A study on the structure-property relationship of microwave irradiated Sunn Hemp fiber reinforced polymer composite

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Abstract. The current investigation has been performed on the microwave irradiated plant-derived cellulosic Sunn Hemp fiber and its composites. The fibers are pretreated by microwave irradiation at a power of 160 watts with different exposure times (2, 4, 6 and 8 minutes). The significant change in fiber and hence composite due to microwave treatment are characterized both in structural and mechanical property. A reasonable increment in cellulose crystallinity with crystallite size, rough surface with fine fibrillation in fiber may lead to improve the mechanical strength in the composite for 4min treatment. The macromolecular structure of the fiber is unaltered by the microwave radiation as indicated by Fourier Transmission Infrared Spectra.

1. Introduction
Production of polymeric composite material from Sunn Hemp natural fiber have gained enough attention by reserachers and industry when environment and health become a major concern. This help to reduce CO₂ level from atmosphere so ecofriendly and moreover it is biodegradable, abundant and recycle. Sunn Hemp fibers are widely being popular due to their possession of high aspect ratio (500-600), cost effective and as reinforcing material in order to fabricate composite[1].Sunn Hemp as reinforcing material also provide good strength to weight ratio, high toughness, resistance to fatigue and corrosion. But the major drawback include in NFRC is their inherent hydrophilic nature. Due to the intra- and inter- molecular hydrogen bonding with hydroxyl group (-OH) of plant fiber, they are very much likely to absorb air molecules and moisture from the atmosphere. In contrast, the polymer matrix in hydrophobically crosslinked, so there is a huge mismatch between reinforcementing fiber and polymer matrix than can adhere to the properties of composite material. To avoid this problem, various kind of modifications(physical/chemical) are adopted in order to modify the structure of fiber[2,3,4]. In the regard of physical modification, microwave irradiation pretreatment has gained a substantial attention to provide a better interface for fiber-matrix composite. The physical method for fiber treatment is chosen in order to get ride over the toxicity and water when compared to various chemical process [5]. Microwave frequencies (300 MHz-300 GHz) lies in between radio and infrared frequencies in electromagnetic spectrum and is popularly used in communication as well as radar purposes. The present research work is focused on the effect of microwave pretreatment on sunn hemp fiber and hence it’s composite. Microwave heating of material is very much effective over conventional heating as the material under microwave get energy and convert it into heat where the conventional heating to the material are concentrated on the surface[6]. There are some literatures says...
the microwave techniques towards fibers is one of the effective physical pretreatment to modify the structure of the fibers[7,8,9].

2. Materials and Methodology

Sunn Hemp fibers are collected from Central Research Institute for Jute and Allied Fibers (CRIJAF), Barrackpore, Kolkata-700120, India in bundled form. The general purpose matrix used in this study is thermosetting “EPOXY L-12” polymer having density- 1.17 g/cm³ and the catalyst to accelerate the curing process is “HARDENER K-6” having density- 0.98 g/cm³ which were procured from Himedia Laboratories pvt. Ltd, Mumbai, India. For the physical modification, cooking microwave oven is used.

2.1. Fiber pretreatment

Sunn Hemp fibers were washed with normal detergent to remove the dirts from the surface. For purification, the fibers are dewaxed with the help of a couple of chemical ethanol:benzene (1:2) subjected to water bath under temperature variator electric heater. The purpose of dewaxing the fiber is to remove extra impurities (wax/oil/fatty substances) from the fiber surface and stack the cellulose layers maintain the space between them. The fiber are then collected, washed thoroughly with running tap water and dried under vacuum at 80 °C. The fiber is named as raw sunn hemp (RSH) fiber. In later process, the dried fibers are placed under microwave oven at 160 watt power setting for different exposure times (2, 4, 6 and 8 minutes). The fibers were then collected, cooled and stored in desiccator. The treated specimen are named as 160W 2m, 160W 4m, 160W 6m and 160W 8m where 160 denote the power setting and the suffix denote as the different exposure timings.

