

# Cellulose Nanofibres and Cellulose Nanowhiskers Based Natural Rubber Composites: Diffusion, Sorption, and Permeation of Aromatic Organic Solvents

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**ABSTRACT:** This article investigates the transport behavior of three aromatic organic solvents, viz. benzene, toluene, and *p*-xylene in natural rubber nanocomposite membranes containing cellulose nanofibres (CNFs) and cellulose nanowhiskers (CNWs) isolated from bamboo pulp. The solvent molecules act as molecular probes to study the diffusion, sorption, and permeation through the nanocomposites, and provide information on the nanocomposite structure and matrix–filler interactions. Both the nanocelluloses were found to decrease the uptake of aromatic solvents in nanocomposite membranes, but the effect was more significant in the case on nanofibers compared to nanowhiskers. Furthermore, the uptake decreased with increased penetrant size; being the highest for benzene and the lowest for *p*-xylene. Transport parameters such as diffusion coefficient, sorption coefficient,

and permeation coefficient have been calculated. Comparison of the experimental values of equilibrium solvent uptake with the predicted values indicated that both the nanocelluloses have restricted the molecular mobility at the interphase and thereby decreased the transport of solvents through the materials; being more significant for nanofibers. The results showed that both the used cellulosic nanomaterials act as functional additives capable of manipulating and tailoring the transport of organic solvents through elastomeric membranes, even at concentrations as low as 2.5 wt %. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 1614–1623, 2012

**Key words:** cellulose nanowhiskers; cellulose nanofibers; diffusion coefficient; sorption coefficient and permeation coefficient

## INTRODUCTION

Studies on the transport properties through polymeric materials aid our understanding of the internal structure and morphology as well as the application of these materials as permeable or semipermeable membranes for selective separation or fractionation of liquid or gaseous mixtures.<sup>1–3</sup> The molecular transport through polymeric systems is a kinetic parameter depending on the free volume within the material, segmental mobility of polymer chains, and the size of the penetrant molecule. Molecular transport phenomena are influenced greatly by the physical and chemical nature, morphology, crosslink density of polymers, and the temperature, shape, and size of the probe penetrant molecules.<sup>4,5</sup> Molecular transport of organic liquids through polymer membranes has been the subject of investigations over the past several years to understand the internal

structure as well as to understand the commercial potential of membranes.<sup>6–8</sup>

Thomas and coworkers<sup>9–16</sup> have done several studies on transport properties of various rubber/rubber blends, thermoplastic elastomers, interpenetrating networks, and natural fiber or particulate-filled blends and composites. Jacob et al.<sup>17</sup> analyzed the absorption of biofibers (sisal and oil palm)/natural rubber (NR) polymer composites in water. The influence of temperature on water sorption of the composites was also analyzed and they analyzed the mechanism of diffusion in the gum sample and it was found to be Fickian in nature, while in the loaded composites, it was non-Fickian. Jacob et al.<sup>18</sup> also investigated the water sorption characteristics of woven sisal reinforced NR composites. These 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.

In recent years enormous efforts have been made to develop, characterize, and utilize bio-based materials, and bio-based nanocomposites belong to the new generation of bio-based materials. Bio-based

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nanocomposites are a relatively new class of nanomaterials and are of great interest in nanocomposite research owing to their biodegradability, biocompatibility, and environmental friendliness.<sup>19,20</sup> Utilization of bio-based nanoparticles was found to improve water vapor barrier, mechanical properties, and thermal stability without affecting the transparency of the biopolymers to any great extent.<sup>21</sup> Most of the diffusion studies were focused on the water uptake by different bionanocomposites, and were aimed at understanding how the water susceptibility was affected by bio-based nanomaterials.<sup>22–24</sup> Though bionanocomposites are being studied extensively these days, there are very few detailed reports on the diffusion of solvents through bionanocomposites.<sup>25</sup> Solvent diffusion through bio-based nanocomposites are expected to be influenced by polymer chain entanglement densities, the composition, and morphology of the nanocomposite. Another factor that influences the diffusion process is the free volume of the polymer nanocomposite which is a function of the interaction between the polymers matrix and the nanoreinforcement. Nair and Dufresne have reported NR-based nanocomposites reinforced with chitin whiskers, produced by the solution casting method.<sup>26</sup> Recently, Dufresne and coworkers<sup>27</sup> studied the swelling behavior of NR reinforced with waxy maize starch nanocrystals. They found that the solvent uptake of NR decreases upon the addition of starch nanocrystals. In these materials, the formation of a three-dimensional percolating network formed by polysaccharide nanoreinforcements could be a barrier limiting the diffusion of solvents within the material, leaving a fraction of the matrix material unsusceptible to swelling.

