



## Mechanical and Transport Properties of Natural Rubber Reinforced with Piassava (*Raphia Hookeri*) Fibre Composites

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### Keywords

- ✓ Natural rubber,
- ✓ Piassava Fibre,
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### Abstract

We report the preparation and studies on the mechanical and transport properties of natural rubber reinforced piassava fibre composites. The influence of piassava fibre and its modification on properties such as tensile and tear strength, tensile modulus, elongation at break, hardness, and bound rubber content on composites evaluated. Increasing the fibre content to 30 phr, for instance, resulted in a decrease of about 6.47 %, 7.23 %, and 15.67 %, 16.86 %, of tensile and tear strengths for both modified and unmodified samples respectively. However, modulus at 100% strain and hardness had a direct relationship with the fibre content. SEM analysis revealed that fibre particles at low content showed good dispersion in the natural rubber matrix. Uptake of organic solvents by the composites and transport coefficients were investigated. They were found to decrease with increase in filler content, modification, and solvent size but with an increase in temperature. The mechanism of transport and activation energy were also determined, and the former was found to be close to Fickian.

## 1. Introduction

The introduction of fillers into polymer matrix help to improve some fundamental properties and as well makes the materials less expensive. In rubber products fabrication, for instance, fillers are vital components be it synthetic or natural. These fillers could be reinforcing or non-reinforcing in nature. Reinforcing fillers offer an improvement on the mechanical properties of the rubber products whereas non-reinforcing fillers provide little or no effect on the material properties.

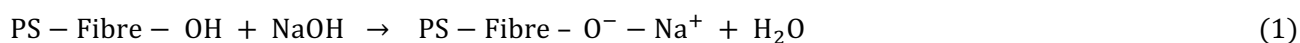
Natural Rubber (NR) occurs naturally in the form of isoprene (2-methyl-1,3-butadiene). Milky natural rubber latex is extracted from the *Hevea brasiliensis* tree and is widely used to prepare many rubber products. The presence of NR in rubber products gives the material beneficial technical characteristics such as considerable tensile strength, excellent resilience, high flexibility and resistance to impact and wear [1, 2]. However, less resistant to oxidation, ozone, weathering, solvents and a wide range of chemicals due to its unsaturated chain structure and polarity are some of its disadvantages [3]. These limitations hinder the use of natural rubber, mainly for technical and engineering applications. However, these shortcomings could be overcome via chemical manipulation of the polymer chain or blending with other polymers and materials.

Piassava fibres are a class of natural leaf fibres of *Raphia Palms* and are available in plenty in the Amazons; said to belong to the Brazilian palm family. There exist various species of the *Raphia* fibres (*funifera*, *vinifera*, *taedigera*, *textilis*, *hookeripiassavas*) due to their origins. West African Piassava fibre obtained from *Raphia Palm* trees that grow majorly in the swamp and riverine areas of Nigeria and other parts of West Africa. In Nigeria, *Raphia Palm (Raphia Hookeri)* is one of the native genera of the palms, which include *Eremospatha*,

*Borassus, Elaeis, Hyphaene, Phoenix, Ancistrophyllum, Calamus, Raphia, Oncocalamus, Sclerosperma* [4]. *Raphia Palm* is hapaxanthic. It implies that, after a period of vegetative growth, it produces flowers and fruits only once and dies [4]. The fibre obtained from the leaf-bases (stalks) of *Raphia Palm*, is cheap and used locally for the weaving of fish traps, hats, and baskets. Other useful applications include making of brooms, brushes, cables, ropes for climbing and for tying of animals like goats, sheep, and fowls as well as canoes to post [4] and thread for tying yam tubers in the barn.

The use of natural polymers as fillers in polymer matrices has continued to dominate the field of polymer composites in recent years. Precisely, the use of fibres from agricultural products and their wastes in the reinforcement of natural rubber has received the attention of researchers. Such fibres investigated include Sisal [5], Oil Palm fibre [6], Pineapple leaf [7], Coir fibre [8, 9], Jute [10], Groundnut shell [11], Cocoa pod and Rubber seed shell [12]. These agricultural fibres investigated exhibited different performance characteristics on natural rubber composites. The availability of these natural fibres in every part of the world has endeared researchers, scientists, and industrialists the opportunities to use their natural resources in composite fabrications. Despite the unique characteristics, very few works have been reported in the literature on piassava as a reinforcing fibre for composites [13-16]. Some of these works show that the interfacial shear strength of the composites was found to be comparable to that of glass fibre/thermoset composites [17, 18].

The desire to use piassava fibre as a filler is motivated mainly due to environmental reasons. No doubt, using piassava fibre as a replacement filler for commercial fillers in NR is of immense importance. On the other hand, poor wettability, incompatibility when combined with some polymeric matrices, and moisture absorption are some challenges that limit its use in polymer composites [19]. Modification of fillers is applied to improve the effectiveness of filler-matrix adhesion. Such change exposes more reactive sites on the filler surface, thus promoting efficient and effective interaction with the polymer matrix. The treatment achieved via isocyanate treatment [20], silane coupling agents [21], alkali treatment [22], acetylation treatment [23], maleic anhydride coupling agents [24], and graft method [25], and so on, to better the fibre/matrix adhesion. Alkalization of natural fillers is a way to obtain the improved structure-property relationship of composites [26-28]. The incorporation of aqueous sodium hydroxide into natural fibre facilitates the ionisation of the hydroxyl group to alkoxide [29-31]. The following is the schematic representation of piassava fibre as a result of alkali treatment.



