APPENDIX I
Papers published/communicated in International Journals

1. Banana Fibre Reinforced Polyester Composites Mechanical, Failure and Aging Characteristics

2. Polyester Composites of Short Banana Fibre and Glass Fibre Tensile and Impact Properties

3. Determination of Polarity Parameters of Chemically Modified Cellulose Fibres by Means of the Solvatochromic Technique


5. Dynamic Mechanical Analysis of Banana Fibre Reinforced Polyester Composites

6. Viscoelastic Properties of Chemically Modified Banana Fibre Reinforced Polyester Composites
   L. A. Pothan, Z. Oommen and S. Thomas, *Polymer* (Communicated)

7. Effect of Chemical Modification on the Electrokinetic Measurements of Cellulose Fibers

8. Static and Dynamic Mechanical Properties of Banana/glass Woven Fabric Composites
   L. A. Pothan, Petra Potschke and S. Thomas, *Composites* Part A. (Accepted for publication)

10. Review on natural fibre reinforced thermoset composites
   L A Pothan, M Jacob and S Thomas *Progress in Polymer Science*
   (Communicated)

11. Dynamic Mechanical Analysis of Banana/Glass hybrid fiber composites
    (communicated to L. A. Pothan, and S. Thomas *Journal of Materials Engineering, Malaysia*)

12. Water absorption behaviour of banana fiber/polyester composites,
    L. A. Pothan and S. Thomas *Journal of Applied Polymer Science*
    (Communicated)

**Papers Presented in National/International Conferences and workshops**


APPENDIX II
CURRICULUM VITAE

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Research Interests

Textile composites of natural fibre and synthetic fibre
Fibre surface modification and characterisation
Fibre filled polymer composites
Particulate filled polymer composites, Fibre/matrix interface
Ageing, Degradation and Diffusion.

Computer background

Operating systems: DOS, Windows 98
Tools and packages: MS office, Microcal Origin, Chemwindow, Harvard Graphics
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<td>M.Phil. (Polymer Chemistry)</td>
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<td></td>
<td>Pursuing Ph.D. (Topic: Banana Fibre reinforced polyester composites)</td>
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<td><strong>Teaching Experience</strong></td>
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<td><strong>Research Experience in India</strong></td>
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<td><strong>Research Experience Abroad</strong></td>
<td>Polarity parameter measurements on chemically modified natural fibres in the department of polymer chemistry, Technical University, Chemnitz, Germany</td>
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<td>Project on Woven composites of sisal/polyester under Prof. Y.W.Mai in the City University of Hong Kong.</td>
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<td>Associate Member of the Royal Society of Chemistry (London)</td>
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<td><strong>Project being handled</strong></td>
<td>Design and Development of fibre (banana/glass reinforced Polyester composites Funding agency: State Committee on Science Technology and Environment, Government of Kerala, INDIA</td>
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<td><strong>Duration</strong></td>
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Determination of Polarity Parameters of Chemically Modified Cellulose Fibers by Means of the Solvatochromic Technique

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ABSTRACT: The surface polarity of organically functionalized cellulose fibers has been characterized with linear solvation energy relationships. The Kamlet-Taft hydrogen-bond-donating ability, the hydrogen-bond-accepting ability, the dipolarity/polarizability, Gutman’s acceptor number (an indicator of the electron-accepting ability), and Reichardt’s $E_{1430}$ parameter have all been used to quantitatively represent the polarity of the chemically treated and untreated fiber surfaces. Three different probe dyes, cis-dicyanobis(1,10-phenanthroline)-iron(II), Michler’s ketone, and aminobenzofurane, have been used as indicators to measure the polarity with correlation analysis of the energy of the ultraviolet-visible absorption maxima. Solvatochromic methods have been proven to be effective in characterizing chemically modified lignocellulosic fibers. Different silanes, NaOH, and long alkyl groups, used to modify the cellulose fiber surface, have changed the hydrogen-bond-donating ability of the fiber. © 2000 John Wiley & Sons, Inc.

Keywords: solvatochromism; probe dye; cellulose fiber; polarity parameters

INTRODUCTION

Lignocellulosic materials are abundant and underutilized and are finding applications in various engineering materials.1,2 Cellulosic fiber obtained from the pseudostem of the banana plant (Musa sapientum) is a bast fiber with relatively good mechanical properties. Table 1 contains the mechanical properties of banana fibers of various diameters. X-ray studies of the fibers have shown that the cellulose content of the fibers has a cellulose 1 structure, giving a characteristic X-ray peak around $d = 0.386$, 0.533, and 0.597 nm. The fiber has a high degree of crystallinity with a good alignment of crystallites parallel to the fiber axis. The crystalline cellulose in banana fiber is arranged in the form of a helix at an angle of 11–12° for fibers 100–200 μm in diameter. The major chemical constituents of the fiber, which is lignocellulosic, are cellulose (63–64%), hemicellulose (19%), and lignin (5%). The hemicellulose component is 4-O-methyl glucose xylan.3–6 In our earlier studies, cellulose fiber was found to be an effective reinforcement in the polymer matrix for making cost-effective composites.7 To improve the adhesion between the fiber and the polymer, various chemical treatments have been suggested by several authors.8 Silanes that are widely used to improve adhesion promotion in glass fibers have
Table I. Mechanical Properties of Banana Fiber

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Diameter of Fiber (μm)</th>
<th>Initial Young’s Modulus (Giga Newton m⁻²)</th>
<th>SD$^a$ Initial Young’s Modulus (Giga Newton m⁻²)</th>
<th>Breaking Strength (Mega Newton m⁻²)</th>
<th>Strain (%)</th>
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</table>

been found to be effective for natural fibers as well. Various silanes have been tried to improve the surface of cellulose fibers. In addition, alkali of different concentrations and acetylation have been tried. A knowledge of the surface characteristics is important for understanding the forces responsible for the fiber–matrix adhesion in composites.

Diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy was used to analyze the surface of chemically modified cellulose fiber and proved inadequate to clearly distinguish the various functional groups.

The acid or basic properties of solid surfaces are interesting aspects of surface structures. An increase in acidic or basic properties improves the interaction with other surfaces. Therefore, better adhesion of the surface with the polymer can be expected. Of the phenomena employed to determine (1) the key characteristics of solvents that can influence reactivity, (2) the relative importance of those characteristics for particular solvents, and (3) the importance of those characteristics with respect to individual solutes, solvatochromism has made a spectacular contribution.

In electronic spectra, ultraviolet-visible (UV-vis) solvatochromism of probe dyes is expected if the solvent polarity is changed. Bathochromic shifts (to lower frequencies) are found with increasing solvent polarity when the excited state is more polar than the ground state. $E_T$, also called $E_T(30)$, is an empirical scale of solvent polarity that is defined as the $\pi-\pi^*$ transition energy of the dissolved dye 2,5-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenolate in kilocalories per mole. This $E_T(30)$ solvent polarity scale has been applied to describe a great variety of solvent-dependent chemical processes in organic chemistry during the last 3 decades.

The sum of all possible interactions between a surface group and an adsorbed molecule or ion is termed surface polarity. Attempts to measure the surface-polarity parameters with the solvatochromic shift of the polar indicator dyes are reported in the literature. In well-behaved regular solvents, the thermal motions of the solvent molecules surrounding the solvatochromic probe dye cause an average polarity. Consequently, a specific probe dye reflects the specific sum of interactions operative between the relevant surface groups and the relevant sites of the probe molecule. When probe dyes are adsorbed onto suspended solid materials from solution, there are many factors that determine the extent of interaction. The thermal motions at the surface of the solid material will be lower than those of an adsorbed probe dye contacting the liquid. The probe dye should interact with the site on the surface corresponding to a minimum of the free energy. Accordingly, the interactive forces differ with the polarity indicator used.

The fundamental Kamlet-Taft equation, which employs the different linear solvation energy (LSE) relationships, describes the manifold influence on a solvent-dependent solute property, $XYZ$, studied with four terms, $\alpha$, $\beta$, $\pi^*$, and the Hildebrand solubility parameter ($\delta_H$), as represented in eq 1:

$$XYZ = (XYZ)_0 + h\delta_H^2 + s(\pi^* + d\delta) + a\alpha + b\beta$$  

$(XYZ)_0$ is the solute property of a reference system (e.g., a nonpolar medium or the gas phase), $\alpha$ is the hydrogen-bond-donating (HBD) ability, $\beta$ is the hydrogen-bond-accepting (HBA) ability, and $\pi^*$ is the dipolarity/polarizability of the solvents. The term $\delta$ is a polarizability correction term that is 1.0 for aromatic solvents, 0.5 for polyhalogenated solvents, and 0 for aliphatic solvents, and $a$, $b$, $s$, $d$, and $h$ are solvent-independent coefficients.
They reflect the susceptibility of the solute with respect to these properties. For solvent effects on spectra, the $h^{12}$ term is important.\textsuperscript{12} Spange and Reuter\textsuperscript{17} reported the application of Fe(phen)$_2$(CN)$_2$ and Michler's ketone as suitable surface-polarity indicators to analyze the $\alpha$ and $\pi^b$ terms of modified silica particles and also the application of the Kamlet-Taft parameters $\alpha$, $\beta$, and $\pi^b$ as a reference system to parameterize the surface polarity. The solvatochromism of well-characterized probe dye indicators and solvent polarity scales based on such dyes have been established as important tools for investigating the polarity and donor-acceptor properties of different media.\textsuperscript{18–21} Spange et al.\textsuperscript{21} established that the solvatochromic method introduced by Kamlet and Taft\textsuperscript{14} based on nitrosubstituted aromatics as polarity indicators is not applicable to acidic surfaces. Cellulose surfaces possess dipolar and HBD properties and cannot be characterized by the polarity indicators introduced by Kamlet and Taft.\textsuperscript{14} Spange et al.\textsuperscript{21} reported the determination of solvatochromic parameters of cellulose fibers by choosing a set of carefully characterized indicators.

This article represents the characterization of chemically modified cellulose fiber surfaces with three carefully chosen probe dye indicators, dicyano-bis(1,10-phenanthroline) iron(II) (1), Michler's ketone (2), and aminobenzodifuranone (3), and the calculation of the polarity parameters with different multiple correlation equations.

**EXPERIMENTAL**

**Materials**

Cellulose fiber was obtained from Sheeba Fibres and Handicrafts, Povvancode, Tamil Nadu. The various silanes, A174, A151, A1100, and Si-69 were obtained from Sigma-Aldrich, India. F8261 was obtained from ABCR GMBH and Co. All the other chemicals were commercial-grade.

**Silane Treatment for Cellulose Fibers**

About 0.3–0.6% of the respective silane was mixed with an ethanol/water mixture in the ratio 6/4 and was allowed to stand for 1 h. The pH of the solution was maintained at 4 with the addition of acetic acid. Neatly separated and cut cellulose fiber was dipped in this solution and was allowed to remain there for 1.5 h. The ethanol/water mixture was drained out, and the fiber was dried in air for 0.5 h and then in an oven at 70 °C until the fiber was completely dry.

**Treatment with C18-T**

C18-T was synthesized according to the procedure described by Zadorecki and Flodin.\textsuperscript{22} The dried cellulose fibers were first immersed in a 0.1 N NaOH solution, then dried, and finally soaked in a solution of C18-T (10 wt % of the fibers) in acetone for 3 min at room temperature. After evaporation of the solvent, the fibers were cured at 60 °C for 2 h in an inert atmosphere.

**Treatment with NaOH**

Cleaned and well-separated cellulose fibers were dipped in 0.25 and 0.5% solutions of NaOH for 0.5 h and then washed in very dilute acid to remove any particles of alkali. Washing was continued until the fibers were alkali-free. The washed fibers were then dried in an oven at 70 °C for 3 h. In another case, the fibers were refluxed in 0.25% alkali for 1 h, taken out, washed free of alkali, and then dried.

