A Study on the Moisture Sorption Characteristics in Woven Sisal Fabric Reinforced Natural Rubber Biocomposites

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Received 03 June 2006; accepted 11 December 2005 DOI 10.1002/app.24061 Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Textile biocomposites were prepared by reinforcing natural rubber with woven sisal fabric. Sisal fabric was subjected to various chemical modifications like mercerization, silanization, and thermal treatment. The moisture uptake of the textile composites was found to depend upon fiber content as well as architecture. The mechanism of diffusion in the composites was found to be fickian in nature. The effect of chemical modification of sisal fabric on moisture uptake was also analyzed. Mercerization was seen to increase the water uptake in the composites while thermally treated fabric reinforced composites exhibited lower water uptake. The influence of temperature on water sorption of the biocomposites is also analyzed. The thermodynamic parameters of the sorption process were also evaluated. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 416–423, 2006

Key words: biocomposite; woven fabric; textile; diffusion

INTRODUCTION

Lignocellulosic fibers have become the wonder materials of this era. Plant fiber reinforced composites have grabbed the attention of the scientific world for their desirable properties like low specific gravity, enhanced mechanical properties, and biodegradability. While the history of natural fiber reinforced composites dates back to several thousand years, modern need of an environmentally friendly system has renewed the interest in this area and a new insight is being discovered.

The applications of lignocellulosic fiber reinforced composites are enormous. The natural fiber reinforced composites in automotive applications is enjoying a double-digit growth. Plastic/wood fiber composites are being used in a large number of applications in decks, docks, window frames, and molded panel components.¹ It has been reported that 460 million pounds of plastic/wood fiber composites were produced in 1999.² Recent statistics show that the production of these composites in 2001 has increased to 700 million kilograms.³ Another innovative approach is the use of natural fibers in concrete, which provides a daunting challenge to the house construction industry especially in nonindustrialized countries.⁴ Another recent application is the production of needle-punched non-

wovens of pure natural fibers or needle-punched hybrid nonwovens of natural fibers and polypropylene fibers, which are used as semifabricated forms for technical components.⁵

A serious problem relating to the use of lignocellulosic fibers and fabrics in composites is their affinity towards moisture. The presence of hydroxyl groups in the cellulosic units in the fibers allows them to form hydrogen bonds with water molecules and it is essential to examine the durability of fiber reinforced composites under wet and humid conditions. Therefore, it is quite imperative to realize the water sorption characteristics of natural fiber reinforced composites.

The water absorption in natural fibers like sisal, coir, luffa sponge, and cellulose (from pulp) reinforced polypropylene composites were investigated by Espert et al.⁶ The authors carried out the experiments at three different temperatures, 23, 50, and 70°C. The process of absorption of water was found to follow the kinetics and mechanisms described by Fick's theory. In addition, the diffusivity coefficient was found to be dependent on the temperature as estimated by means of Arrhenius law. A decrease in tensile properties of the composites was demonstrated, showing a great loss in mechanical properties of the water-saturated samples compared to the dry samples.

In a recent study, the water and steam uptake of natural fiber reinforced novolac resin was studied by Mishra et al.⁷ In this work, natural and maleic anhydride esterified fibers of banana, hemp, and sisal were used. The absorption of water was found to increase

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Journal of Applied Polymer Science, Vol. 102, 416–423 (2006) © 2006 Wiley Periodicals, Inc.

with increase in time from 2 to 30 h in all fiber composites tested. Among all the composites, the maximum absorption of water was found in hemp fiber composite and the minimum in maleic anhydride treated sisal fiber composite. Among all six composites, steam absorption was found to be maximum in untreated hemp fiber composite and minimum in maleic anhydride treated banana fiber composite.

Another interesting study involving biodegradable composites was analyzed by Tserki et al.⁸ The authors used cotton waste as a source of reinforcing fibers in biodegradable polyester (bionolle 3020). Maleic anhydride-grafted bionolle (bionolle-*g*-MA) was used as a compatibilizer. The compatibilizer was found to decrease the water sorption characteristics of the composites.

