Modification of Lignocellulosic Fibre for Enhanced Oleophilicity

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Abstract - Crude oil is currently the most important raw material and energy source worldwide. Oil sometimes gets accidentally introduced into the environment during production, transportation, and refining process causing adverse effects on aquatic life and human economic activities. It is thus important to use oil sorbent in order to prevent such adverse effects of oil spills. Moreover, contrary to synthetic polymer sorbents which are being used during oil spillage, natural fibre like jute is safe to the environment as it is biodegradable and does not lead to supplementary pollution. This work reports the use of Jute nonwoven fabric that was modified with fatty acid to enhance its oleophilicity. The modified nonwoven fabric was characterized by FT-IR, TG, SEM and its Acid value was also calculated. It is found that nonwoven jute grafted with fatty acid exhibited better sorption capacity than unmodified fabric for crude oil.

Keywords - Jute, nonwoven, fatty acid, esterification, acid value, oil sorbent

1 INTRODUCTION

Oil is a major source of ground water contamination and ocean pollution. The vast majority of this oil enters the ocean from oil spills on ships that transport petroleum or from manufacturing operations on land. However oil can also seep into the ocean naturally from cracks in the sea floor (Wei, 2003). Oil well and oil tanker accidents at sea account for a small portion of ocean oil pollution, yet the lasting effects of these accidental spills can be disastrous (Boopathy, 2000). Oil spill also cause strong odor that can be felt miles away and also there is excessive growth of green algae which alters the color of sea and landscape (Annunciado, 2005). Removal of oil by sorption technique has been observed to be one of the most effective techniques for complete removal of spilled oil under ambient conditions. Various sorbents such as exfoliated micas, chalk powder, ekoperl, straw, sawdust, foams of polyurethane or polyther, fibres of nylon, polyethylene etc. have been studied for this purpose. However, the treatment of water containing oil pollutants by these sorbents is expensive because of the high costs of most of the sorbent materials (Hussein, 2009). This has prompted academic and industrial interests in developing methods for marine oil spill recovery using natural materials. The utilization of biomass has gained an increased importance due to threats of limited petroleum availability and concerns about the environmental pollution. Eco friendly, renewable and biodegradable materials prepared by using lignocellulosic fibres of plant origin have become the most required material in the present time (Bledzki, 2009).

Wood and other lignocellulosic materials are three-dimensional, polymeric composites made up primarily of cellulose, hemicelluloses, and lignin. These polymers make up the cell wall and are responsible for most of the physical and chemical properties of these materials. Lignocellulosic materials have been used as engineering materials because they are economical, renewable, and strong and have low processing-energy requirements. They have, however, several undesirable properties, such as dimensional instability due to moisture sorption with varying moisture contents, flammability and degradability by ultraviolet light, acids and bases. These types of degradation are chemical in nature and it should be possible to eliminate them or decrease their rate by modifying the basic chemistry of the lignocellulosic cell wall polymers.

Jute is one of such lignocellulosic, low-cost, multicellular, fibre produced in large quantities every year in south and Southeast Asia, especially in India and neighboring Bangladesh. It consists of α-cellulose, hemicellulose, lignin, pectin’s and waxes. The former two components are hydrophilic and the latter ones are hydrophobic (Rowell, 1998). In other words, the cellulose and hemicelluloses being more hygroscopic than lignin and are mainly responsible for moisture uptake. These properties can be modified chemically using fatty acids. The hydroxyl groups attached to cellulose, lignin and hemicellulose are responsible for its hydrophilicity. This paper highlights the use of Oleic acid to change the surface characteristic of a nonwoven jute fabric and hence increase the hydrophobicity of the nonwoven fabric.

\[
\text{Jute-OH} + C_{17}H_{33}COOH \rightleftharpoons \text{Jute-OCOC}_{17}H_{33} + H_2O
\]

2 MATERIALS AND METHODS

Jute nonwoven fabric was obtained from BTRA (Mumbai, India). Oleic acid, Sulfuric acid and all other chemicals were purchased from S.D Fine Chemicals Mumbai India. Crude oil used for the testing purpose was supplied by HPCL.
2.1 Preparation of Fatty Acid-Grafted Jute nonwoven

One gram of nonwoven jute fabric was treated with required amount of fatty acid in the presence of one to three drops of concentrated sulfuric acid as catalyst. The mixture was refluxed in a Dean-Stark apparatus at required temperature for an optimized period of time. The treated fabric was washed with n-hexane, dried in oven at 70°C till constant weight and stored in an air tight container till further use (Banerjee, 2006). The amount of grafted fatty acid was estimated by weight percent gain (WPG) as follows.

\[ WPG = \frac{W_2 - W_1}{W_1} \times 100 \]

2.2 Oil sorption capacity

Oil sorption capacity was determined by using method reported in literature (Sun, 2004). A fixed quantity of machine oil (50 g) was suspended in water in a beaker. The modified jute non woven fabric (1g) was added at room temperature and allowed to absorb oil for 1hr. The fabric was then removed and held to drain off the excess amount of oil. The fabric was then reweighed to determine the oil absorbptivity.