The structures of the various chemical agents used are given in Chart 1.

**Solvents Used for Solvatochromic Measurements**

1,2-Dichloroethane (DCE) and cyclohexane were dried over calcium hydride (CaH$_2$) and freshly distilled before use.

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**Chart 1.** Structures of the various chemical agents used for the treatments of banana fibers.
CHEMICALLY MODIFIED CELLULOSE FIBERS 2549

Chart 2. Formulae of the probe dyes used.

Solvatochromic Probe Dyes

The probe dye indicator 1 was prepared according to Schilt.23 2 was purchased from Merck (Darmstadt), recrystallized twice from ethanol, and carefully dried before use. 3 was kindly provided by BASF Aktiengesellschaft, Manchester, England. The formulae of the probe dyes are given in Chart 2.

Solvatochromic Measurements

The fibers were weighed and covered with 20 mL of the respective solvent. Stock solutions of the probe dyes of the specified concentrations were prepared. For dye 1, a concentration of $2 \times 10^{-3}$ mol/L in DCE was used; for dyes 2 and 3, a concentration of $1 \times 10^{-3}$ mol/L in cyclohexane was used. The stock solution (4 mL for 1 and 2 mL for 2 and 3) was added to the fibers in the respective solvent (DCE or cyclohexane). The fibers with the probe dyes were shaken overnight. The solvent was then decanted off, and the fibers were washed with the respective solvents to remove any dye particles adhering. The fibers were dried in vacuo at 30 °C for 12 h. The dried samples were used for UV–vis measurements. The equipment employed was an MCS 400 UV–vis spectrometer with glass fiber optics (ZEISS GmbH). UV–vis spectra of fibers were recorded by a special reflectance technique. The fibers were placed between two quartz plates. The sensor head for measuring reflectance spectra was located under one of those quartz plates, and the UV–vis spectrum of the adsorbed dye was monitored. The absorption maxima were detected with a software program. Chart 3 gives a schematic representation of the investigation.

Calculation of the Polarity Parameters

The solvatochromism and properties of the indicators and the mathematical procedure for the determination of the individual LSE approaches of the indicators are described in detail in the literature.18,24

The following multiple correlation equations are used in this article to separate the polarity parameters from the unit of measurement of each $\nu_{\text{max}}$(indicator):25

$$\alpha = -7.900 + 0.453 \nu_{\text{max}}(1) \cdot 10^{-8} (\text{cm}^{-1})$$
$$+ 0.021 \nu_{\text{max}}(2) \cdot 10^{-3} (\text{cm}^{-1}) \quad (2)$$

$$\pi^a = 13.889 - 0.251 \nu_{\text{max}}(1) \cdot 10^{-3} (\text{cm}^{-1})$$
$$- 0.320 \nu_{\text{max}}(2) \cdot 10^{-5} (\text{cm}^{-1}) \quad (3)$$

$$\beta = (-1/2.93)(\nu_{\text{max}}(3) \cdot 10^{-3} (\text{cm}^{-1}) - 18.6$$
$$+ 0.91 \pi^e - 0.97 \alpha) \quad (4)$$

$$AN = 0.0137 \nu_{\text{max}}(1)(\text{cm}^{-1}) - 207.8 \quad (5)$$

Chart 3. Schematic representation of the investigation.
Figure 1. UV–vis absorption spectra of dye 1 on untreated and alkali-treated banana fibers: (1) untreated, (2) 0.25% NaOH, and (3) 0.5% NaOH.

For well-behaved regular solvents, the following LSE equation of the $E_r(30)$ parameter was calculated by Marcus; this equation can also be used for natural fibers:

$$E_r(30) = 31.2 + 15.2\alpha + 11.5\pi^{*}$$ \hspace{1cm} (6)

**RESULTS AND DISCUSSION**

The UV–vis spectra of untreated and chemically treated cellulose fibers were analyzed with the probe dyes Fe(phen)$_2$(CN)$_2$ (1), Michler's ketone (2), and aminobenzodifuranone (3). The analysis was done with DCE as the solvent for dye 1 and with cyclohexane as the solvent for dyes 2 and 3. DCE was chosen as a standard solvent because it bears only very weak HBA properties. Figure 1 shows the UV–vis spectrum of untreated cellulose fibers and cellulose fibers treated with 0.25 and 0.5% NaOH when probed with dye 1.

The spectra show a definite change in the absorption peak compared with the untreated fiber, showing a reduction in the number of acidic sites. An increase in the concentration of the alkali gives a bathochromic band shift, as can be seen in Figure 1. The broader absorption peak can be attributed to the changes in the surface structure of the fiber. The changes in the surface structure can be explained by the changes in the manifold surface properties due to the interaction with alkali. Table II shows the UV–vis absorption maxima for the three dyes used on differently treated fibers. Clear absorption peaks are not visible for 2 adsorbed onto the fibers treated with silanes A174 and A1100, acetylated, or treated with C18-T. The $\nu_{max}$ values for 3 are the lowest. However, clear absorption peaks are not visible for 3 adsorbed onto fibers treated with C18-T, probably because of the inability of the dyes to attach to the long alkyl chains because of the low surface acidity. Only 3 could locate the centers on the fibers treated with A1100.

Figure 2 shows the UV–vis absorption bands of dye 1 adsorbed on fibers treated with silane A174. The absorption spectrum is broad for 1 adsorbed onto fibers treated with the more concentrated alkali. The pretreatment of the fiber with a 0.25% alkali gives a higher (HBD) acidity value. When a mild alkali is used, there is not much disturbance to the supramolecular structure. When the fibers treated with 0.5% alkali are further treated with silane, more coverage of the surface area by silane occurs because of the additional cavities available from the dissolution of hemicellulose and lignin. These multilayers, other than forming ether linkages with the fiber surface, self-condense to give polysiloxanes. Table III contains the Kamlet–Taft polarity parameters calculated for the various fibers.
Figure 2. UV–vis absorption spectra of dye 1 on untreated and silane-treated banana fibers: (1) untreated, (2) 0.25% NaOH + A174, and (3) 0.5% NaOH + A151.

The Kamlet–Taft HBD ability $\alpha$ is lowest for fibers treated with silane A174. An increase in the concentration of the alkali decreases the HBD ability $\alpha$. The increase in the $\alpha$ value can be attributed to the changes in the manifold surface properties that make new reaction sites available. The hemicellulose of the cellulose fiber is sensitive to the action of alkali and is subjected to dissolution. In addition to the hemicellulose, the lignin component dissolves out. This makes additional reaction sites available for the silanol. The polysiloxane bridges are responsible for the low HBD $\alpha$ values. The AN values calculated for these fibers, which are indicative of the electron-accepting ability or acidity, also show the same trend.

The $E_f(30)$ parameter calculated by the Marcus equation (eq 6) is given in Table IV. This parameter also shows the same value when a higher alkali concentration is used. The $E_f(30)$ parameter reflects the polarity of the environment.

The $\alpha$ value is lower when silane A174 is used. Unlike silane A151, silane A174 has a polar carbonyl group. The HBD acidity is lowered because of the presence of the polar group. Spange et al. reported a decrease in the value of the $\alpha$ parameter through an increased degree of functionalization on the silica surface. Something else that can be attributed to the low $\alpha$ value is the inability of the bulky dye particles to attach themselves to the hydrogen atoms within the crevices of the cellulose. The value of the $\pi^e$ parameter, however, increases. This may be due to the dispersion forces between the dye and the siloxane bridges.

Figure 3 represents the UV–vis spectra of dyes 1, 2, and 3 adsorbed onto the fibers after treatment with silane A151.

The $\alpha$ values of the fibers treated with silane A151 show the same trend as those of A174, as shown in Figure 2. The dissolution of hemicellu-
Figure 3. UV–vis absorption spectra of dyes 1, 2, and 3 adsorbed onto banana fibers after treatment with silane A151.

Lose and lignin attributed to A174 can be given as the reason in this case also. However, the π* value is lower. This can be explained as due to the differences in the functional groups of the two silanes. The AN values calculated for the fibers treated with silanes A151 and A174 are lower at higher alkali concentrations.

The UV–vis spectra of dyes 1, 2, and 3 adsorbed onto the fibers treated with silane F8261 are shown in Figure 4.

In Figure 4, only one peak is visible for dyes 1 and 2, but two peaks are visible for dye 3. The UV–vis absorption maxima obtained for dye 3 are at $\lambda_{max} = 528$ nm and $\lambda_{max} = 674$ nm. The two peaks represent two surface centers, one due to $\text{CF}_2$ and the other due to $\text{CH}_2$.

The $\alpha$ value of the F8261 fiber is low compared with that of the ones treated with A174 and A151. The value of the $\pi^*$ parameter, which represents the overall polarity, is also lower than that of the fiber treated with silane A174. Treatment with silane Si 69 also gives a value nearer to that of F8261 and an overall polarity value nearer to that of the fibers treated with the fluorinated silane.

The indicator dyes 1 and 2, however, could not give any absorption peak when adsorbed onto the fibers treated with silane A1100. However, 3 was able to give a broad absorption with two absorption maxima; 3 can locate both acidic and basic centers.

However, for fibers treated with C18-T, no UV–vis absorption peaks are visible because of the low surface acidity of the functional groups. Solvatochromic measurements carried out on alkyl-modified silica also did not provide any measurable influence on the chromophoric $\pi$ system.28 The large bulky alkyl groups possibly prevent the dyes from attaching to the polar surface centers of the fiber. Chart 4 shows the schematic representation of the large alkyl group preventing the probe dye from reacting with the fiber surface.

Dye 1, we would suggest, is ideal for locating acidic centers on chemically modified cellulose fibers also.

Chart 4. Schematic representation of the large alkyl group preventing the probe dye from reacting with the fiber surface.
Unlike dye 1, dye 2 gave sharp UV-vis absorption bands in almost all cases. Fibers treated with the various silanes, namely, A151, Si 69, and F8261, were all characterized by the indicator dye 1. The absorption bands obtained due to 2 are at a lower wavelength than those due to 1. The UV-vis absorption peaks due to 2 are due to a $\pi-\pi^*$ transition.

As evident from Table II, for samples treated with A174 pretreated with 0.25% NaOH, the UV-vis absorption maximum obtained at $\lambda_{\text{max}}(2) = 390$ nm and that obtained at $\lambda_{\text{max}}(2) = 401$ nm for fibers treated with 0.5% NaOH and A174 correlate well with the dipolarity/polarizability of the silanol group environment, as reported by others for silica samples. Other silane-treated fibers also gave an UV-vis absorption maximum at these wavelengths. Dye 2 can be used to detect silanol groups on cellulose fiber surfaces also.

However, the indicator dyes 1 and 2 did not give any UV-vis absorption maxima. For the amino silane-treated cellulose fibers, dye 3 was able to give an UV-vis absorption band with a shoulder indicating the absorption due to both the NH$_2$ and OH groups. Dye 3 adsorbed onto samples treated with the other silanes, namely, A174 and A151, could also give broad UV-vis absorption bands with two absorption maxima; 3 can locate both acidic and basic sites within the cellulose fiber.

**CONCLUSION**

Chemically modified cellulose fibers have been characterized with a solvatochromic technique. The HBD acidity $\alpha$, the basicity $\beta$, the dipolarity/polarizability $\pi^*$, the AN, and the $E_1(30)$ parameter values were determined in a few cases for the chemically modified cellulose fibers. In this study, the HBD acidity was the lowest for fibers treated with silane A174 after pretreatment with 0.5% NaOH. The highest AN value was for fibers treated with silane A151. The $E_1(30)$ parameter, an indicator of the overall polarity, was greatest for fibers treated with silane A151. The probe dye aminobenzodifuranone (3) has been proven to be the best for identifying the acidic and basic centers in chemically modified cellulose fiber.

