COMPARISON OF INTERACTION OF AROMATIC SOLVENTS IN HYBRID AND TEXTILE BIOCOMPOSITES

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Abstract

Natural rubber was reinforced with sisal – oil palm hybrid fibers. Composites were prepared by varying the weight content of the fibers and chemical modification of the bio- fibers. The interaction of three different types of aromatic solvents, namely, benzene, toluene and xylene with the rubber composites was analyzed. Textile composites were also prepared by sandwiching a single sheet of sisal fabric between two pre-weighed rubber sheets. The diffusion behaviour of the textile composites in benzene, toluene and xylene was also analyzed. The mechanics of diffusion was found to be different for hybrid and textile biocomposites. The swelling index factor was also calculated for all the composites. Swelling was found to be predominantly dependent on the aromatic solvent used and chemical treatments. Chemically modified composites were found to be less prone to solvent permeation.

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1. INTRODUCTION

Bio-fiber reinforced composites are finding tremendous applications in various fields ranging from the automotive industry to the construction industry. The most attractive aspect about natural fiber reinforced composites is their positive environmental impact. Also the fact that they are low cost, light weighted, have enhanced mechanical properties and are free from health hazard makes it all the more interesting.

The latest research and development results dealing with natural fiber reinforced plastics have shown the possibilities of partial replacement of inorganic fibers in interior components of cars and trucks such as door linings, parcel racks and column trim[1]. Plastic/wood fiber composites are being used in a large number of applications in decks, docks, window frames and molded panel components[2]. It has been reported that 460 million pounds of plastic/wood fiber composites were produced in 1999[3]. Recent statistics show that the production of these composites in 2001 has increased to 700 million pounds[4]. Another innovative approach is the use of natural fibers in concrete, which provides a daunting challenge to the house construction industry especially in non-industrialized countries[5]. As these fibers are cheap and readily available the energy required for the processing of these composites is low; also the incorporation of random vegetable fibers in cement matrices requires only a small number of trained personnel in the construction industry.

The use of vegetable fiber reinforced foamed materials have attracted attention because of the possibility of reducing automobile construction due to the hollow cellular structure of fibers. Natural fiber reinforced polyurethane foams have been found to have low densities while in the case of natural fiber reinforced epoxy foams; they combine excellent tensile properties with low specific mass[6]. Another recent application is the production of needle-punched non-wovens of pure natural fibers or needle-punched hybrid non-wovens of natural fibers and polypropylene fibers, which are, used as semi-fabricated forms for technical components[7].

Diffusion in organic solvents is an important study in elastomeric compounds because it can be used as a measure of their long term behaviour in a liquid environment. It can also be an indirect estimation of the interfacial adhesion in rubber composites. The factors that affect swelling are type of solvent used, temperature, structure of rubber compound and presence of fillers or fibers. The presence of fibers is of utmost importance as it influences the sorption behaviour in rubber composites. The reinforcement of natural fiber in rubber composites and their applications has been well documented[8].

In the case of systems containing hybrid lignocellulosic fibers the intrinsic characteristics of both the fibers come into play. Generally it has been seen that the presence of fibres restrict the entry of organic solvents. But anomalous results were found in the transport of organic solvent through coir fiber reinforced natural rubber composites[9] . The authors found that the presence of coir fibers did not completely restrict the passage of solvent. At high levels of fiber loading it was found that sorption decreased. Also composites containing chemically treated fibers were found to be less prone to solvent sorption.

In another interesting study the interfacial adhesion in sisal fiber reinforced SBR composites was analysed by Kumar and Thomas[10]. They observed a marked reduction in swelling behaviour upon the incorporation of fiber and chemical modification. This was attributed to increased hinderance and good fiber-rubber interactions due to the presence of bonding agents.

In a study involving hybrid fiber composites, the interfacial adhesion of short sisal/coir hybrid fibre reinforced natural rubber composites was investigated by restricted equilibrium swelling technique by Haseena et al[11]. The authors found that as fibre content and penetrant size increased, the solvent uptake was found to decrease due to the increased hindrance and good fibre–rubber interaction. The bonding agent added mixes showed enhanced restriction to swelling and it was seen that the ratio of change in volume fraction of rubber before and after swelling to the volume fraction of rubber before swelling (V_o - V_r/V_0) was lower for bonding agent added composites, when compared to an unbonded one.

It is obvious from the literature that the solvent sorption of hybrid bio-fiber reinforced natural rubber biocomposites has not been extensively studied. Also the sorption characteristics of woven biocomposites need to be addressed. This manuscript investigates the sorption uptake of organic solvents in hybrid and woven biocomposites.

