

Effect of Chemical Modification on Properties of Hybrid Fibre Biocomposites

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Abstract

The effects of chemical modification of fiber surface in sisal-oil palm reinforced natural rubber green composites have been studied. Composites were prepared using fibers treated with varying concentrations of sodium hydroxide solution and different silane coupling agents. The vulcanisation parameters, processability conditions and tensile properties and swelling characteristics of these composites were analysed. The fiber reinforcing efficiency of the chemically treated biocomposites was compared with that of untreated composites. The extent of fiber alignment and strength of fiber-rubber interfacial adhesion was analysed from the swelling measurements. Composites containing chemically treated fibers were found to possess enhanced mechanical properties. The hardness and abrasion resistance of the untreated and treated composites were also analyzed. Surface characterization of treated and untreated sisal fibers by XPS showed the presence of numerous elements on the surface of the fiber. The fracture mechanism of treated and untreated fiber reinforced rubber biocomposites was investigated from SEM studies.

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1. INTRODUCTION

Biopolymers or synthetic polymers reinforced with natural (or bio) fiber, frequently termed biocomposites, can be viable alternatives to glass fiber reinforced composites. The use of biofibers like sisal, jute, flax, oil palm from both renewable and non-renewable resources to produce composite materials that are competitive with synthetic composites is gaining attention over the last decade¹ because they are renewable, biodegradable and environmentally friendly.

Short fibers are used in rubber compounding due to considerable processing advantages, improvement in certain mechanical properties and for economic consideration. The reinforcement of biofibers in rubber composites has been well documented by Joseph et al². Though natural fibers have appealing properties they also suffer from some serious setbacks due to their hydrophilic character. This limitation is remedied by several methods like grafting functional moieties onto the fibers, introduction of coupling agents or pretreatment of fibers with suitable agents. An enormous amount of research has been invested in studying the modification of natural fibers and their subsequent characterization in composites.

The influence of different chemical treatments such as mercerization, acetylation, benzoylation and silanation on the mechanical properties of isora fiber reinforced natural rubber composites was investigated by Mathew et al³. They observed a marked improvement in the properties after chemical modification. The effect of alkali treatment on the mechanical properties of *Hildegardia populifolia* reinforced styrenated polyester composites was reported by Varada Rajulu et al⁴.

In another recent study involving biodegradable matrix Bairado et al.⁵ employed heterogeneous esterification reactions on flax fibers to improve fiber / matrix adhesion. The matrix in question was an aliphatic polyester (butylene adipate/succinate copolymer) Bionolle 3020. The authors observed an increase in strength for the chemically treated

composites. In another interesting study⁶ sugar cane bagasse fibers were modified by surface treatments using physical and chemical methods in order to improve their adhesion to polystyrene matrices. The surface treatment methods used were alkaline treatment, treatment with silane coupling agents, physical coating with polystyrene and grafting of polystyrene with and without crosslinker. The improvement of the adhesion between sugar cane modified fibers and polystyrene was assessed by micromechanical pull-out and by macromechanical Iosipescu tests. The authors observed substantial improvements in fiber-matrix compatibility from the interfacial shear strength values (IFSS).

The interface modification and mechanical properties of newsprint, kraft pulp and hemp fiber reinforced polyolefin composite products was investigated by Sain et al.⁷. The effect of a low-molecular weight, maleated type coupling agent, on the mechanical properties of these natural fiber-filled PP composites was also investigated and it was found that the optimum level of the coupling agent was found to be around 3-4 percentage by weight of the composite.

The influence of 4,4'-thiodiphenol (TDP) on the interfacial properties of flax fiber reinforced poly(3-hydroxybutyrate) was studied by Wong et al.⁸ Scanning electron microscopic studies revealed good adhesion between fiber and matrix while FTIR confirmed the presence of hydrogen bonds between additive and matrix.

In an interesting study using cardanol based bio-composites Maffezzoli et al.⁹ used silane coupling agent to improve the adhesion between the natural fiber and matrix. The fibers used were hemp, ramie, flax and jute fabric. The authors observed that void content decreased in composites containing chemically treated fibers. An attempt to study the mechanical characteristics of hybrid systems was performed by Mishra et al.¹⁰. The composite systems chosen were sisal / glass and pineapple /glass fiber reinforced polyester composites. Composites were prepared by varying the concentration of glass fiber and by subjecting the bio-fibers to different chemical treatments. The modifications employed were mercerization, cyanoethylation and acetylation. The surface modification

of sisal fibers such as alkali treatment was found to produce optimum tensile and impact strengths, while cyanoethylation resulted in the maximum increase in flexural strength of the hybrid composites. Ismail et al¹¹ looked into the effect of addition of silane coupling agent in bamboo fiber reinforced natural rubber composites. The authors observed a marked increase in mechanical properties due to better fiber / matrix adhesion.

Another investigation utilizing mercerization was attempted by Boynard et al.¹².The authors looked into the aspects of alkali treatment of sponge gourd (*Luffa cylindrica*) fibers on the flexural properties of polyester composites. The authors observed significant morphological changes on the surface of luffa fibers and that a 5 % concentration of NaOH provided the best flexural mechanical properties.

It is apparent from the above literature that chemical treatment has a profound influence on the properties of fiber reinforced composites. It can also be seen that studies involving the chemical modification of hybrid bio-fiber systems have not been addressed so far. Among the different natural fibers sisal and oil palm fibers are anticipated to be promising materials because of the high tensile strength of sisal fiber and hardness of oil palm fiber. Therefore any composite comprising of these two fibers may exhibit the above desirable properties of the individual constituents

In this paper, we report on the effect of various chemical modifications of sisal and oil palm fibers on improving its suitability as reinforcement in natural rubber composites. The chemical modifications comprise of treatment with various silanes. Alkali treatment has also been performed with varying concentrations with a view to improve adhesion. Swelling experiments have also been performed to analyze the extent of fiber/matrix adhesion.

2. EXPERIMENTAL

Sisal fiber was obtained from Sheeba Fibers, Poovancode, Tamil Nadu. Oil palm fiber was obtained from Oil Palm India Limited, Kerala. Natural rubber used for the study was procured from Rubber Research Institute of India, Kottayam. All the other ingredients used were of commercial grade.

3.FIBER SURFACE MODIFICATION

One of the most important factor for obtaining good fiber reinforcement in the composite is the strength of adhesion between fiber and polymer matrix. Due to the presence of pendant hydroxyl and polar groups in various constituents of fiber, moisture absorption of fiber is very high which leads to poor interfacial bonding with the hydrophobic matrix polymers. Therefore in order to develop composites with better mechanical properties it is necessary to impart hydrophobicity to the fibers by suitable chemical treatments. Such treatments not only decrease the moisture absorption but would also increase the wettability of fibers with the rubber matrix. Surface modification is therefore necessary to obtain better performance of the resulting composites. The chemical modification and characterization of lignocellulosic fibers has been highlighted by Jacob et al¹³. The chemical constituents and physical properties of fibers are given in Table I & II. Sisal and oil palm fibers were first separated from undesirable foreign matter and pith material.

3.1 ALKALI TREATMENT

Sisal and oil palm fibers of lengths 10 mm and 6 mm were treated for 1 hour with NaOH solutions of concentrations 0.5,1,2,4 % respectively. The fibers were further washed with water containing acetic acid. Finally the fibers were washed again with fresh water and dried in an oven.

3.2 SILANE TREATMENT

The silanes used were fluorosilane (F8261), 3-aminopropyl tri-ethoxy silane (A1100) and vinyl triethoxy silane (A151). 0.4 % of the respective silanes was prepared by mixing with an ethanol / water mixture in the ratio 6 / 4 and was allowed to stand for 1 hour. The pH of the solution was maintained at 4 with the addition of acetic acid. Sisal and oil palm fibers were dipped in this solution and were allowed to stand for 1.5 hours. The ethanol / water mixture was drained out and the fiber was dried in air and then in an oven at 70°C until the fibers were completely dry.

4. PREPARATION OF COMPOSITE

Formulation of mixes is shown in Table III. Natural rubber was masticated on the mill for 2 minutes followed by addition of the ingredients. The composite materials were prepared in a laboratory two-roll mill (150 x 300mm). The nip-gap, mill roll, speed ratio, and the number of passes were kept the same in all the mixes. The samples were milled

for sufficient time to disperse the fibers in the matrix at a mill opening of 1.25 mm. The bonding system consisting of resorcinol and hexamethylene tetramine was incorporated for mixes containing treated fibers. The chemically treated fibers were added at the end of the mixing process, taking care to maintain the direction of compound flow, so that the majority of fibers followed the direction of the flow.