In this study, we have prepared cellulose nanofibre (CNF) and cellulose nanowhisker (CNW)-based NR nanocomposites and solvent molecules were used as molecular probes to understand the morphology and internal structure of cellulose-based nanocomposites. The diffusion of benzene, toluene, and xylene through the nanocomposites has been investigated in detail. Attempts have been made to correlate the transport with filler/matrix interaction and the extent of dispersion of nanoreinforcements in the matrix phase.

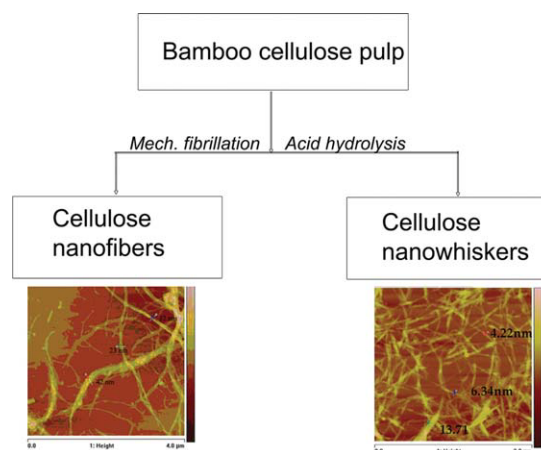
## EXPERIMENTAL

### Materials

NR was supplied in latex form and solid form by RRI, Kottayam, Kerala, India, and used as matrix material. Waste bamboo cellulose pulp was supplied by Piravam Paper Mill, Kerala, India.

### Isolation of nanocelluloses

CNFs were obtained through mechanical fibrillation of bamboo pulp. The pulp was dispersed homo-



**Figure 1** Process for the isolation of nanofibres and nanowhiskers from bamboo pulp. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

geneously in distilled water using a laboratory shear mixer (Silverson L4RT, Silverson Machine Ltd., England), and then a slurry with a cellulose concentration about 1% w/w was ground using a super mass-colloider (MKCA6-3, Masuko Sanyo Co, Ltd., Japan). In the present study, the fibrillation was done using contact mode grinding, where the final gap distance between the grinding stones (from 0-point) was further decreased by 10  $\mu\text{m}$  during the grinding. The grinding speed was approximately 3600 rpm and the total processing time was around 20 min.

CNW were prepared by acid hydrolysis of the bamboo pulp following the method developed by Bondeson et al.<sup>28</sup> The hydrolysis was completed by heating the suspension at 45°C for 130 min with continuous stirring, and then stopping the process by adding cold distilled water. Removal of excess acid was achieved by centrifugation with distilled water and this process was repeated until the supernatant became turbid. The resulting suspension was collected and dialyzed against distilled water, and then sonicated in an ice bath for 5 min. The process flow-chart showing the isolation of the two types of nanocelluloses, viz. nanofibres (CNFs) and nanowhiskers (CNWs), from bamboo pulp is shown in Figure 1.

Both processes resulted in nanosized materials, as shown in the atomic force microscopy (AFM) images. The obtained nanofibres had diameters in the range of 23–42 nm and lengths are estimated to be in micrometer scale, whereas the acid-hydrolyzed nanowhiskers had diameters in the range of 5–14 nm and lengths in the range of 300–400 nm.

### Nanocomposite processing

Nanocomposites of CNFs and CNWs with NR as a matrix were prepared via a two-step process involving (a) master-batch preparation in NR latex and (b)

**TABLE I**  
Formulations for the Prepared Compounds

Sample code	NR	Cellulose	Vulcanizing ingredients (phr)			
			ZMBT	ZO <sub>2</sub>	Sulphur	ZDC
NR	100	0	0.5	0.2	1.5	0.75
NR-CNF <sub>2.5</sub>	97.5	2.5	0.5	0.2	1.5	0.75
NR-CNF <sub>5</sub>	95	5	0.5	0.2	1.5	0.75
NR-CNF <sub>10</sub>	90	10	0.5	0.2	1.5	0.75
NR-CNW <sub>2.5</sub>	97.5	2.5	0.5	0.2	1.5	0.75
NR-CNW <sub>5</sub>	95	5	0.5	0.2	1.5	0.75
NR-CNW <sub>10</sub>	90	10	0.5	0.2	1.5	0.75

ZO<sub>2</sub>, zinc oxide; ZMBT, zinc mercapto benzothiazole; ZDC, zinc dithiocarbamate.

two-roll mill mixing of the master batch with solid NR and vulcanizing agents followed by subsequent curing. In the master batch processing step, NR latex and CNF or CNW in aqueous medium are mixed together, casted, and dried into films with a final nanocellulose concentration of 20 wt %. This master batch is then powdered and diluted in the next processing step, where the master batch is compounded with solid NR and vulcanizing agents in a two-roll mixing-mill which results in different weight percentages of CNFs and CNWs in the final formulations. The formulations are given in Table I.