2.3 Recovery of Sorbed Oil and Reusability of Sorbents

In order to examine the reusability of these sorbents, method described by Choi and Moreau (1993) was followed which has limitation that gives only an approximate value of oil sorption. In this method machine oil (50 g) was suspended in water in a beaker. The modified fabric (1g) was added and mixed for 1 min at room temperature and allowed to sorb oil for 1hr. The sorbent with oil was weighed and then squeezed between two rollers at a pressure of 10k gf/cm before it was reweighed to determine the amount of recovered oil. The squeezed sorbent was again used in the sorption process as before. The efficiency of sorbent reusability was determined by oil sorption capacity of each sorbent after repeated sorption and mechanical desorption cycles (Ansari, 2003).

3 CHEMICAL CHARACTERIZATION

3.1 FT IR

The IR spectra of original and modified jute fibre samples were recorded using FTIR spectrophotometer (Shimadzu 8400s, Japan) using ATR sampling technique by recording 45 scans in % T mode in the range of 4000 to 600 cm\(^{-1}\).

3.2 TGA

Thermal gravimetric analysis (TGA) of the unmodified and modified jute nonwoven fabric was carried out by regular method. The thermograms of samples were recorded on Shimadzu 60H DTG machine using aluminum pan between temperature range 30-500°C and under the inert atmosphere of N\(_2\) at a flow rate of 50ml/min.

3.3 Scanning electron microscopy (SEM)

Analysis of the morphology of dried and modified sample was carried out using scanning electron microscope (JEOL, Japan), from Institute of Chemical Technology. The samples were sputter coated with gold layers and images were recorded using scanning electron microscope.

3.4 Acid Value

The acid value is the number of milligrams of sodium hydroxide necessary to neutralize the free acids in 1 gram of sample. A suitable quantity of sample was taken into a 250 ml flask. To this flask neutralized alcohol was added and the temperature was raised to boil and allowed to stand for at least 30 mins. This was followed by addition of 1ml of phenolphthalein indicator and it was titrated against 0.1N sodium hydroxide solution until a faint color persists for at least 10 seconds. It is necessary to shake the contents of the flask continuously and as violently as possible during the titration, since in general the fibre is not soluble in the alcohol and free fatty acids have to be brought out from the fibre phase to the alcoholic one. (Williams, 1966)

\[ \text{The Acid Value} = \frac{N \times 4.0}{W} \]

Where,
N= number of milliliters of 0.1 N alkali required
W= weight of fabric taken in grams
4 RESULTS AND DISCUSSION

Results, in Table 1 show the effect of various parameters on WPG and on oil absorbency of the final product.

4.1 Effect of Time on WPG

Results with respect to effect of reaction time on WPG are shown in Table 1. There was increase in the WPG as the reaction time increased from 1 to 3h. This initial increase was due to the condensation reaction of greater number of fatty acid molecules with those of hydroxyl groups of the jute fibre. After 3h, the percentage grafting did not increase appreciably, even though time was increased to 5h. This leveling of grafting with time could be mainly due to leveling off of maximum accessibility of jute fibre for the reactants indicating near stagnancy in level of WPG. Also the oil sorption capacity at 3h grafted sample was maximum i.e. 18.33g/g.

4.2 Effect of Temperature on WPG

In this experiment duration of the reaction (3h) and the fatty acid concentration was 100% on the weight of fibre was kept constant, while temperature was varied. It was observed that while initial increase in temperature from 55°C to 65°C, brought about increase in WPG, beyond this temperature no significant increase in WPG was observed. Also the oil sorption capacity of the jute nonwoven fabric at 65°C was significantly higher than that of those samples obtained using other temperatures and hence 65°C was taken as optimum temperature.

4.3 Effect of Concentration of Oleic Acid on grafting

The results from Table 1 indicate that when concentration of oleic acid was varied from 50%, 100% and 150% on the weight of fibre, the extent of acylation increased with increasing concentration of Oleic acid which was mainly because of increased amount of reactant available for reaction with fibre enhancing its proper penetration inside the fibre. However, beyond 100% concentration there was no significant increase in the extent of acylation as seen in WPG as well as in extent of oil absorption. Hence, 100% concentration is considered to be optimum one. Acid value of the optimized sample was also calculated to confirm the grafting of oleic acid on jute fabric and it was found to be 36.07.

Table 1 Effect of Different Parameters of Fatty acid modification on Oil Absorption

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Time (hrs)</th>
<th>Temperature (°C)</th>
<th>Conc. Oleic Acid (owf)*%</th>
<th>** WPG (%)</th>
<th>Oil absorption (g of oil/g of fibre)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Effect of Time</td>
<td>A</td>
<td>1</td>
<td>65</td>
<td>100</td>
<td>12.67</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>3</td>
<td>65</td>
<td>100</td>
<td>19.13</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>5</td>
<td>65</td>
<td>100</td>
<td>19.15</td>
</tr>
<tr>
<td>2. Effect of Temperature</td>
<td>A</td>
<td>3</td>
<td>55</td>
<td>100</td>
<td>16.28</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>3</td>
<td>65</td>
<td>100</td>
<td>19.13</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>3</td>
<td>75</td>
<td>100</td>
<td>19.01</td>
</tr>
<tr>
<td>3. Effect of Conc. of Oleic Acid</td>
<td>A</td>
<td>3</td>
<td>65</td>
<td>50</td>
<td>12.7</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>3</td>
<td>65</td>
<td>100</td>
<td>19.13</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>3</td>
<td>65</td>
<td>150</td>
<td>19.12</td>
</tr>
</tbody>
</table>