**REFERENCES AND NOTES**


Short Banana Fiber Reinforced Polyester Composites: Mechanical, Failure and Aging Characteristics

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ABSTRACT: This paper describes the tensile, impact, flexural properties and aging behavior of short banana fiber reinforced polyester composites with special reference to the effect of fiber length and fiber content. Maximum tensile strength was observed at 30 mm fiber length while impact strength gave the maximum value for 40 mm fiber length. Incorporation of 40% untreated fibers gave a 20% increase in the tensile strength and a 341% increase in impact strength. On treatment with silane coupling agent, composites showed a 28% increase in tensile strength and a 13% increase in flexural strength. Aging studies showed a decrease in tensile strength of the composites. The experimental tensile strength values were compared with theoretical predictions according to Piggot equation. Scanning electron microscopy studies were carried out to understand the morphology of the fiber surface, fiber pullout and interface bonding. Water absorption studies showed an increase in water uptake with increase in fiber content. Finally, the properties of banana fiber reinforced polyester composites have been compared with other natural fiber reinforced composites.

KEY WORDS: banana fiber; polyester; coupling agent; aging.

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INTRODUCTION

Natural fibers are relatively inexpensive and these renewable resources which are abundantly available and underutilized have the potential to be fillers and reinforcements in polymers [1]. Studies have been carried out with other natural fibers like coir [2], sisal [3], pineapple leaf fiber [4], oil palm empty fruit bunch fiber [5], etc. Results of the above studies carried out in this laboratory by Thomas and coworkers have shown natural fiber to be an effective reinforcement in plastic. Studies have also been carried out on the effect of fiber treatment on various natural fibers to improve fiber matrix bonding [6]. Natural fibers are themselves cellulose reinforced materials and the cellulose content and microfibril angle determine the mechanical behavior of the fiber [7]. The high cellulose content (64%) and low microfibrillar angle (11°) of banana fiber indicate that it has potential as a reinforcing material [8]. Composites made out of banana/cotton hybrid fabric have been found to be useful in the preparation of low strength material [9]. It has been reported that addition of banana fiber to polymeric matrices can make composite products adequate for building application [10]. This study focuses on the effect of banana fiber on the mechanical properties of polyester composites. The influence of fiber loading and fiber length on the tensile, flexural and impact properties has been analyzed. Several studies have been reported based on the surface modification of fibers [11-16] to improve interfacial bonding between fiber and matrix. Effect of the coupling agent, vinyl triethoxy silane, on the mechanical properties of the composites has also been studied. The tensile and flexural failure surfaces of the samples have been examined by scanning electron microscopy to understand the nature of failure, fiber matrix adhesion, fiber breakage and pullout. Percentage decrease in tensile strength of samples subjected to aging has also been studied. Finally the properties of banana fiber reinforced polyester composites have been compared with other natural fiber reinforced thermoset composites.

EXPERIMENTAL

Banana fiber was obtained from Sheeba Fiber and Handicrafts, Poovancode, Tamil Nadu, India. The polyester used for the study was unsaturated polyester resin HSR 8131 (Sp. gr 1.12, viscosity 650 cps, gel time 25 min) obtained from M/s Bakelite Hylam Ltd., Hyderabad, India. Vinyl triethoxy silane was obtained from Merck, Germany. Methyl ethyl ketone peroxide and cobalt naphthanate were of commercial grade obtained from M/s Sharon Enterprises, Cochin, India. The characteristics of polyester and banana fiber are given in Tables 1 and 2.

The well separated fibers were cut into the desired length of 10, 20, 30 and 40 mm. The matrix was prepared by taking a definite amount of resin to which 0.9% (volume per cent) cobalt naphthanate and 1% (volume per cent) methyl ethyl ketone peroxide were added. Curing of laminates was done at room temperature for 24 h. Composites were prepared using treated and untreated fibers. Fiber treatment was done by immersing the chopped fibers in water/ethanol mixture in the ratio 40:60 containing different concentrations of silane (0.3, 0.6, 1 and 2%) for 1 1/2 h. The pH was maintained between 4 and 7 by adding acetic acid. The
Table 1. Typical properties of the liquid resin.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>A clear pale yellow liquid</td>
</tr>
<tr>
<td>Viscosity @25°C (cps) (Brookfield viscometer)</td>
<td>650</td>
</tr>
<tr>
<td>Specific gravity @25°C</td>
<td>1.11</td>
</tr>
</tbody>
</table>

Typical properties of cured unreinforced resin (specimens cured for 24 h at room temperature followed by post-curing for 4 h at 80°C).

- Tensile strength (psi): 9000
- Flexural strength (psi): 16,000
- Water absorption at 25°C (%), 28 days: 0.65

Table 2. Physical and mechanical properties of banana fiber.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose content</td>
<td>63-64%</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>19%</td>
</tr>
<tr>
<td>Lignin</td>
<td>5%</td>
</tr>
<tr>
<td>Moisture content</td>
<td>10-11%</td>
</tr>
<tr>
<td>Initial modulus</td>
<td>20-51 MPa</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>520-750 MPa</td>
</tr>
<tr>
<td>Density</td>
<td>1.35 g/cc</td>
</tr>
</tbody>
</table>
fibers were dried in air followed by drying in an oven at 70°C for 30 min. The tensile properties of samples were determined in accordance with ASTM D 638-76 at a cross head speed of 5 mm/min using Zwick model 1465. The tensile strength and modulus were determined from the stress strain curves. Five samples were tested in each set and the mean value was taken. Flexural strength of the specimen was done by three point bend tests as per ASTM D790-91 at a cross head speed of 4 mm/min. Charpy impact test on unnotched specimen was determined using a pendulum impact testing machine. Water absorption of composites was tested as per ASTM D570-81. Aging studies of the composite were carried out by subjecting the conditioned specimens to accelerated and natural aging.

RESULTS AND DISCUSSION

The performance of a composite is judged by its properties. The mechanical properties of short fiber reinforced composites which include the strength, modulus, mode of failure are all dependent on the properties of the banana fiber and polyester matrix and also on the fiber content and fiber orientation.

Tensile Properties

The tensile strength of the banana fiber is seen to vary from one variety to another and also from one locality to another [17]. The fibers have an initial modulus of 20–51 GN/m², tensile strength 520–750 MN/m² and extension at break 1.8–3.5%. The stress-strain curve of single banana fiber is given in Figure 1. The curve shows three distinct regions elastic, inelastic and crystalline. The initial portion, i.e., up to 3% elongation shows elastic behavior and after that it shows inelastic behavior. The increase in modulus at higher stress is due to the orientation of crystalline regions in the fiber.

Figure 2 delineates the effect of fiber loading on the tensile properties of the composite. At low fiber loading fibers act as flaws and the volume percent of fiber is not enough to impart high strength to plastic [18]. The tensile strength shows a linear increase after the initial decrease for 10% loading. The stress-strain curve of the composite as a function of fiber loading is given in Figure 3. The tensile stress is found to increase with fiber loading, the value being a maximum for 40% loading. At a loading of 30 and 40 percent, the stress-strain curves seem to overlap emphasizing the maximum allowable fiber content. There seems to be an increase of 159% in stress for a 40 weight percent composite compared to a 10 weight percent composite. However, compared to neat polyester the increase in stress is about 20%. Figure 4 delineates the effect of fiber content on tensile modulus. The tensile modulus is found to be maximum for 20% loading followed by a decrease at higher loading.

Figure 5 shows the effect of fiber length on the tensile strength of the composite. In a discontinuous fiber composite the stress along the fiber is not uniform. A certain fiber length called critical fiber length is required for the effective transfer of stress between fiber and matrix. From the figure it is clear that tensile strength gives a maximum value for 30 mm fiber. Tensile strength of the compos-
Figure 1. Stress-strain curve of banana fiber.

Figure 2. Effect of fiber content on the tensile strength of the composites (fiber length 20 mm).
Short Banana Fiber Reinforced Polyester Composites

Figure 3. Stress-strain curves of banana polyester composite at different fiber content under tension (fiber length 20 mm).

The stress shows a linear increase with fiber length. Curtis and Bader [19] found that the ends of fiber acted as notches and generated considerable stress concentrations which could initiate micro cracks. Tensile strength therefore is low for smaller fiber lengths. However, there is a decrease in tensile strength at 40 mm fiber length. At higher fiber lengths dispersion problems and fiber to fiber interactions can occur. Moreover, fiber curling will occur reducing the fiber length and thereby effective stress transfer.

Silane-coupling agents which are widely used on glass fiber to form stable covalent bonds to both the mineral surface and the resin are potentially suitable for use on cellulosic fibers [20]. Figure 6 shows the effect of silane concentration on the tensile strength of the composites. The increase in tensile strength is found to be 11% at 0.3% silane concentration while it is 28% at 0.6% concentration. At a higher concentration the improvement is only negligible. The silane coupling agent undergoes hydrolysis to form silanols which serves to bridge the interface. The silane by coreacting with the polymer modifies the morphology at the interface to improve stress transfer. This involves a tightening up of the polymer structure through increased crosslinking and increase in rigidity [21]. The mechanism of adhesion of the silane on to the fiber can be represented as follows.

\[
\text{CH}_2=\text{CH-} \text{Si(OC}_2\text{H}_5)_3 + 3\text{H}_2\text{O} \rightarrow \text{CH}_2=\text{CH-Si(OH)}_3 + 3\text{C}_2\text{H}_5\text{OH} \quad (1)
\]

\text{silineol}
In the presence of moisture the silanol reacts with -OH groups attached to the glucose units of the cellulose molecule in the cell wall thereby bonding itself to the cell wall by further rejection of water. The tensile modulus also showed maximum value between 0.3 and 0.6% silane concentration (Figure 7).

The experimentally observed tensile strength values of short banana fiber reinforced polyester with different fiber loading have been compared with theoretical predictions. The Piggot equation according to which the strength of a composite is given by

\[ T_c = T_f K_1 K_2 V_f + T_m (1-V_f) \]

where

- \( T_c \) = composite strength
- \( T_f \) = fiber strength
- \( V_f \) = volume fraction of fibers
- \( K_1 \) = fiber orientation factor
- \( K_2 \) = fiber length factor \((l/2l)\)
- \( l \) = length of the fiber

**Figure 4.** Effect of fiber content on the tensile modulus of the composites (fiber length 20 mm).
Figure 5. Effect of fiber length on the tensile strength of banana polyester composites (fiber content 20%).

Figure 6. Effect of silane concentration on the tensile strength of banana-polyester composites (fiber length 20 mm; fiber content 20%).
The values calculated using Piggot's equation showed agreement with the experimental values (Figure 8). However, deviation was found to be large at low fiber concentration.

Figures 9 and 10 are the SEM photomicrographs of untreated and silane treated banana fiber. The treated fiber has a rough surface topography. Development of a rough surface topography offers better fiber-matrix adhesion and an increase in mechanical properties. Figures 11 and 12 are the tensile fracture surface morphology of the untreated and silane treated banana polyester composite, respectively. The better fiber-matrix bonding can be seen from the polyester particles sticking to the fiber surface in the case of treated fibers (Figure 12). The clean fiber pull out regions in the case of untreated fibers show weak interfacial bonding (Figure 11).

**Flexural Properties**

Stress-strain characteristics of banana-polyester composites under flexure at different fiber loading are given in Figure 13. The flexural strength of the composite is found to be lower than that of neat polyester at lower fiber loading. Similar results have been observed by other workers. Zhu et al. [22] has reported that unlike other natural fiber composites flexural strength of banana fiber reinforced polyester composites is lower than that of neat polyester at low fiber loading. The
Figure 8. Comparison of theoretical and experimental values of tensile strength at different fiber loading.

Figure 9. SEM photograph of banana fiber surface.
Figure 10. SEM photograph of the surface of silane treated banana fiber.