The development of textile technologies such as weaving, knitting and braiding has resulted in the formation of composites that have superior mechanical properties, as continuous orientation of fibers is not restricted at any point. In an interesting study using braided synthetic fiber composites, the moisture absorption of three-dimensionally braided carbon fiber epoxy composites were investigated by Wan et al.⁹ The authors observed that moisture uptake reduced the mechanical properties of the composites. Also the moisture uptake of epoxy resin was found to be much higher than the reinforced composite as braided carbon fiber did not absorb water. The experimental values were also found to be higher than the theoretical data. This was attributed to the wicking effect of fibermatrix interfaces and microcracks within the composites.

The micromechanics modeling of moisture diffusion in woven composites was reported by Tang et al.¹⁰ The authors observed that woven composites exhibited quicker diffusion than that of a unidirectional laminate with the same overall fiber volume fraction. The plain weave with a lenticular tow and large waviness was seen to exhibit the quickest diffusion process.

Pothan et al.¹¹ investigated the water sorption characteristics of woven sisal fabric reinforced polyester composites. The authors observed that the diffusion mechanism in the textile composites followed a fickian pattern.

It is quite clear that though studies on water sorption behavior of short fiber reinforced composites are prevalent, studies of lignocellulosic fabric reinforced composites are limited and therefore need to be addressed in detail. This manuscript attempts to explore the moisture uptake characteristics of woven sisal fabric reinforced natural rubber composites. The water uptake at three different temperatures viz. 30, 50, and 70°C are analyzed. The thermodynamic parameters of the sorption process have also been evaluated.

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EXPERIMENTAL

Materials

Sisal fabric was obtained from local sources. Natural rubber used for the study was procured from Rubber Research Institute of India, Kottayam. The other ingredients used to vulcanize natural rubber were zinc oxide, stearic acid, TDQ (2,2,4 trimethyl-1,2-dihydro quinoline), CBS (*N*-cyclohexylbenzothiazyl sulfenamide), and sulfur, and it was obtained from local rubber chemicals suppliers.

Processing of sisal fibers

Sisal fiber

Sisal plantations were developed by the Mayas in Mexico before the arrival of Europeans. The name sisal originated from the port town Yucatan in Mexico and the literal meaning is cold water. Large-scale production of sisal started in 1888 and thereafter its plantation has been propagated throughout tropical and subtropical regions. There are now 57 species of sisal known to date.¹²

This fiber is extracted from the leaves of the plant *Agave sisalana* that is widely cultivated in the Western Hemisphere, Africa, and Asia. The agaves have rosettes of fleshy leaves, usually long and narrow, which grow out from a central bud. As the leaves mature, they gradually spread out horizontally and are 1–2 m long, 10–15cm wide and about 6 mm thick at the center. The fibers are embedded longitudinally in the leaves and are most abundant near the leaf surfaces. The leaves contain about 90% moisture but the fleshy pulp is very firm and the leaves are rigid. The fiber is removed when the leaves are cut because dry fibers adhere to the pulp. The fiber is removed by scraping away the pulpy material, generally by a mechanical decortication process.

In the decortication process, the leaves are fed through sets of crushing rollers. The crushed leaves are held firmly at their centers and both ends are passed between pairs of metal drums on which blades are mounted to scrape away the pulp, and the centers are scraped in the same way. The fiber strands are then washed and dried.

Sisal yarn

Sisal yarns are obtained from a spinning process, which depends upon the grade of sisal fiber used. Sisal must be softened and lubricated with batch oil so that the fiber may be processed without excessive fiber breakage and waste. Fibers are drawn evenly into slivers or loose untwisted strands and then drawn out to the desired yarn thickness.



Figure 1 SEM of weave pattern of sisal fabric.

Sisal fabric

In this particular analysis a unidirectional type of fabric weave having a count of 20 is used. (Fig. 1). The properties of woven sisal fabric are given in Table I.

