Study of the surfactants role in natural fibres reinforced composites for structural applications

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Abstract. In this study, hemp fibres were used as reinforcements in polypropylene (PP) resin to form composite materials for structural applications. Adhesion between the fillers and holding matrix was enhanced using alkalisation, KMnO4 treatments respectively on the fibre surface thus developed. Spectroscopic analysis such as Fourier transforms infrared (FTIR) and scanning electron microscope (SEM) was carried out to determine interferential adhesion and homogeneous distribution of fibres in the holding matrix. Based on the results obtained fibres treated with both NaOH and KMnO4 treatment showed better mechanical properties than the treatments done in isolation. Among the results obtained fibres specifically treated with specific composition of 5% NaOH and 0.6% KMnO4 exhibited better mechanical properties compared to those with treated and untreated fibre composite samples.

Keywords: Hemp fibres, Sodium hydroxide (NaOH) treatment, Potassium permanganate (KMnO4) treatment, Poly propylene (PP), FTIR, SEM.

1. Introduction:
With increasing universal population, ecological complications are becoming more and more problematic. Rapid economic development of a country to meet increased societal needs has led to severe environmental problems. This has necessitated search for novel eco-friendly materials that are renewable in nature and the need to adopt innovative technologies facilitating use of such materials [1]. A composite material is a material that is made from two or more constituent materials with significantly dissimilar physical or chemical properties that, when combined, produce a material with characteristics different from the individual components. The individual components when used remain separate and distinct within the finished structure. The new material that is stronger, lighter or less expensive when compared to traditional materials can address the problems adequately [2].

Fibre is a natural or manmade substance that is considerably longer than its width. Fibres are often used in the manufacturing of other materials [3]. There are two kinds of fibres: natural fibres and
manmade fibres. Several researchers have studied composites based on these fibres [4, 5]. Because of
the outstanding properties and superior advantages of natural fibre over synthetic fibres in terms of
lower weight, lower price, good mechanical properties such as flexural modulus and tensile modulus,
better surface finish of moulded parts, lower density, unlimited availability, recyclability, biodegradability and minimal health hazards they are more preferred in various structural applications
[6-12]. Natural fibres reinforced polymer composites find different locomotive applications by several
locomotive corporations such as Cambridge industry (an auto industry in USA) and German auto
companies (Audi Group, Volkswagen, BMW, Ford, Daimler Chrysler, and Benz). In addition, they
find application in building and construction, packaging, sports, aerospace industries. Vehicle interior
parts such as door trim panels made from natural fibre-polypropylene (PP) and exterior parts such as
engine and transmission covers from natural fibre-polyester resins are already into use [13,14]. Some
of the complications related with natural fibre-reinforced composites include poor interfacial bonding
between the cellulose fibres and the thermoplastic matrix, limited thermal stability of the composites
and poor fibre separation and dispersion within the composites developed [15]. From the exhaust
literature survey undertaken on the utilization of natural fibres as fillers treated with different
chemicals it is found that limited work on KMnO₄ treated fibres in PP has been investigated with
respect to strength aspects of the composites for structural applications. The main objective of the
present work is to develop novel PP composites reinforced with NaOH and KMnO₄ treated hemp
fibres and to study their suitability for structural applications.

2. Materials and Method adopted:
Poly propylene composites were developed with treated and untreated filler materials as
reinforcements. The material used in the preparation of natural fibre composites were hemp fibre,
Sodium hydroxide (NaOH), Potassium permanganate(KMnO₄), distilled water, PH paper, Polypropylene (PP) and Acetic acid respectively.
Hemp used in the study was procured from the Canada. Table1 show the chemical composition of the
hemp fibre which influences the characteristic of the composites developed. Figure 1 shows the hemp
fibre. Fibres of length 2000 mm in length were chopped to 5mm by fibre chopping machine. Table 2
shows the nomenclature of the test specimens used in the study.

Table 1. Chemical composition of hemp fibres

| Pectin | Cellulose | Waxes and oils | Hemicelluloses | Lignin |
|--------|-----------|---------------|---------------|--------|
| 0.88%  | 76.34%    | 2.4%          | 17.88%        | 2.16%  |

Figure 1. Hemp fibre

Table 2. Nomenclature of the test specimens
| SL.NO | Weight %      | Nomenclature of the test specimen |
|-------|--------------|----------------------------------|
| 1     | Untreated fibre | UF                               |
| 2     | 3% NaOH       | S1                               |
| 3     | 5% NaOH       | S2                               |
| 4     | 7% NaOH       | S3                               |
| 5     | 0.3% KMnO₄    | P1                               |
| 6     | 0.6% KMnO₄    | P2                               |
| 7     | 0.9% KMnO₄    | P3                               |

2.1 Surface treatment:
This section explains the method on chemical treatment of hemp fibres used as fillers in the polymer based composites.