Figure 11. Tensile fracture surface of untreated banana fiber-polyester composites.
Figure 12. Tensile fracture surface of treated banana fiber-polyester composites showing broken fiber and also adhering polyester particles.

Figure 13. Stress-strain curve of banana polyester composites under flexure at different fiber loading.
Flexural strength is found to be a maximum for 40% loading of fibers. For every 10% increase in fiber loading there is approximately an increase of about 13% in flexural strength. Figures 14 and 15 show the effect of fiber content on the flexural modulus and flexural strength. The flexural modulus is low for 10% loading but the modulus values increase appreciably when the fiber loading is increased to 20%. For 30% loading also the flexural modulus shows a comparatively higher value and the modulus does not show increasing trend after 30%.

Figure 16 shows the effect of fiber length on the flexural strength and flexural modulus at constant loading of 20%. The flexural strength and flexural modulus are found to be maximum when the fiber length is 20 mm.

The effect of silane concentration on the flexural strength and flexural modulus is given in Figure 17. Both flexural strength and flexural modulus give a high value at 1% silane concentration. The flexural strength of silane treated composites showed a 13% increase in strength. SEM photographs of the fracture surfaces of untreated and silane treated composites are given in Figures 18 and 19, respectively. Fracture surface of untreated fiber composite shows fiber pullout which is an indication of adhesion between fiber and matrix. Figure 19 shows fibrillation and also broken fibers in the case of treated fiber composites. This suggests improved fiber-matrix interaction.

Impact Properties

Impact strength of the samples were measured under varying fiber length and

![Graph](image.png)

**Figure 14.** Variation of flexural modulus of banana-polyester at different fiber content (fiber length 20 mm)
Figure 15. Effect of fiber content on the flexural strength of composite (fibre length 20 mm).

Figure 16. Variation of flexural modulus and flexural strength with fiber length of banana-polyester composites (fiber content 20%).
Figure 17. Effect of silane concentration on the flexural strength and flexural modulus of banana-polyester composites (fiber length 20 mm; fiber content 20%).

Figure 18. Fracture surface of untreated banana fiber-composite under flexure.
fiber loading. Figures 20 and 21 show the effect of fiber loading and fiber length on the impact strength of the composites. For a given fiber length of 40 mm, the impact strength increases linearly with increasing fiber concentration. The percentage increase in impact strength is 177 for 20% fiber loading while the value changes to 270 and 341 for 30% and 40% loading. At a loading of 40% the impact strength at room temperature becomes maximum when the fiber length is 40 mm (Figure 21).

The high impact strength shown by composites with 40 mm length can be attributed to the extra energy dissipation mechanisms due to plastic deformation as shown in Figure 22 [23-25]. For shorter fiber length, the fiber being pulled out of the matrix is more likely than a plastic deformation. High impact strength for 40 mm fiber over the shorter fiber lengths can be explained as due to plastic deformation [24].

Water Absorption and Aging Studies

The slightest amount of water can significantly alter the key mechanical properties of natural fiber filled composites. The percentage increase in weight of the specimens after immersion in water for various time intervals (in days) is calculated to the nearest 0.01% as follows.

\[
\text{Increase in wt}\% = \left( \frac{\text{Net wt} - \text{Conditioned wt}}{\text{Conditioned wt}} \right) \times 100
\]
Figure 20. Effect of fiber loading on the impact strength of the composite (fiber length 40 mm).

Figure 21. Effect of fiber length on the impact strength of the composite (fiber content 40%).
Since the percentage of soluble matter lost during immersion in water is practically nil the increase in weight percent is equal to the percentage of water absorbed. The samples were soaked in water for about one month till the increase in weight almost leveled off. The percent absorption of water against time is shown graphically in Figure 23.

Water absorbed by the neat polyester was negligibly small, i.e., only 0.8% after a period of 35 days. The water uptake for samples with 10, 20 and 30% were found to increase regularly and leveled off at longer periods which is an indication of saturation. The leveling off period increases with the increasing concentration of fiber. The uptake is also due to the hydrophilic nature of cellulose and also due to the capillary action when fiber ends are exposed to water. The maximum water uptake was found to be for samples with 30 wt%, i.e., 29%.

Figure 24 shows the stress-strain curves of composite samples subjected to accelerated and natural aging. The stress is found to be maximum for the unaged sample. The stress of samples subjected to thermal aging is not much different from the unaged sample. While the unaged sample has shown a tensile strength of 903.16 MPa, the samples subjected to thermal aging has shown a value 845.5 MPa. The lowering of tensile strength is about 6%. Samples exposed to sun and rain continuously for six months have also shown only a 9% decrease in tensile strength. However, samples subjected to accelerated water aging have shown a 32% decrease in tensile strength. Other workers have also reported a decrease in mechanical properties of composites exposed to high humidity [26-28]. The water molecules act as a plasticizer by influencing the fibers, matrix and interface simultaneously and disturbing the mechanical integrity of the composite system [29]. Fiber-resin debonding may be initiated by the development of osmotic pressure pockets at the surface of fibers due to the leaching of water soluble substances from the fiber surface [30,31]. Also, initiators sometimes do not completely disappear but become converted into other substances which are capable
of acting as osmotic solutes [32]. The degradation of composites may thus occur not only with the degradation of the individual constituents but also with the loss of interaction between them [29,33]. Table 3 shows the variation in tensile strength of the composites with aging. This study indicates that banana fiber reinforced polyester composite can withstand normal exposure to environment without any appreciable change in tensile strength and reconfirms its utility as a substitute for timber in building purposes. The surface topology of banana fiber polyester composite shows wood like appearance. The composite has a smooth surface finish and resembles wood.

Comparison with Other Natural Fiber Reinforced Polyester Composites

In Table 4, the mechanical properties of banana polyester composites have been compared with other natural fiber composites. In fact, tensile, flexural and impact properties of banana fiber reinforced polyester composites have been compared with other natural fiber composites. Banana fiber composites have tensile and flexural strength comparable with other natural fiber composites while impact strength values are much higher than that of other composites.

CONCLUSIONS

Banana fiber has good potential as a reinforcing agent due to its high cellulose

![Figure 23. Effect of immersion time in water on the water absorbed (%) by banana-polyester composites](image-url)
content and low microfibrilar angle. Banana fiber composites are promising as a substitute for timber in building industry. The influence of fiber length and loading on the mechanical and aging characteristics of the composite has been investigated. The stress-strain behavior in tension indicated that the addition of fiber makes the composite more ductile. The tensile strength of the composite was found to increase with increasing concentration of fiber, after an initial decrease in tensile stress for 10% loading. The initial decrease in tensile stress can be attributed to the volume fraction being not enough to impart high strength to the composite. In the present study, maximum tensile strength and tensile modulus were observed for 40% and 20% loading, respectively.

**Table 3. Variation in tensile strength of composites with aging.**

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Tensile Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unaged</td>
<td>903.16</td>
</tr>
<tr>
<td>Thermally aged</td>
<td>845.50</td>
</tr>
<tr>
<td>Water aged</td>
<td>614.15</td>
</tr>
<tr>
<td>Naturally aged</td>
<td>821.90</td>
</tr>
</tbody>
</table>
Table 4. Properties of natural fiber polyester composites prepared by hand lay up (30%).

<table>
<thead>
<tr>
<th>Composite</th>
<th>Tensile Strength (MPa)</th>
<th>Flexural Strength (MPa)</th>
<th>Impact Strength (kJm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jute-polyester</td>
<td></td>
<td>66.25</td>
<td>14.67</td>
</tr>
<tr>
<td>Straw-polyester</td>
<td></td>
<td>47.00</td>
<td>2.6</td>
</tr>
<tr>
<td>Sisal-polyester</td>
<td>28</td>
<td>53.00</td>
<td>11.00</td>
</tr>
<tr>
<td>PALF-polyester</td>
<td>52.7</td>
<td>80.2</td>
<td>24.2</td>
</tr>
<tr>
<td>Banana-polyester</td>
<td>47.6</td>
<td>53.5</td>
<td>31.3</td>
</tr>
<tr>
<td>Coir-polyester</td>
<td>18.61</td>
<td>31.15</td>
<td>3.910</td>
</tr>
</tbody>
</table>

Silane treatment has been found to increase the tensile strength of the composite by about 28%. A silane concentration of 0.6 volume percent used in this study has given the maximum improvement in tensile strength. SEM photographs of the tensile fracture surface of treated fiber composites showed improved adhesion between fiber and matrix. Theoretical predictions of tensile strength made according to Piggot’s equation showed good agreement with experimental values.

In the case of flexural strength an increase in fiber content by about 10% has resulted in an increase of about 13%. The maximum value of flexural strength and flexural modulus was obtained for 40% loading. Impact strength of the composite showed a linear increase with fiber content. The improvement in impact strength at a fiber loading of 40% was found to be 341%.

Aging studies showed a decrease in tensile strength of about 6% for samples subjected to thermal aging, while it is 9% for samples kept exposed to sun and rain for six months. However, samples subjected to accelerated water aging showed a decrease of 32%. Water uptake of the composite was found to increase with fiber content and leveled off at longer periods. The leveling off period increases with increasing fiber concentration.

Comparison of the properties of banana fiber composites with other natural fiber composites has shown comparable tensile and flexural strength values but much higher impact strength values than other composites.

Banana fiber serves as an effective reinforcement in polyester composites. A fiber length of 30-40 mm and a fiber loading of 40% used in this study has given the best properties. These properties together with the inexpensive nature of the indigenous fiber make the composite attractive for industrial application. The surface topology of banana fiber polyester composite shows wood-like appearance. The composite has a smooth surface finish and resembles wood. The results suggest that banana fiber reinforced polyester composites have an edge over the conventional materials used in building industry.

REFERENCES

Polyester composites of short banana fibre and glass fibres.
The tensile and impact properties

Summary — Variations in tensile and impact properties of banana fibre reinforced polyester composites caused by the addition of glass fibre have been analysed. Banana fibre in combination with glass is excellent for making cost effective composite materials. The effects of the arrangement of glass and banana fibres in the preparation of composites have also been studied. A volume fraction of 0.11 glass mixed with banana fibre gives a 54.5% increase in the tensile strength and a 196% increase in the impact strength of the composites. The tensile strength increases linearly as the glass content is raised and attains the highest value when the glass volume fraction 0.17 is used and an interleaving arrangement of glass and banana fibres is followed. At lower volume fractions of glass, an intimate mixture of banana fibre and glass shows the highest tensile strength. The impact strength shows the highest value when a glass volume fraction of 0.11 is used.

Key words: cellulose, hybrid, random fibre, banana fibre, layering.

Multicomponent composite materials comprising two or more families of fibres have been recently attracting attention of researchers. This is because the use of one type of fibre alone has proved to be inadequate in satisfactorily tackling all the technical and economic problems confronted with in making fibre-reinforced composites. These types of composites introduce additional degrees of compositional freedom and provide yet another dimension to the potential versatility of fibre-reinforced composite materials. Combination of a high performance fibre with a low performance fibre provides versatility in the performance of the product. Various reports on hybrid composites of natural fibres reveal reduction in the material cost due to the low cost of the natural fibres used. The mechanical and physical properties of natural fibre reinforced plastics reach the values typical of a glass fibre-reinforced system only under certain conditions. Investigations on lignocellulosic fibre composites have shown that the properties of the fibre can be better utilised in hybrid composites [1—7]. Mohan and Kishore [2] have reported that glass has got good reinforcement effect along with jute. Clark and Ansell [3] have reported improvement of various mechanical properties of jute-glass hybrid laminates with different arrangements of jute and glass in the laminate. Pavithran et al. [4] have studied the mechanical properties of jute-glass hybrid laminates containing varying amounts of glass fibre. They have noticed a considerable enhancement in the mechanical properties on incorporation of a very small volume fraction of glass. Studies on sisal-glass in polyester have showed a linear increase in the work of fracture by varying the volume fraction of the glass at the core [5]. Attempts have been made in our laboratory to prepare hybrid composites of sisal and glass in polyethylene and oil palm empty fruit bunch fibre and glass in phenol formaldehyde (PF). It has been reported that addition of glass has improved the orientation characteristics and thereby the tensile strength of the composites [6]. A ratio of 0.26 : 0.74 volume fraction of glass to oil palm fibre has given a 23% improvement in the Izod impact strength of the composite. Better properties have been given by intimately mixed hybrid composites [7].