*OWF: on weight of fabric

** WPG: weight percent gain
4.4 FT-IR Analysis

The analysis of the IR spectra of modified nonwoven fabric and unmodified jute nonwoven fabric is a simple way to confirm the esterification of cellulose hydroxyl groups with fatty acids. Clear evidence of esterification reaction is observed by the emergence of a new ester carbonyl band at 1737 cm\(^{-1}\). The decrease in the intensity of the broad band at about 3300 to 3400 cm\(^{-1}\) is assigned to the cellulose O-H vibration. The IR analysis confirms the enhancement of the hydrophobic character of the cellulose fibres after esterification with fatty acids and the intensity of the band, at around 1500 cm\(^{-1}\), assigned to absorb water molecules, decreases significantly. Indeed, this band is almost completely absent in the IR spectra of esterified fibres.

![FT-IR Spectrum of Raw Jute nonwoven fabric](image)

4.5 Thermal analysis

Fig. 3 shows the thermograms of raw and modified nonwoven fabric. In the initial stage weight loss of raw and modified samples were 8.16% and 9.93% at 200°C respectively; beyond this temperature the drastic decomposition of the sample resulted into the significant weight loss which was 59.32% for raw and 57.39% for modified sample at 360°C which was more or less similar. However the total weight loss at 500°C was found to be 95.94% for unmodified fabric and 95.1% for fatty acid modified sample respectively. This clearly indicates that the modified sample showed more or less the same thermal stability as unmodified fibre.
4.6 SEM analysis

The SEM micrograph of modified Jute fibre (Fig. 4b) clearly shows a surface deposition, which is absent in the non-modified substrate (Fig. 4a). This confirms the presence of grafted fatty acid on the cellulose backbone of the fibre. The Fig. 4a indicates that the untreated fibre surface is smooth where as Fig. 3b indicates the internal ‘channels’ in the fibre being open up and at the same time became straighter and confer greater rigidity upon the fibre. It is for this reason oleophilicity of the treated fibre increases. Increased thickness, roughening of surface and micro pores developed during modification seen in the fatty acid modified jute fibre.
Fig 4 Scanning electron micrograph of Raw and modified Jute fibre.

4a. SEM of Raw Jute fibre

4b. SEM of Modified Jute fibre

4.7 Oil absorption

Modified jute fabric was tested for its oil sorption capacity and it was found that modified optimized sample showed significant increase in oil absorbency. The capacity of oil sorption at room temperature of the modified samples was 18.33 g/g (refer Table 1) which in general, increased with the increment of WPG. Acylation of jute nonwoven fabric led to a substantial increase in acetyl groups. The oil sorption capacity of unmodified fabric
was 8.63 g/g and these values for modified jute samples were much higher than those for the synthetic sorbents (Choi & Cloud, 1992; Hill, Jones, Strickland, & Cetin, 1998).

### 4.8 Reusability of sorbents

Squeezing of oil from the sorbent is a simple, economical and practical method of recovering the oil sorbed. Hence recovery of the oil from the sorbent material and also the feasibility of reusing the sorbents were studied.

The results in Table 2 indicate that the fatty acid modified jute fabric shows higher oil uptake in the first cycle and then its sorption capacity decreased significantly in the subsequent cycles. This may be due to the collapsing of lumen during the mechanical squeezing (Hill et al., 1998) and masking of acetyl groups in modified fabric. Thus the capacity of oil sorption decreased from 18.33 g/g to 12.95 g/g in the third cycle as show in Table 2.

<table>
<thead>
<tr>
<th>Table 2 Reusability of Fatty acid modified Jute fabric</th>
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<tbody>
<tr>
<td>First cycle</td>
</tr>
<tr>
<td>Second cycle</td>
</tr>
<tr>
<td>Third cycle</td>
</tr>
</tbody>
</table>

### 5 CONCLUSION

The jute nonwoven fabric has been modified successfully with fatty acid to replace the hydroxyl groups of the cellulose of jute fibres. The reaction parameters like time, temperature and concentration of Oleic acid were optimized and maximum WPG obtained was 19.13% and oil sorption capacity of the optimized modified sample was 18.33 g/g. The carbon long chain incorporated with the fatty acid induced hydrophobicity to the fibre surface. FTIR and SEM confirmed the modification brought out in the jute fibre by reaction with oleic acid. Slight improvement in the thermal stability of the modified sample in the region of 200°C to 360°C was observed. Acid value of optimized fabric was determined to confirm the modification. It was also possible to reuse the modified jute nonwoven fabric for oil sorption at least 3 times. Hence a low cost, high capacity, effective oil sorbent which is easy to desorb oil can be obtained by modifying jute nonwoven fabric.

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## References