Natural rubber-based products have found their applications in electrical insulation, telecommunication cable manufacturing, component encapsulation and waterproofing, corrosion protection and packaging of materials. Such exposition makes them have contact with varieties of chemicals and solvents which adversely affect their shelf life. The transport behaviour of fluids through rubber blends is significant regarding barrier applications. Some researchers have reported the use of equilibrium swelling technique for finding out the interaction of different fillers with natural rubber and blends. For example, the interaction of peanut shell powder with natural rubber, and their blends by an equilibrium swelling method has been studied by Sareena et al. [11]. Joseph et al. [32] investigated the role of fibre content, and interfacial adhesion on the transport of aromatic solvents through the oil palm microfibre filled natural rubber. Similarly, the diffusion and transport of organic solvents through lignin-filled natural rubber composites in the temperature range 25–45°C, have been reported [33]. So far there is no report to our knowledge of the literature on the fabrication of natural rubber/piassava fibre composites. Thus, this present work seeks to investigate the mechanical properties and transport behaviour of aromatic solvents (benzene, toluene, and xylene) through piassava fibre filled natural rubber at different temperatures.

## 2. Materials and Method

### 2.1 Materials

A local farmer in Ehime Mbanjo, Imo State kindly provided the Piassava (*Raphia Hookeri*) fibre (PSF) and validated at the Department of Forestry and Wildlife Technology, Federal University of Technology, Owerri, Nigeria. Sodium hydroxide (Sigma-Aldrich, Czech Republic) and Acetic acid (BDH Analar, England) were used as received. Natural rubber (NSR 10) and other compounding ingredients such as zinc oxide, stearic acid,

sulphur, processing oil (dioctyl phthalates, DOP), N-cyclohexyl-2-benzothiazole sulphenamide (CBS) and 2, 2, 4-trimethyl-1, 2-dihydroquinoline (TDQ), were purchased from a local vendor in Zaria, Kaduna State. The solvents, benzene, toluene, and xylene were of analytical grade and used without further purification and their properties presented in Table 1.

**Table 1:** Properties of solvents used

Solvent	Density, (gcm <sup>-3</sup> )	Molecular Weight, (gmol <sup>-1</sup> )	Solubility Parameter, (Mpa) <sup>1/2</sup>
Benzene	0.876	78.12	18.7
Toluene	0.867	92.14	18.3
Xylene	0.865	106.17	18.2

## 2. 2 Purification and Modification of Piassava fibre

The previously extracted piassava fibre was washed with hot water detergent, rinsed four times with tap water and finally once with deionised water, then dried in a vacuum oven at 65 °C for 24 h. Afterward, a portion of the piassava fibres was treated with alkali (NaOH) solution to obtain modified piassava fibre (MPSF). Briefly, one gramme of piassava fibres were put in 10 mL (5 % NaOH) solution for 5 h with continuous stirring using a mechanical stirrer and kept for 24 h. The fibres were then treated with dilute acetic acid to remove any trace of sodium hydroxide remaining and finally washed again with deionised water and dried in vacuum oven at 65° C for 24 h for further use. Both the untreated and treated dried fibres were pulverised and sieved to obtain 150µm particle size.

## 2. 3 Sample Preparation

Before compounding, we accurately weighed all the materials and ground where necessary. The compounding ingredients used were of the same quantity, save for the amounts of piassava fibre which varied from 10 to 30 phr (parts per hundred of rubber) and presented in Table 2. Mixing was done using a two-roll mill at 27°C in line with ASTM D15-627. Mixing time was kept to a minimum to avoid sticking of the rubber mixes to the mill rolls. The two-roll temperature was not held too high to prevent premature curing during mixing. Cooling has achieved this. The nip gap rolls speed ratio, time of mixing (12 min) and the order of addition of the ingredients kept the same for all the blends. The rubber mixes were then cured in a hydraulic press to the optimum cure time at the same temperature with a pressure of 6.7 MPa and compressed at 150°C. The vulcanizates obtained for both unmodified and modified (alkali-treated) fibres respectively and conditioned for 24 h before further use.

**Table 2:** Mixing Formulation for NR/PSF composites

Compounding Ingredients	Contents (parts per hundred of rubber, phr)
NR	100
ZnO	5
Stearic Acid	2
CBS	0.5
TDQ	1
DOP	10% based on filler content
Piassava Fibre	Variable (10, 20, 30)
Sulphur	2.5

## 2. 4 Bound rubber content estimation

The bound rubber content obtained by extracting the unbound from the rubber composites such as ingredients and free rubbers. The technique reported by [34] was used to evaluate the amount of bound rubber. The following equation gives the amount of bound rubber in weight % of initial rubber content of the compound;

$$\text{BRC (\%)} = \frac{M_{rc} - M_{erc}}{M_{rc}} \times 100 \quad (2)$$

where  $M_{rc}$  is the rubber content in the sample and  $M_{erc}$  is the extracted rubber content using toluene for 72 h at room temperature with solvent renewal after 24 h.

## 2. 5 Mechanical Properties

The tensile testing of the various NR/PSF vulcanizates performed using a Universal Testing Machine INSTRON-3365 (Series IX, model-441, USA) in line with ASTM D 412-1998, at a crosshead speed of 500 mm/min. Cut out dumbbell-shaped test samples were stretched at room temperature ( $25 \pm 2$  °C). Tear strength also determined in line with ASTM D 624. The average value of each composite also obtained from three specimens. Hardness (Shore A) of the samples was also measured by ASTM D 2240.

## 2. 6 Scanning Electron Microscope Analysis

A TESCAN-VEGA 3 (Czech Republic) scanning electron microscope was used to analyse the morphology of modified and unmodified NR/PSF samples. Before analysis, each sample was gold coated.