There is a conservative notion that the strength of a collection of fibres is governed by the fibre component with the smallest elongation at break. The traditional belief is that materials with significant differences in breaking strains will not share the same load path. Based on this view, when a collection of fibres is uniformly strained, the collection tends to break as the
straining level reaches the breaking strain level of the fibre which has the smallest breaking strain level. A subsequent infinitesimal increase in strain causes all those fibres characterised by the smallest breaking strain to fail. The sudden transfer of load to the remaining unbroken fibres is presumed to lead to catastrophic failure. Therefore, the ultimate strength of the system is the stress level at which the elongation of the system has reached the ultimate elongation of the fibre family [8]. The two fibres in the group are strain compatible only if strain compatibility parameter, \( \lambda \), has a value \(-1\) [8]. In the banana-glass system, the value of \( \lambda \) is 0.7, i.e., \(-1\). Therefore the two fibres are strain compatible.

In our earlier studies, banana fibre was found to be an effective reinforcement in polyester composites [9]. In this study, attempts have been made to improve the mechanical properties of the composite by the incorporation of glass fibre, based on the reports of other researchers [1—7]. Composites with different volume fraction of glass have been prepared and analysed.

**EXPERIMENTAL**

**Materials**

Banana fibre obtained from Siveeva Fibre and Handicrafts, Poovancode, Tamil Nadu, was used in this study. The chemical and mechanical characteristics of the banana fibre are given in Table 1. Unsaturated isophthalic polyester HSR 8131 obtained from M/s Bakelite Hylam, Hyderabad, India, was used as matrix. The important

<table>
<thead>
<tr>
<th>Table 1. Chemical and mechanical characteristics of banana fibre</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
</tr>
<tr>
<td>Hemicellulose</td>
</tr>
<tr>
<td>Lignin</td>
</tr>
<tr>
<td>Moisture</td>
</tr>
<tr>
<td>Initial modulus</td>
</tr>
<tr>
<td>Tensile strength</td>
</tr>
<tr>
<td>Density</td>
</tr>
</tbody>
</table>

**Table 2. Characteristics of isophthalic polyester**

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity</td>
<td>600 cps</td>
</tr>
<tr>
<td>Specific gravity at 25°C</td>
<td>1.11</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>9000 psi</td>
</tr>
<tr>
<td>Flexural strength</td>
<td>16000 psi</td>
</tr>
<tr>
<td>Water absorption at 25°C (24 hrs)</td>
<td>0.05%</td>
</tr>
<tr>
<td>Gel time</td>
<td>35 min</td>
</tr>
</tbody>
</table>

Characteristics of the polyester resin are given in Table 2. Multidirectional glass strand mat used for the study was supplied by Ceat Ltd., Hyderabad, India. Methyl ethyl ketone peroxide and cobalt naphthenate were of commercial grade supplied by Sharon Enterprise, Cochin.

**Preparation of composites**

Randomly oriented glass mats and neatly separated banana fibre cut at a uniform length of 30 mm were evenly arranged in a mould measuring 150x150x3 mm in the required layering pattern for preparing the samples. Composite sheets were prepared by impregnating the fibre with the polyester resin to which 0.9 volume percent cobalt naphthenate and 1% methyl ethyl ketone peroxide were added. The resin was degassed before pouring and air bubbles were removed carefully with a roller. The closed mould was kept under pressure for 12 hours; samples were post-cured and test specimens of the required size were cut out from sheets. Different volume fractions of glass were used for the preparation of samples as detailed in Table 3. In all these samples, glass was used as the core material. Samples with different layering patterns were also made in combinations A, C, and F as given in Table 4 and the pattern is depicted in Fig. 1.

**Table 3. Description of composite samples with different glass volume fraction**

<table>
<thead>
<tr>
<th>Sample marking</th>
<th>Volume fraction of glass</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.03</td>
</tr>
<tr>
<td>B</td>
<td>0.07</td>
</tr>
<tr>
<td>C</td>
<td>0.11</td>
</tr>
<tr>
<td>D</td>
<td>0.15</td>
</tr>
<tr>
<td>E</td>
<td>0.16</td>
</tr>
<tr>
<td>F</td>
<td>0.17</td>
</tr>
</tbody>
</table>

**Table 4. Explanation of the various layering patterns**

<table>
<thead>
<tr>
<th>Sample marking</th>
<th>Layering pattern</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1</td>
<td>G-B-G-B-G-B-G-C</td>
</tr>
<tr>
<td>L2</td>
<td>Intimate mixture of G and B</td>
</tr>
<tr>
<td>L3</td>
<td>G-B</td>
</tr>
<tr>
<td>L4</td>
<td>G-B-G-C-B-C</td>
</tr>
<tr>
<td>L5</td>
<td>G-B</td>
</tr>
</tbody>
</table>

where: G — glass, B — banana

**Fig. 1. The layering pattern of composite specimen marked A, C and F**

**Mechanical tests**

Test specimens were cut from composite sheets. Tensile testing was carried out by using HIE electronic tensile testing machine TNE-500 according to ASTM D 63-
Five samples were tested in each set and the average value is reported. Impact test was done on a Charpy impact tester instron Wolpert PW5 according to ASTM D256. Minimum of four samples were tested in each case and the average value is reported. Fractography of the failure surfaces of the composites were examined by a Scanning Electron Microscope after the surfaces had been sputtered with gold.

RESULTS AND DISCUSSION

Tensile stress-strain behaviour

Figure 2 represents the tensile stress-strain behaviour of a neat polyester and a banana polyester with a fibre volume fraction of 0.4. Figure 3 delineates the tensile stress-strain behaviour of banana glass hybrid composites with a constant fibre volume fraction of 0.4 (with in experimental error) and varying glass volume fractions. The response of the material when subjected to an increasing stress is shown in Fig. 3. An increase in the glass volume fraction changes the general nature of the stress strain curve. Aveston et al. have reported on the general nature of the stress-strain curve of hybrids. The hybrid stress-strain curve, theoretically, has different slopes in the initial and final portions [10]. When subjected to tension, the fibres break over a range of stress instead of a single value predicted by theory. The stress-strain curves of the hybrid composites with different glass volume fractions show an inflection point. The point of inflection shifts upward as the glass content in increased, except for samples marked D. The point of inflection corresponds to the limiting elongation of a high modulus glass. Short and Summerscales [11] have observed that the minimum strength of the hybrid is proportional to the critical content of the low modulus fibres. If the content of the low modulus fibres in the composite is greater than the critical content, an inflection occurs in the stress-strain curve, corresponding to the limiting elongation of the high modulus material. The fibre/matrix interface has a lot to do with the form of the stress-strain curve [12]. An increase in glass content helps in the mutual reinforcement of strength characteristics by the low elongation glass and high elongation banana fibre.

Tensile modulus

Figure 4 shows the variation of tensile modulus with glass volume fraction. Fibre length, fibre aspect ratio, relative moduli of the fibre and matrix, thermal expansion mismatch are all important variables that control the performance of a composite. Stiffness of the mate-
Material has been calculated as tangent modulus at an elongation of 2%, 4% and 5%. The modulus values increase as the glass volume fraction is raised. Glass fibre has a higher tensile modulus than has banana fibre and incorporation of a high modulus glass increases the tensile modulus of the composite.

Tensile strength

Figure 5 shows the variation of tensile strength of the samples with respect to the variation of glass fibre volume fraction when the total volume fraction of the two fibres is kept constant. Tensile strengths of the samples increase linearly with the increases in glass volume fraction. Harris and Bunsell [13] have noticed that occurrence of a hybrid effect, negative or positive, will depend on the relative volume fraction of the two fibres. Analysis of the fracture surface of samples subjected to tension have shown that the mode of failure of the samples is proceeded by the failure of glass fibre, the low elongation component in the hybrid composite. As a result, the strength of the hybrid composite in tension uniformly increases with glass content. However, at relatively higher glass content failure by delamination occurs and the tensile strength values show only a slight enhancement. Optical photographs of the failed samples in Figure 6d, e and f show delamination between the fibre layers. In hybrids of carbon and glass the presence of higher extension glass fibre has been found to reduce the probability of failure of the lower extension carbon fibre resulting in a higher breaking strength of the carbon fibres [14]. In the present study, the increased tensile strength of the hybrid can be attributed to the presence of high modulus glass fibres. When the volume fraction of glass is changed from 0.11 to 0.15, the
increase in tensile strength is only marginal. At a high glass volume fraction, the fracture occurs in the composite mainly by interlayer delamination.

SEM photographs of the composites with glass volume fractions of 0.03, 0.11 and 0.15 are shown in Figures 7a, b and c, respectively. The fractograph of the sample with glass volume fraction 0.15 shows delamination of a glass/banana and also a matrix crack propagation.

The effect of banana glass layering on the tensile strength

Different layering patterns were tried for composites marked A, C and F. Figure 8 represents the tensile strength values of the different layering patterns. In the composites marked A and C, an intimate mixture of the two fibres gave the highest tensile strength. Fischer et al. [15] have reported that when the fibres are more intimately mixed, failure by delamination will be more difficult to occur because of the greater energy involved in creating the large amount of a new surface in an intimate mix than that required to cause delamination of a layered hybrid. In the composite marked F, the tensile strengths for layering $L_3$ and $L_5$ are almost similar. In intimately mixed hybrids, the area of the high elongation component to the low elongation component interface per unit volume will be high compared to the composites where the fibres are not intimately mixed. In an intimately mixed composite there will be only a small
distance from the failed fibre to the fibre which did not fail. The full reinforcing strength therefore, will be re-developed within the failed fibre within a short distance of the fracture surface. When individual glass and banana layers are made, the tensile strength values are found to be lower than that in an intimate mixture for composites with a low glass content. Bader and Manders [16] have noted that the hybrid effect was maximum only when the layer thickness had a certain minimum value. Mohan and Kishore [2] also noted that when the glass reinforced plastic shell thickness was small, the resistance to withstand strain was insufficient and thus the specimen failed prematurely by fibre buckling.

The impact strength of banana-glass hybrid composites

The impact performance of fibre reinforced composites depend on many factors including the nature of the constituents, fibre/matrix interface, the construction and geometry of the composite and test conditions. The impact strength of the composites with respect to glass volume fraction is shown in Fig. 9. The impact energy of a composite occurs by factors like matrix fracture, fibre/matrix debonding and fibre pull out. Even though fibre pull-out is believed to be the important energy dissipation mechanism in long fibre reinforced composites it occurs in short fibre composites as well [17]. The applied load, transferred by shear to the fibres, may exceed the fibre/matrix interfacial bond and debonding may occur. Optical photographs of the fractured samples show crack propagation through the fibre/matrix interface. The frictional force along the interface may transfer the stress to the debonded fibre. If the fibre stress level exceeds the fibre strength, fibres may fracture. The fractured fibres may be pulled out of the matrix, which involves energy dissipation [18]. Many authors have stated that the energy dissipated by fibre fracture is small [19]. The impact strength of the composites increased linearly up to an optimum value of 0.11 and then decreases slightly. The slight lowering of the impact strength can be attributed to a change in the energy dissipation mechanism. At high glass contents, the fracture mechanism is mainly fibre fracture, due to the brittle nature of glass. However at lower glass volume fractions, the fracture mechanism is mainly fibre pull-out due to the presence of a higher volume fraction of banana fibre. A synergistic effect of the two fibres leads to a linear increase initially.

