Surface modification of abaca fiber by benzene diazonium chloride treatment and its influence on tensile properties of abaca fiber reinforced polypropylene composites

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Abstract

In this investigation, the effect of surface modifications of abaca fiber by alkali and benzene diazonium chloride on the tensile strength of abaca fiber reinforced polypropylene matrix composites was studied. Natural fibers are having low cost, low density and are biodegradable. All these points are on the positive side but they are hydrophilic. Their water absorption property limits the use of these fibers as potential reinforcement in the preparation of composites. Polymer matrix is hydrophobic in nature. This makes fiber and matrix incompatible and results in poor interfacial bonding between the fiber and the matrix. The main objective of this chemical treatment is to reduce their water absorption property and also to improve the compatibility with polymer matrix. Abaca/Polypropylene composites with 20-50 wt% fiber loading have been developed by hot compression moulding technique and were then analysed for tensile strength. The study revealed that there is significant change in tensile strength of abaca composites upon alkali and benzene diazonium chloride treatment. The results showed that the tensile strength of the composites increased with increase in fiber loading up to 40% and beyond 40% it showed a decrease in tensile strength. The results indicated that chemically treated abaca fibers can be used as promising materials as reinforcement in the preparation of biocomposites.

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1. Introduction

In the manufacture of composite materials and structures, measurement of mechanical properties plays a significant role in quality control. Tensile strength, the force required to pull something to the point till it breaks, is one of the basic important mechanical properties of a composite that is required for analysis and design of composite materials and structures. A tensile test result helps one to select a material for an application; can predict how a material will react to different types of forces. With the advancement in composite technology, the composite test methods and test equipment have become sophisticated. Tensile strength is an intensive property and hence its value does not depend on the size of the
test specimen but depends on the methods of preparation of the specimen, presence of surface defects and the temperature of the test environment and material.

Natural fibers as reinforcement in the production of green products are gaining attention because of ecological concerns and increasing environmental awareness. Natural fibers mainly consist of cellulose, hemicelluloses, pectin, lignin and waxes [1-3]. This composition can vary for the same fiber depending on the growing and harvesting conditions [4].

Cellulose is a semi crystalline polysaccharide consisting of D-anhydro glucose repeating units joined by β-1, 4 glycosidic linkages at c1 and c4 positions [5]. Each repetitive unit consists of three hydroxyl groups and their ability to hydrogen bond makes natural fibers hydrophilic. Hemicelluloses are amorphous polysaccharide with low molecular weight compared to cellulose. It differs from cellulose mainly in three aspects. Firstly, cellulose contains 1,4-β-D-glucopyranose units whereas hemicelluloses contain different sugar units. Secondly, hemicelluloses exhibits chain branching with pendant side groups giving rise to non-crystalline nature, whereas cellulose is a linear polymer and finally, degree of polymerization of native cellulose is 10 to 100 times higher than that of hemicelluloses. Because of the presence of hydroxyl groups, hemicelluloses are hydrophilic in nature [6]. Lignin is amorphous and hydrophobic in nature and has little effect on water absorption. The structural units of lignin molecules are derivatives of 4-hydroxy-3-methoxy phenyl propane. It gives rigidity to the plants.

Pectin is a hetero polysaccharide and holds the fibers together. It provides flexibility to the plants. Waxes consist of different types of alcohols [6, 7].

Natural fibers like abaca, sisal, jute, hemp, coir etc. are acting as good reinforcements in thermoplastic and thermosetting resins. These fiber reinforced composites are extensively used in automotive applications, in construction sector and in packaging industries [8]. Abaca fibers are extracted from the pseudo stem of Musa Textilis and are bast fibers. Nowadays abaca fiber reinforced composites are gaining importance due to the innovative applications of abaca fibers in under floor protection for passenger cars by Daimler Chrysler [9]. Ease of availability, sustainability, high tensile strength, resistance to rotting and specific flexural strength nearer to that of glass fibers make abaca fibers superior [10].

These fibers are waste products of abaca cultivation and hence are cheaper and the use of these fibers results in weight reduction, enhances heat and noise insulation and are biodegradable [11]. But the constraints in using these natural fibers as reinforcing materials in the preparation of composites are incompatibility between natural fiber and resin due to hydrophilic nature of natural fibers and high level of water absorption leading to poor wettability. This results in degrading the properties of composites. This also nullifies the weight reduction advantage.