Fabrication of composites

Formulation of mixes is shown in Table II. Natural rubber was masticated on the mill for 2 min followed by addition of the ingredients. The rubber sheet was prepared in a laboratory two-roll mill ($150 \times 300 \text{ mm}^2$). The nip-gap, mill roll, speed ratio, and the number of passes were kept the same for all the mixes. The bonding system consisting of resorcinol and hexamethylene tetramine was also incorporated. The sisal fabric—natural rubber textile composites were prepared by sandwiching a single layer of sisal fabric between two layers of preweighed rubber sheets which was then compression molded at 150°C for 8 min.

Chemical modification of sisal fabric

The different chemical modifications performed were as follows:

Alkali treatment

Sisal fabric was treated for 1 h with NaOH solution of concentration 4%. The fabric was further washed with water containing acetic acid. Finally the fabric was washed again with fresh water and dried in an oven.

Silane treatment

The silanes used were 3-aminopropyl triethoxy silane (Silane A1100) and γ -Metharyloxypropyltrimethox-

ysilane (Silane A174). 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 h. The pH of the solution was maintained at 4 with the addition of acetic acid. Sisal fabric was dipped in this solution and was allowed to stand for 1.5 h. The ethanol–water mixture was drained out and the fabric was dried in air and then in an oven at 70°C until it was completely dry.

[c] Thermal treatment

Thermal treatment is aimed at increasing interfacial adhesion. It results in moisture loss of the fabric thereby enhancing the extent of bonding between fabric and rubber.¹³ Thermal treatment was carried out by keeping the woven sisal fabric in the oven for 8 h at 150°C. The fabric, directly from the oven was used for composite preparation.

MEASUREMENTS

Water sorption is evaluated in terms of weight increase for composite specimen immersed in distilled water at temperatures 30, 50, and 70°C. Circular specimens were dried in vacuum at room temperature for two days and the weight of dried specimen was measured using an electronic balance. The thickness of the samples was also measured. The weighed specimens were then immersed in distilled water at different temperatures. The specimens were periodically removed from water bath and the surface moisture was wiped off. The weight gain of the specimen has been measured as a function of time until equilibrium or saturated state of water uptake has been reached. Moisture absorption was determined by weighing the specimen on an electronic balance. The molar percentage uptake Q_t for water by 100 g of the polymer was plotted against square root of time. The Q_t value is expressed as

$$Q_t = \frac{M_e(w)/M_r(w)}{M_i(s)} \times 100 \tag{1}$$

where M_e (w) is the mass of water sorbed, M_r (w) is the relative molecular mass of water (18) and M_i (s) is the initial mass of the sample. When equilibrium was

TABLE I Properties of Sisal Fabric

Yarn distance (weft)	3 mm
Yarn distance (warp)	5 mm
Twist (turns per mm)	10
Areal density (g/m^2)	1500

Tomulation of Mixes								
	Mixes (phr)							
Ingredients	Gum	Т	TB	TBA	TBAS	TBMS	TT	
NR	100	100	100	100	100	100	100	
ZnO	5	5	5	5	5	5	5	
Stearic acid	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	
Hexa	_	-	4.8	4.8	4.8	4.8	4.8	
TDQ ^a	1	1	1	1	1	1	1	
CBS ^b	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	
Sisal fabric	_	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	
Treated	-	_	_	4% NaOH 1 h	Silane A1100	Silane A174	Thermal	

TABLE II Formulation of Mixes

^a 2,2,4 trimethyl-1,2-dihydro quinoline.

^b N-cyclohexylbenzothiazyl sulphenamide.

reached, Q_t was taken as the molar percentage uptake at infinite time i.e., Q_{∞}

RESULTS AND DISCUSSION

Moisture uptake in textile composites

Figures 2–4 present the water sorption behavior of untreated and treated sisal fabric reinforced natural rubber composites in distilled water at 30, 50, and 70°C respectively. It has been reported that whatever be the fiber material, fiber architecture has been found to influence the composite properties based on the morphological and structural parameters.¹⁴

The amount of water absorbed by the samples at 30°C was closely followed. From Figure 2, it can be seen that all the samples show a fickian mode of diffusion, i.e., sorption begins with a rapid initial mass gain which slowly approaches saturation after pro-

longed immersion i.e., the process takes place by simple diffusion with out any physical as well as chemical reactions.¹⁵