The effect of glass-banana layering on the impact strength

Mallick and Broutman [20] have reported that stacking sequence is more important than composition in determining toughness, and that different lay-ups maximise different toughness parameters such as total energy, initiation energy or propagation energy. In this study also, it is found that the arrangement of the fibre within the composite affects the impact strength. The highest value is obtained when banana and glass are kept as interleaving layers. In this arrangement, the core thickness is very small. When a crack tip approaches a fibre, the crack crosses the fibres and cuts them as well as the matrix. Then, the crack changes its direction and moves through the matrix parallel to the fibres.

Such debonding fracture consumes more energy by creation of more surface area within the sample. The impact strength shows a decrease with the decrease in the number of layers. Unlike tensile strength, intimately mixed composites shows the lowest impact strength.

![Fig. 9. Effect of glass volume fraction on the impact strength](image)

![Fig. 10. Effect of layering on the impact strength of the composites](image)
Short and Summerscales [21] have reported a negative
hybrid effect in fracture tests of intimately mixed com-
posites. Harris and Bursell [13] have reported that inti-
mately mixed composites are inferior to interply lay-
ups in impact resistance because of the finer state of
subdivision.
Figure 10 shows the effect of layering on the impact
strength. Optical micrographs of the hybrid composite
samples are given in Figs. 6a, b, c, d, e. Figures a, b and
c represent the crack propagation at the fibre matrix
interface.

Theoretical Modelling

Hybrid reinforcing effect of the two fibres was theo-
retically calculated by using the parallel and the Hirsch
model [22, 23].

According to Hirsch’s model:

\[ X_c = X_f V_f + X_m V_m \]  \hspace{1cm} (1)

where: \( X_c, X_f \) and \( X_m \) are characteristic strength properties
of composite, fibre and matrix respectively.

According to Hirsch’s model:

\[ X_c = x(X_m V_m + X_f V_f) + (1 - x)X_f V_f + \frac{x}{X_m V_m} \]  \hspace{1cm} (2)

where: \( x \) varies between 0 and 1.

The value of \( x \) determines the stress transfer between
the fibre and the matrix. The value of \( x \) is the deter-
mining factor in describing the real behaviour of short fi-
bre composites [24]. The composite strength calculated
by using the above model was incorporated in the ad-
ditve rule of hybrid mixtures,

\[ X_h = X_f + X_m \]  \hspace{1cm} (3)

where: \( X_h \) is the characteristic property of the hybrid com-
posites.

Theoretically, the increase in volume fraction of glass
increases the tensile strength linearly up to a certain vo-

te fraction and thereafter a slight decrease is predic-
ted. The experimentally determined tensile strength va-

ues are found to be higher than the theoretical predic-
tions emphasizing a positive hybrid effect. Figure 11
represents the comparison of the experimental and the-
oretical values.

CONCLUSION

The above study concludes that the tensile strength
of banana-glass hybrid composites shows a linear in-
crease as the volume fraction of glass is increased. The
gometry or the layering of the fibres affects the mecha-
nical properties of the composites. Tensile strength
shows the maximum value in intimately mixed compo-
site at a low volume fraction of glass. However, when a
high volume fraction of glass is used, an interleaving
arrangement of glass and banana shows a marginal in-
crease in tensile strength of the composite.

The impact strength of the hybrid composite increases
when the glass volume fraction is increased up to 0.11.
A further increase in glass volume fraction lowers the
impact strength slightly. The highest impact strength
value of banana-glass hybrid composites occurs in the
samples made with a glass volume fraction of 0.11 with
the fibres arranged in an interleaving manner.

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Influence of chemical treatments on the electrokinetic properties of cellulose fibres

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Abstract—Changes in the surface composition of chemically treated cellulose fibres obtained from the sheath of banana plants were investigated using electrokinetic (z-potential) measurements. Scanning electron microscopy (SEM) was used to observe changes in the surface morphology of the fibres. Spectroscopic methods were also used to analyse the changes on the cellulose fibre surface. Chemical treatments such as alkali treatment, acetylation, treatment with a triazine coupling agent, various silanes, etc. reduced the hydrophilicity of the fibres. The surface morphology of the fibres showed considerable changes. Chemical treatments reduced the acidity of the already polar cellulose fibre. The high iso-electric point (IEP) of the silane A1100-treated fibres shows that basic groups dominate at these surfaces. The observations are consistent with the values obtained using solvatochromic measurements.

Keywords: Banana fibre; z-potential; chemical modification; iso-electric point.

1. INTRODUCTION

Chemical transformations of macromolecules constitute the most important route to alter their macroscopic properties and to tailor them to specific end uses. The transfer of knowledge regarding low-molecular-weight organic chemistry to the field of polymer chemistry provides a means for refining and upgrading naturally occurring polymeric materials.

The reaction sites for practical relevance for the functionalization of natural cellulose are the three alcoholic hydroxy groups. The reactivity of the hydroxy groups...
groups can be enhanced by several methods. One method of activating the hydroxy group involves loosening of the cellulose supramolecular structure with preservation of the original solid state of the sample. The breaking of inter-chain hydrogen bonds leading to spacing between the chains can be brought about by temporary or permanent chemical interactions. One way to attain this is by treatment with an alkali.

Natural fibres are finding application as reinforcement in various polymeric matrices, such as thermoplastics, thermosets, and rubbers. To improve fibre–matrix adhesion, modification of the natural fibre using various techniques has been suggested. Gonzalez et al. [2] modified henequen fibres using silane coupling agents and observed that the fibre–matrix adhesion was improved. Treatment with alkali was found to be effective for modifying the cellulose fibre surface by Gonzalez et al. [3]. Zadorecki and Rouhult [4] reported on the modification of the cellulose fibre surface by a triazine coupling agent and Mitra et al. [5] reported on the chemical modification of jute fibres to reduce their hydrophobicity.

Zeta potential measurements are commonly carried out to investigate surface properties and possible interactions. Electrokinetic phenomena can be observed by contacting a solid surface with a polar liquid medium, because of the existence of an electrical double layer at the solid–liquid interface [6]. The strength of the interaction is determined by the extents of dispersion and acid–base interactions. A hydrogen bond may be considered as a special case of acid–base interactions [6]. The magnitudes of such interactions depend on the chemical constitution of the adhering members and adsorption layers. Adsorption layers may be due to impurities, modifiers, or water, which is always present.

Bismarck et al. used zeta potential measurements [7] to confirm changes at the surface of oxygen plasma-treated carbon fibres. The surface polarity of grafted carbon fibres was determined by contact angle measurements and confirmed by zeta potential measurements. Stana-Kleinschek and Ribitsch [8] have discussed the electrokinetic properties of processed cellulose fibres. In this study, the changes in surface properties by chemical purification of cellulose and its acid–base properties were investigated. The characterization of solid surfaces by electrokinetic phenomena was reported by Jacobasch [9]. Surface, interphase, and composite property relationships in fibre-reinforced polymers have been studied by Mäder et al. [10].

Extensive research studies carried out in our laboratory by Thomas and co-workers [11–14] have shown natural fibres such as sisal, pineapple leaf fibres, oil palm empty fruit bunch fibres, and banana fibres to be an effective reinforcement in polymer matrices. In the present investigation, in order to modify the fibre–matrix adhesion, banana fibres were subjected to different chemical treatments.

Banana fibres obtained from the sheath of banana plants have been characterized in detail. The cellulosic fibre obtained from the pseudo-stem of banana plant (Musa sepientum) is a bast fibre with relatively good mechanical properties. Table 1 lists the mechanical properties of banana fibres. X-ray studies on the fibres have
shown that the structure is that of cellulose 1. The fibre has a high degree of crystallinity, with good alignment of crystallites parallel to the fibre axis. The crystalline cellulose in a banana fibre is arranged in the form of a helix at an angle of 11–12° for fibres of diameter 100–200 μm. The major chemical constituents of the fibre, which is lignocellulosic, are cellulose (63–64%), hemicellulose (19%), and lignin (5%). The hemicellulose component is 4-O-methyl glucose xylan [15–17].

Recently, in our laboratory, cellulose fibres obtained from banana have been used as reinforcement in the polyester matrix [18]. In the present study, the fibres were modified chemically to improve their adhesion to the polyester matrix. The modified fibres were characterized using FTIR, SEM, and solvatochromism. Electrokinetic measurements were made to measure the surface polarity and to determine the acid–base properties of the treated fibres.

### 2. EXPERIMENTAL

#### 2.1. Materials

Banana fibre was obtained from Sheeba Fibres and Handicrafts, Poovancode, Tamil Nadu, India. The various silanes, A174 (γ-methacryloxypropyltrimethoxysilane), A151 (vinyl triethoxysilane), and A1100 (γ-aminopropyltriethoxysilane), were obtained from Sigma-Aldrich, India. Dynasylan F8261 (1H,1H,2H,2H-perfluoroctyltriethoxysilane) was obtained from ABCR GmbH and Co. 2,4-Dichloro 6-n-octadecyloxy-s-triazine (C18-T) was synthesized in our laboratory. Si 69 [bis(3-triethoxysilylpropyl)-tetrasulphone] was obtained from Degussa AG Germany. NaOH and all other chemicals were of commercial grade. The chemical structures of the various chemical agents used are shown in Fig. 1.

#### 2.2. Silane treatment of banana fibres

A 0.6 wt% solution of the silane in an ethanol–water mixture (6:4) was prepared and allowed to stand for 1 h. The pH of the solution was maintained at 4 by adding acetic acid. Neatly separated and cut banana fibres were dipped in the above solution and left there for 1.5 h. The ethanol–water mixture was drained out and the fibres
were dried in air for 30 min, followed by drying in an oven at 70°C until the fibres were completely dry.

2.3. Treatment with the triazine coupling agent (C18-T)

The triazine coupling agent (2,4-dichloro-6-n-octadecyloxy-s-triazine) (C18-T) was synthesized according to the procedure described by Zadorecki and Rouhult [4]. The dried cellulose fibres were first immersed in 0.1 N NaOH solution, dried, and then soaked in a solution of C18-T (10 wt% of the fibres) in acetone for 3 min at room temperature. After evaporation of the solvent, the fibres were dried at 60°C for 2 h in an inert atmosphere.

2.4. Treatment with NaOH

Cleaned and well-separated banana fibres were dipped in 0.25% and 0.5% aqueous solution of NaOH for 30 min and then washed in very dilute hydrochloric acid to remove the unreacted alkali. Washing was continued until the fibres were alkali-free. The washed fibres were then dried in an oven at 70°C for 3 h.

2.5. Treatment with acetic anhydride

Acetylation of the fibres was carried out as follows. The fibres were dipped in glacial acetic acid for 30 min, the acid was drained, and the fibres were dipped in acetic anhydride containing a few drops of concentrated sulphuric acid for 5 min, washed in distilled water, and then dried.