In order to use natural fibers as successful reinforcement, surface modification is a must, which can be brought about by various chemical treatments like alkali treatment, permanganate treatment, acylation, acetylation, benzene diazonium chloride treatment etc. After chemical treatment surface of fibers becomes rough and enhances mechanical interlocking with resin. These treatments lead to decrease in moisture absorption as well as improving the wettability of fibers by matrix. This results in imparting better mechanical properties to the composites [12-16].

One of the most extensively used plastics both in developed and developing countries is polypropylene because of its inherent advantages with regard to economy, ecological (recycling behaviour) and technical requirements (higher thermal stability) [17].

The cost of producing lignocellulosic polymeric composites is quite low. Hence, these composites have attracted much attention and are becoming increasingly important for the production of a large variety, cheap, light–weight, environmental friendly composites [18]. Chopped natural fiber reinforced PP composites have been widely studied in an attempt to benefit from the cost and mechanical properties of these natural fibers [19-26].

Although there have been numerous studies on mechanical behaviour of other natural fiber composites, only a few references are available on mechanical behaviour of benzene diazonium chloride-treated natural fiber reinforced polymer composites and found to have a good flexural strength, adhesion and tensile properties [27, 28]. However, no literature is available on benzene diazonium chloride treated abaca-polypropylene composites fabricated by compression moulding technique. In the present study, untreated, alkali-treated and benzene diazonium chloride-treated fibers were used for the development of abaca–polypropylene composites. The aim of this study is to investigate the effect of surface modification of natural abaca fiber on tensile strength of abaca/polypropylene composites.
2. Materials and methods

2.1. Materials

Abaca fibers were collected from the Maruthi Peach Finishing Company, Tirupur, Chennai, India and Analytical grade reagents were purchased from Qualigens Company and used as received.

2.2. Alkali treatment of fibers

Abaca fibers were soaked in a beaker containing 6% NaOH solution at room temperature (30-32 °C) for 1h. The alkali treated fibers were immersed in distilled water for 24 h to remove the residual NaOH. Final washing was done with distilled water containing a small amount of acetic acid. Fibers were then dehydrated in an oven at 70 °C for 3 h.

2.3. Preparation of benzene diazonium chloride

8 cm³ of concentrated hydrochloric acid was added to a boiling tube containing 3 cm³ of phenyl amine (aniline) and 10 cm³ of water, the mixture was shaken until the amine has dissolved, and then the solution was cooled to 5 °C by cooling it in an ice bath. After that a solution of sodium nitrite (3 g in 8 cm³ of water), pre-cooled to 5 °C was added. The temperature of the mixture was maintained below 10 °C during the addition of sodium nitrite [29].

2.4. Benzene diazonium treatment of abaca fiber

The abaca fibers were chopped to a length of 10 mm, washed with distilled water, and were then dehydrated in an oven at 70 °C for 24 h. The dried fibers were immersed in a 6% NaOH solution taken in a 2.0 L glass beaker for 10 minutes at about 5 °C. A freshly prepared diazo solution was then poured slowly into the above mixture with constant stirring. Fibers were then taken out, washed with soap solution followed by distilled water, and finally dried in an open air for 48 h [27].

2.5. Composite fabrication

Abaca fibers and polypropylene filament were chopped into a length of 10 mm and they were mixed. The weight fractions 20, 25, 30, 35, 40, 45 and 50% of fiber was carefully controlled during the mixing of two ingredients. The resulting material was compression moulded to the dimensions of 300 x 300 x 2.0 mm. The composite preparation process was performed in the following order. First, the heat press was pre-heated to 60 °C. Then the pressure was set as 0 MPa and the temperature raised to 100 °C. After that pressure and temperature raised to 5 MPa and 190 °C, respectively. Further, raised the pressure to 15 MPa, maintained the pressure and temperature for 30 min. Finally, lowered the pressure to 0 MPa, lowered the temperature to 30 °C and composite plate was removed from the heat press. The specimens were post cured for 24 h before the test [30].

2.6. Tensile strength of composites

Specimens prepared for the tensile strength test were cut and the measurement was carried out according to ASTM D3039 standards. A rectangular shape specimen with the total length of 250 mm, a gauge length of 150 mm, width of 25 mm and a uniform thickness of 2.0 mm is considered for the test. The specimen was loaded in the universal testing machine until the failure of the specimen occurs at laboratory conditions (temperature, 30±2 °C; RH 65%).

2.7. Morphological study

The surfaces of the specimens are examined directly by Scanning electron microscopy (SEM) JEOL JSM - T330A at the accelerating voltage of 20 KV. The samples are mounted on stubs with silver paste. To enhance the conductivity of the samples, a thin film of platinum is vacuum-evaporated onto them before the photomicrographs are taken.