(a) Alkali (NaOH) Treatment:
In order to enhance the strength of the fibres alkali treatment was carried out using sodium hydroxide (NaOH). Alkali treatment was carried out with varied concentration levels viz, 3, 5 and 7% by weight of fibres. The fibres were soaked in the sodium hydroxide solution for two hours and were washed with 2% acetic acid and distilled water until its pH value reaches to 7. The soaked fibres were then dried in hot air oven at 60°C for 24 hours in order to remove moisture. The composites were prepared by adding 20% of fibre to the weight of resin used. In order to check the efficiency of treatment method on composites untreated natural fibre reinforced composites were prepared as control beams. Six specimens were prepared for each composition considered. Tensile tests were carried out in Universal testing machine (UTM).

(b) Potassium permanganate (KMnO₄) treatment
Potassium permanganate (KMnO₄) was used as surfactant at varying concentration levels. Among the alkali treated specimen S2 has given optimum results. The S2 specimen were further soaked in acetone and KMnO₄ solution for 3 minutes which were dried in hot air oven for a period of 24 hours at 60°C in order to remove the moisture. All the specimens were prepared keeping the concentration level of fibres at 20% by weight of resin. Specimen was prepared by varying the concentration levels of KMnO₄ viz., 0.3, 0.6, and 0.9% by weight of fibres. Six specimen were prepared for this same composition and averaged out readings on the results obtained are plotted for the result analysis. Tensile tests were carried out using Universal testing machine (UTM).

2.2 Experimental methods
For the preparation of the composites the fillers used were chopped into 2-3 millimetre in length by fibre chopping machine. Fibres along with polypropylene are melted in the furnace and the resulting blended mixture was then added to injection moulding machine. The consequent injecting operation was carried out at 220°C and a pressure of 1.5 MPa for 12-15 minutes. The mould was removed from the injection moulding machine and allowed to cool down at room temperature. The volume fraction of fibres was kept fixed at 20% for all the composites developed. The tensile test was performed as per ASTM norms D3039. The natural fibre reinforced composites reinforced with treated and untreated fibres was subjected to tensile loading in a Universal Testing Machine (UTM) of capacity 750 kgf load cell at a crosshead speed of 3 mm/min at room temperature.

3. Results and Discussion:
The following section presents the mechanical properties of the composites reinforced with NaOH and KMnO₄ treated hemp fibres and the analysis of the results as well. In the first phase the fibres were treated with NaOH followed by KMnO₄.
Table 3 shows the ultimate load carrying capacity and tensile strength of untreated and alkali treated Hemp fibre reinforced composites. From the table it follows that with increased NaOH concentration used for fibre treatment, the load carrying capacity of the specimens increased. However further increase in NaOH concentration beyond certain limit resulted in decreased tensile and ultimate load carrying capacity. The reason for this trend could be attributed to the fact that beyond 5% alkali treatment the fibres tend to coagulate leading to reduced fibre waviness which enhances the brittleness of the specimens.

| Sl no | Nomenclature of testing specimen | Ultimate load in kN | Tensile strength in kN/mm² |
|-------|----------------------------------|---------------------|---------------------------|
| 1     | UF                               | 0.425               | 0.01048                   |
| 2     | S1                               | 0.4133              | 0.0102                    |
| 3     | S2                               | 0.48                | 0.0118                    |
| 4     | S3                               | 0.36                | 0.024                     |

The ultimate load and tensile strengths of the hemp fibre-reinforced PP composites are shown in Figure 2(a) and (b) respectively. The tensile strength and ultimate load of the UF control composites were found to be 0.01048 and 0.425 kN/mm² respectively. After alkali treatment, the tensile strength and ultimate load of composites increased and were higher than the UF composites. The reasons for enhanced load carrying capacity of the alkali treated specimen could be attributed to the removal of excess lignin and pectin of the natural fibre leading to enhanced waviness and load bearing ability. Figure the Figure 2(a) it follows that the S2 composite demonstrated the highest tensile and ultimate load values. Further increasing the NaOH chemical treatment has no bearing on the mechanical properties and accordingly S3 composites showed decreased performance when compared to S2.

Figure 2 (a). Ultimate load of NaOH treated fibre reinforced composites
In the second phase the optimized percentage of NaOH treated fibres used as fillers in the composites were further treated with KMnO$_4$ and its combined effect on the mechanical properties of the developed composites are presented below. Table 4 shows the ultimate load and tensile strength of potassium permanganate (KMnO$_4$) treated hemp fibre reinforced composites. This treatment enhanced the chemical interlocking at the interface of the fibre and provided better adhesion with the matrix. When the potassium permanganate concentration was increased, the load bearing ability of the specimen increased to a certain extent and beyond 0.6% a detrimental effect on the strength of composites was observed. In case of P2 composites the presence of metal traces from KMnO$_4$ such as K and Mn has shifted the polymer to metallo-polymer systems further leading to enhanced ductility as ductility is the inherent property of the metal component. Increasing the KMnO$_4$ beyond certain limit has led to decreased strength in the specimen. Accordingly, P3 composites have shown reduced mechanical properties due to higher reinforcement proportion of the metal traces as well as rigidity of natural fibres which will break the polymer chain mobility enhancing the brittleness of the specimen.