5. MEASUREMENT OF PROPERTIES

Curing properties were measured in a Monsanto R-100 rheometer, at a temperature of 150°C.

Stress-strain measurements were carried out at a crosshead speed of 500 mm per minute. Tensile strength and tear strength was measured according to ASTM methods D412-98 and D624-00, respectively. The tensile tests were done using dumbbell samples cut longitudinally and transversely with respect to the orientation of fibers.

Anisotropic swelling studies were carried out using rectangular samples (2.5 x 1 x 0.2 cm) cut at different angles with respect to orientation of the fiber from the tensile sheets and swollen in toluene at room temperature for 3 days. Length, breadth and thickness of the samples were measured before and after swelling.

Hardness measurements were measured by Shore A type Durometer according to ASTM methods D2240-03. Abrasion resistance was measured on an abrader according to DIN 53516.

Equilibrium swelling measurements of the vulcanizates was performed in toluene at room temperature. Circular shaped samples having a diameter of 2mm, punched out of tensile sheets were used. The samples were allowed to swell for 72 h in toluene.

ESCA studies were carried out on Axis Ultra Photoelectron Spectrometer (KRATOS ANALYTICAL, Manchester, U.K.) Spectrometer was equipped with a monochromatic Al K α X-ray Source ($h\nu = 1486.6$ eV) of 300W operating at 15kV. The kinetic energy of photoelectrons was determined with a hemispherical analyzer set to pass energy of 160 eV. During all measurements, electrostatic charging of sample was overcompensated by

means of a lower energy source working with combination with a magnetic immersion lens. All recorded peaks were corrected for electrostatic charging by setting the component of saturated hydrocarbon in the C 1s spectrum 285 eV. In all experiments, the base pressure in the analysis chamber was less than 10^{-8} mbar.

Scanning electron microscopic studies were conducted using JEOL, JSM 5800 to analyse the fracture behaviour of the composites. The fracture ends of the tensile and tear specimens were mounted on aluminium stubs and gold coated to avoid electrical charging during examination.

6. RESULTS AND DISCUSSION

6.1. Processing characteristics

6.1.1 Effect of bonding agent and chemical modification

The minimum torque gives an indication of the filler content in the rubber while the maximum torque in the rheograph is a measure of crosslink density and stiffness in the rubber. In general, for all the mixes the torque initially decreases, then increases and finally levels off. The initial decrease in torque to a minimum value is due to the softening of the rubber matrix while the increase in torque is due to the crosslinking of rubber. The levelling off is an indication of the completion of curing. It is found that generally the presence of fibers increases the maximum torque

Table IV shows the maximum torque, minimum torque and cure time of the gum, untreated, alkali treated and silane treated composites. It is seen that upon treatment maximum torque increases indicating greater crosslinking due to better adhesion between fiber and matrix. Maximum torque value is exhibited by composite L indicating maximum crosslinking for alkali treated composites. Cure time does not show any systematic trend upon treatment.

6.2 Mechanical properties

The variation of tensile strength with alkali treatment is seen in Figure 1. The two factors that are apparent are that composites containing treated fibers possessed greater tensile strength compared to untreated composite and also that composites treated with 4 %

NaOH showed maximum tensile strength. It has been reported that alkali treatment leads to fiber fibrillation i.e. breaking down of fiber bundles into smaller fibers which increases the effective surface area available for contact with the matrix¹⁴. Alkali treatment results in improvement in the interfacial bonding by giving rise to additional sites of mechanical interlocking, thereby promoting more resin / fiber interpenetration at the surface. The reason why composites composed of fibers treated with 8 % NaOH showed a decrease in tensile strength is that at such high concentrations of alkali the lignocellulosic sisal and oil palm fibers undergo degradation leading to lowering of tensile strength.

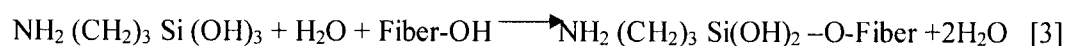
The effect of chemical modification on tensile strength is given in Figure 2. It can be seen that the strength of the fiber composites is less than that of gum. Natural rubber inherently possesses high strength due to strain-induced crystallization. When fibers are incorporated into natural rubber, the regular arrangement of rubber molecules is disrupted and hence the ability for crystallization is lost. This is the reason why fiber reinforced natural rubber composites possess lower tensile strength than gum compounds.

Among the silane treated composites it can be seen that composites prepared of fluorosilane treated fibers possess the maximum tensile strength. The potential advantages of using silane coupling agents are their inherent natural attraction with both the natural fiber and rubber matrix.

The reaction mechanisms can be explained as follows. First silane reacts with water to form silanol and an alcohol.



In the presence of moisture the silanol reacts with hydroxyl group attached to the cellulose molecules of the fiber through an ether linkage with removal of water.



Similar reactions take place for fluoro silane and vinyl silane coupling agents. The rubber matrix gets attached to the organo functional group of silane coupling agent either through a covalent bond or hydrogen bond. Here the possibility of hydrogen bonding is greater due to the presence of nitrogen in amino group and fluorine in fluoro silane group, while no such possibility exists in vinyl group. This kind of bonding cannot be possible for the vinyl silane group. The hydrogen bond formed by the fluorine to the matrix will be stronger than hydrogen bond formed by nitrogen to the matrix due to the high electronegative character of fluorine atom. Thus, in fluoro-silane treated composites fiber / matrix adhesion will be stronger compared to amino-silane treated and vinyl-silane treated composites.

A schematic sketch of the interaction between silane coupling agent and fibers is shown in Figure 3. In addition to the self-condensation of silanes and the condensation on the cellulose fibre surface, amino silane molecules can interact with the cellulose's OH groups via their Brønsted-basic amino groups.

The use of XPS to study the chemical modification of banana fibers has been reported¹⁵. In the present study, XPS data revealed that silane treatment was found to introduce a considerable amount of silicon on the surface of the fiber. The [O]/[C] ratio was also found to decrease for the F8261 treated fibers. Figure 4 (a) and (b) presents the XPS survey spectra of raw and silane F8261 modified sisal fibres. It can also be seen that there is a considerable increase in the concentration of fluorine on surface of fiber.

This results in better interaction between sisal and oil palm fibers and rubber matrix. It can also be seen that composites in which the fibers are longitudinally oriented possess greater tensile strength than transversely oriented composites. When fibers are longitudinally oriented the fibers are aligned in the direction of force and the fibers transfer stress uniformly. When transversely oriented, the fibers are aligned perpendicular to the direction of load and they can transfer stress but not as efficiently.

Figure 5 shows the variation of elongation at break of the untreated and treated composites. It can be seen that elongation at break for treated composites is lower than that for untreated composites at similar loading. This can be attributed to better strength and stiffness achieved from strong adhesion between treated fiber and rubber matrix. Higher extension is obtained from weak interfacial adhesion as seen for untreated composites.

The variation of modulus at 100 % elongation with chemical modification is shown in Figure 6. It is clear that the modulus of a well bonded composite arises from the fact that the load transfer between the fiber and matrix occurs through the strong fiber/matrix interface. Here one can see that the modulus of the chemically treated composites exhibit higher modulus values than untreated composite. It can be seen that that this is due to the presence of a strong interface between the treated fibers and matrix. Composite containing fluorosilane treated fibers possessed the maximum modulus.

Figure 7 shows the variation of tear strength with chemical modification. It can be seen that the tear strength of treated composites is higher than that of untreated composites. The reason why tear strength of filled composite increases with that of gum compound is because the increased strain between closely packed fibers decreases tearing and increases the tear strength. In the case of treated sisal and oil palm fibers, the fiber surface is transformed into a more reactive one with the ability to bind active groups with the rubber matrix. Therefore rubber / fiber chemisorption increases leading to greater tear strength.

The variation of hardness with chemical modification is presented in Figure 8. It can be seen that chemical modification has resulted in an increase of hardness. The composite containing 4 % alkali treated fiber exhibits maximum hardness (L). It has also been observed by the authors in an earlier study that composite containing fibers treated with 4 % NaOH shows the maximum tensile strength.¹⁶ Therefore this can be attributed to a strong interface as well as a close packing arrangement in the composite. Among the composites containing silane treated fibers maximum hardness is shown by fluorosilane

treated composite and the minimum hardness is given by the vinyl silane treated composites.

The abrasion resistance of a solid body is defined as its ability to withstand the progressive removal of material from its surface as the result of mechanical action of a rubbing, scraping or erosive nature¹⁷. The variation of abrasion resistance with loading is given in Figure 9. It can be seen that abrasion loss decreases with loading. Chemically modified composites are also found to be less prone to wearing (Figure 10).