![Chemical structures of the various chemical agents used](image_url)
2.6. ζ-potential measurements

ζ-potential measurements were made with the electrokinetic analyser EKA (Anton Paar KG, Graz, Austria) based on the streaming potential method. Details of the measuring technique are reported elsewhere [119]. An electrolyte solution was forced by an external pressure through a bundle of capillaries (fibre plug). The potential resulting from the motion of the ions in the diffuse layer was measured. By measuring the pH dependence of the ζ-potential, the acidity or basicity of solid surfaces can be determined qualitatively. If the solid surface investigated contains acidic functional groups, the negative ζ-potential increases with increasing pH, due to increasing dissociation of these groups, and remains constant above a given pH, due to their complete dissociation. The pH dependence of the ζ-potential was determined in a 1 × 10^{-3} M KCl electrolyte solution and to keep the ionic strength constant, the pH value in the range 3–11 was altered by the addition of 0.1 M HCl or KOH solution. The special fibre cell used for the investigation is shown in Fig. 2. From the ζ = f (pH) shape (Fig. 3), it can be determined whether an adsorption or a dissociation process is predominant. When the formation of the electrical double layer is caused by the dissociation of the acidic functional surface groups, a plateau area in the alkaline range for the pH dependence of the ζ-potential is obtained. If there is a change in the sign of the ζ-potential in the acidic range, this is caused, first, by repressing the dissociation of the acidic surface groups and, second, by the adsorption of the potential-determining ions. An analogous trend in the ζ-potential is present if there are any alkaline surface groups. The iso-electric point (IEP), where ζ = 0, is also a measure of the acidity or basicity of a solid surface if the dissociation of surface groups is the predominant mechanism for the formation of the electrical double layer. The solid surface displays an acidic character if the value of IEP is low. If the IEP is situated in the alkaline range, the solid surface

![Figure 2. Special fibre cell used for the investigation of ζ-potential.](image)
contains basic surface groups. The shifts of IEP in $\zeta = f(pH)$ due to solid surface modifications indicate the concentration of dissociable surface groups.

2.7. Surface morphology

All treated fibres were analysed by SEM to observe changes in the surface morphology. Fibres were investigated with a scanning electron microscope (JEOL 35 C model). Treated fibres were sputtered with gold before microscopic analysis.

2.8. Solvatochromism

Solvatochromism of well-characterized probe dye indicators and solvent polarity scales based on such dyes have been established as important tools for investigating the polarity and donor–acceptor properties of different materials [6]. Cellulose

![Schematic diagrams of $\zeta = f(pH)$ for Brønsted acidic and alkaline surfaces (steady values represent completely dissociated states).](image_url)
surfaces possess dipolar and hydrogen bond properties. In our previous paper [21], we reported on the characterization of chemically modified cellulose fibre surfaces using the probe dye indicators dicyano-bis(1,10-phenanthroline) iron(II) (1), Michler's ketone (2), and aminobenzodifuranone (3), and the calculation of the polarity parameters using different multiple correlation equations.

3. RESULTS AND DISCUSSION

3.1. Untreated fibres

Lignocellulosic materials are abundant, but under-utilized, and are finding applications in various engineering materials [21, 22]. Cellulosic fibres obtained from the stem of banana plant (*Musa sapientum*) are bast fibres with relatively good mechanical properties. The major constituents of the fibre are cellulose and hemicellulose. The hemicellulose component is 4-O-methyl glucose xylam. Cellulose is a linear condensation polymer consisting of D-anhydroglucopyranose units joined together by \(\beta-1,4\) glycosidic bonds [23, 24]. These pyranose rings are in the \(\beta\)-conformation, which means that the \(-\text{CH}_2-\text{OH}\) and \(-\text{OH}\) groups, as well as the glycosidic bonds, are equatorial with respect to the mean planes of the rings.

Figure 4 shows the DRIFT (diffuse reflectance infrared Fourier transform) spectrum of the untreated fibre. The characteristic peaks obtained for the untreated fibres are as follows. The strong peak at 3429 cm\(^{-1}\) is characteristic of the hydrogen-bonded \(-\text{OH}\) stretching vibration. The strong peak at 2922 cm\(^{-1}\) is due to CH stretching vibrations [25]. The peak at 1778 cm\(^{-1}\) is the characteristic band for car-

![Figure 4. DRIFT spectrum of the untreated banana fibre.](image)
bonyl (C=O) stretching. The band near 1245 cm\(^{-1}\) is due to the \(-C=O-C-\) bond in the cellulose chain. The peak near 900 cm\(^{-1}\) is characteristic of \(\beta\)-linkages.

Figure 5 shows the SEM micrograph of the raw banana fibre surface. The fibre surface is comparatively smooth, with fibrils arranged uniformly. The multi-fibrillar nature of the fibre is clear from the SEM micrograph. Figure 6 shows the pH dependence of the \(\zeta\)-potential for the raw, acetylated, alkali-treated, and C18-T-treated fibres. In the case of untreated banana fibres, a plateau region is obtained in the pH range starting from 4. The natural cellulose fibres are negatively charged, due to the presence of carboxyl and hydroxyl groups [8]. The plateau region could be obtained only up to pH 6. In the case of the untreated fibres, the hemicellulose, pectins, waxes, etc. are dissolved on treatment with water. These dissolved materials cause measurement problems since they are adsorbed on the fibre surface as well as on the measuring device. The hydrophilicity of the fibres also causes problems. The relationship between the hydrophilicity and the \(\zeta\)-potential may be explained by the competitive adsorption between the ions forming the electrical double layer and water. The interaction between cellulose and water occurs due to the presence of the hydroxy groups (Fig. 7). There is competition for hydrogen bond formation with the hydroxy group of a cellulose chain and a water molecule.

The observed decrease in the \(\zeta\)-potential with time was caused by water adsorption. This effect depends on the hydrophilicity of the solid [8]. One of the reasons for the decrease in the \(\zeta\)-potential could be the swelling of the solid. This would lead to a transfer of the electrochemical double layer into the solid and, therefore, of the shear plane into the electrolyte solution. Another cause could be the removal of

![Figure 5. SEM micrograph of the untreated banana fibre.](image)
Influence of chemical treatments on the electrokinetic properties of cellulose fibres

Water-soluble components from the surface (and/or bulk): this would also decrease the solid surface potential.

The surface polarity of functionalized cellulose fibres has been characterized using linear solvation energy (LSE) relationships. Kamlet-Taft's hydrogen-bond donating ability ($\alpha$), hydrogen-bond accepting ability ($\beta$), the dipolarity/polarizability ($\pi^*$), Gutmann's acceptor number $AN$, which is indicative of the electron accepting ability, and Reichardt's $E_T(30)$ parameter have all been used to represent quantitatively the polarity of chemically treated and untreated fibre surfaces [20].

**Figure 6.** pH dependence of the $\zeta$-potential on untreated, alkali-treated, acetylated, and C18-T-treated fibres.

**Figure 7.** Schematic representation of the interaction of cellulose with water molecules [1].
The acceptor number calculated for the untreated fibres is 61.36 and the $E_T$ parameter calculated for the fibres is 58.58. The results are consistent with the $\zeta$-potential values. The molecular structure of cellulose is responsible for its supramolecular structure and this, in turn, determines many of its chemical and physical properties. Hemicellulose, which is another principal component of the cellulose fibre, comprises a group of polysaccharides (excluding pectin) that remain associated with the cellulose after lignin has been removed. Hemicellulose differs from cellulose mainly in that it contains several different sugar units, whereas cellulose contains only 1,4-$\beta$-D-glucopyranose units. Hemicellulose also has a considerable degree of chain branching, whereas cellulose is linear. The degree of polymerization of cellulose is also ten to a hundred times higher than that of hemicellulose.

Lignins are complex hydrocarbon polymers with both aliphatic and aromatic constituents. Their chief monomer units are various ring-substituted phenyl propanes [26]. Pectin is a collective name for heteropolysaccharides, which consist essentially of polygalacturon acid. Pectin is soluble in water after partial neutralization with an alkali.

Waxes, which make up a part of the fibres, consist of different types of alcohols and acids (palmitic, oleaginous, and stearic acids).

### 3.2. Treated fibers

#### 3.2.1. Alkali treatment

The NaOH treatment removes practically all non-cellulose components except waxes. The number of dissociable groups does not change. The swelling itself causes a reduction in the $\zeta$-potential. Swelling of the fibre leads to a transfer of the electrochemical double layer and the shear plane of the fibre to the electrolyte solution. Another cause could be the removal of water-soluble components from the surface (and/or bulk): this would also decrease the solid surface potential.

On interaction with water, the first layer of water molecules is associated very tightly with cellulosic hydroxy groups in the disordered regions, while further sorption causes the water molecules to be bound less tightly. Cellulose–water interaction can be understood as hydrogen bond formation between a hydroxy group of a cellulose chain and a water molecule or a water cluster [11]. The interaction between cellulose and aqueous alkali hydroxides results in swelling and uptake of both alkali and water. The process of alkali absorption destroys the hydrogen bonds within the cellulose, opening up the structure. There is a decrease in the supramolecular order in the chain conformation of cellulose. Usually, hydroxy anions are seen to be responsible for the primary interaction with the cellulosic hydroxy groups in the ordered regions of the structure, while hydrated cations are responsible for the resulting swelling. Hemicellulose, which consists principally of xylan, polyuronide, and hexosan, is very sensitive to the action of caustic soda, which exerts only a slight effect on lignin or $\alpha$-cellulose. When the hemicellulose
Influence of chemical treatments on the electrokinetic properties of cellulose fibres

Figure 8. IR spectrum of the alkali-treated fibre.

is removed, the interfibrillar region is likely to be less dense and less rigid, making the fibrils more capable of rearranging themselves [27].

Figure 8 shows the IR spectrum of the alkali-treated fibre. The peak at 3376 cm\(^{-1}\) is due to the \(-\text{OH}\) stretching vibration. The shift of the peak from 3424 to 3376 cm\(^{-1}\) indicates the participation of some free hydroxyl groups in the chemical reaction. The medium band at 1739 cm\(^{-1}\), due to \(-\text{C-}-\text{O}\) stretching in the parent cellulose fibre, disappeared in the alkali-treated fibre. In alkali treatment, a substantial portion of uronic acid, a constituent of hemicellulose xylan, is removed, resulting in the disappearance of this peak.

The changes in the surface features of the cellulose fibre after treatment with alkali are shown in the SEM micrograph (Fig. 9). The fibrillar structure is clearer in the alkali-treated fibres than in the untreated ones. Dissolution of waxy material increases the inter-fibrillar region and gives the surface a rough texture, as is clear from the micrograph. Other substances associated with the cellulose matrix, namely non-cellulosics, polysaccharides, fatty and waxy substances, as well as inorganic components, dissolve out.

The pH dependence of the \(\zeta\)-potential on the alkali-treated fibres (Table 2) shows an iso-electric point (IEP) of 3.8. The value in the case of the untreated fibre is 2.6, which indicates a highly acidic surface, and the treatment with alkali decreases the acidity. At lower pH values, the adsorption of protons, which are potential-determining ions, is the predominant process, which gives rise to the positive value
Figure 9. SEM micrograph of the alkali-treated fibre.

Table 2.
Iso-electric points and $E_T(30)$ parameters of the treated fibres

<table>
<thead>
<tr>
<th>Treatment</th>
<th>IEP</th>
<th>$E_T(30)$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>2.6</td>
<td>58.58</td>
</tr>
<tr>
<td>Silane A151</td>
<td>3.4</td>
<td>65.83</td>
</tr>
<tr>
<td>Silane A174</td>
<td>3.2</td>
<td>60.44</td>
</tr>
<tr>
<td>Silane A1100</td>
<td>5.4</td>
<td>—</td>
</tr>
<tr>
<td>NaOH</td>
<td>3.8</td>
<td>61.01</td>
</tr>
<tr>
<td>Acetylation</td>
<td>2</td>
<td>—</td>
</tr>
<tr>
<td>Dynasylan F8261</td>
<td>—</td>
<td>60.65</td>
</tr>
<tr>
<td>Si69</td>
<td>3</td>
<td>59.01</td>
</tr>
<tr>
<td>C18-T</td>
<td>2.8</td>
<td>—</td>
</tr>
</tbody>
</table>

of the $\zeta$-potential. In this case, the dissociation process of the functional groups leads to a negative value of the $\zeta$-potential. A plateau region is obtained in the pH range from 5 to 10.

Solvatochromic measurements carried out on alkali-treated fibres showed a definite change in the absorption peak compared with the untreated fibre, indicating a reduction in the number of acidic sites [20]. The changes in the surface structure can be explained as due to the changes in the supramolecular structure because of interaction with the alkali. The acceptor number calculated using the solvatochromic measurements is lower than that of the untreated fibre [20]. The results are consistent with the $\zeta$-potential measurements.