3. Results and discussion

3.1. IR spectra

The reaction scheme for the synthesis of benzene diazonium chloride is presented in Scheme 1 and the coupling reaction between fiber cellulose and benzene diazonium chloride yielding benzene diazocellulose is shown in Scheme 2.
In FTIR a Fourier transform is required to turn the raw data into the actual spectrum. It is an effective analytical instrument for detecting functional groups. This is more accurate and faster. FTIR of untreated, alkali-treated and benzene diazonium-treated abaca fibers was taken and the spectrum was analysed to know the various chemical constituents present. The infrared spectra for treated and untreated single abaca fibers were obtained by using FTIR spectrometer in the region 500 cm\(^{-1}\) and 4000 cm\(^{-1}\) and they are presented in Figure 1 and Figure 2, respectively. The obtained absorption peaks are explained in Table 1.

Chemical treatment of abaca fibers resulted in significant differences in the infrared spectra. The spectrum of untreated fiber is dominated by the peak at 3430-3450 cm\(^{-1}\) which is mainly related to the hydroxyl groups and O-H stretching vibrations present in carbohydrate (cellulose + hemicelluloses). In the spectra of alkali-treated abaca fibers, band assigned to alcoholic group was reduced due to the removal of the hemicelluloses. Lignin, waxy materials, and impurities were removed by alkali treatment. This treatment reduces hydrogen bonding and also causes loss of ordered structural arrangement of cellulose. In the spectra of untreated fiber, the carbonyl absorption band at 1727 cm\(^{-1}\), corresponding to hemicelluloses; can no longer be observed in alkali-treated abaca fiber. This is due to the fact that upon alkali treatment, hydrolysis occurs which breaks down the ester bond or ether bond, resulting in the absence of this peak. Another peak due to the alcoholic group of cellulose OH deformation appeared at 1310 cm\(^{-1}\) was also reduced by alkali treatment. The large peaks at 1593 and 777 cm\(^{-1}\) shown in untreated fiber spectra are due to the presence of lignin, and they seem to be removed upon alkali treatment. Also, the peak at 1245 cm\(^{-1}\) appeared in the spectra of untreated fiber found to disappear in alkali treated fibers. Alkali treatment removed the waxy epidermal tissue, adhesive pectin and hemicelluloses that bind fiber bundle to each other. The C-O-C symmetric glycosidic stretch at 1100 cm\(^{-1}\) is due to the polysaccharide component that was largely cellulose and appeared for both untreated and treated abaca fibers [31-33].

An infrared spectrum of benzene diazonium chloride treated abaca fiber (Figure 2) confirms the interaction between the fiber cellulose and benzene diazonium chloride to form diazocellulose compound. In the IR spectra, the characteristic absorption peaks at around 1500 and 1650 cm\(^{-1}\) are mainly related to the presence of NO group and peaks at 1400 and 1460 cm\(^{-1}\) are assigned to \(-N=N-\) group found in the fiber-cellulose compound. Also, the absorption band observed at 1310 cm\(^{-1}\) is attributed to NO\(_2\) symmetric deformation. It can be summarized that the treatments with alkali and benzene diazonium chloride had removed most of the lignin and hemicelluloses components from the fiber surface. Further, the treatment had changed the hydrophilic nature of the natural abaca fibers to hydrophobic nature.

In FTIR a Fourier transform is required to turn the raw data into the actual spectrum. It is an effective analytical instrument for detecting functional groups. This is more accurate and faster. FTIR of untreated, alkali-treated and benzene diazonium-treated abaca fibers was taken and the spectrum was analysed to know the various chemical constituents present. The infrared spectra for treated and untreated single abaca fibers were obtained by using FTIR spectrometer in the region 500 cm\(^{-1}\) and 4000 cm\(^{-1}\) and they are presented in Figure 1 and Figure 2, respectively. The obtained absorption peaks are explained in Table 1.

Table 1. FTIR peaks position of abaca fibers

<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>FTIR peak origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>3200-3500</td>
<td>Hydroxyl group and bonded OH stretching</td>
</tr>
<tr>
<td>2924</td>
<td>C-H stretching vibration</td>
</tr>
<tr>
<td>1732</td>
<td>C=O stretching vibrations (carboxylic group and ester groups)</td>
</tr>
<tr>
<td>1650</td>
<td>NO group</td>
</tr>
<tr>
<td>1593</td>
<td>Lignin components</td>
</tr>
<tr>
<td>1500</td>
<td>NO group</td>
</tr>
<tr>
<td>1460</td>
<td>(-N=N-) group</td>
</tr>
<tr>
<td>1310</td>
<td>Alcohol group</td>
</tr>
<tr>
<td>1310</td>
<td>NO(_2) symmetric deformation</td>
</tr>
<tr>
<td>1245</td>
<td>Hemicelluloses and pectin</td>
</tr>
<tr>
<td>1100</td>
<td>C-O-C symmetric glycosidic stretch</td>
</tr>
<tr>
<td>777</td>
<td>Lignin components</td>
</tr>
</tbody>
</table>
3.2. Fiber image analysis