All the above observation show that the chemical treatment of sisal and oil palm fibers result in superior tensile properties due to better interaction between fiber and rubber matrix.

We can also say that on comparing the two treatments, alkali treated composites exhibited better tensile properties than silane treated composites. This suggests that the economical alkali treatment is a much more effective chemical modification than the expensive silane treatments.

6.3 Equilibrium swelling studies

6.3.1 Rubber- Fiber Interaction and extent of reinforcement

The extent of interaction between rubber and fiber can be analysed using Kraus equation¹⁸. The Kraus equation is

$$\frac{V_{ro}}{V_{rf}} = 1 - m \left[\frac{f}{1-f} \right] \quad [3]$$

where V_{ro} = volume fraction of rubber gum vulcanizates.

f = volume fraction of fiber

m = polymer – fiber interaction parameter.

V_{rf} is the volume fraction of elastomer in the solvent swollen filled sample and is given by the equation by Ellis and Welding.

$$V_{rf} = \frac{(d - fw)p_p^{-1}}{(d - fw)p_p^{-1} + A_s p_s^{-1}} \quad [4]$$

where d = deswollen wt. of sample

f = volume fraction of fiber

w = initial weight of sample

p_p = density of polymer

p_s = density of solvent

A_s = amount of solvent absorbed by sample

V_{r0} = volume fraction of elastomer in solvent swollen unfilled sample

The ratio V_{r0} / V_{rf} represents the measure of swelling of the rubber matrix due to the presence of fiber and is given in Table V. It can be seen that Mix L has the lowest V_{r0} / V_{rf} value. This can be associated with enhanced fiber - rubber adhesion in the composite due to better reinforcement. Since there is better bonding between fiber and matrix, there is a strong interface, which restricts the entry of solvent. As concentration of alkali used increases solvent uptake decreases. This causes an increase in V_{rf} values which in turn reduces the ratio of V_{r0} / V_{rf} . It can also be seen that among silane treated composite P shows the minimum V_{r0} / V_{rf} value while Q exhibits the maximum value.

6.4 Swelling index and crosslink density determination

The swelling index which is a measure of the swelling resistance of the rubber compound is calculated using the equation:

$$\text{Swelling index \%} = \frac{A_s}{W} \times 100 \quad [5]$$

where A_s = amount of solvent absorbed by sample

W = initial weight of sample before swelling.

The diffusion mechanism in rubbers is essentially connected with the ability of the polymer to provide pathways for the solvent to progress in the form of randomly generated voids. As the void formation decreases with fiber addition, the solvent uptake also decreases. Table VI shows the swelling index values of the different composites. The gum compound shows the maximum value for swelling index indicating maximum swelling and minimum crosslinks. As fiber is added to the matrix swelling decreases since the fibers restrict the entry of the solvent. Among the alkali treated fibers I show maximum swelling index value and L shows minimum swelling index. This suggests that for composites treated with 4 % NaOH there exists a strong interface due to better adhesion between rubber and fiber and this prevents entry of solvent and results in minimum swelling. Among the silane treated composites fluorosilane treated composite exhibits minimum swelling index value and vinylsilane treated composites give maximum swelling index value. This shows that fluorosilane treated fiber provide better adhesion than other silanes.

The extent of crosslinking can be determined from the reciprocal swelling values $1/Q$ where Q is defined as the amount of solvent absorbed by 1g of rubber is given by the equation.

$$Q = \frac{\text{Swollen wt. - dried wt.}}{\text{Original wt.} \times 100 / \text{formula wt.}} \quad [6]$$

Table VII shows the apparent crosslinking values in various mixes. Mix L shows the maximum crosslink density indicating maximum interaction between fiber and matrix among alkali treated composites while for silane treated composites P shows the highest value. Crosslink density can also be calculated from the equation:

$$M_c = \frac{-\rho_r V_s V_{rf}^{1/3}}{\ln(1 - V_{rf}) + V_{rf} + \chi V_{rf}^2} \quad [7]$$

where M_c = molecular weight of polymer between crosslinks

ρ_r = density of polymer

V_s = molar volume of solvent

χ = interaction parameter

χ is given by Hildebrand equation

$$\chi = \beta + \frac{V_s (\delta_s - \delta_p)^2}{RT} \quad [8]$$

where β = lattice constant

V_s = molar volume

R = universal gas constant

T = absolute temperature

δ_s = solubility parameter of solvent

δ_p = solubility parameter of polymer

V_{rf} = volume fraction of elastomer in the solvent swollen filled sample.

Figure 11 represents the crosslink density of the various mixes. It can be seen that upon chemical treatment the number of cross links increases whereby the above observations are supported.

6.5 Anisotropic swelling studies

Information about anisotropy caused by the orientation of fibers and matrix /fiber adhesion can be obtained from anisotropic swelling studies. This provides an idea about the extent of fiber orientation also. Geethamma et al.¹⁹ estimated the extent of fiber orientation and fiber / matrix interfacial adhesion in coir reinforced natural rubber composites.

For short fiber reinforced rubber composites, the swelling ratio in any direction forming an angle θ with the fiber orientation is given by the expression:

$$a_{\theta}^2 = (a_T^2 - a_L^2) \sin^2 \theta + a_L^2 \quad [9]$$

where a_L and a_T are the dimensional swelling ratios in the longitudinal and transverse directions, respectively. Fig. 12 shows dimensional swelling variation with angle θ in

accordance with the above equation where various values of θ were assumed. For all the mixes, the swelling increases with θ and is found to be maximum when θ becomes 90°C. The line corresponding to gum compound which does not contain fibers is positioned above those for the other mixes. This shows that short fibers restrict the transport of solvent into the composite. It can also be seen that composites prepared from fibers treated with 4 % NaOH show less swelling compared to the untreated composite. This suggests the presence of a strong interface in mix L due to greater interaction between fibers and matrix.

The extent of fiber alignment can be understood from the slope values given in Table VIII. It has been reported that the steeper the line the higher the degree of fiber alignment. Mix P shows the maximum slope value among the various mixes. It shows that the composite containing fluorosilane treated fiber has the highest degree of fiber alignment.

6.6 Scanning electron microscopy studies

Scanning electron microscopy is a common method to analyze the level of fiber/ matrix adhesion. Enormous amount of studies has been conducted to evaluate the bonding between matrix and fiber. Analysis of the morphological features of fracture surfaces by SEM is an important tool for observing the surface morphology of fibers, the cause of crack initiation and the failure process in composites. The tensile fracture surfaces of polypropylene-sawdust composites were investigated by means of scanning electron microscopic studies.²⁰ The authors observed that the addition of higher maleated propylene content to the composites produced better adhesion of saw dust to polypropylene matrix. The interfacial adhesion as a function of fiber loading of sisal-oil palm hybrid reinforced natural rubber composites was analyzed by Jacob et al.²¹ . The authors found that at low and high levels of fiber loading the interfacial adhesion was quite poor while at intermediate levels of loading interfacial adhesion was found to be good as the population of fibers was just right for uniform stress transfer.

Figure 13 (a) show the tensile fracture surface of untreated sisal / oil palm fiber filled rubber composite at 30 phr loading. The presence of cavities is clearly visible. This

indicates that the level of adhesion between the fibers and the matrix is poor and when stress is applied it causes the fibers to be pulled out from the rubber easily leaving behind gaping holes. Figure 13 (b) depict the tensile fracture surface of 2 % NaOH treated sisal / oil palm fiber filled rubber composite at the same loading. The figure shows the smooth surface of the fibers indicating that the chemical modification has significantly altered the fiber structure.

Figure 13 (c) show the tensile fractures surface of 4 % NaOH treated sisal –oil palm fiber reinforced rubber composite at 30 phr loading. Here again the presence of a number of short broken fibers projecting out of the rubber matrix can be clearly seen indicating that alkali treatment definitely improves the bonding between the fibers and matrix. Figure 13(d) shows the tensile fracture surface of fluorosilane treated sisal / oil palm hybrid fiber reinforced rubber composites at 30 phr loading. Here one can see the presence of a number of broken fibers. This observation supports the high tensile strength and low swelling index value of fluorosilane treated sisal-oil palm hybrid fiber composites.

CONCLUSIONS

The processability characteristics and mechanical properties of sisal-oil palm hybrid fiber reinforced natural rubber green composites have been investigated as a function of different chemical modifications. It was observed that upon chemical treatment the torque values increased indicating greater crosslinking. As the degree of crosslinking increases the rubber chains are immobilized leading to higher torque values. Maximum torque value was exhibited by alkali treated composites. Cure time did not show any systematic trend with different chemical modifications.