## 2. 7 Sorption Experiments

The sorption behaviour of the modified and unmodified natural rubber/piassava fibre vulcanizates as prepared was studied at three different temperatures viz. 30, 50, and 70°C. Square shaped specimen of dimensions, (25 x 25) mm<sup>2</sup> were cut out from each vulcanizate and dried in vacuum desiccators over anhydrous CaCl<sub>2</sub> at room temperature for about 24 h. The original weight and an average thickness of each specimen measured before the sorption experiment. The sample specimen was immersed in 20 mL of solvents in closed diffusion bottles and kept in a thermostatically controlled water bath. The change in weights of the swollen sample was measured at specified time intervals until equilibrium swelling reached. During the weighing of the samples, efforts were made to minimise the error due to the evaporation of the solvent.

# 3. Results and Discussion

## 3. 1 Bound rubber content analysis

Bound rubber measurements provide vital information about the filler network density. It defines the resistance of the uncured rubber portion to be extracted by a suitable solvent due to adsorption of rubber molecules to the filler surface. For any given rubber blends, the amount of bound rubber at a fixed filler content depends on some factors, like the size, structure and surface activity of the filler, the dispersion state [35]. We investigated the variation of bound rubber content with filler content in toluene. Table 3 presents the change in the bound rubber content with the filler content for NR/PSF vulcanizates. The increase in filler content from 10 to 30 phr gave rise to the bound rubber increase from 25.87 to 36.79 % and 53.79 to 76.86 % for modified and unmodified composites under study respectively. NR/MPSF composites showed higher bound rubber content when compared with NR/PSF composites. This behaviour could be possible due to nature (high surface area and topography) and structure of the modified filler which allowed for a satisfactory mix between the filler and the NR matrix. The bound rubber study also underscores the interaction effect of MPSF with the rubber matrix.

**Table 3:** The variation of bound rubber content for NR/PSF and NR/MPSF composites

Sample	NR	NR/MPSF			NR/PSF		
Filler, phr	0	10	20	30	10	20	30
Bound rubber (%)	19.77	25.87	38.16	53.79	36.75	52.78	76.86

## 3. 2 Mechanical properties

Table 4 presents the mechanical properties results of NR/PSF composites. From the table, the mechanical property parameters of the composite samples as realised from the experimental work were found to be reasonably affected by increasing filler content on neat NR sample. The inclusion of piassava fibre into NR matrix led to the growth in the tensile strength up to an optimum of 10 phr of piassava fibre content. The wetting and interaction between the rubber matrix and filler have hindered efficiently polymer chains segmental motion [36, 37] leading to strong adhesion of the filler to the matrix. However, a shift in PSF content beyond this point resulted in the reduction in the tensile strength of the composites. Thus, filler particles agglomeration which promotes weak interfacial regions may be responsible for the decrease in tensile strength. This behaviour suggests that at filler content below 10 phr, a sizeable interfacial area of contact is provided resulting in uniform

distribution and better interfacial adhesion. Modified composite samples (NR/MPSF) had higher tensile strength than the unmodified counterparts. This scenario indicates that the degree of adhesion between the fibres and the rubber matrix improved significantly after modification.

**Table 4:** Mechanical Properties of NR-PSF and NR-MPSF composites

Sample	NR	NR/PSF			NR/MPSF		
Filler, phr	0	10	20	30	10	20	30
Tensile strength (MPa)	18.5±0.6	21.6±0.5	19.7±0.3	15.6±0.4	24.4±0.2	21.9±0.3	17.3±0.5
Elongation at break (%)	680±3	452±5	380±4	300±2	594±6	435±5	365±4
Modulus at 100% (MPa)	1.4±0.3	2.5±0.2	3.2±0.5	3.9±0.4	2.7±0.6	3.6±0.3	4.1±0.6
Tear strength (N/mm)	33.2±0.4	36.5±0.7	33.8±0.3	27.6±0.8	39.4±0.5	35.1±0.3	30.8±0.7
Hardness (Shore A)	35.4±1	43.7±3	49.6±1	53.5±1	48.8±2	54.2±2	61.4±2

Table 4 also shows a continuous increase in composite stiffness on the introduction of PSF into the NR/PSF composites. This increase in tensile modulus with PSF suggests a typical behaviour of filled polymer systems [38]. For the elongation at break, a steadily decrease observed as the PSF content increased for all the samples. This action attributes to the stiffening effect of the filler caused by the segmental chain restriction thereby reducing the rate of deformation of the stiff interface between the piassava fibre and the NR matrix. The reduction in elongation at break of the composites corroborates the increase in cross-link density. The volume fraction of filler, the degree of dispersion of the filler and the interaction between the filler and the matrix have been reported to affect the elongation at break of composites [39]. As seen in Table 4, the hardness of the NR/PSF samples was found to increase with the increase in filler content. The reason is that the incorporation of filler into the rubber matrix hinders rubber chain mobility, resulting in stiffer vulcanizates. Table 4 also revealed that the tear strength followed the same trend with the fibre content in the composite, as the tensile strength. Above all, the modified samples had better properties over the unmodified samples due to improved bond adhesion between the filler and matrix as observed in the SEM images.

### 3. 3 Scanning Electron Microscopic Analysis

Figure 1 shows the SEM micrographs of NR, PSF, and different NR/PSF composites. The surface of the NR filled blend appears rougher when compared with the unfilled blend as evident in the illustration. Impurities like pectin, wax, and oil present in the fibre contribute to poor adhesion and surface interaction between filler and matrix, which are dominant in the unmodified NR/PSF composites. The images showed poor distribution and interaction at high fibre concentration indicating fibre agglomeration and suggests the low values of tensile strength and tear strength recorded. The modified samples showed better reinforcement with NR matrix as shown in the figure and are evident in the observed higher mechanical properties compared to unmodified composites.