3.2.2. C18-T (2,4-dichloro-6-n-octadecyloxy-s-triazine) treatment. Figure 1 shows the structure of C18-T. The principle of chemical bonding of specific func-
Influence of chemical treatments on the electrokinetic properties of cellulose fibres

1. Trichloro-s-triazine
2. Stearyl alcohol
3. 2,4-dichloro-6-n-octadecyloxy-s-triazine (C18-T)

Figure 10. Schematic representation of the interaction of cellulose with C18-T.

![Chemical Reaction](image)

1. Trichloro-s-triazine
2. Stearyl alcohol
3. 2,4-dichloro-6-n-octadecyloxy-s-triazine (C18-T)

Figure 11. DRIFT spectrum of the C18-T-treated fibre.

![DRIFT Spectrum](image)

Wavenumber (cm⁻¹)

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Transmittance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3318</td>
<td>50</td>
</tr>
<tr>
<td>2919</td>
<td>60</td>
</tr>
<tr>
<td>2851</td>
<td>70</td>
</tr>
<tr>
<td>2135</td>
<td>80</td>
</tr>
<tr>
<td>1562</td>
<td>90</td>
</tr>
<tr>
<td>814</td>
<td>50</td>
</tr>
<tr>
<td>719</td>
<td>40</td>
</tr>
</tbody>
</table>

The IEP of the C18-T-treated fibre is 2.8 (Table 2). The increase in IEP from that of the untreated fibres indicates a less acidic character of the fiber. Solvatochromic measurements carried out on the fibre surface treated with C18-T gave absorption peaks only with one dye, as reported in our earlier paper [20]. However, consistent results were obtained in the case of the electron-accepting ability of the fibres from solvatochromic measurements carried out on the fiber surface. Table 3 shows the calculated AN (acceptor number) value for the C18-T-treated fibre to be 56.38, compared with 61.36 for the untreated fibres. The sum of all possible interactions...
Table 3.
Acceptor numbers (AN) and $E_\tau(30)$ parameters of the untreated and variously treated banana fibres

<table>
<thead>
<tr>
<th>Banana fibres</th>
<th>AN</th>
<th>$E_\tau(30)$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>61.36</td>
<td>58.58</td>
</tr>
<tr>
<td>0.25% NaOH</td>
<td>57.91</td>
<td>61.01</td>
</tr>
<tr>
<td>0.5% NaOH</td>
<td>60.57</td>
<td>62.68</td>
</tr>
<tr>
<td>A174</td>
<td>43.86</td>
<td>43.86</td>
</tr>
<tr>
<td>A174 + 0.25% NaOH</td>
<td>51.42</td>
<td>60.45</td>
</tr>
<tr>
<td>A174 + 0.5% NaOH</td>
<td>45.24</td>
<td>60.99</td>
</tr>
<tr>
<td>A151 + 0.25% NaOH</td>
<td>69.11</td>
<td>65.83</td>
</tr>
<tr>
<td>A151 + 0.5% NaOH</td>
<td>66.90</td>
<td>63.64</td>
</tr>
<tr>
<td>F8261</td>
<td>54.38</td>
<td>60.65</td>
</tr>
<tr>
<td>S69</td>
<td>53.39</td>
<td>59.01</td>
</tr>
<tr>
<td>A1100</td>
<td>33.73</td>
<td></td>
</tr>
<tr>
<td>C18-T</td>
<td>56.38</td>
<td></td>
</tr>
<tr>
<td>Acetylated</td>
<td>54.87</td>
<td></td>
</tr>
</tbody>
</table>

between a surface group and an adsorbed molecule or ion is termed the surface polarity. The overall polarity $E_\tau(30)$ for the untreated fibres could not be measured, because a clear absorption maximum could be obtained only with one probe dye.

3.2.3. Acetylation. During acetylation, the typical reaction taking place on the fibre surface can be represented as

$$\text{Cellulose-OH} + (\text{CH}_3\text{CO})_2\text{O} \rightarrow \text{Cellulose-OCOCH}_3 + \text{CH}_3\text{COOH}.$$  

A peak at 1730 cm$^{-1}$ in the acetylated fibre indicates the presence of the ester groups.

The SEM micrograph of the acetylated fibre also shows clear changes in the surface morphology. Acetylation has rendered the fibre surface rougher. Also, the fibres have become stiffer.

The $\zeta$-potential measurements gave a negative $\zeta$-value and a non-measurable IEP (Fig. 17 extrapolated to pH $\approx$ 2). Variation in the pH leads to a more negative value. The fibre surface is expected to be more acidic than the surface of the untreated fibre.

Solvatochromic measurements, however, gave an acceptor number less than that of the untreated fibre $^{[13]}$.

3.2.4. Silane treatment. The structures of the various silanes used are given in Fig. 1. The general scheme of reaction of cellulose with a silane is also given in Fig. 12 $^{[28, 29]}$.

All the silanes used in this work have two functional groups, a hydrolysable group able to condense with the hydroxyls of the banana fibre and an organofunctional group capable of interacting with the polymer matrix. The hydrolysed silane
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Figure 12. General scheme of the reaction of cellulose with a silane.

The reaction of cellulose with a silane involves the formation of a bond between the cellulose and the silane. The silanol groups are chemically attached to the fibre through an ether linkage.

3.2.4.1. Silanes A151 and A174. The FTIR spectra (not shown) of the silane A151 and A174-treated fibres show the presence of absorption bands at 765 cm⁻¹ corresponding to the –\( \text{Si}–\text{C}– \) symmetric stretching band and at 700 cm⁻¹ corre-
Figure 13. SEM micrograph of the silane A151-treated fibre.

Figure 14. SEM micrograph of the silane A174-treated fibre.

Corresponding to the $-\text{Si}-\text{O}-\text{Si}^-$ symmetric stretching [$30$]. The band around 1150 cm$^{-1}$ can be attributed to the asymmetric stretching of the $-\text{Si}-\text{O}-\text{Si}^-$ and/or to the $-\text{Si}-\text{O}-\text{C}^-$ bonds. The former bond is indicative of the polysiloxanes deposited on the fibre and the latter points to a condensation reaction between the silane coupling agent and the fibre. The characteristic absorption bands around 1035 and 1178 cm$^{-1}$ further confirm the presence of polysiloxanes. The bands around 860 cm$^{-1}$ reveal the presence of a few residual $-\text{Si}-\text{OH}$ bonds.
Fibers subjected to treatment with silanes A151 and A174 after pretreatment with the alkali gave IEP values of 3.4 and 3.2, respectively (Table 2). The increase in IEP values indicates a less acidic surface than the untreated fibres.

Figures 13 and 14 show, respectively, the SEM micrographs of the silane A151- and A174-treated fibres. The surface of the fibres treated with silane A174 is rougher than that of the A151-treated fibre.

3.2.4.2. Silane F826l. The scheme of reaction is the same as that given for the other silanes (Fig. 12).

Figure 15 shows the DRIFT spectrum of the silane F826l-treated fibre. The peak at 1150 cm\(^{-1}\) can be attributed to the asymmetric stretching of the \(-\text{Si}-\text{O}-\text{Si-}\) and/or to the \(-\text{Si}-\text{O}-\text{C-}\). The surface of the F826l-treated fibre is shown in Fig. 16. Compared with the untreated fibre, the silane F826l-treated fibre surface shows fine hairy structure on its surface and the surface is rougher than that of the untreated fibre.

The pH dependence of the \(\zeta\)-potential of the Dynasylan F826l-treated fibre is shown in Fig. 17. The \(\zeta\)-potential shows a negative value and a plateau region is observed after pH 4.5.

3.2.4.3. Silane A1100. The chemical interaction between the aminopropyltriethoxysilane and the cellulose fibre can be represented schematically as shown in Fig. 18. In addition to the ether linkage, the interaction between the cellulose and the silane also takes place by electrostatic attraction.

![Figure 15. DRIFT spectrum of the silane F826l-treated fibre.](attachment:figure15.png)
Figure 16. SEM micrograph of the silane F8261-treated fibre.

Figure 17. pH dependence of the $\zeta$-potential on untreated and silane-treated fibres.

Figure 19 shows the IR spectrum of the silane A1100-treated fibre. The band around 1150 cm$^{-1}$ can be attributed to the asymmetric stretching of the $-\mathrm{Si}-\mathrm{O}-\mathrm{Si}-$ and/or to the $-\mathrm{Si}-\mathrm{O}-\mathrm{C}-$ bonds. The peak around 1150 cm$^{-1}$ is attributed to the amino group.
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Figure 18. Scheme of the interaction of aminosilane with cellulose.

Figure 19. IR spectrum of the silane A1100-treated fibre.
Figure 20. SEM micrograph of the silane A1100-treated fibre.

Figure 20 shows the SEM micrograph of the silane A1100-treated fibre. Treatment with silanes has led to fibrillation and thereby an increased surface area of the fibres. The IEP shows the highest value in the case of the A1100-treated fibre, proving the basic nature of the fibre surface (Table 2). The basic nature and the IEP value of 5.4 can be explained as due to the presence of the NH$_2$ group.

Table 2 shows the chemical treatments and the corresponding IEP values. It is interesting to note that except in the case of acetylated fibres and F8261-treated fibres, in all the other cases, the IEP values are higher than that of the untreated fibres, showing a decreased acidity. Whereas the untreated fibres show an IEP value of 2.6, the alkali and silane-treated fibres have an IEP greater than 3.2. The maximum IEP value was found for the A1100-treated fibre. The results are consistent with the acceptor number calculated using solvatochromic measurements and are presented in Table 3.

In the electronic spectra, UV/visible solvatochromism of the probe dyes is expected if the solvent polarity is altered. Bathochromic shifts are found with increasing solvent polarity when the excited state is more polar than the ground state. $E_T$, also called $E_T(30)$, is an empirical scale of solvent polarity which is defined as the $\pi-\pi^*$ transition energy (in kcal/mol) of the dissolved dye 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio) phenolate. This $E_T(30)$ solvent polarity scale has been employed to describe a great variety of solvent-dependent chemical processes in organic chemistry [20]. Table 3 gives the acceptor number and the $E_T(30)$ values of the variously treated and untreated fibres. The lowest acceptor number was observed for the silane A1100-treated fibre, consistent with the observations from the solvatochromic measurements [20]. However, the $E_T(30)$ polarity parameter of the silane A1100-treated fibres could not be determined because absorption peaks could not be obtained with all three probe dyes.
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3.2.4.4. Silane Si69. The silane Si69-treated fibres show an IEP value of 3, slightly higher than that of the untreated fibre. The \( E_T(30) \) polarity parameter value is also approximately equal to that of the untreated fibre. This suggests that treatment with the silane Si69 is not very effective for cellulose fibre.

4. CONCLUSION

Electrokinetic measurements have been shown to be successful in characterizing the polarity of chemically modified banana fibres. The results obtained were found to be consistent with the values obtained using solvatochromic measurements carried out earlier. The untreated banana fibre surface was found to be acidic. All IEPs, except those of the acetylated fibres and F8261-treated fibres, are higher than that of the untreated fibres. Treatment with NaOH changed the IEP to 3.8. Treatment with the silanes A174 and A151 covered some basic groups and the IEPs of the fibres changed to 3.2 and 3.4, respectively. Acetylation of the fibres generated a lower IEP value of \( \approx 2 \), showing the presence of more acidic groups. In the case of the silane A1100-treated fibres, the surface changed to basic properties with an IEP of 5.4, due to the effect of the \(-\text{NH}_2\) group. SEM micrographs of the silane-treated and acetylated fibres, which show a change in the IEP values, clearly revealed changes in morphology, compared with the untreated fibres.

REFERENCES