After the compounding process the materials was pressed to obtain vulcanized sheets. The cure time for the vulcanization was determined using a Monsanto rheometer and optimum curing times ( $t_{90}$ ) was calculated. The nanocomposite preparation is schematically represented in Figure 2.

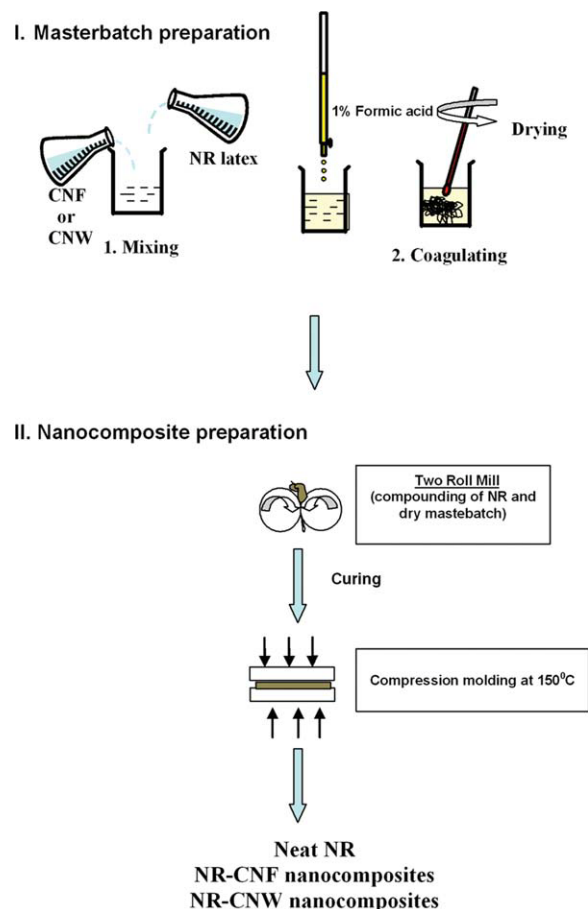
### Solvent uptake studies

Circular samples of 1 cm in diameter were cut from the vulcanized sheets by means of a standard circular die. The thickness and initial weight ( $W_0$ ) of the samples were measured. The thickness of the samples was in the range 1.5–2 mm and the experiments were conducted under ambient conditions (25°C). The samples were removed at specific intervals ( $t$ ) and weighed ( $W_t$ ) to the nearest  $\pm 0.1$  mg using an electronic balance until equilibrium weight ( $W_a$ ) was attained. Before each weighing, the surfaces of the samples were cleaned gently without any pressure using filter paper to remove the adhering solvents. The experiments were carried out using benzene, toluene, and *p*-xylene as solvents. To conduct the experiments at elevated temperatures (40 and 50°C), a thermostatically controlled air oven was used. All the experiments were conducted in duplicate and the data showed agreeing results. All presented values are considered representative of the material behavior.

## RESULTS AND DISCUSSION

### Organic solvent uptake behavior

In this study transport of three different organic solvents through NR-based cellulose nanocomposites containing CNFs and CNWs as reinforcements is compared. Vulcanized NR has good affinity to the used solvents, benzene, toluene, and xylene and readily absorb these solvents and swell. The solvent uptake is determined by the sorption of solvents as well as the diffusion and permeation of the solvent molecules in the material. The cellulosic nanomaterials used in the study have no affinity to the solvents and therefore their addition will reduce the solvent uptake. However in addition to that, the solvent uptake is manipulated in presence of the nanocelluloses. Any reduction in the solvent uptake is therefore an indirect measure of the interaction between the matrix and the reinforcements and the presence of interphase where the polymer chain mobility is totally arrested or limited. On the other hand, in cases where the matrix–filler interactions are weak the solvent uptake may increase due to the possible accumulation of solvents at the interface.