The most important problem of natural fiber composites originates from the hydrophilic nature of the fiber and hydrophobic nature of the matrix. The inherent incompatibility between these two phases results in weakening of bonding at the interface. Chemical treatments on reinforcing fiber can reduce its hydrophilic tendency and thus improve compatibility with the matrix [34-36]. Alkali treatment of abaca fiber changes the orientation of highly packed crystalline cellulose order forming an amorphous region. In the amorphous region, cellulose micro molecules are separated at large distances and the spaces are filled by water molecules. Alkali sensitive hydroxyl groups present among the molecules are broken down, which then react with water molecules (H-OH) and move out from the fiber structure. The remaining reactive molecules form abaca fiber-cell-O-Na groups between the cellulose molecular chains [6]. Due to this, hydrophilic hydroxyl groups are reduced and increases the fibers moisture resistance property. The alkali treatment of fibers also takes out a certain portion of hemicelluloses, lignin, pectin, wax and oil covering materials [1, 37, 38]. As a result, the fiber surface becomes clean. In other words, the fiber surface becomes more uniform due to the elimination of micro voids and thus the stress transfer capacity between the ultimate cells improves. In addition to this, it reduces fiber diameter and thereby increases the aspect ratio. This increases the effective fiber surface area for good adhesion with the matrix [39]. Hence, tensile behaviour of the composites would improve significantly by alkali treatment.

Figure 3 presents the images of the abaca fiber, before and after chemical treatment. Treated fibers have lower lignin content, partial removal of waxy and oil cover materials and distension of crystalline cellulose order.

Fig. 3. SEM images of (a) untreated, (b) alkali treated and (c) benzene diazonium chloride treated abaca fiber.

It is seen that the chemical treatment has removed the surface debris from the fiber, most of the lignin and partial removal of wax and oil resulting in rough surface. This rough surface facilitates both mechanical interlocking and the bonding reaction due to the exposure of the hydroxyl groups to the matrix, thereby increasing the fiber–matrix adhesion. As a consequence: (i) the interfacial interaction between the fiber and matrix enhances, (ii) this increases the effective surface area available for contact with the matrix, and (iii) the possibility of efficient load transfer between the matrix and the reinforcing fibers.

Comparing the images of untreated and benzene diazonium-treated abaca fiber reveals that benzene diazonium chloride in the fiber formed a rough coating and interaction on the fiber surface, which enhanced the morphological properties. Furthermore, benzene diazonium treatment partially filled the voids spaces of fiber and aligns uneven fiber, which provided smoother surface texture than raw abaca fiber. This result also suggests that the chemical reaction formed a strong interface with fiber cell walls, accounting for the observed increase in tensile properties of composites [40].

3.3. Tensile strength of composites

The ability of a material to resist breaking under tensile stress is one of the most important and widely measured properties of composite materials used in structural applications. The force per unit area (N/mm² or MPa) required to break composite material is the ultimate tensile strength or tensile strength at break. The composites were prepared by reinforcing untreated, alkali-treated and benzene diazonium chloride-treated abaca fibers in polypropylene matrix. Each piece of the fabricated abaca composite plate was cut into five specimens. Each result is an average of five measurements. The test specimen is in the form of rectangular shape. The two ends of the specimen are called shoulders and the area in between the two shoulders is the gauge section. The shoulders of the specimen are meant for gripping in the machine and the actual deformation and failure occurs in the gauge section.

Fibers are very effective in improving the fracture resistance of the matrix since a reinforcement having a long dimension discourages the growth of incipient cracks normal to the reinforcement that might otherwise lead to failure, particularly with brittle matrices.

It is necessary to find out the best possible fiber loading to achieve maximum tensile property [41, 42]. Generally, chemically treated fiber reinforced composites have higher tensile strength than the untreated fiber reinforced composites. The observed tensile strength values of composites can be understood in terms of chemical constituents of fiber.
The effect of fiber loading on tensile strength of abaca composites is presented in Figure 4.