EXPERIMENTAL

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

Fiber Preparation

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. The fibers were then chopped to different lengths. Sisal and oil palm fibers of lengths 10 mm and 6 mm were treated for 1 hr. with sodium hydroxide solutions of varying concentrations viz., 0.5, 1, 2 and 4 %. Finally the fibers were repeatedly washed with water and air-dried.

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

Preparation Of Composite

Formulation of mixes is shown in Table IV a & b. 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 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.

The sisal fabric – natural rubber textile composites were prepared by sandwiching a single layer of sisal fabric between two layers of pre-weighed rubber sheets which was then compression moulded at 150° C under a pressure of 120 for 8 minutes [See Figure 1]. The formulation of different composites is given in Table V.

5. MEASUREMENT OF PROPERTIES

Solvent sorption is evaluated in terms of weight increase for composite specimen immersed in solvents benzene, toluene and xylene at room temperature. Circular specimens of thickness 2 mm 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 the solvents. The specimens were periodically removed from water bath and the surface solvent was wiped off. The weight gain of the specimen has been measured as a function of time until equilibrium or saturated state of solvent uptake has been reached. The molar percentage uptake Q_t for the composite samples was determined using the following equation:

$$Q_t = \frac{(W_2 - W_1)/M_s}{W_1} x100 \qquad [1]$$

where W_2 is the weight of the sample after swelling , W_1 is the weight of the sample before swelling and M_s is the molecular mass of the solvent. The sorption data were evaluated by plotting the mole percentage uptake of the composite versus square root of time for different solvents.

6. RESULTS AND DISCUSSION

6.1. Hybrid Biocomposites

6.1.1 Effect of fiber loading on solvent uptake

The variation of toluene sorption with time as a function of fiber loading is shown in Figure 2. Here it can be seen that maximum solvent sorption is exhibited by the gum compound. Upon biofiber incorporation, solvent uptake decreases and minimum uptake is shown by 50 phr composite. This is due to the fact that the uptake of organic solvents is predominantly dependent on voids that are present in natural rubber. The presence of fibres in rubber matrix will thus restrict the entry of solvent. Biofibres are composed of hydrophilic cellulosic units and therefore do not show affinity to organic solvents. Hence solvent uptake decreases upon biofibre incorporation.

The variation of solvent uptake in different organic solvents (benzene, toluene and xylene) as a function of fibre loading is presented in Figure 3. Here it can be seen that solvent uptake is dependent on the size of solvent molecules. Uptake is maximum when the solvent used is benzene and minimum uptake occurs when xylene is used as the solvent. We can also co-relate the diffusion process with speed of the diffusing solvent molecules. Diffusion is related to the velocity of the diffusing molecules by the equation given below:

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

where $\bar{c}$ = mean velocity of molecules

λ = mean free path (distance traveled by molecules between two consecutive collisions)

Since the velocity decreases with size of penetrating molecules, diffusion also decreases upon using high molecular weight solvents.

6.1.2 Effect of chemical modification on solvent uptake

Mercerization is an economical and effective method used for improving the interfacial incompatibility between the matrix and the fiber .It improves the fiber surface adhesive characteristics by removing natural waxy materials, hemicellulose and artificial impurities by producing a surface topography[12]. In addition to this, alkali treatment can lead to fibrillation ie 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. As the strength of NaOH increases, the amount of surface area created increases,
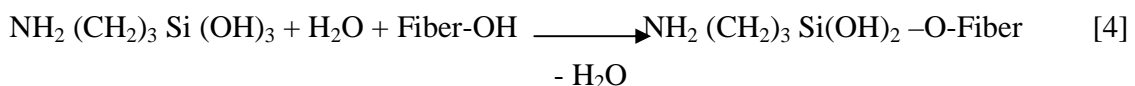
providing better mechanical interlocking between the fiber and matrix. Besides the removal of hemicellulose and waxes, the treatment with NaOH solution promotes the activation of hydroxyl groups of cellulose unit by breaking the hydrogen bond. The authors in a previous study observed that mercerization of sisal and oil palm fibers in natural rubber composites resulted in enhanced tensile properties[13].

Figure 4 presents the variation of toluene sorption with time as a function of chemical modification. From the graph it can be seen that compared to untreated, the composites containing treated fibres show lower solvent uptake. Among the composites containing treated fibres, minimum solvent uptake is shown by composites containing 4 % NaOH treated fibres. This clearly indicates that stronger interfacial adhesion is present in alkali treated composites. Due to the presence of a strong interface, there are fewer gaps in the interfacial region which makes it difficult for solvent to enter the interfacial region. Another factor is that stronger adhesion results in tighter packing within the rubber- fiber network due to which, the distance traveled by the diffusing solvent molecules between two consecutive collisions decrease (mean free path) and consequently results in lowering of solvent uptake (See equation 2).