**Figure 2** Schematic representation of the CNF and CNW nanocomposite preparation. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**TABLE II**  
**The Weight Percent Uptake of Different Organic Solvents in Natural Rubber and its Nanocomposites Containing Cellulose Nanofibres and Nanowhiskers**

Sample	Equilibrium weight percent solvent uptake (%)			Equilibrium mole percent solvent uptake ( $Q_2$ ) (%)		
	Benzene	Toluene	Xylene	Benzene	Toluene	Xylene
NR	379	328	322	4.9	3.6	3.0
NR-CNF <sub>2.5</sub>	298	273	269	3.8	2.9	2.5
NR-CNF <sub>5</sub>	262	213	231	3.4	2.3	2.2
NR-CNF <sub>10</sub>	232	205	181	3.0	2.2	1.7
NR-CNW <sub>2.5</sub>	370	317	314	4.7	3.4	3.0
NR-CNW <sub>5</sub>	363	287	289	4.6	3.1	2.7
NR-CNW <sub>10</sub>	289	268	280	3.7	2.9	2.6

Therefore, a careful analysis of transport of solvents through the nanocomposite helps to understand the internal structure and predict their mechanical performance. In addition, this study will provide quantified information on the barrier properties, solvent stability, and dimensional stability of the cellulose-based nanocomposites with respect to matrix.

The percent uptake of the solvent at different time intervals is calculated using the equation<sup>24</sup>

$$\text{Solvent uptake (wt\%)} = 100 \times (W_t - W_0)/W_0 \quad (1)$$

$W_t$  is the mass of the nanocomposite at time  $t$ ,  $W_0$  is the initial mass of the sample. Table II shows the weight percentage uptake of benzene, toluene, and xylene in NR and the two types of nanocomposites with 2.5, 5, and 10 wt % of nanocelluloses. NR shows an uptake of 379, 328, and 322% in benzene, toluene, and xylene, respectively, which was reduced with the addition of CNFs and CNWs, even at concentrations as low as 2.5%.

Figures 3–5 show plots of solvent uptake (weight %) versus  $t^{1/2}$  for the benzene, toluene, and *p*-xylene in the NR nanocomposites with different weight percentages of CNFs and CNWs. All figures show a similar pattern for the curves, indicating a relatively rapid uptake in the initial stage and a plateau region in the later stage. In all the figures, two well-separated zones were observed at shorter times (zone I:  $(\text{Time})^{(1/2)} \min^{(1/2)} < 15$ ) and longer times (zone II  $(\text{Time})^{(1/2)} \min^{(1/2)} > 15$ ) for all the solvents. In zone I, a rapid increase in solvent uptake occurs at less than 15 min and in zone II, the rate of solvent absorption decreases. It may, however, be noted that the equilibrium uptake depends on various parameters such as the nature of the penetrants and the concentration and nature of the used nanomaterials. In addition to the composition of the material the solvent resistance of the nanocomposites is greatly dependent on the temperature, molecular weight of solvent, and polymer/solvent interactions.

#### Effect of nanocellulose content

The sorption curves in the used solvents such as benzene, toluene, and *p*-xylene are strongly influenced by the nanocellulose content of both types of nanocomposite. It is observed from Table II that neat NR membranes have maximum-equilibrium mole percent uptake and in both cases there is a gradual decrease in equilibrium solvent uptake with an increase in nanocellulose content. The table shows that the sorption behavior varies in the order NR > NR-CNF 2.5% > NR-CNF 5% ≥ NR-CNF 10%, i.e., the equilibrium solvent uptake decreases with increasing percentage of cellulose content in the composites. Similarly, nanocomposites with 10 wt % CNW have the lowest equilibrium mole percent uptake compared to neat NR and nanocomposites with 2.5 and 5 wt % CNWs in all the three studied organic solvents.

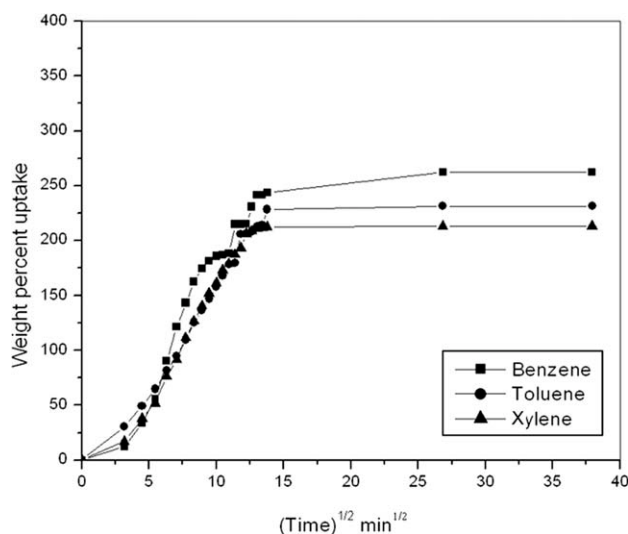
#### Effect of the penetrant size

The influence of penetrant size on the respective solvent uptake in neat NR and the different NR nanocomposites can be seen in Table II. In NR matrix, as well as CNF nanocomposites and CNW nanocomposites, benzene showed the highest uptake and xylene showed the lowest uptake, while toluene showed intermediate uptake. Figures 3 and 4 show the effect of mole percent uptake of the three aromatic solvents benzene, toluene, and *p*-xylene in NR composites with 5 wt % CNWs and 5 wt % CNFs, respectively. The same trend is followed at 2.5 and 10 wt % of nanofibres and nanowhiskers. This decrease in uptake is directly dependent on the penetrant size or molecular weight of the solvent. Increased molecular weight increases the bulkiness of the penetrant and restricts the mobility of the solvent molecules through the NR matrix.