It can also be seen that minimum water sorption is shown by sample containing bonding agent alone (TB) and maximum uptake is exhibited by composite containing alkali treated sisal fabric (TBA). Generally it has been seen that chemical modification of fibers results in lowering of water uptake in composites. In fact, in a previous study,¹⁶ we found that composites containing alkali treated sisal and oil palm fibers exhibited minimum water uptake compared to untreated composite. But in the present case, contrary to expectations, alkali and silane treated textile composites exhibit higher water uptake than the untreated composite. Only the thermally treated composite (TT) shows lower water uptake than the untreated sample.

The higher uptake of water by samples TBA, TBAS, and TBMS with respect to untreated one can be explained as follows. The mechanics of water diffusion



Figure 2 Sorption curves of untreated and treated sisal fabric reinforced natural rubber composite at 30°C.



Figure 3 Sorption curve of untreated and treated sisal fabric reinforced natural rubber composite at 50°C.

Figure 4 Sorption curve of untreated and treated sisal fabric reinforced natural rubber composite at 70°C.

in short fiber composites is different from that of textile composites. In the case of short fiber composites, chemical treatment improves the fiber surface adhesive characteristics by removing natural waxy materials, hemicellulose and artificial impurities and by producing a surface topography.¹⁷ In addition to this, alkali treatment can lead to fibrillation i.e., breaking down of fibers into smaller ones. All these factors provide a large surface area and give a better mechanical interlocking between the fiber and matrix and thus reduce water absorption. Besides the removal of hemicellulose and waxes, the treatment with NaOH solution also promotes the activation of hydroxyl groups of cellulose unit by breaking the hydrogen bond.

In the case of textile composites, chemical treatment of sisal fabric results in the partial unwinding of yarns (as hemicellulose dissolves off) and hence the alignment of the yarns gets antagonized. Another aspect is that as sisal fabric is composed of thick strands and knots, the alkali and silane coupling agents cannot penetrate into the fabric and therefore the interfacial properties between the sisal fabric and rubber matrix has not been improved enough.¹⁸ As there is not effective bonding between fabric and rubber matrix, water can easily penetrate into the voids and interfacial gaps that are present in the interfacial area causing higher water uptake.

Another aspect is that when the fibers are made into yarn form, the hydrophilic character comparatively gets reduced. Because of the twisted structure, some of the hydrophilic —OH groups may not be very activated to form H-bonds with water. This can further explain lower water uptake shown by the untreated composite. However on treatment with NaOH, there may be a chance of activation of all the hydroxyl groups which is now able to form H-bonds with water and increase the uptake of water significantly. Aminosilane treated (TBAS) composite shows a lower uptake than methyl silane treated (TBMS) composite because of the strong hydrogen bond formed between the matrix and fiber (Fig. 5). Such a possibility does not exist in TBMS because of the nonpolar nature of methyl group; the bond formed between fabric and matrix in this case is very weak.

From Figure 2, it can be seen that thermally treated samples show a lower uptake then untreated one. The thermal treatment results in moisture loss of the fabric thereby enhancing the extent of bonding between fabric and rubber and the rubber-fabric network becomes more compact. This increases fiber-matrix adhesion and leads to lower water uptake.

The minimum water uptake exhibited by sample TB can be attributed to the improved adhesion between rubber and sisal fabric in the presence of bonding agents. The same result has been observed from the calculation of diffusion coefficient (Table III).

The rate of diffusion of water is time and temperature dependent. As temperature increases, activation of diffusion increases and hence uptake of water also increases. Diffusion is related to the velocity of the diffusing molecules by the equation given below:

$$D = \frac{1}{3}\lambda \bar{c} \tag{2}$$

where \bar{c} = mean velocity of molecules

 γ is the mean free path (distance traveled by molecules between two consecutive collisions). Since the mean velocity increases with temperature, diffusion also increases with temperature.