2.2. Composite preparation

The composites of treated and untreated reinforced fiber were developed by using Hand lay out technique. Two different kinds of rectangular specimens of dimension (90×12×5)mm³ and (165×19×5)mm³ were fabricated for the 3-point bending and tensile test according to the ASTM standard of D7254 and D3039 respectively. A measured (weight of 100 gram and 48 gram) amount of epoxy was taken and was presonicated for 1 hr followed by degassing under vacuum for 8 hr at 80°C and after a mild cooling the catalyst was mixed (epoxy:hardner=10:1) in order to crosslink the curing process. Finally the chopped fiber of 3mm length was mixed in the solution and poured into the mould which was designed using glass slabs and spayed using an heavy duty silicon sparay prior to pouring for easy removal of the composite. The mould was covered using an plastic sheet and a roller was used to remove the extra resin and air bubbles from the mixture. After 24 hours of curing, the specimen were collected from the mould and ready for the mechanical tests.

2.3. Instrumentations

For fine structural characterization of fiber, X-Ray Diffraction (XRD), Fourier Transmission Infrared (FTIR) spectroscopy and Field Emission Scanning Electron Microscopy (FESEM) were carried out to investigate the crystallographic information, functional group and surface morphology respectively. X-Ray spectral patterns of both untreated and microwave treated Sunn Hmep were recorded by Ultima IV- Rigaku, Japan diffractometer using CuKα radiation. Data were taken at Bragg angle range from 10° - 50° and scanning rate of 3°/min with step size 0.05. Functional groups of untreated and treated fiber were investigated by FTIR PerkinElmer Spectrum with averaged over 8 scans using a nominal resolution of 4 cm⁻¹. The surface morphology were carried out by using (Nova Nanosem 450, Japan) FESEM at 10KV accelerating voltage. The mechanical test was executed by a Universal testing Machine (Instron-5967, UK) with environment chamber by applying a cross head speed of 3mm/min.
3. Results and Discussions

3.1. XRD analysis

![XRD pattern of untreated and treated fiber](image)

Figure 1. XRD pattern of untreated and treated fiber

The XRD pattern of untreated and microwave treated Sunn Hemp fiber is shown in Figure 1. There are two peaks are observed at the Bragg angle of 15.6° and 22.6° of miller indices [101] and [002] which are ascribed to crystalline cellulose I region and pure cellulosic component in nature. Cellulose known to be a biphasic material which consist of both crystalline and amorphous phases. To know the relative amount of crystalline material present in the cellulose, Segal and his co-workers found a technique called ‘Peak height method’ where they approached the height of 100% intensity peak into the consideration and subtracted it from the amorphous phase. In this pattern, the region between [101] and [002] peak is considered as cellulosic amorphous components. The microwave treatment does not seem to change the crystalline structure of the cellulose chain rather than change the arrangement. The crystallite size is calculated using Schere’s formula. The relative amount of crystalline material which is also named as Crystalline index (CI) and Crystallite size are found to be high in case of 160W 6m followed by 160W 4m, 160W 8m, 160W 2m and RSH. All the values are listed in tabular form shown in the Table 1.

| Fiber name | Crystalline Index (CI) in % | Crystallite size (L) in Å |
|------------|-----------------------------|--------------------------|
| RSH        | 72.5                        | 31.2                     |
| 160W 2m    | 78.1                        | 37.6                     |
| 160W 4m    | 78.1                        | 40.3                     |
| 160W 6m    | 79.9                        | 40.5                     |
| 160W 8m    | 77.2                        | 39.0                     |

The reason of appreciable increment in treated fiber may be due to the arrangement of amorphous cellulosic chain arrangement in the crystalline domain. Treatment with irradiation time up to 6m leads to formation of reasonable modification in bond chain than leads to formation of new crystallites. Such behaviour reduce the possibility of distortion and enhance the crystallite dimensions. It also remove the extra amount of impurities and non cellulosic compounds from fiber. Treatment with higher time lead to degradation of cellulose polymer chain and increased the amorphous cellulosic content amout along with crystalline cellulose.