#### Effect of nanocellulose type

In this study, nanofibers and nanowhiskers were used as the functional additives. The effect of





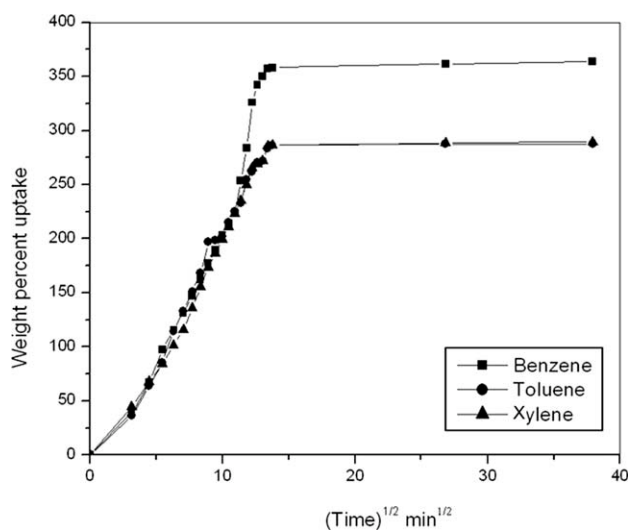
**Figure 3** Plots of solvent uptake (wt %) versus  $t^{1/2}$  for the benzene, toluene, and *p*-xylene in NR nanocomposites with 5 wt % CNFs.

nanocelluloses type on the uptake can be compared in Table II. The representative curves showing the evolution of the benzene uptake versus time for nanocomposites with 5 wt % CNFs and CNWs are given in Figure 5. In all three solvents, CNF-based nanocomposites showed lower uptake than the corresponding CNW-based ones.

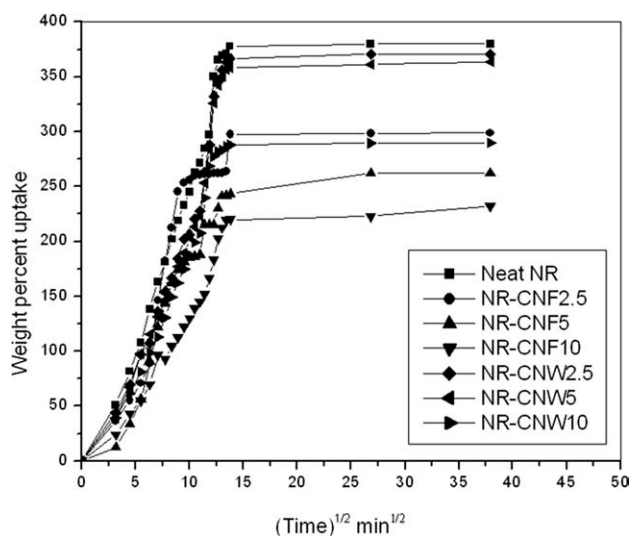
#### Diffusion, sorption, and permeation coefficients

The mole percent uptake  $Q_t$  of the solvents by the materials is given by the equation<sup>10,16</sup>

$$Q_t = 100 \times \frac{[(W_t - W_0)/M_w]}{W_0} \quad (2)$$



**Figure 4** Plots of solvent uptake (wt %) versus  $t^{1/2}$  for the benzene, toluene, and *p*-xylene in NR nanocomposites with 5 wt % CNWs.



**Figure 5** Sorption curves of NR and the nanocomposites with CNF and CNW 2.5, 5, and 10 wt % in benzene.

$W_t$  is the mass of the nanocomposite at time  $t$ ,  $W_0$  is the initial mass of the sample and  $M_w$  is the molecular weight of the solvent. The equilibrium mole percent uptake ( $Q_\infty$ ) values are given in Table II. This follows the same trend as equilibrium weight percent uptake. The mole percent uptake  $Q_t$  of the solvent by neat NR and NR-based nanocomposites was plotted as a function of square root of time and used to study the kinetics of diffusion, sorption, and permeation. The diffusion coefficient of a polymeric sample immersed in an infinite amount of solvent can be calculated using the equation<sup>29,30</sup>

$$Q_t/Q_\infty = 1 - (8/\pi^2) \sum_{n=0}^{\infty} [1/(2n+1)^2 \exp[-D(2n+1)^2\pi^2t/h^2]] \quad (3)$$