Table 4. KMnO$_4$ treated fibre reinforced composites

| Sl no | KMnO$_4$ treated | Ultimate load in kN | Tensile strength in kN/mm$^2$ |
|-------|------------------|---------------------|------------------------------|
| 1     | P1               | 0.79                | 0.019                        |
| 2     | P2               | 0.81                | 0.0205                       |
| 3     | P3               | 0.673               | 0.0166                       |

From the two different surface treatments carried out it is found that KMnO$_4$ showed optimum results as compared to the alkali treatment as depicted in figures 3 (a) and (b). Among the KMnO$_4$ treated composites P2 demonstrated good mechanical properties as compared to P1 and P3 respectively.
Table 5 and Figure 4 show the comparison on ultimate load between treated and untreated fibre reinforced composites using two different surface treatments. When compared to the untreated fibre the alkali treatment showed an increase in the ultimate load of the composites by 12.94% while potassium permanganate treatment increased ultimate load by 90.58%.
Table 5. Ultimate load comparison of treated and untreated fibres

| Sl no | Comparison                                | % increase in Ultimate load |
|-------|-------------------------------------------|-----------------------------|
| 1     | NaOH compared with untreated fibre        | 12.94                       |
| 2     | KMnO4 compared with untreated fibre       | 90.58                       |

Similarly, Table 6 and Figure 5 shows the tensile strength comparison between treated and untreated fibre reinforced composites. When compared to the untreated fibre reinforced composite alkali treatment showed increased tensile strength of the composites by 12.59% while the potassium permanganate treatment showed increased tensile strength by 95.61%. Figures 6 and 7 shows the SEM images of the composites reinforced with NaOH and KMnO4 treated fibres and the effect of the surfactant used. From the Figure 6&7 it is clear that untreated fibres in the polymer composites were covered with a membrane layer of pectin, lignin, and hemicelluloses impurities respectively. Alkali treatment has retained the required proportion of these impurities for enhanced mechanical properties which can be seen in Figure 6 and results are in good agreement with those published in the literature on NaOH treated composite works.

From Figure 7 it can be observed that the shiny particles of potassium (K) and manganese (Mn) in and around the fibres which facilitate shifting the system from general polymers to metallo-polymer systems leading to enhanced ductility or load bearing ability of the specimens developed. Metallo-polymer systems lead to increase in the mechanical properties. A unique combination obtained from varied alkali treatment followed by potassium permanganate treatment blending the reinforcing agents such as lignin, pectin and hemicelluloses and metal traces such as potassium (K) and manganese (Mn) will shift favourably to metallo-polymer systems. The interference of alkali treatments and metallo-polymer structure has given enhanced results. Figure 8 shows the FTIR spectra for untreated, NaOH and KMnO4 treated fibres reinforced in the PP. The spectra show many transmittance bands. C-H symmetrical stretch at 2924 cm\(^{-1}\) is present in all fibres. The HCH and OCH peak at 1423 cm\(^{-1}\) present in all fibres. CH\(_2\) rocking vibration at C6 present in all fibres. The C=O (carbonyl) peak at 1742 cm\(^{-1}\) present in the untreated as well as NaOH but disappeared in the KMnO\(_4\) treatment and this is due to the removal of the reducible hemicelluloses from the fibre surfaces.
Table 6. Tensile strength: Treated v/s untreated hemp fibre

| Sl no | Comparison                                | % increase in tensile strength |
|-------|-------------------------------------------|-------------------------------|
| 1     | NaOH compared with untreated fibre       | 12.59                         |
| 2     | KMnO4 compared with untreated fibre      | 95.61                         |

Figure 5. Tensile strength comparison for treated and untreated hemp fibre
Figure 6. SEM images of NaOH treated fibres reinforced in PP matrix

Figure 7. SEM images of KMnO₄ treated fibres reinforced in PP matrix
Conclusions:
From the exhaustive experimentation carried on the two surfactant coating for natural fibre hemp reinforcement in the PP it can be concluded that the alkali treatment has increased ultimate load to 12.94% and tensile strength to 12.59% when compared to untreated fibres. Whereas a combination of alkali and KMnO4 treatment has further enhanced drastically the ultimate load to 90.58% and tensile strength to 95.61% respectively as compared to untreated fibre. The overall conclusion from the above study is that the polymer composite fabrication with individual treatments suffers from reduced mechanical properties while an optimized combination of different treatments can give enhanced results.

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