## 3. 4 Analysis of Sorption Data

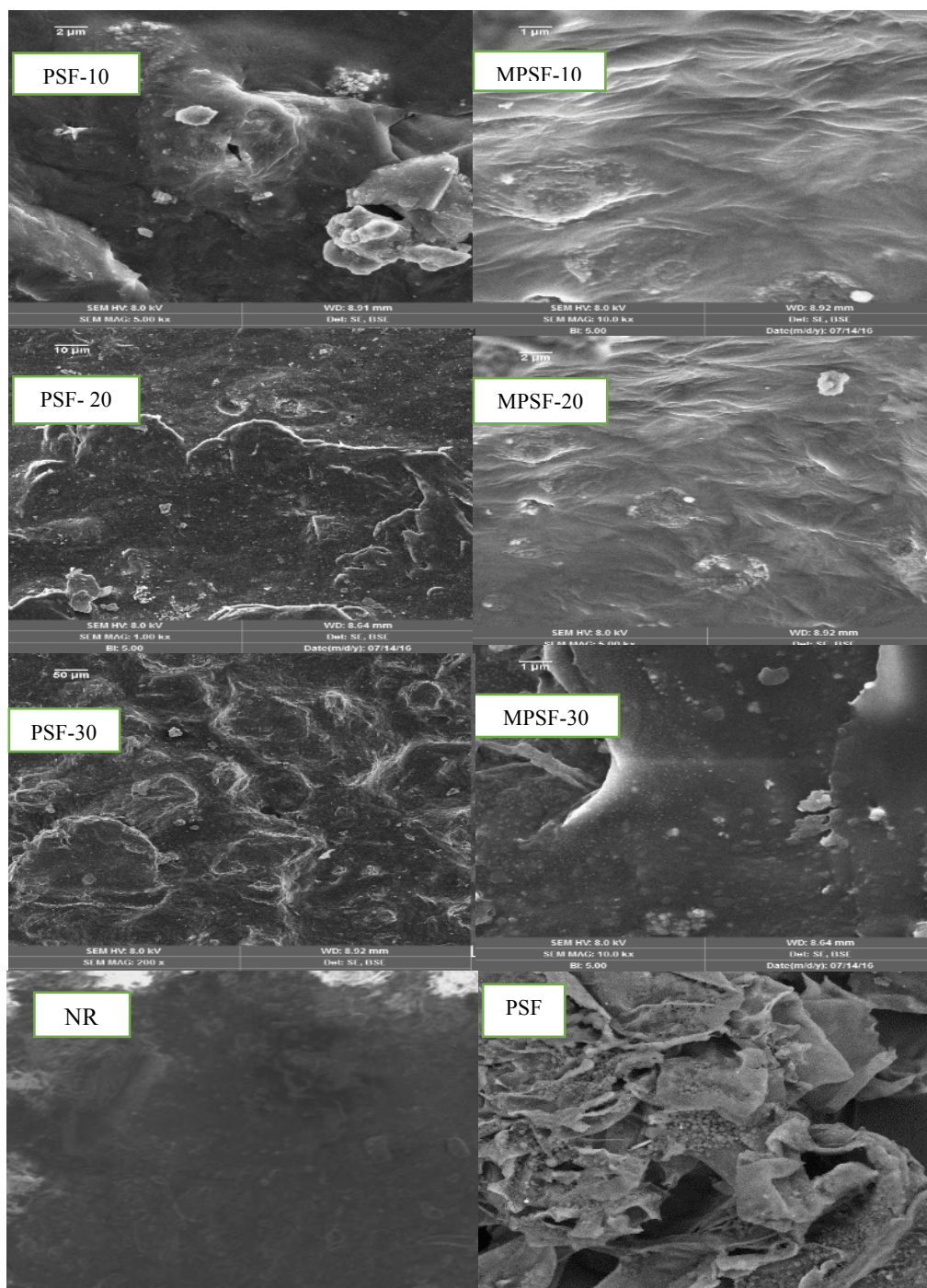
### 3. 4. 1 Determination of $M_t$ (mol % solvent uptake)

We investigated the sorption data of different solvents at the following temperatures (30, 50, and 70) °C and filler contents (10, 20, 30) phr into natural rubber (NR) filled piassava fibre (PSF) vulcanizates. The percent solvent uptake as obtained from the molar percentage absorption (%  $M_t$ ) of solvent per gramme of NR/PSF vulcanizates using the equation below [40]:

$$M_t = \frac{(W_t - W_o)/M_s}{w_o} \times 100 \quad (3)$$

Where  $W_o$  and  $W_t$  are the mass of the specimen before, and after swelling at the time,  $t$ , and  $M_s$  is the molar mass of the solvent. At equilibrium sorption,  $M_t$  equals  $M_o$ , i.e., mole absorption at infinite time. The  $M_t$  values