where " $t$ " is the time, " $h$ " the initial thickness of the sample, " $D$ " the diffusion coefficient, and " $n$ " an integer. From this equation it is understood that a plot of " $Q_t$ " versus " $t_{1/2}$ " is linear at short time and " $D$ " can be calculated from the initial slope. The equation for short time limiting is,<sup>29,30</sup>

$$Q_t/Q_\infty = 4/h(D/\pi)^{1/2}t^{1/2} \quad (4)$$

By rearranging this equation, the diffusion coefficient can be calculated using the equation,<sup>31</sup>

$$D = \pi(h\theta/4Q_\infty)^2 \quad (5)$$

where " $D$ " is the diffusion coefficient,  $h$  the thickness of each sample, " $\theta$ " is the slope of the linear portion of the curve and " $Q_\infty$ " is the equilibrium weight in moles. From the slope " $h$ " of the initial

**TABLE III**  
**D, S, and P Values of the Nanocomposite Samples in Different Solvents**

Sample	Diffusion coefficient $D \times 10^{-8} \text{ (m}^2 \text{ s}^{-1}\text{)}$			Sorption coefficient, $S$ , $(\text{g g}^{-1})$			Permeation coefficient, $P, \times 10^{-10} \text{ (m}^2 \text{ s}^{-1}\text{)}$		
	Benz	Tolu	Xyln	Benz	Tolu	Xyln	Benz	Tolu	Xyln
NR	1.3	1.3	1.1	4.79	4.28	4.22	6.2	5.6	4.6
NR-CNF <sub>2.5</sub>	1.2	1.3	1.1	3.98	3.73	3.39	4.7	4.8	3.6
NR-CNF <sub>5</sub>	1.0	1.1	1.0	3.62	3.13	3.31	3.6	3.3	3.3
NR-CNF <sub>10</sub>	0.9	1.0	0.9	3.32	3.05	2.81	2.9	3.1	2.6
NR-CNW <sub>2.5</sub>	1.3	1.3	1.1	4.79	4.28	4.22	6.3	5.6	4.5
NR-CNW <sub>5</sub>	1.0	1.0	0.9	4.70	4.17	4.14	4.5	4.2	3.8
NR-CNW <sub>10</sub>	0.9	1.0	0.9	4.63	3.87	3.89	4.2	3.7	3.6

linear portion of the sorption curves the diffusion coefficient, “ $D$ ” was calculated using the equation.

The permeation of penetrant through polymer membranes depends on the diffusivity as well as the solubility or sorptivity of the penetrant. Hence, sorption coefficient, which is the maximum saturation sorption value, is calculated using the equation<sup>29–31</sup>

$$S = M_{\infty}/M_0 \quad (6)$$

where  $S$  is the sorption coefficient,  $M_{\infty}$  is the mass of polymer sample at infinity, and  $M_0$  is the initial mass of polymer sample.

The permeability coefficient  $P$  can be calculated from the equation,<sup>29,30</sup>

$$P = DS \quad (7)$$

where  $P$  is the permeability coefficient,  $D$  the diffusion coefficient, and  $S$  the sorption coefficient. Diffusion coefficient of the CNFs and CNW-based nanocomposites is given in Table III. The neat NR membranes showed diffusion coefficients of 1.3, 1.3, and  $1.1 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$  in benzene, toluene, and *p*-xylene, respectively. For all the three solvents the  $D$  value decreases systematically from neat NR to 10 wt % nanocellulose content. Thus, when the concentration of CNWs increased, the diffusion coefficient values decreased. On comparing the CNFs and CNWs, it can be seen that the diffusion coefficient values are lower for NR-based CNF nanocomposites for benzene and toluene, but higher for *p*-xylene than the corresponding NR-CNW ones.<sup>29,30</sup> Diffusivity is a kinetic parameter which depends on the polymer segmental mobility, which is related to the amount of free volume in the matrix. The diffusion of solvent depends upon the concentration of available space that is large enough to accommodate the solvent molecule. A penetrant molecule may exist in a hole of sufficient size and can jump into a neighboring hole once it acquires sufficient energy.<sup>29,30</sup> The addition of nanocellulose to NR may lead to reduced availability of spaces and restrict the mobility of chain segments in the nanocomposites. There-

fore, the addition of cellulose fibers and whiskers results in a progressive increase in the stiffness of the NR matrix, especially in the vicinity of the nanocellulose. In addition, it may be noted that the  $D$  values decrease as the penetrant size increases.