3.2. FTIR analysis

FTIR spectra of untreated and microwave treated Sunn Hemp fiber is shown in Figure 2. It was observed that all the spectra follow an equivalent pattern as the treatment looks like unaltered the macromolecular structure of the cellulose. But there is a disappearance of 2852 cm⁻¹ peak upon higher
order timing exposure in 160W 8m. This peak is specially meant to wax presence in the fiber surface which is mainly net to amorphous impurity. It is also noticed that the transmittance peak at 3401 cm$^{-1}$ of RSH peak that is attributed to –OH group show the presence of water molecule is shifted to 3341 cm$^{-1}$, 3343 cm$^{-1}$ and 3351 cm$^{-1}$ attribute to lowering of water molecules due to absorbance by radiation[10]. There are no other major change observed in the transmittance peak which suggest that the microwave irradiation of fiber did not change the molecular arrangement of polymer chain.

| RSH (cm$^{-1}$) | 160W 2M (cm$^{-1}$) | 160W 4M (cm$^{-1}$) | 160W 6M (cm$^{-1}$) | 160W 8M (cm$^{-1}$) |
|----------------|--------------------|--------------------|--------------------|--------------------|
| 3403           | 3401               | 3341               | 3343               | 3351               |
| 2924           | 2920               | 2921               | 2922               | 2901               |
| 2852           | 2851               | 2851               | 2849               | -                  |
| 1732           | 1739               | 1735               | 1744               | 1734               |
| 1633           | 1633               | 1633               | 1633               | 1638               |
| 1374           | 1383               | 1372               | 1372               | 1371               |

**Figure 2.** FTIR spectra of (a) untreated and treated fiber (b) zooming of 1732 cm$^{-1}$ peak

**Table 2.** Comparison of wavenumbers of untreated and treated Sunn Hemp fibers

### 3.3. FESEM analysis

The visibility in surface change of fiber in comparison to untreated was shown in figure 3. It was observed that increase in high irradiation time increase the surface roughness of fiber. The single fiber was splitted into many microfibrills in case of 160W 4m, 160W 6m and 160W 8m with making space in between them. The surface area is effectively increased at the higher irradiation time but got degradation on the surface in case of 160 8m. Such damaging effect appear may ascribe to degradation of internal macromolecular chain structure. The surface roughness and increased surface area of fiber make an easy flow of the resin and strengthen the fiber-matrix interface.

**Figure 3.** FESEM images of (a) untreated (b) 160 2m (c) 160 4m (d) 160 6m (e) 160 8m fibers
3.4 Mechanical analysis

Figure 4. Mechanical strength of untreated and treated composite

3-point bending test or flexural test and tensile strength of untreated and treated composite are shown in figure 4. Increasing relative amount of crystallinity and crystallite size strengthened the fiber. Sunn Hemp fiber possess a higher amount of cellulose (70-78%) after cotton (85-95%). A higher quantification of cellulose always make the fiber strong and stiff. Moreover upon treatment, the increment in surface roughness and surface area facilitated the mechanical binding between fiber-matrix. Failure in mechanical strength at higher irradiation time of 8m degraded the cellulose structure which also lead to form a poor adhesion between fiber-matrix.

3.5 Microstructure

Figure 5. FESEM images of (a) untreated(b) 160 2m (c)160 4m (d)10 6m (e)160 8m composite

The adhesion between fiber-matrix of both untreated and microwave treated composite was observed from the fracture micrograph in figure 5. Due to weak bonding between fiber-matrix, RSH fiber experience debonding around the fiber periphery and also the matrix region is layered over by over. This suggest a sign of poor adhesion at interface. But upon treatment, the adhesion got stronger due to the increment in cellulose crystallinity in fibre which lead to a stronger interface. The splitting of fiber was observed in all treated case but there is a formation of secondary fibers was noticed in case of 160W 6m. This is obviously a scenario of initiation of the fiber weakening but due to strong adhesion, no debonding was marked rather than breakage at the fiber edge. Treatment at 8m exposure time lead to degradation of fiber due to absorbing a lot of electromagnetic radiation which provide a poor wetting of fiber into matrix.
4. Conclusions
Sunn Hep fiber was physically modified by microwave irradiation technique for making it applicable for various potential applications such as composites widely. The treatment unaltered the macromolecular stucture of cellulose which is confirmed from FTIR spectra. Higher crystallinity and crystallite size were found in case of 160W 6m fiber which suggests the rearrangement of crystalline cellulose polymer chain and increment in crystallite dimensions. Surface roughness are observed in all treated fibers but a better splitting with adequate surface area was the main focus for 160 6m. Mechanical strength of Sunn Hemp composite was found to be higher in case of 160 6m due to better wetting and adhesion between fiber-matrix. So the microwave irradiation of fiber at power 160 watt with different exposure times was could have the best mechanical strength at 6 minute. This technique of microwave irradiation is quite doable in the favrication of obtaining safer and effective treatment for heating rather than conventional heating.

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