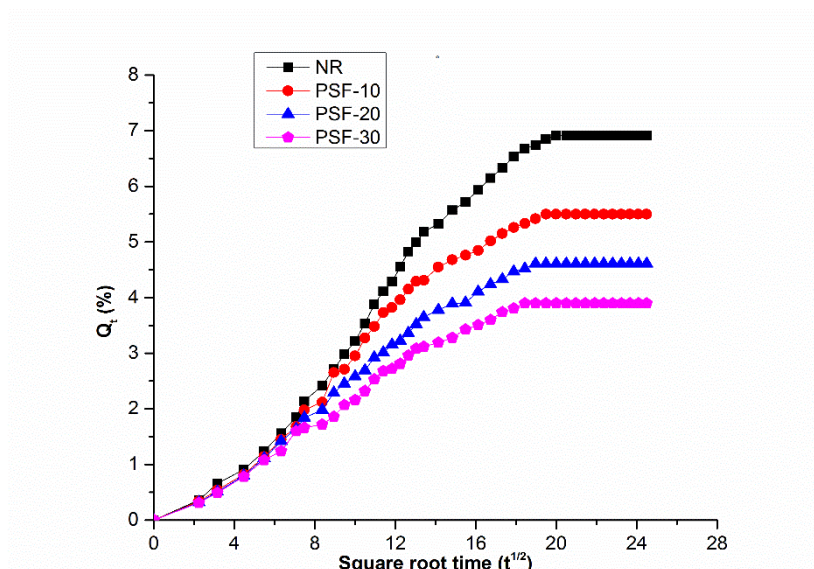
got were plotted as a function of the square root of time, to generate the sorption curves. The mole percent absorption of the three solvents taken by the NR and NR/PSF composites plotted against the square root of time ( $\sqrt{t}$ ) are illustrated in the subsequent figures on the effect of filler content, modification, solvent molecular size, and temperature. All the sorption plots irrespective of nature of the filler show a gradual increase in the mass of the solvent sorbed, and the mass of the absorbed solvent remained constant, till there was equilibrium plateau.



**Figure 1:** SEM images of NR, PSF and NR-PSF Composites

### 3. 4. 2 Effect of filler content and modification

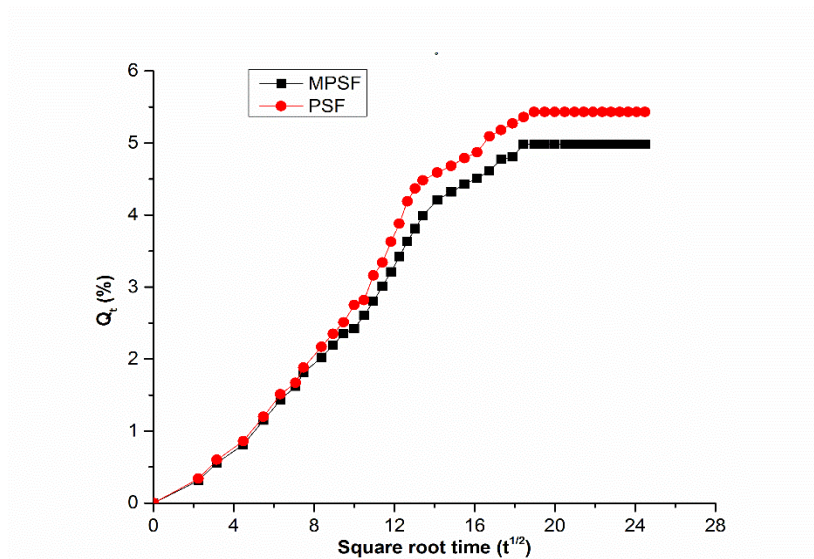
Figure 2 illustrates the effect of piassava fibre content on the absorption of benzene taken at 30°C in NR/PSF composites. The sorption behaviour for toluene and xylene showed a similar trend. The degree of dispersion, the nature of filler, free space, and interface adhesion with the polymer matrix are some of the factors that govern the solvent diffusion in filled polymer composites. The figure shows that the solvent ingress decreases as the filler content increases.



**Figure 2:** Effect of filler content on NR-PSF composites at 30°C

This action can be explained based on polymer chain mobility. Even after vulcanisation, the polymer chains get restricted by the addition of fillers thus improving the solvent resistance [41]. The decrease in solvent diffusion in the filled polymer systems is also indicative of the tortuous path created by the fillers. The extent of tortuosity has to do with the volume fraction of the filler, the shape, and orientation of the particles [42].

Figure 3 shows that the mole percent uptake of the solvents for any solvent used is lower for modified NR/PSF composites when compared to their unmodified counterparts. In this case, there are fewer voids in the interfacial region, due to the existence of a stable interface, which makes it difficult for solvent molecules to enter the interfacial area. Furthermore, stronger adhesion results in tight packing within the rubber-fibre network; hence, the distance travelled by the diffusing solvent molecules between two consecutive collisions decreases and reduces the rate of solvent uptake by the samples.