Alkali treatment increased the tensile strength of the composites and the maximum tensile strength was observed for composites prepared with 4 % NaOH treated fibers. Composites prepared from fluorosilane treated fibers exhibited better mechanical among the other silane treated composites. Swelling studies indicated that among the alkali treated fibers composites treated with 0.5 % NaOH show maximum swelling index value and those treated with 4 % NaOH showed minimum swelling index value. This suggest that for composites treated with 4 % NaOH there exists a strong interface due to better adhesion between rubber and fiber and this prevents the entry of solvent and results in

minimum swelling. Among the silane treated composites, fluorosilane treated composites exhibits minimum swelling index value and vinylsilane treated composites show maximum swelling index value. Surface characterization by XPS showed the presence of numerous elements on the surface of the fiber. Anisotropic swelling studies revealed that composite containing fluorosilane treated fiber reinforced composites has the highest degree of fiber alignment.

CAPTIONS TO FIGURES

Figure 1 – Variation of tensile strength with alkali treatment.

Figure 2 – Variation of tensile strength with chemical modification.

Figure 3- Scheme of interaction of silanes with cellulose

Figure 4- XPS survey spectra of raw and chemically modified sisal fibres: (a) Untreated sisal fibres (b) fibres grafted with the fluorosilane F8261.

Figure 5- Variation of elongation at break with chemical modification.

Figure 6 – Variation of modulus at 100 % elongation with chemical modification.

Figure 7 – Variation of tear strength with chemical modification.

Figure 8- Variation of hardness with chemical modification.

Figure 9- Variation of abrasion with fiber loading.

Figure 10- Variation of abrasion with chemical modification.

Figure 11 – Variation of crosslink density with chemical modification.

Figure 12 – Variation of dimensional swelling ratio as a function of the angle of measurement, θ

Figure 13 – SEM tensile fracture surface at 30 phr loading of (a) untreated composite (b) composite K (c) composite L (d) composite P

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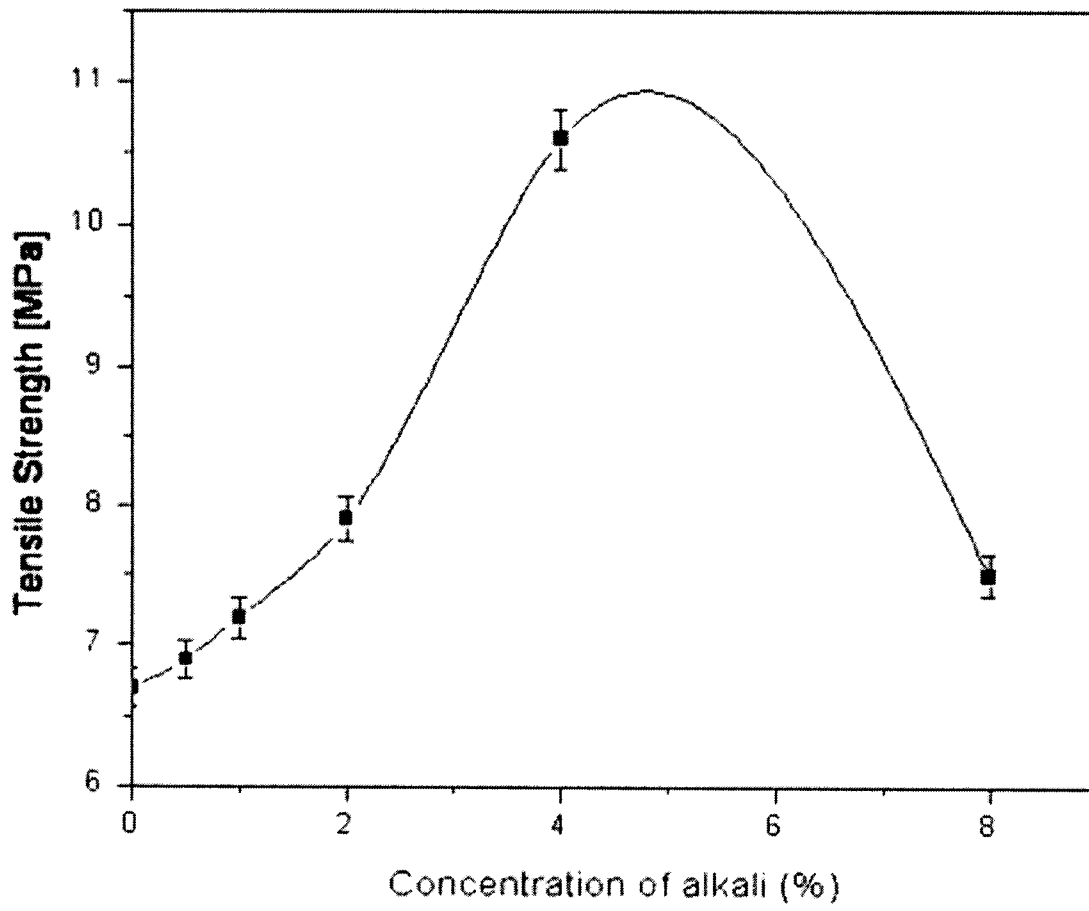
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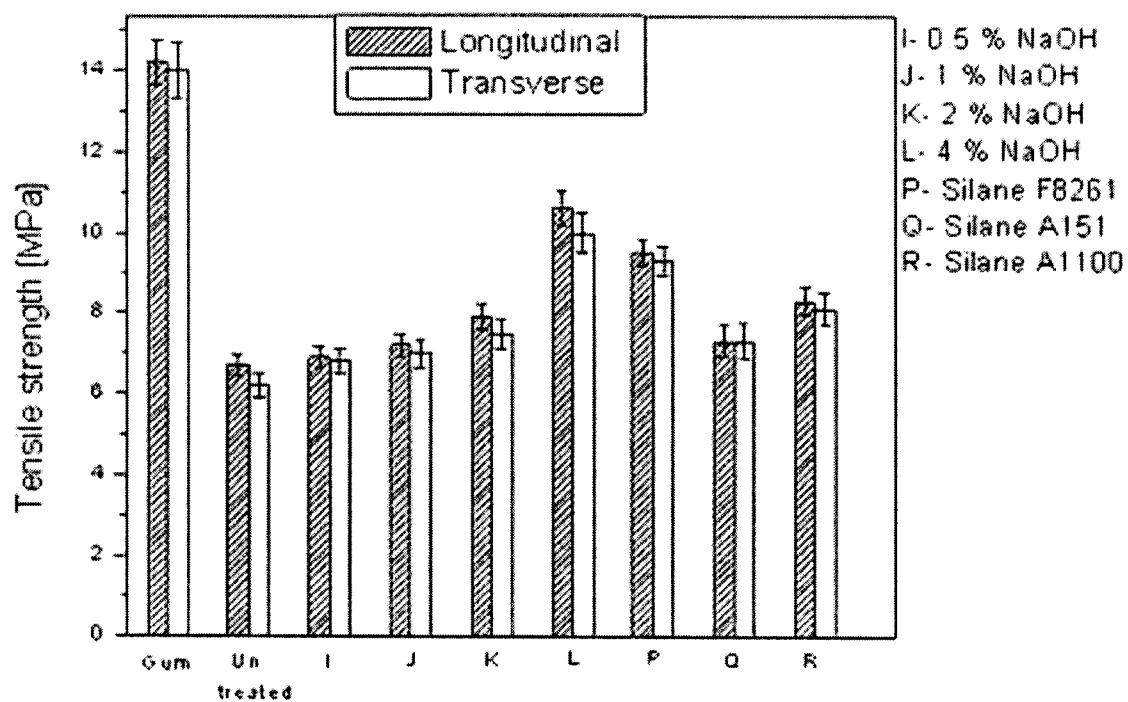
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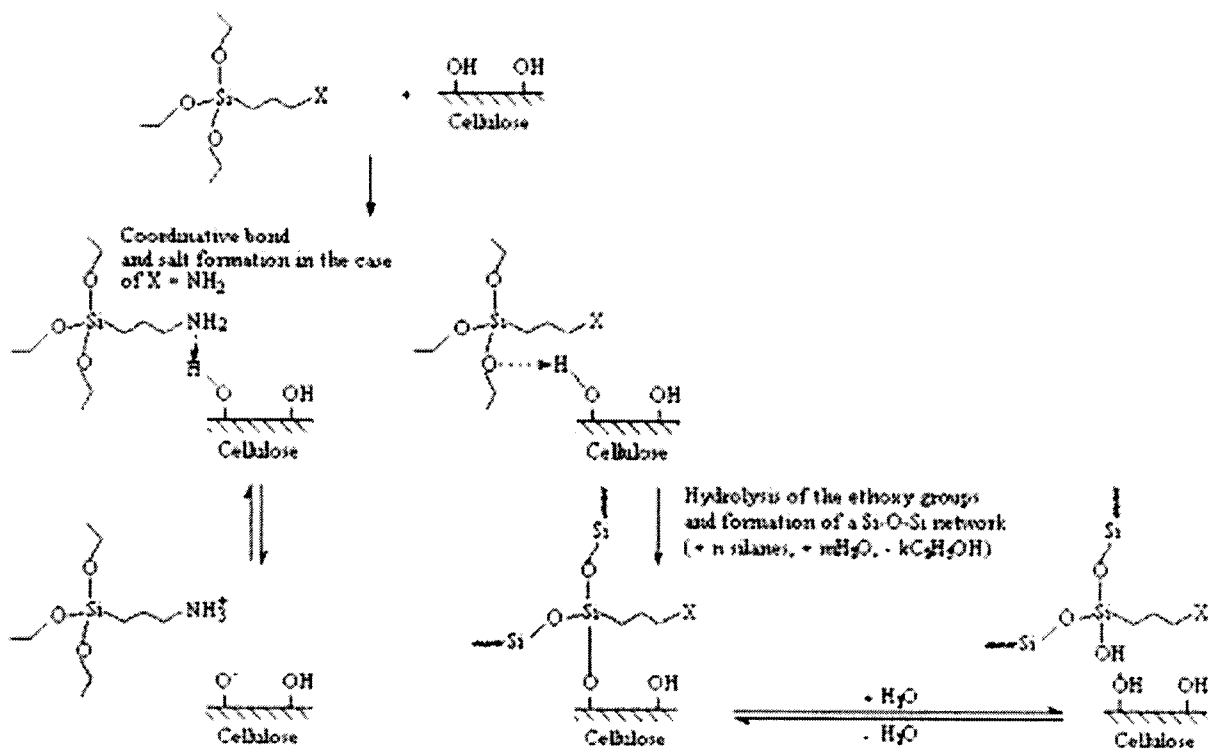
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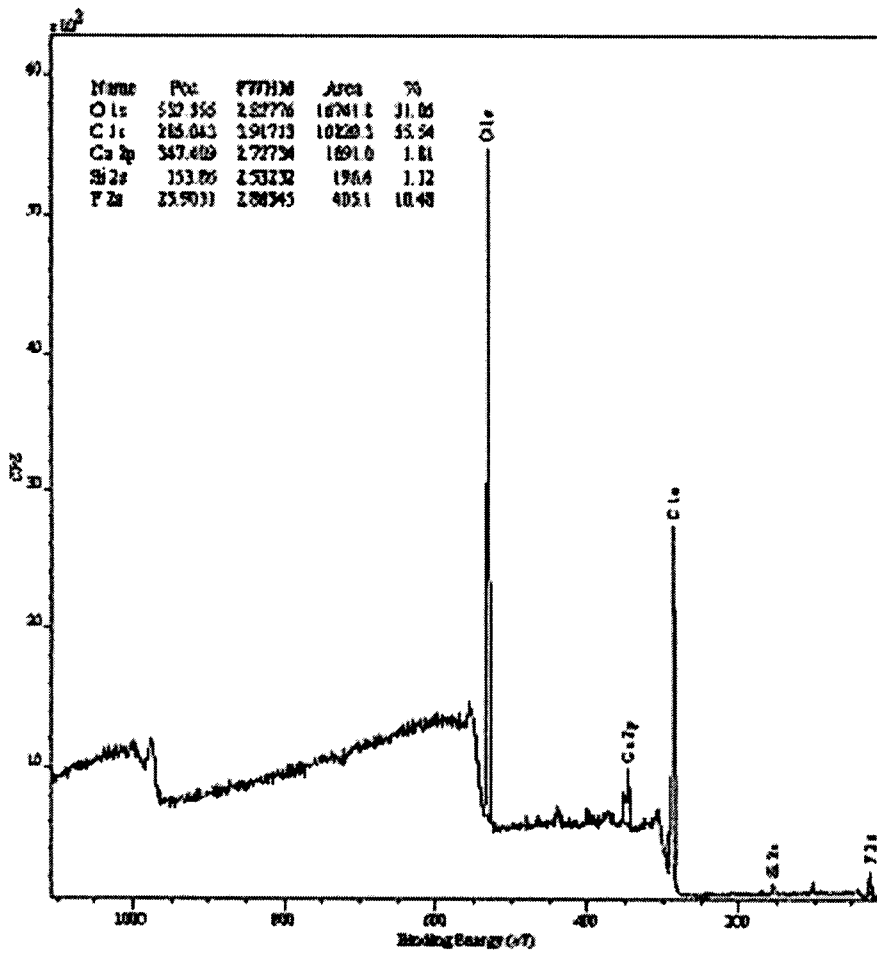