The sorption coefficient of the neat NR membranes was reduced in the presence of CNFs and CNWs within the nanocomposites and decreased gradually as the concentration of nanocelluloses increased. In all cases, the CNW-based NR composites showed higher sorption coefficient than the corresponding CNF-based ones, indicating that sorption is more restricted by the nanofibres than by the nanowhiskers. Permeation is a phenomenon which is dependent on diffusion and sorption. The permeability coefficients of NR film and different compositions of CNF and CNW nanocomposites are given in Table III. The permeation coefficient is significantly lower for the nanocomposites compared to the matrix and decreases as a function of nanocellulose concentration. This is because the presence of cellulose nanomaterials restricts the polymer chain mobility and the movement of solvent molecules between the polymer chains. In the case of permeation coefficient, the values are also higher for nanowhisiker-based composites than the corresponding nanofibre based ones. It may be noted that the equilibrium solvent uptake closely follows the trend of diffusion, sorption, and permeation coefficients, indicating that the transport phenomenon is controlled by these three phenomena. Diffusion, sorption, and permeation are lower for nanofibre-based composites and are reduced with increased penetrant size and nanocellulose content, and the equilibrium uptake also shows the same trend.

### Transport mechanism

The mechanism of transport in NR nanocomposites was analyzed using the relationship<sup>10,31–33</sup>

$$\log(Q_t/Q_{\infty}) = \log k + n \log t \quad (8)$$

where  $Q_t$  and  $Q_{\infty}$  are the mol % solvent uptake at time “ $t$ ” and at equilibrium respectively, “ $k$ ” is a

**TABLE IV**  
**"n" and "k"(in g g<sup>-1</sup>min) Values of Diffusion of**  
**Aromatic Hydrocarbons Through Natural Rubber and**  
**the Nanocomposites**

Samples	Benzene (30°C)		Toluene (30°C)		Xylene (30°C)	
	<i>n</i>	<i>k</i> × 10 <sup>2</sup>	<i>N</i>	<i>k</i> × 10 <sup>2</sup>	<i>n</i>	<i>k</i> × 10 <sup>2</sup>
NR	0.64	4.23	0.52	4.10	0.50	3.93
NR-CNF <sub>2.5</sub>	0.67	4.13	0.53	4.04	0.51	3.86
NR-CNF <sub>5</sub>	0.68	4.10	0.54	4.00	0.52	3.81
NR-CNF <sub>10</sub>	0.69	3.98	0.54	3.90	0.52	3.75
NR-CNW <sub>2.5</sub>	0.69	4.02	0.55	3.87	0.53	3.70
NR-CNW <sub>5</sub>	0.71	3.76	0.55	3.85	0.53	3.70
NR-CNW <sub>10</sub>	0.715	3.54	0.56	3.82	0.53	3.68

constant which depends on the structural characteristics of the polymer and gives information about the interaction between the solvent and polymer and "n" indicates the mechanism of sorption.

When the value of *n* = 0.5, the mechanism of transport is termed as Fickian and this occurs when the rate of diffusion of the penetrant molecule is much less than the relaxation rate of the polymer chains. When *n* = 1, the mechanism of transport is termed as non-Fickian (case II-relaxation controlled) which arises when the rate of diffusion of the penetrant molecule is much greater than the relaxation process. However, the value of "n" between 0.5 and 1 indicates anomalous transport behavior and it is due to the fact that the rate of diffusion of the penetrant molecule and the relaxation rate of the polymer are similar.

The values of *n* and *k* for NR/CNW nanocomposites were obtained by regression analysis of the plot of log (*Q<sub>t</sub>/Q<sub>∞</sub>*) versus log *t* and the results are given in Table IV. The correlation coefficient value is found to be 0.99. Since, the value of "n" lies in between 0.52 and 0.59, the mode of transport is close to Fickian. Similar Fickian mode transport of several semicrystalline and elastomeric polymers has already been reported.<sup>30</sup> As the concentration of cellulose whisker in the nanocomposites increases, there

is a slight decrease in the value of *n* and the sorption behavior approaches the Fickian mode.

### Diameter variation of the composites

The diameter variation of the nanocomposites was determined by the equation<sup>25</sup>

$$DV = (d - d_0)/day_0 \quad (9)$$

*d*<sub>0</sub>, diameter before swelling (10 mm) and *d*-diameter after 24 h. The diameter variation of the neat NR film and different nanocomposites was measured before and after sorption in three different solvents. It clearly appears that swelling of the material systematically decreases with increasing amount of filler content in the NR matrix.

This observation was quantified by measuring the diameter of the discs after 24 h of swelling in solvents. Diameters and diameter variations of the neat NR and the nanocomposites are given in the Table V. The diameter variation was lower for the nanocomposites compared to the neat NR, in all the three solvents. However the diameters were higher for CNF nanocomposites, despite that the CNW nanocomposites which is an unexpected trend. However in all cases the diameter variation decreased with increasing the nanocellulose content.