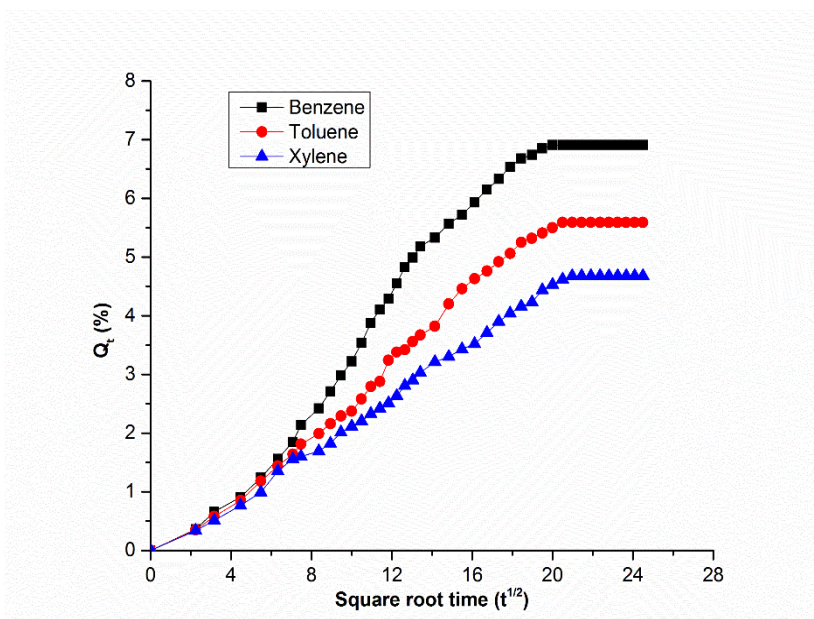


**Figure 3:** Effect of modification on 20 phr NR-PSF composites at 50°C

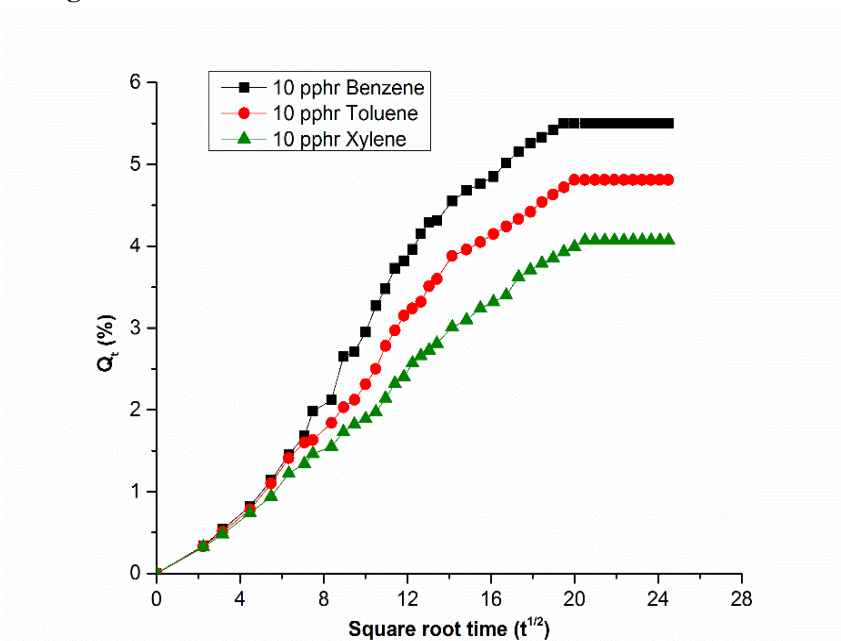
### 3. 4. 3 Effect of solvent molecular size

The mole percent uptake of NR/PSF composites indicates that there is a decrease in the value of  $M_t$  (%) with an increase in the solvent molecular size in all the systems studied (Figures 4 and 5). The decline in  $M_t$  mol% uptake with the increase in solvent molecular size has been attributed to change in activation energy required for activation of the diffusion process [43]. Increasing the solvent molecular size results in the lower kinetic energy of solvent molecules and this, in turn, decreases the solvent diffusion through the rubber matrix. All the

composites showed maximum uptake of solvent in benzene and minimum absorption in xylene but with lower absorption in modified composites. The behaviour suggests that as the solvent molecular size increases, the interaction between the solvent molecules and the matrix reduces, particularly in the case of the filled matrices.



**Figure 4:** Effect of solvent molecules on NR vulcanizates at 30°C



**Figure 5:** Effect of molecules on 10 phr NR-PSF composites at 30°C

#### 3. 4. 4 Effect of temperature

Figure 6 illustrates the behaviour of NR/PSF composites at three different temperatures, viz; 30°C, 50°C, and 70°C in benzene for 10 phr filler content. The figure depicts that as the temperature increased from 30 to 70°C, the rate of diffusion increases for both modified and unmodified composites but with lower effects for the modified counterparts. Similar behaviour holds for toluene, and xylene solvent systems studied for different filler contents. Again, the figure indicates that diffusion of the solvent into the composites is time and temperature dependent. Undoubtedly, activation of diffusion takes place with an increase in temperature which results in the disruption of the filler/matrix interface. Some researchers have reported the growth in the mass of solvent sorbed by rubbers and rubber filled composites with an increase in temperature [11, 32, 43, 44].



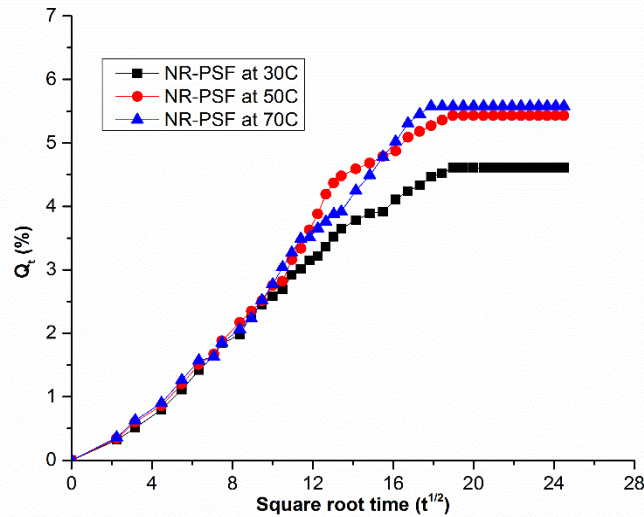


Figure 6: Effect of temperature on 20 phr NR-PSF composites

### 3. 5. Kinetic Parameters

#### 3. 5. 1. The Coefficient of Diffusion, (D).

The coefficient of diffusion of a polymer specimen soaked in a solvent can be calculated using the relation [45];

$$M_t/M_\infty = 1 - \sum_{x=0}^{\infty} \frac{8}{(2x+1)^2 \pi^2} e^{-(2x+1)^2 \pi^2 \left(\frac{Dt}{h^2}\right)} \quad (4)$$

Where D is the coefficient of diffusion,  $h$  is the thickness of the specimen,  $t$  is the time, and  $x$  is an integer. For the small period of swelling, we used a modified short-time equation as shown below [46];

$$M_t/M_\infty = (4/h)(Dt/\pi)^{\frac{1}{2}} \quad (5)$$

A plot of  $M_t$  vs.  $t^{1/2}$  gives a curve with an initial linear part. On the rearrangement of Eq. 5, D can be determined using Eq. 6.

$$D = \pi \left( \frac{h\beta}{4Q_\infty} \right)^2 \quad (6)$$

Where  $h$ , is the initial sample thickness,  $\beta$  is the slope of the linear portion of the sorption curve of the plot of %  $M_t$  against  $t^{1/2}$  and  $Q_\infty$  is the equilibrium absorption.