It can also be seen that among the composites containing silane treated fibres, minimum solvent uptake is exhibited by fluorosilane treated composites (P) and maximum by vinylsilane treated composites (Q). The reaction mechanism can be explained as follows. First silane reacts with water to form silanol and an alcohol.

$$NH_2(CH_2)_3Si(OC_2H_5)_3 + 3H_2O \longrightarrow NH_4 (CH_2) Si (OH)_3 + 3C_2 H_5\text{-}OH \qquad [3]$$

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.

$$NH_2 (CH_2)_3 Si (OH)_3 + H_2O + Fiber\text{-}OH \underset{- H_2O}{\longrightarrow} NH_2 (CH_2)_3 Si(OH)_2 \text{–}O\text{-}Fiber \qquad [4]$$

Similar reactions takes place for fluro 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 fluro silane group, while no such possibility exists in vinyl group. The schematic sketch of the interaction between rubber, amino and fluoro silane coupling agent and fiber is shown in Figure 5.

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 the high electronegative character of fluorine atom . Thus in fluro-silane treated composites fiber / matrix adhesion will be very stronger compared to amino-silane treated and vinyl-silane treated composites. Due to the stronger fiber / matrix adhesion, the uptake of solvent will be less in flurosilane treated composite as seen in the figure. Thus fluro-silane treated fiber containing composites show lowest solvent uptake compared to other silane treated samples. The sample Q i.e. composite containing vinyl silane treated fiber exhibits the largest uptake of solvent. As the fiber-matrix adhesion is very weak in vinyl silane treated composite, maximum uptake of solvent takes place. Composites containing amino-silane treated fibers show medium water uptake. In these composites the adhesion to the matrix is not as strong as in fluro silane, but stronger than vinyl silane treated composite.

The improved interfacial adhesion in chemically modified composites can be further understood by looking into fracture topography of the system. Figure 6 depicts the scanning electron micrographs (SEM) of tensile fracture surfaces of untreated, alkali treated (4 %) and silane treated composites. Figure 6 (a) shows the tensile failure surface of composite containing untreated composite. The presence of cavities is clearly visible in both the figures. 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 cavities. The SEM of composite containing fibers treated with 4 % NaOH is presented in Figure 6 (b). This figure shows short broken fibers projecting out of the rubber matrix. This indicates that the extent of adhesion between the fibers and rubber matrix is greatly improved and when stress is applied the fibers break and do not wholly come out of the matrix. Figure 6 (c) presents the tensile fracture of

composite containing fluorosilane treated fiber. Here we can see the presence of rubber particles adhering to the fiber surface and no considerable cavities indicating good interfacial adhesion.

The variation of solvent uptake in different organic solvents (benzene, toluene and xylene) as a function of chemical modification is presented in Figures 7. As expected uptake is found to be maximum when the solvent used is benzene and minimum uptake occurs when xylene is used as the solvent. The reason is the same as explained in Section 6.1.

6.2. Textile biocomposites

Figure 8 presents the variation of toluene uptake of untreated and treated composites. Contrary to expectations, it can be seen that composites containing chemically modified fabric show higher solvent uptake than untreated, indicating that poor interfacial adhesion is present in the composites. The minimum solvent uptake is exhibited by composite containing thermally treated sisal fabric. This suggests the better interfacial bonding in the composite due to removal of water and increased crystallinity of fabric.

The variation of solvent uptake in different organic solvents (benzene, toluene and xylene) is depicted in Figure 9. Here also we can see that uptake is maximum when the solvent used is benzene and minimum uptake occurs when xylene is used as the solvent.

6.3 Swelling index values

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

$$\text{Swelling index \%} \quad = \quad \frac{A_s}{w} x 100 \tag{5}$$

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 composites at different fiber

loadings and that of composites containing chemically treated fibres in different organic solvents.

It can be seen that for all the solvents, the gum compound shows the maximum value for swelling index indicating maximum swelling and minimum crosslinks. As fibre is added to the matrix, swelling decreases since the fibres restrict the entry of the solvent. Among the alkali treated fibres, I shows 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 fibre 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 fibres provide better adhesion than other silanes.

The swelling index values of the various textile composites in different organic solvents are given in Table VII. It can be seen that for all the solvents, swelling index value is maximum for composites containing alkali treated sisal fabric. This indicates that swelling is maximum in composite TBA suggesting the level of adhesion and extent of crosslinks between sisal fabric and rubber matrix is less. One can also see swelling index value is minimum for composite containing heat treated sisal fabric indicating that swelling is minimum in this composite. This is attributed to the fact there is a great deal of bonding between the matrix and fabric due to the presence of larger number of crosslinks. This show that thermally treated composites provide better adhesion and a stronger interface than other chemical modifications.