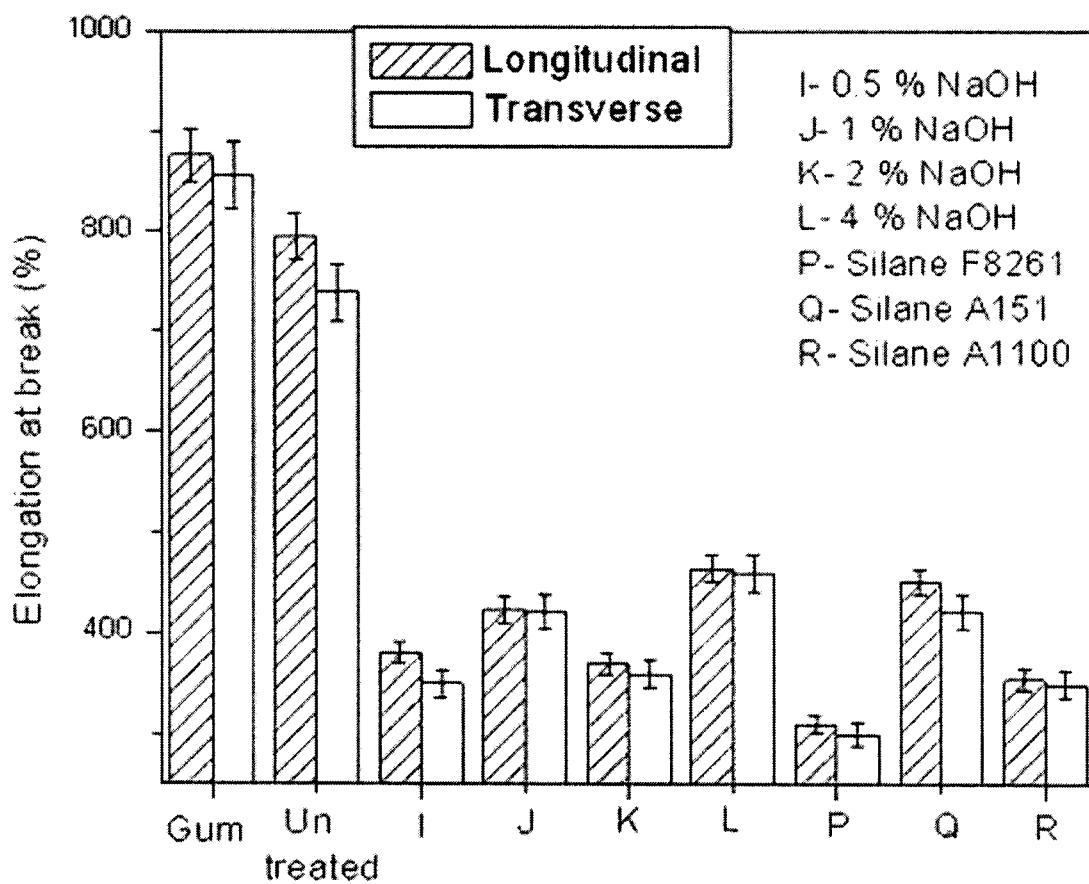
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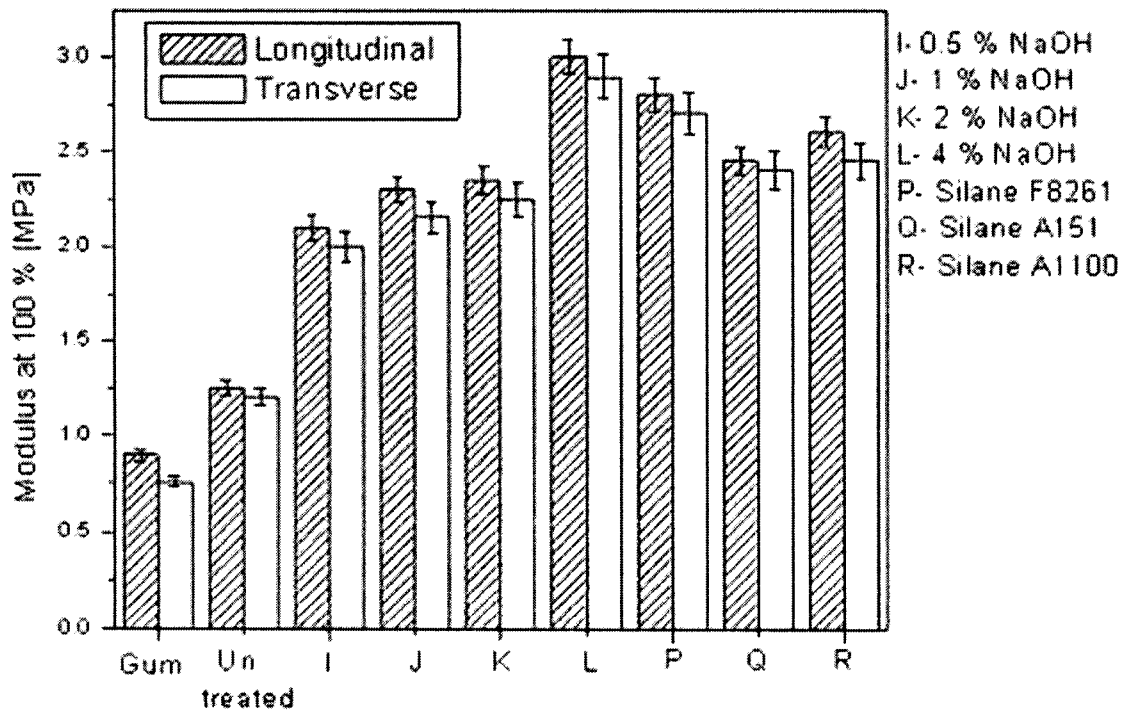
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File Acquisition Time: 2003/11/12 12:14:20
Acquired On: 2003/11/12 12:14:20
Scan 1: All