#### 3. 5. 2. Coefficient of sorption, (S)

The coefficient of sorption, S, depends on the strength of the polymer-solvent molecule interaction and was calculated using equation 7;

$$S = \frac{M_\infty}{M_p} \quad (7)$$

Where,  $M_\infty$  is the mass of polymer sample at equilibrium, and  $M_p$  is the initial mass of the polymer sample. The coefficient of sorption is related to the equilibrium sorption of the solvent.

#### 3. 5. 3. Coefficient of permeation, (P)

The coefficient of permeation of a solvent in a polymer composite is dependent on the diffusion and sorption of the solvent in the polymer composite. The coefficient of permeation, P, is obtained using Eq. 8 [47];

$$P = D \times S$$

(8)

Table 5 shows the values of the coefficient of diffusion for the different fibre contents at 30°C. The trend is similar for all other temperatures studied. The coefficient of diffusion mainly decreases as the filler content increases. Reduced diffusion coefficient confirms that the sample absorbs a lesser amount of solvent. From the table, the diffusion coefficient values were also found to decrease with increase in the molecular weight of the solvents used, where the order of the molecular weight of the solvents is benzene < toluene < xylene. The diffusion coefficient was also found to be lower for the alkali treated fibre composites. The lower diffusion coefficient values have been attributed to the lesser void content and higher fibre /matrix adhesion. A small degree of the coefficient of diffusion further means that the specimen absorbed only a small amount of solvent and it is lower for treated fibre composites.

**Table 5:** Values of D, S, and P of NR-PSF composites in different solvents at 30°C

Sample	Filler, phr	Diffusion Coefficient, $D \times 10^{-4}$ (cm <sup>2</sup> /s)			Sorption Coefficient, S (mol %)			Permeation Coefficient, $P \times 10^{-4}$ (cm <sup>2</sup> /s)		
		Benzene	Toluene	Xylene	Benzene	Toluene	Xylene	Benzene	Toluene	Xylene
NR	0	1.79	1.36	1.15	7.636	7.324	7.156	13.67	9.96	8.23
NR-PSF	10	1.33	1.17	1.10	5.919	4.724	4.421	7.87	5.53	4.86
	20	1.20	1.12	1.05	4.961	4.503	4.073	5.95	5.04	4.28
	30	1.14	1.06	0.95	4.197	4.008	3.776	4.78	4.25	3.59
NR-MPSF	10	1.19	1.11	1.04	5.428	4.342	4.044	6.46	4.82	4.21
	20	1.02	0.97	0.88	4.516	4.128	3.796	4.61	4.00	3.34
	30	0.86	0.81	0.74	3.824	3.676	3.321	3.29	2.98	2.46

The values of the coefficient of sorption and coefficient of permeation for various NR/PSF composites are also given in Table 5. Permeation and sorption coefficients follow a similar trend as the diffusion coefficient, i.e., their values decrease with PSF content and with an increase in temperature and time for both modified and unmodified fibres. The general decrease in the values as fibre content increases confirms the lack of interaction between hydrophilic fibres and non-polar solvents. Similar behaviour of the same aromatic solvents in natural rubber reinforced with natural fillers have been reported [11, 32].

### 3. 6. Transport Mechanisms

The mechanism of transport of the solvents through natural rubber filled composites was analysed using the relation [48];

$$\log \left( \frac{M_t}{M_\infty} \right) = \log k + n \log t \quad (9)$$

Where  $M_t$  and  $M_\infty$  are the mol % sorption at time  $t$ , and equilibrium respectively.  $k$  is a constant which is dependent on the polymer structural characteristics, and its interaction with the solvent. The value of  $n$  indicates the nature of the transport mechanism. When the value of  $n$  is 0.5, the mechanism of transport is said to be Fickian. This action occurs when the rate of diffusion of the solvent molecule is much lower than the relaxation rate of the polymer chains. When  $n$  is 1, it is said to be relaxation controlled (non-Fickian, case II). This scenario happens when the relaxation process is lower than the diffusion rate of the solvent molecule. When the value of  $n$  is between 0.5 and 1, it is anomalous transport behaviour. It occurs when the rate of diffusion of the solvent molecule and the relaxation rate of the polymer are alike. Super-case II transport happens when  $n$  is higher than

1.0, and the release rate is said to be time-dependent, and when  $n$  is less than 0.5, it is less Fickian (pseudo-Fickian). Table 6 gives the estimated values of  $n$  and  $k$  for the NR/PSF composites. From the table, the values of  $n$  are between 0.45 and 0.51 for the three different solvents, filler content, and temperatures indicating that the mode of transport showed Fickian and pseudo-Fickian behaviour. The variation observed in Fickian sorption is associated with the time taken by polymer chains to respond to swelling stress and the rearrangement to accommodate the solvent molecules [49]. The values of  $k$  give an insight into the interaction between the NR/PSF composites and the solvent. Table 6 indicates further that the values of  $k$  are higher for the modified composites. The behaviour is due to the existence of higher interfacial adhesion between the treated fibre and the NR matrix.