It is interesting to note that in textile biocomposites chemical modification of sisal fabric has resulted in higher swelling index value which is the reverse to what we observed in hybrid biocomposites. We must keep in mind that the mechanics of diffusion in textile composites is different from short fiber composites. The major contribution to interfacial strength in textile composites is the alignment of yarns in warp and weft direction. Chemical treatment results in the partial unwinding of yarns (as hemicellulose dissolves off) and hence the alignment gets antagonized. This results in lowering of strength of

composites. Another reason is that as sisal fabric is composed of thick strands and knots, the alkali and silane coupling agents did not penetrate into the fabric and therefore the interfacial properties between the sisal fabric and rubber matrix has not been improved enough. It can be seen that the highest swelling index is exhibited by alkali treated composite while the lowest values are exhibited by thermally treated composites. This could be attributed to the fact that upon heat treatment the crystallinity of cellulose increases due to the rearrangement of molecular structure at elevated temperatures.[14] The thermal treatment also results in moisture loss of the fabric thereby enhancing the extent of interfacial bonding between fabric and rubber making it difficult for solvent to penetrate the rubber-fabric interface.

CONCLUSIONS

The diffusion of organic solvents in hybrid biocomposites and textile composites was investigated. Hybrid biocomposites were fabricated by reinforcing natural rubber with sisal and oil palm fibres. Textile biocomposites were fabricated by incorporating woven sisal fabric in natural rubber. The mechanics of diffusion were found to be different for hybrid and textile biocomposites. In hybrid biocmposites, solvent uptake was found to be predominantly dependent on natural rubber and fibre incorporation resulting in lower solvent uptake. Composites containing chemically modified biofibres exhibited lower solvent uptake due to increased interfacial adhesion. Among the different organic solvents used, diffusion was found to be minimum for xylene and maximum for benzene. In the case of textile biocomposites, chemically modified composites exhibited higher solvent uptake. Uptake was found to be maximum for textile composite containing sisal fabric treated with 4 % NaOH. This was attributed to the weak interfacial adhesion due to partial disruption of the alignment of yarns in the fabric.

Table I

PROPERTIES OF SISAL FIBRE

Chemical constituents (%)

Cellulose	78
Hemicellulose	10
Lignin	8
Wax	2
Ash	1

Physical properties of sisal fibre

Diameter (mm)	0.1212
Tensile strength (MPa)	530-630
Young's modulus (GPa)	17-22
Microfibrillar angle	20-25
Elongation at break (%)	3-7

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

Cellulose	65
Hemicellulose	-
Lignin	19
Ash content	2

Physical properties of oil palm fibre

Diameter μm	150-500
Tensile strength (MPa)	248
Young's modulus (MPa)	6700
Elongation at break %	14
Microfibrillar angle (°)	46

Table III

Properties of sisal fabric

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

Table IV a (Hybrid biocomposites)

Formulation of mixes A to E (Fiber Loading)

	Mixes [phr]					
Ingredients	Gum	B	C	A	D	E
NR	100	100	100	100	100	100
ZnO	5	5	5	5	5	5
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5
TDQ[a]	1	1	1	1	1	1
CBS[b]	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
Sisal fiber Fiber length, (10mm)	-	5	10	15	20	25
Oil palm fiber Fiber length (6 mm)	-	5	10	15	20	25

a- 2,2,4 trimethyl-1,2-dihydro quinoline
b- N-cyclohexylbenzothiazyl sulphenamide

Table IV b (Hybrid biocomposites)

Formulation of mixes (I to R)

Ingredients	I	J	K	L	P	Q	R
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	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
CBS	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 fiber	21	21	21	21	21	21	21
Treatment Fiber length, (10 mm)	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	9	9	9	9	9	9	9
Treatment Fiber length (6 mm)	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 V (Textile biocomposites)

Ingredients	Gum	T	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[a]	-	-	4.8	4.8	4.8	4.8	4.8
TDQ	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	-	✓	✓	✓	✓	✓	✓
Treatment	-	-	-	4% NaOH 1 hr	SilaneA 1100	Silane A174	Heat

c- 2,2,4 trimethyl-1,2-dihydro quinoline
d- N-cyclohexylbenzothiazyl sulphenamide

Table VI

Samples	Swelling index		
	Benzene	Toulene	Xylene
Gum	618.97	540.6	258.9
B	506.4	474.8	198.7
C	500	470.6	192
A	516.8	469.4	189
D	480	422.9	185
E	390.7	349.6	182.69
I	290.9	220.8	135
J	268.7	206.4	131.5
K	250.1	201.3	129.6
L	181.2	166	123
P	310.3	280.7	210.5
Q	376	333.9	240
R	339.5	310	228

Table VII

Samples	Swelling index		
	Benzene	Toulene	Xylene
T	425.6	386	295
TB	498	382.3	265
TBA	587.2	538.2	362
TBAS	383.6	348.7	296.3
TBMS	561	519.1	321
TT	332.9	306.9	256

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