rate. Though, at the initial stage the both the data follow approximately similar trend. But a large difference is observed in the final phase of water absorption.

4.8. Field emission scanning electron microscope images of samples

The FE-SEM image of untreated fiber surface is depicted in figure 20 (a-c) at different magnification. Uneven fiber surface is observed in the untreated fiber. Some impurities such as waxes and debris are also observed in untreated fiber surface. The FE-SEM image of H_2O_2 treated fiber surface is depicted in figure 21 (a-c) at different magnification. The
impurities which were observed in untreated fiber surface was removed. A rough surface was created to facilitate fiber–matrix mechanical interlocking. The FE-SEM image of NaOH treated fiber surface is depicted in Figure 22 (a–c) at different magnification. The impurities which were observed in untreated fiber surface was removed. A rough surface was generated which promotes better fiber–matrix mechanical interlocking. Some voids are also observed, which may be an indication of fiber surface degradation due to long treatment time.

The FE-SEM image of untreated fiber composite is depicted in Figure 23 (a–c) at different magnification. Poor attraction between fiber and matrix was observed in the untreated fiber composite. Some voids are also seen. The FE-SEM image of NaOH treated fiber composite is depicted in Figure 24 (a–c) at different magnification. Good fiber matrix bonding was observed in NaOH treated fiber composite, which results in better properties than the untreated one. The FE-SEM image of H₂O₂ treated fiber composite is depicted in Figure 25 (a–c) at different magnification. Good interfacial bonding between the fiber and the matrix is evident. The good interfacial bonding is a prerequisite for better mechanical properties. The FE-SEM image of MAPP treated fiber composite is depicted in Figure 26 (a–c) at different magnification. The inclusion of MAPP, which provides a link between the fiber and the polymer matrix, results in good interfacial attachment between the reinforcement and the continuous phase. Better mechanical properties are the result of good interfacial bonding.

The FE-SEM image of tensile fractured untreated fiber composite are depicted in Figure 27 (a–c) at different magnification. The lumen of the fiber was clearly visible. A large gap was remained between fiber and matrix interface which indicates untreated fiber has poor attraction towards the polymer matrix due to its hydrophilic nature. The resulting poor properties than the other composite can also be verified from the FE-SEM image. The FE-SEM image of tensile fractured NaOH treated fiber composite are depicted in Figure 28 (a–c) at different magnification. The poor bonding between fiber and matrix is usually identified by matrix yielding or fiber debonding but these two phenomena was not observed in case of NaOH treated fiber composite. Rather fibers were teared which is an indication of good fiber matrix attraction and good mechanical properties. The FE-SEM image of tensile fractured MAPP treated fiber composite are depicted in Figure 29 (a–c) at different magnification. Similar to NaOH treated fiber good interfacial bonding is observed in MAPP treated fiber composite. The FE-SEM image of tensile fractured H₂O₂ treated fiber composite are depicted in Figure 30 (a–c) at different magnification. Fiber fracture as the failure mode of the composite was observed which indicates good interfacial bonding as well as good mechanical properties.

5. Comparison with coir fiber polypropylene composite

The property of the composite largely depends on the constituents of fiber. Specifically, the cellulose content of the fiber. Therefore, composite those having similar cellulose percentage or little less or much less than the nypa would be a good choice for comparison. Coir fiber has cellulose percent around 36–43% and density is around 1.2 g/cm³ [45] which closely resembles the percentage of the nypa fiber. Therefore, coir fiber would be a great choice for comparison. A study of injection molded coir fiber PP composite was done by Arrakhiz et al. [46]. In that study different percentage of coir, Alfa and bagasse fiber reinforced was prepared and tested. From those, only the properties of coir are chosen for comparison Figure 31.

30% coir fiber volume is used in coir PP composite. From Figure 31 it is evident that nypa fiber treated with different chemical gives better tensile property than the coir fiber PP composite. Though, the young modulus of the treated composite was less than that of coir PP composite, which probably due to individual coir fiber has higher modulus of elasticity than the nypa fiber. The maximum strength which was got in case of MAPP treated fiber is approximately 25% higher than the coir PP composite.