**Table 6:** Values of  $n$  and  $k$  ( $\text{g/g}\cdot\text{min}^{-n}$ ) of NR-PSF composites

Temp. °C	Filler, phr	Transport Mechanism											
		n						k					
		Benzene		Toluene		Xylene		Benzene		Toluene		Xylene	
		PSF	MPSF	PSF	MPSF	PSF	MPSF	PSF	MPSF	PSF	MPSF	PSF	MPSF
30	0	0.48	0.48	0.47	0.47	0.45	0.45	2.53	2.53	2.44	2.44	2.38	2.38
	10	0.51	0.52	0.48	0.49	0.50	0.51	2.61	2.65	2.54	2.62	2.49	2.54
	20	0.49	0.47	0.47	0.52	0.49	0.47	2.88	2.94	2.82	2.93	2.77	2.81
	30	0.48	0.48	0.50	0.49	0.46	0.48	3.02	3.08	3.01	3.06	2.94	3.02
50	0	0.49	0.49	0.46	0.46	0.45	0.45	2.84	2.84	2.68	2.68	2.61	2.61
	10	0.50	0.51	0.51	0.51	0.48	0.45	2.68	2.77	2.70	2.75	2.64	2.70
	20	0.51	0.49	0.50	0.50	0.46	0.47	3.01	3.06	2.94	3.01	2.82	2.94
	30	0.49	0.48	0.47	0.49	0.45	0.48	3.10	3.09	3.05	3.10	3.03	3.08
70	0	0.49	0.49	0.45	0.45	0.46	0.47	2.98	2.98	2.93	2.93	2.87	2.87
	10	0.48	0.47	0.46	0.46	0.50	0.48	3.02	3.07	2.96	2.99	2.90	2.95
	20	0.46	0.48	0.50	0.50	0.51	0.53	3.06	3.11	3.03	3.07	2.85	3.01
	30	0.50	0.49	0.50	0.51	0.51	0.47	3.12	3.15	3.09	3.13	3.04	3.08

### 3. 7. Activation Energy Estimation

The temperature dependence of transport properties can be used to analyse the activation energy obtained from three different temperatures using the Arrhenius relationship [50];

$$\log X = \log X_0 - \frac{E_x}{2.303RT} \quad (10)$$

Where,  $X$  is  $D$  or  $P$ , and  $X_0$  represents  $D_0$  or  $P_0$ , which is a constant;  $E_x$  is the energy of activation,  $R$  is the universal gas constant, and  $T$  is the absolute temperature. From the slopes of the Arrhenius plots of  $\log D$  and  $\log P$  against the inverse of  $T$ ,  $E_p$ , and  $E_D$  can be calculated by linear regression analysis. We observed that for any given solvent, the  $E_D$  and  $E_p$  values increase with the increase in PSF content up to 20 phr after which the values showed a decrease as presented in Table 7.

**Table 7:** Values of activation energy of diffusion and permeation of NR-PSF composites

Sample	Filler, phr	Activation Energy of Diffusion, $E_D$ KJ/mol			Activation Energy of Permeation, $E_p$ KJ/mol		
		Benzene	Toluene	Xylene	Benzene	Toluene	Xylene
NR		12.694	10.538	9.614	14.839	14.294	13.465
NR-PSF	10	15.243	14.938	12.675	18.224	17.923	17.572
	20	18.562	17.714	15.367	22.537	20.714	19.326
	30	16.934	15.843	13.938	21.276	20.366	20.012
NR-MPSF	10	16.426	15.836	15.324	19.798	19.427	18.884
	20	21.035	19.763	17.432	24.636	22.736	20.258
	30	18.242	17.642	15.774	24.023	23.281	21.314

The behaviour is due to the reinforcement of the NR matrix, which reduces the matrix-free volume and restricts the movement of the polymer chain due to the bound network of the matrix. Furthermore, the activation energies are dependent on the size of the solvent molecules used and observed to be highest for benzene and lowest for xylene. The activation energies as expected are higher for the NR filled composites compared to the neat NR in all the three solvents studied, indicating that the PSF fillers hinder the rate of diffusion. However, the decrease in the values beyond 20 phr may be attributed to the inability of the matrix to engulf and wet the fibre particles. In all cases, the modified composites showed higher activation energy than the unmodified ones signifying that the presence of strong interfacial adhesion restricted solvent movement.

## Conclusions

We have conducted the preparation, and studies on the mechanical and transport properties of natural rubber filled with piassava fibre composites. Tensile and tear strength for both composites increased up to 20 phr of PSF content while tensile modulus showed an upward trend. Percent elongation at break decreased steadily with the rise in fibre content due to chain movement restriction caused by the presence of PSF particles. Good dispersion of the piassava fibre in the natural rubber matrix at low filler content is evident from the SEM micrographs. The transport coefficients of diffusion, sorption, and permeation values were found to decrease with increase in filler content and were lower for modified composites in all cases due to strong interactions and good interfacial adhesion of the matrix and filler phases. With the increase in the solvent molecular size, there is a corresponding decrease in solvent uptake value for all the systems. The mode of transport study revealed that the value of ' $n$ ' is independent of temperature and filler content and was observed mostly to be Fickian. The ' $k$ ' value increases with the increase in sorption temperature and filler content. The activation energies of diffusion and permeation for NR/PSF composites were all positive and observed to rise with the addition of filler up to 20 phr. The vulcanizate could find its application in low strength materials such as valve oil seals and gaskets.

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