Figure 3 presents the water uptake of textile composites at 50°C. The maximum water uptake is exhibited by TBA sample while minimum water uptake is shown by TB sample. An interesting feature in this graph is the anomalous behavior shown by TT sample which shows higher water uptake than untreated



Figure 5 Interaction between aminosilane treated fabric and rubber matrix.



Sample	Temperature (°C)	Diffusion coefficient (cm ² /min)	Sorption coefficient (g/g)	Permeability coefficient ($P = D \times S$) (cm ² /min)
Т	30	5.481×10^{-10}	0.1816	9.95 $\times 10^{-11}$
	50	2.57×10^{-9}	0.2227	5.723×10^{-11}
	70	1.4667×10^{-8}	1.66029	2.435×10^{-11}
TB	30	2.45×10^{-10}	0.16368	4.010×10^{-11}
	50	1.1696×10^{-9}	0.17009	1.989×10^{-11}
	70	1.186×10^{-8}	0.1966	1.336×10^{-11}
TBA	30	4.18×10^{-8}	0.31797	1.329×10^{-8}
	50	4.595×10^{-7}	0.34801	$1.5226 imes 10^{-8}$
	70	1.687×10^{-7}	1.76307	2.995×10^{-11}
TBAS	30	5.5 $\times 10^{-10}$	0.20218	$1.1122 imes 10^{-10}$
	50	1.46×10^{-9}	0.2023	$2.9535 imes 10^{-11}$
	70	1.188×10^{-9}	1.2025	$1.4292 imes 10^{-11}$
TBMS	30	7.713×10^{-10}	0.21286	$2.1286 imes 10^{-10}$
	50	1.2017×10^{-9}	0.29589	$2.3504 imes 10^{-11}$
	70	1.1726×10^{-9}	1.0574	$1.2399 imes 10^{-11}$
TT	30	2.64×10^{-10}	0.16885	4.457×10^{-11}
	50	8.324×10^{-9}	0.21831	$2.2704 imes 10^{-10}$
	70	7.4172×10^{-8}	0.9739	$7.2236 imes 10^{-12}$

 TABLE III

 Diffusion, Sorption, and Permeability Coefficient of Composites

composite. The results are also apparent from the diffusion coefficient calculated i.e., diffusion increases with increase in temperature.

In the case of amino silane treated (TBAS) and methyl silane treated samples (TBMS), the water absorption becomes lower than that of untreated composite. Also the uptake of water in TBMS is lesser than TBAS which is reverse to the sorption curve of the sample at 30°C. This may be due to weaker fabricmatrix adhesion in TBMS. Water will easily penetrate into the interfacial gaps in the initial stages. This causes the yarns to swell, reducing the distance between the fiber bundles or interstitial positions which will gradually result in decreased water uptake by the sample.

In the case of thermally treated sample, its uptake is found to be greater than untreated composite. This can be explained as follows. At higher temperatures like 50°C, there may be chance of breakage of the additional H-bonds created in the cellulosic network and this paves way for diffusion through these additional sites. Thus, the diffusion through the normal sites as well as through the additional sites increases the absorption of water compared to all other samples.

Figure 3 represents the water uptake at 70°C. It can be seen that maximum water uptake is exhibited by mercerized sample while minimum water uptake is shown by the thermally treated sample. Another interesting observation is that none of the samples have any tendency to attain saturation point.

In the case of mercerized sample, as explained earlier, the —OH groups in TBA are highly activated due to mercerization and because of prolonged exposure, the swelled fibers will have a tendency to escape from the yarn structure and there may occur fabric–matrix debonding. The weave architecture will be completely destroyed resulting in the formation of a large number of interstitial gaps which can increase water uptake abnormally.

Another aspect is that the sisal fabric–matrix adhesion decreases at elevated temperatures which further facilitate the water flow through the hydrophilic fabric and there may be a chance of fabric–matrix debonding leading to abnormal water uptake. Thus, uptake of water increases due to the fiber debonding from the matrix as exposure time increases. Moreover, there may a chance of degradation of the sample either by osmotic cracking or by destruction of the weave architechture.