The trend observed in Figure 32 for flexural properties is also analogous to that of the tensile properties. The properties exhibited by the treated nypa fiber composite were higher than the coir PP composite. The flexural properties of the MAPP treated fiber were maximum among all. The flexural strength was 23% higher than the coir fiber composite, which may be due to the strong interfacial bonding between fiber and matrix.

The mechanical properties for different fiber loading of coir/PP composite were studied by Zaman et al. [47]. It was observed that impact strength was increased with the increasing fiber content. A comparison of impact strength is depicted in Figure 33. The impact strength of coir PP composite is little higher than the treated nypa fiber composites. The probable reason for this was that coir fiber absorbs much more energy than the nypa fiber and another reason may be due to high percentage of lignin in coir fiber compared to nypa fiber as lignin gives rigidity to plants.

The moisture resistance characteristic of coir fiber at different fiber loading was depicted in Figure 37. It is evident from Figure 34 that the moisture absorption of 30% coir fiber composite is almost 2% whereas in our present study the water absorption of all the treated samples were almost equal or less than 1% which may be due to the removal of hydroxyl group from the fiber with different chemical treatment.

6. Discussion and conclusion

The use of NFC is still limited only because of their inherent hydrophilicity, which makes them less compatible with the polymer matrix. Various physical or mechanical approach was tried to enhance the interfacial bonding of fiber with matrix. Some of them have produced very promising results and chemical treatment of fiber to make it hydrophobic has a great impact on the properties of the composite. Various chemical treatment results in a different level of improvements in the mechanical properties of the composite. The MAPP treated composite had the highest tensile and flexural strength among all the treatments and untreated composites. NaOH and hydrogen peroxide usually create a rough surface which promotes mechanical interlocking. On the contrary, MAPP creates chemical bonds with fiber and the matrix, which provides much better bonding, i.e., better properties than the other two. The tensile and flexural characteristics of untreated fiber composites were reduced, which was attributable to the fiber's incompatibility with the polymer matrix. The composite's young modulus was trending in the same direction as its tensile characteristics. The impact strength of all the composite was lower than the impact strength of the polypropylene, which may be due to the agglomeration of fibers due to the hydrogen bonding. The increase in hardness number is negligible. Better hardness was observed where fiber was distributed properly. Since the matrix covers the surface of the all, the samples therefore the difference observed was negligible. The thermal stability of the composite was increased, and it was intermediate between the PP and fibers in most the case. The melting temperature was reduced due to the addition of fibers, which may be due to the decrease in crystallinity of the composite. The treated composites showed a significant reduction in moisture absorption, which could be attributed to the fiber's hydrophilic hydroxyl group being removed. The FESEM images of the fractured sample confirm the improvement of properties of the treated composite. MAPP gives better properties than the other treatments as it forms chemical bonds with fiber and the matrix, while other treatments usually create a rough surface which promotes mechanical interlocking. The nypa fiber composite can be used in various applications, except where high impact strength is required. This can be used in automobile dashboard, door panels, packaging boxes, floor panels of automobile and furniture. Adding fibers to the injection molded product would reduce the cost of the product as well as consumption of plastics. Reduced consumption of plastics is nowadays a prime concern of any countries, therefore incorporating the fibers with the chemical treatment that provides augmented bonding will be a great contribution to the environment with minimal plastic consumption.

7. Recommendations

Based on the experiments and results following recommendation can be made:
Various treatments of fiber should be assessed with some biodegradable matrix, such as PLA (Poly-Lactic acid) and vitrimers.

Hybridization can be done by focusing on specific property of the composite. The treatment of fibers can be done with other chemicals as well. Treating fibers with those chemicals, a more detailed comparison can be developed.

Declarations

Author contribution statement

Afnan Hasan: Perform the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

Md. Sanaul Rabbi: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data.

Md. Abdul Hasib: Contributed reagents, materials, analysis tools or data.

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Additional information

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