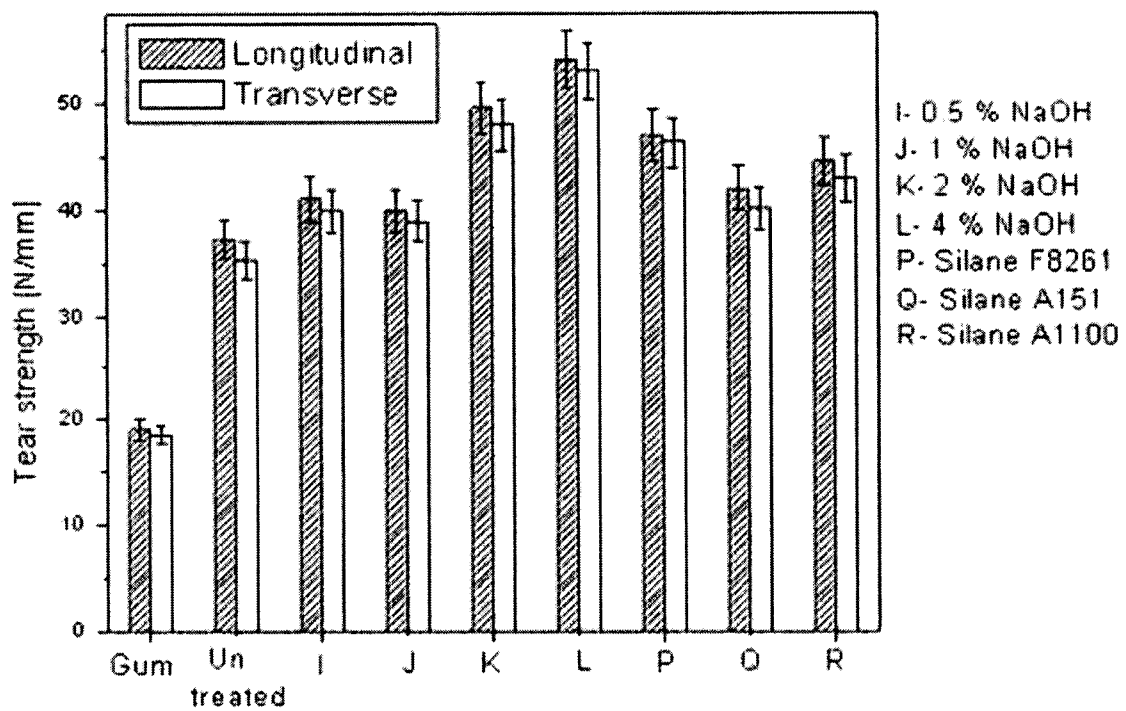




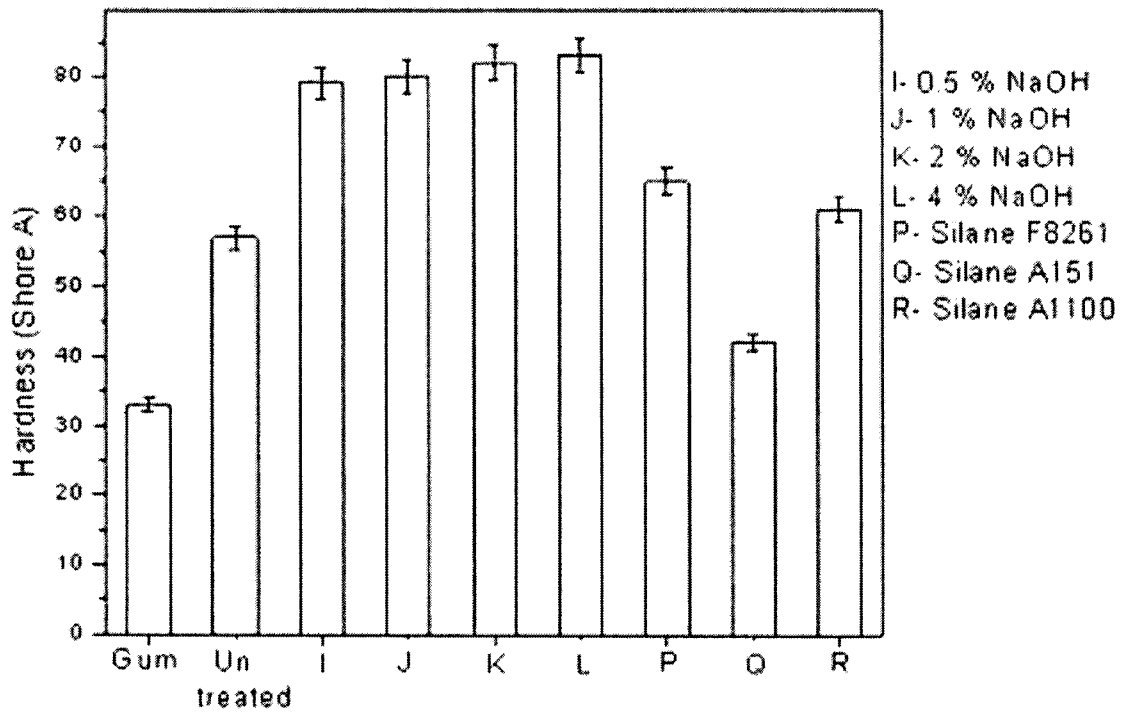
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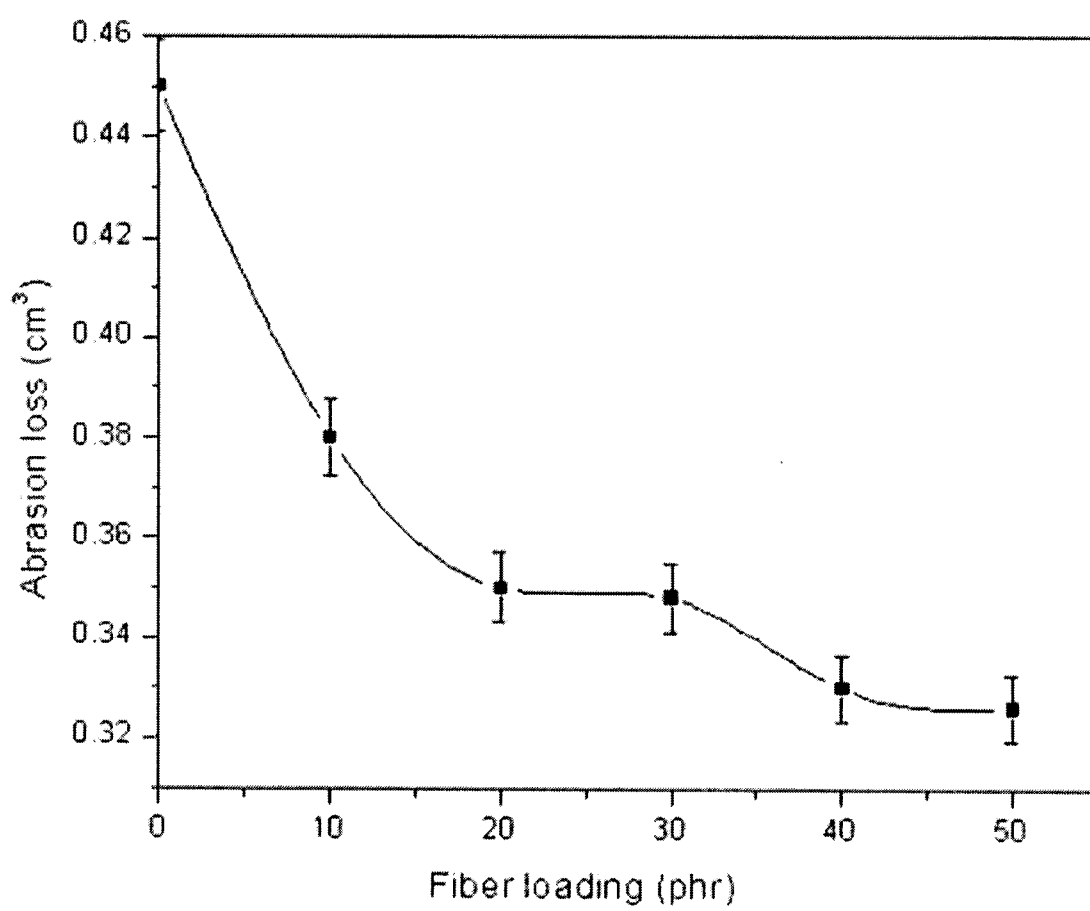