Kinetic parameters

The thermodynamic parameters of sorption process can be calculated from diffusion data. The activation energy can be calculated from the equation:

$$\log D = \log D_o - E_D / RT \tag{3}$$

where *D* is the diffusion coefficient; D_0 , the constant; and E_D , activation energy. Plot of log *D* against 1/T gives the value of activation energy from the slope.

Diffusion coefficient

Diffusion coefficient explains the rate at which a diffusion process takes place. It is the rate of transfer of the diffusing substance across unit area of section divided by the space gradient of concentration. Diffusion coefficient characterizes the ability of water molecules to diffuse into the fiber.

The diffusion coefficient can be calculated by the equation

$$D = \pi \left(\frac{h\theta}{4Q_{\alpha}}\right)^2 \tag{4}$$

where *h* is the thick initial thickness or initial average diameter of the sample θ is the slope of the initial linear portion of the sorption curve. The slope is calculated from the graph Q_t versus root time.

Sorption coefficient

The sorption coefficient (S) is calculated by the equation

$$S = \frac{M_{\alpha}}{M_o} \tag{5}$$

where M_{α} is mass of the water taken up at equilibrium; M_0 , initial mass of the sample. It gives a measure of the extent of sorption

Permeability coefficient

Permeability coefficient gives an idea about the amount of water permeating through uniform area of the sample per second. The permeability coefficient is given by equation

$$P = DS \tag{6}$$

The calculated diffusion coefficient and permeability coefficient are in agreement with the results obtained by analyzing the graph. In case of sisal fabric reinforced NR composite diffusion of water decreases with increase in temperature and the same pattern is obtained on calculating diffusion coefficient and permeability coefficient (Table III) Thermodynamic functions ΔS , ΔH , and ΔG were calculated by linear-regression analysis using the Van't Hoff equation

$$\ln K_s = \Delta S / R - \Delta H / RT \tag{7}$$

$$\Delta G = \Delta H - T \Delta S \tag{8}$$

where K_s is the number of moles of solvent sorbed at equilibrium/mass of the fiber; ΔS the entropy of sorption; ΔH the enthalpy of sorption; ΔG is the free energy change.

The thermodynamic parameters are presented in Table IV. The enthalpy and entropy of sorption are positive indicating that the process is endothermic. It

TABLE IV Kinetic Parameters of Composites

Samples	ΔH (kJ/mol)	ΔS (J/mol/K)	ΔG (kJ/mol)
T TB	45.88663 40 72754	114.9826 95 77728	-34.7938 -28.9798
TBA	35.21727	84.13768	-25.4585
TBAS TBMS	37.18279 33.22025	86.21618 74.39367	-26.0863 -22.5081
TT	36.67222	83.47256	-25.2555

can also be seen that for the composites containing chemically treated fabric, ΔS and ΔH values are lower. The free energy values are found to be negative for all the systems indicating that the diffusion process is a spontaneous reaction due to the presence of hydrophilic sisal fabric.

CONCLUSIONS

An investigation into the water sorption characteristics of woven sisal reinforced natural rubber composites was attempted. Textile composites were prepared by sandwiching a layer of sisal fabric between two layers of rubber sheets. It was found that water uptake was mainly dependent on the properties of the woven fabric. The mechanism of diffusion was found to be fickian for the composites. Among the chemically treated composites mercerized samples exhibited the maximum sorption while the composite containing bonding agent alone showed minimum water uptake. This was attributed to the fact that the treatment with NaOH promotes the activation of hydroxyl groups of the cellulose units. As a result of this treatment, the hydrogen bonding among the layers of cellulose are partially cleaved and the chains undergo modification of their conformation. These activated hydroxyl groups can effectively form hydrogen bond with water which can increase the water uptake of mercerized composites. Minimum water uptake in composites containing bonding agent alone is due to the high adhesion power given by the presence of bonding agents to the rubber matrix compared to all other samples. The rate of diffusion was seen to increase with temperature for all composites. Thermodynamic parameters were evaluated; it was found that free energy of the textile composites were found to be negative indicating that sorption is a spontaneous process.

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