It is observed from Figure 4 that the tensile strength of untreated abaca fiber-polypropylene composites was slightly higher than that of the matrix. This is attributed to the low compatibility between the hydrophilic untreated fiber and hydrophobic polypropylene matrix. However, appreciable higher tensile strength is observed in alkali treated abaca-polypropylene composites and significant increase is observed in the tensile strengths of benzene diazonium chloride-treated abaca fiber composites.

![Fig. 4. Tensile strength of composites.](image)

The tensile strengths of alkali treated abaca fiber composites found to increase up to 40% of fiber loading and then it decreased with increasing fiber load. Compared to untreated fiber composites, the tensile strength increased by 20-60% for alkali treated composites. The tensile strength, however, drops by 54% for composites with 45% fiber loading when compared with 40% fiber loaded composites. This is attributed to the fact that the weak interfacial area between the fiber and matrix increased with increase of fiber load [27].

It was also observed from Figure 4 that the benzene diazonium chloride treatment of abaca fiber showed a similar trend like alkali treatment. The highest tensile strength was observed at 40% fiber loading. This is attributed to the reduction of the hydrophilic nature of abaca fiber due to the coupling of the hydroxyl group of fiber with benzene diazonium chloride. The treatment of fiber also increased interfacial adhesion between the abaca fiber and the polymer matrix material. The highest tensile strength observed in 40% fiber loading can be attributed to the improved fiber distribution in a matrix material and less fiber fracture.

The highest tensile strengths observed at around 40% fiber loading can be explained by better fiber distribution in matrix material and less fiber fractures. Therefore the bond between fiber and matrix communicate whether the fiber will improve the tensile strength of composites by transferring an applied load. The stress transfer between matrix and fibers in a composite is not only determined by the intrinsic properties of the fiber and matrix, but also affected by the geometric parameters and fiber arrangement within the matrix such as fiber distribution [42, 43].

In general, for majority of the composites 50:50 is most effective fiber-volume fraction for better mechanical properties. In case of synthetic fibers, they occupy the largest fraction of the composite and bear the major portion of the load. Consequently, the fiber volume fraction and fiber orientation play an important role in deciding the final composite characteristics. Usually, synthetic fiber is different from natural fiber in many characteristics such as the density, moisture absorption, and the cross section shape and the fiber morphology. Several investigators indicated that the fiber volume fraction is one of the main parameters in the determination of the natural fiber reinforced composite’s mechanical properties; the variation of the fiber volume fraction in natural fiber composites will affect strongly the behavior of its failure. It has been a well-known mechanism that when a fiber composite is under axial tension, the axial displacements in the fiber and in the matrix will be different because of the differences in tensile properties of these two components. As a result, shear strains will be created on all planes parallel to the axes of the fibers. The shear strain and the resulting shear stress are the primary means by which load is transferred to fibers (for a short fiber composite), or distributed between and supported by the two components of composites. Therefore, it is expected that variation of the fiber volume ratio will result in a variation of the strength of the fibers. Also, the lower packing density and less fiber twist will give better and low variability of the natural fiber composites mechanical properties.

It is observed from SEM micrograph (Figure 5) that relatively excess amount of fiber lie down onto each other rather than being mixed with matrix at 50% fiber loads and relatively less amount of fiber and fiber fracture is observed at 30% fiber loads which also leads to reduce stress transfer ability.
It was also observed that relatively less fiber fracture and more homogeneous mixing can be observed at 40% fiber loading. So it may be said that 40% is the optimum fiber loading of abaca fiber reinforced polypropylene composites.

4. Conclusions

A good interfacial bond is required for the effective stress transfer from the matrix to the fiber in the composite. The literature has indicated that the chemical treatment considerably improves the fiber strength, fiber–matrix adhesion, and hence the performance of the natural fiber composites [44]. In the present study both alkali and benzene diazonium chloride treated abaca fibers reinforced polymer composites were fabricated by hot compression moulding technique and their tensile properties were measured. The tensile property is observed to have improved for both alkali and benzene diazonium chloride treatments of fiber. The results show that the tensile strength of the composites increased with increase in fiber loading up to 40% and beyond 40% it showed a decrease in tensile strength. Further, the results indicated that benzene diazonium chloride treated abaca fiber reinforced composites are having higher tensile strength than alkali treated abaca fiber reinforced composites and untreated abaca fiber reinforced composites. Coupling reaction has taken place between benzene diazonium chloride and cellulose of fiber resulting in the formation of a diazocellulose compound. This was confirmed from FTIR spectral analysis which has shown a peak at 1460 cm\(^{-1}\) corresponding to \(-\text{N}=\text{N}-\) group. The treatments improved the adhesive ability of the abaca fiber with the matrix in the fabricated composites, resulting in a greater tensile strength of the material.

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