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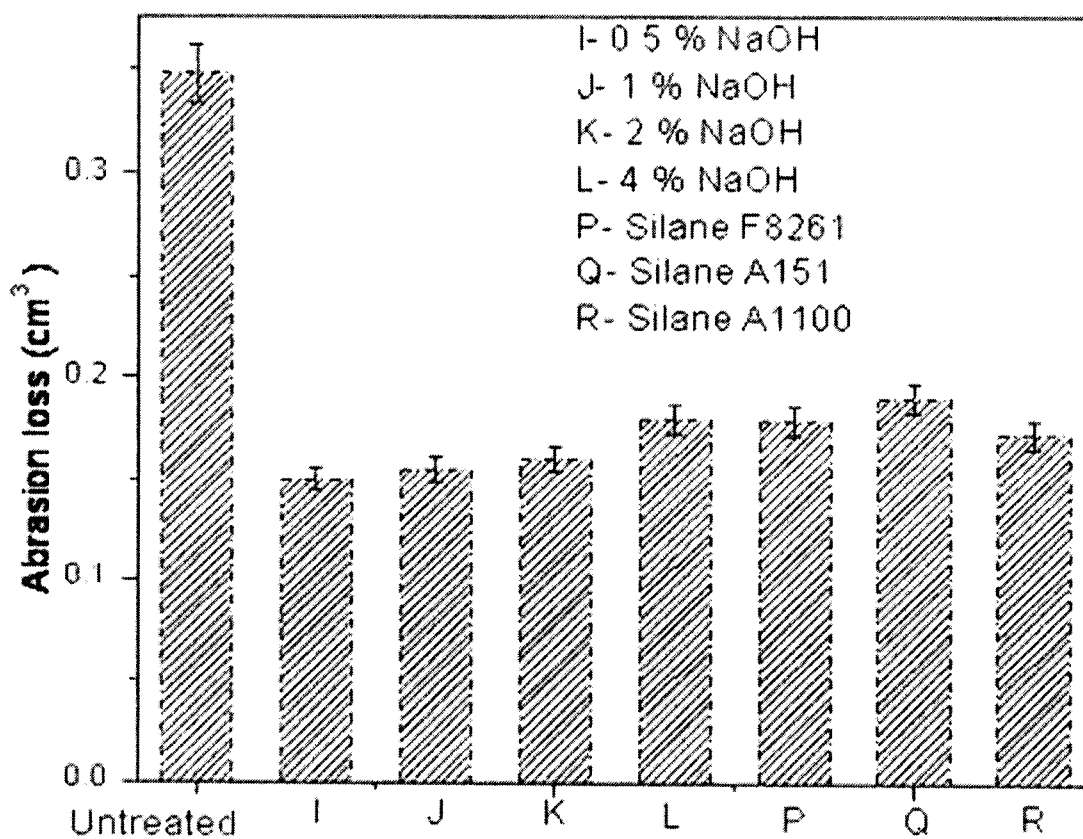


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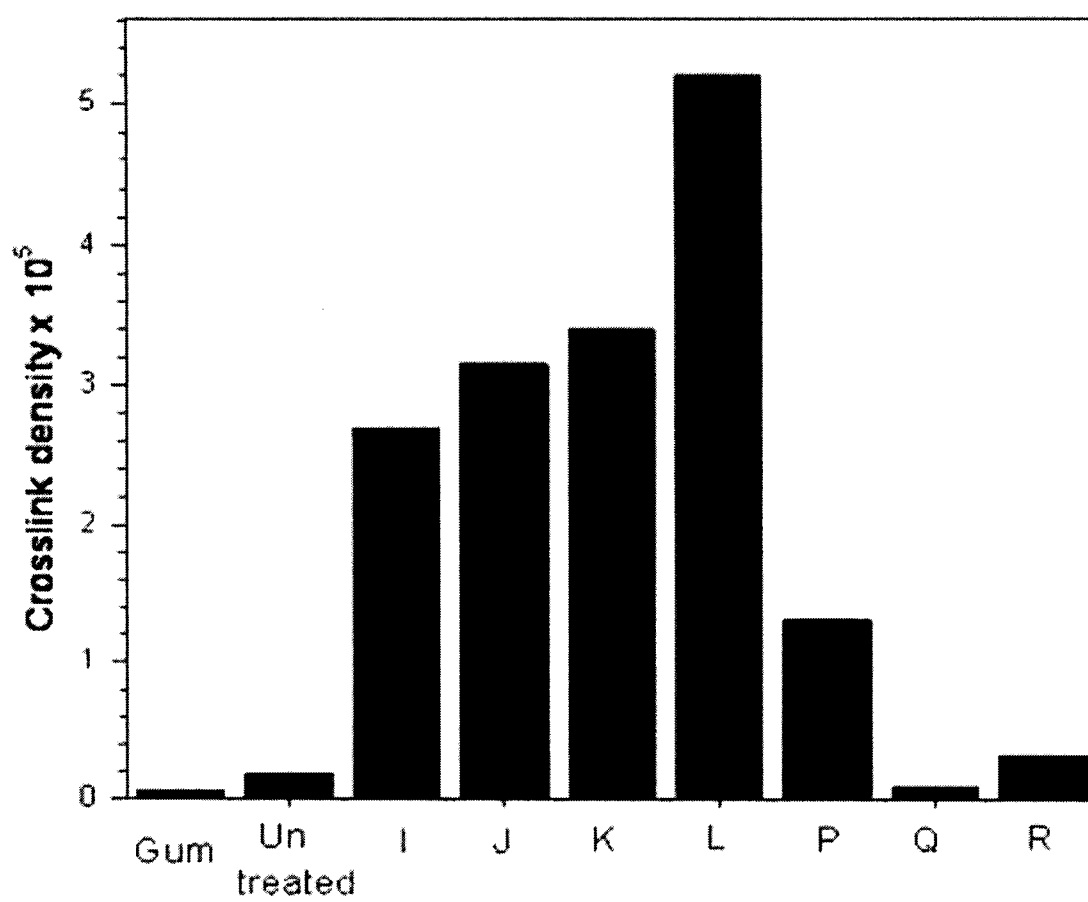


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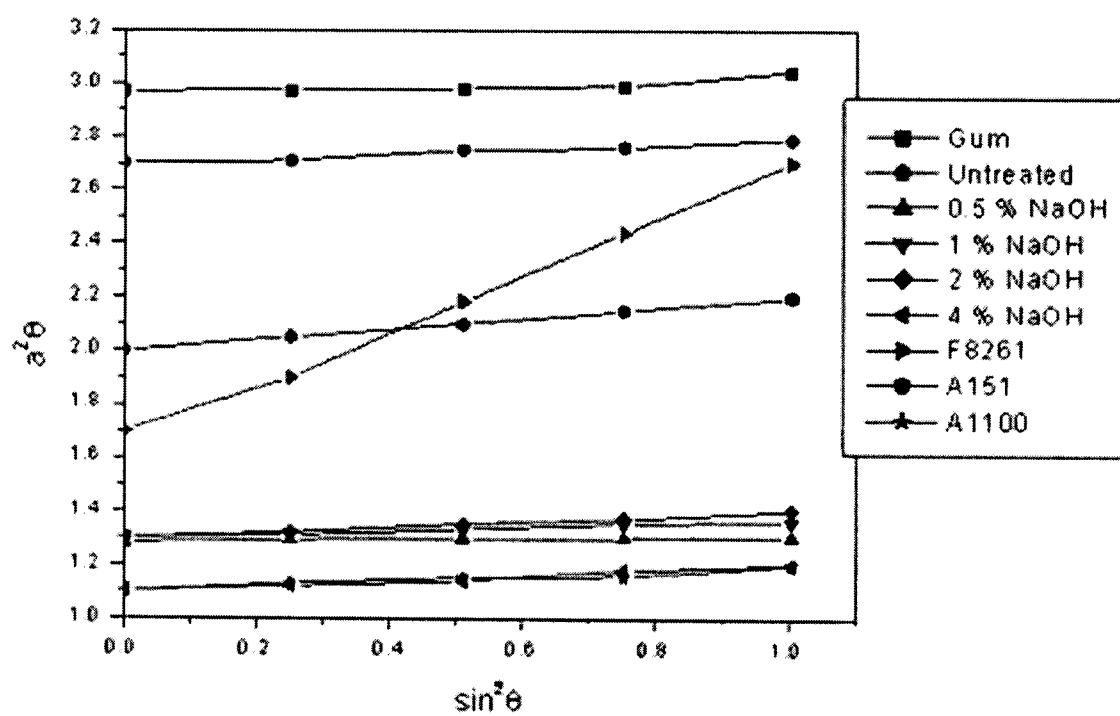




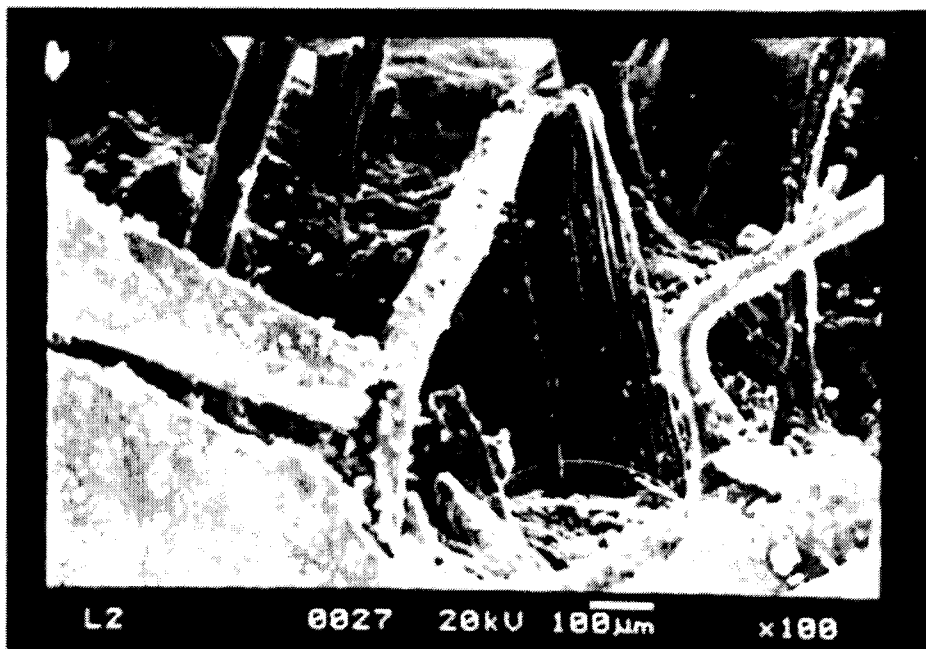
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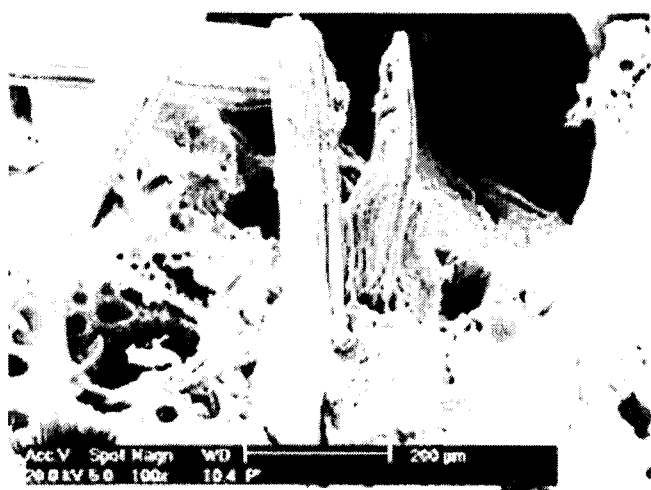


Table I

PROPERTIES OF SISAL FIBER

Chemical constituents (%)

Cellulose	78
Hemicellulose	10
Lignin	8
Wax	2
Ash	1

Physical properties of sisal fiber

Diameter (μm)	50-200
Tensile strength (MPa)	530-630
Young's modulus (GPa)	9.4-22
Microfibrillar angle ($^{\circ}$)	20-25
Elongation at break (%)	3-7

Table II
 PROPERTIES OF OIL PALM FIBER
 Chemical constituents (%)

Cellulose	65
Hemicellulose	-
Lignin	19
Ash content	2

Physical properties of oil palm fiber

Diameter (μm)	150-500
Tensile strength (MPa)	248
Young's modulus (GPa)	3.2
Elongation at break %	25
Microfibrillar angle ($^{\circ}$)	46

Table III

Formulation of mixes (Gum to R)

Ingredients	Mixes [phr]								
	Gum	A	I	J	K	L	P	Q	R
NR	100	100	100	100	100	100	100	100	100
ZnO	5	5	5	5	5	5	5	5	5
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Resorcinol	-	-	7.5	7.5	7.5	7.5	7.5	7.5	7.5
Hexa ^a	-	-	4.8	4.8	4.8	4.8	4.8	4.8	4.8
TDQ	1	1	1	1	1	1	1	1	1
CBS ^b	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Sisal fiber Fiber length, (10 mm)	-	15	15	15	15	15	15	15	15
Treatment	-	-	0.5 % NaOH 1 hr	1 % NaOH 1 hr	2 % NaOH 1 hr.	4 % NaOH 1 hr	0.4 % Fluoro- silane	0.4% vinyl triethoxy silane	0.4% 3-amino propyl tri-ethoxy silane
Oil palm fiber Fiber length (6 mm)	-	15	15	15	15	15	15	15	15
Treatment	-	-	0.5 % NaOH 1 hr	1 % NaOH 1 hr	2 % NaOH 1 hr	4 % NaOH 1 hr	0.4 % Fluoro- silane	0.4% vinyl triethoxy silane	0.4% 3-amino propyl tri-ethoxy silane

a- Hexamethylene tetramine

b- N-cyclohexylbenzothiazyl sulphenamide

Table IV

Samples	Max torque [dNm]	Min torque [dNm]	Cure time t_{90} [min]
Gum	58	6	14
A	66	7	7
I	70	8	7.5
J	72	7	8
K	71	5	7.5
L	81	7.4	8.5
P	72	6	8
Q	67	5	8.3
R	69	7	7.5

Table V

Samples	V_{rd}/V_{rf}
A	1.0079
I	0.5399
J	0.514
K	0.4996
L	0.4396
P	0.660
Q	0.9575
R	0.7519

Table VI

Samples	Swelling index values
Gum	540.6
A	469.4
I	220.8
J	206.4
K	201.3
L	166
P	280.7
Q	333.9
R	310

Table VII

Samples	Apparent crosslink density values [1/Q]
Gum	0.1399
A	0.15015
I	0.2942
J	0.3147
K	0.3219
L	0.388
P	0.2300
Q	0.1471
R	0.1947

Table VIII

Samples	Slope values
Gum	0.1427
A	0.1983
I	0.1267
J	0.064
K	0.1
L	0.104
P	1.04
Q	0.1998
R	0.0737