### Activation energy

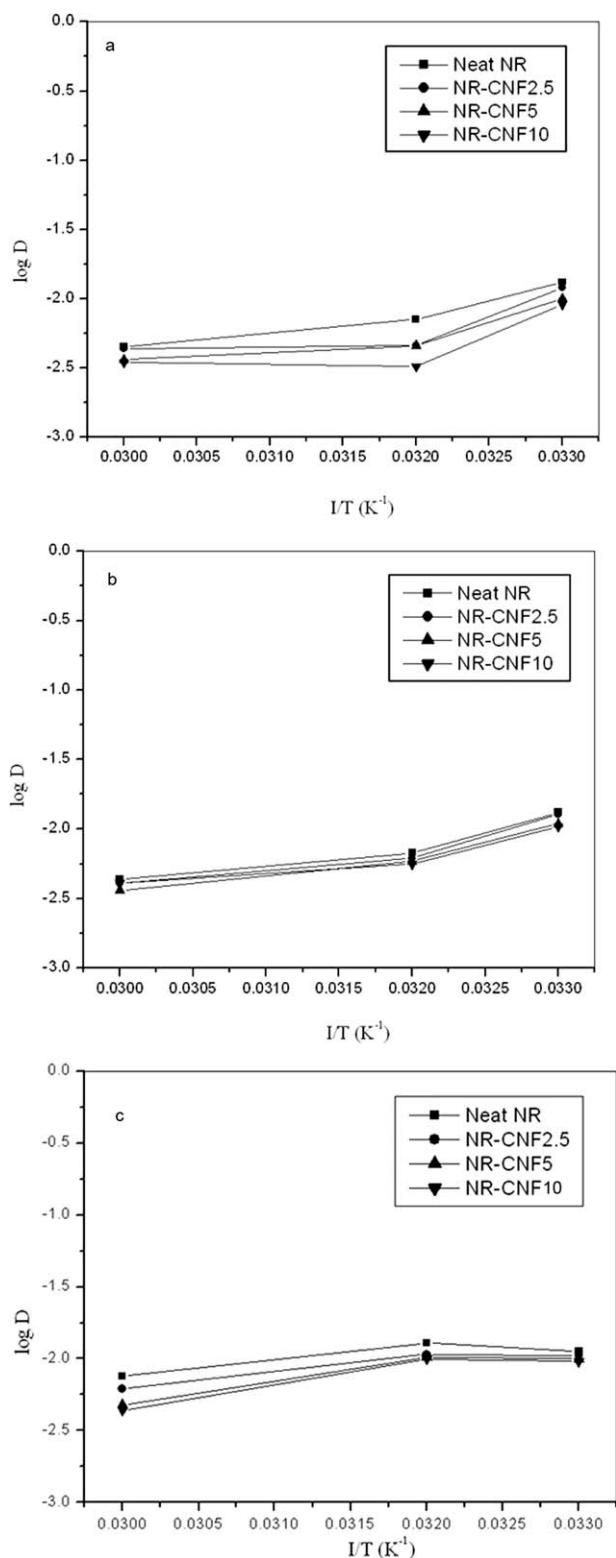
Activation energy of diffusion was calculated from the Arrhenius equation based on diffusion studies of nanocomposites in different solvents in three different temperatures: 30, 40, and 50°C.<sup>5,33</sup> The equation used is

$$\log D = \log D_0 - E_D/2.303RT \quad (10)$$

According to the equation, the slope of the plot log *D* versus 1/*T* gives the value of activation energy of diffusion of the solvents through the studied

**TABLE V**  
**Diameter Variation of the Natural Rubber and its Nanocomposites at Room**  
**Temperature After 24 h of Swelling in Three Different Aromatic Solvents**

Materials	Benzene		Toluene		<i>p</i> -Xylene	
	Diameter (mm)	Diameter variation (%)	Diameter (mm)	Diameter variation (%)	Diameter (mm)	Diameter variation (%)
NR	18.5	79.12	16.7	66.5	16.1	60.5
NR-CNF <sub>2.5</sub>	17.1	66.0	15.6	56.0	15.1	50.5
NR-CNF <sub>5</sub>	16.2	57.3	14.7	47.0	14.6	45.5
NR-CNF <sub>10</sub>	15.5	50.0	14.1	41.0	14.0	39.5
NR-CNW <sub>2.5</sub>	15.7	56.5	14.3	42.5	13.8	38.0
NR-CNW <sub>5</sub>	14.8	47.5	13.4	33.5	13.3	33.0
NR-CNW <sub>10</sub>	14.0	40.0	12.8	27.5	12.7	27.0

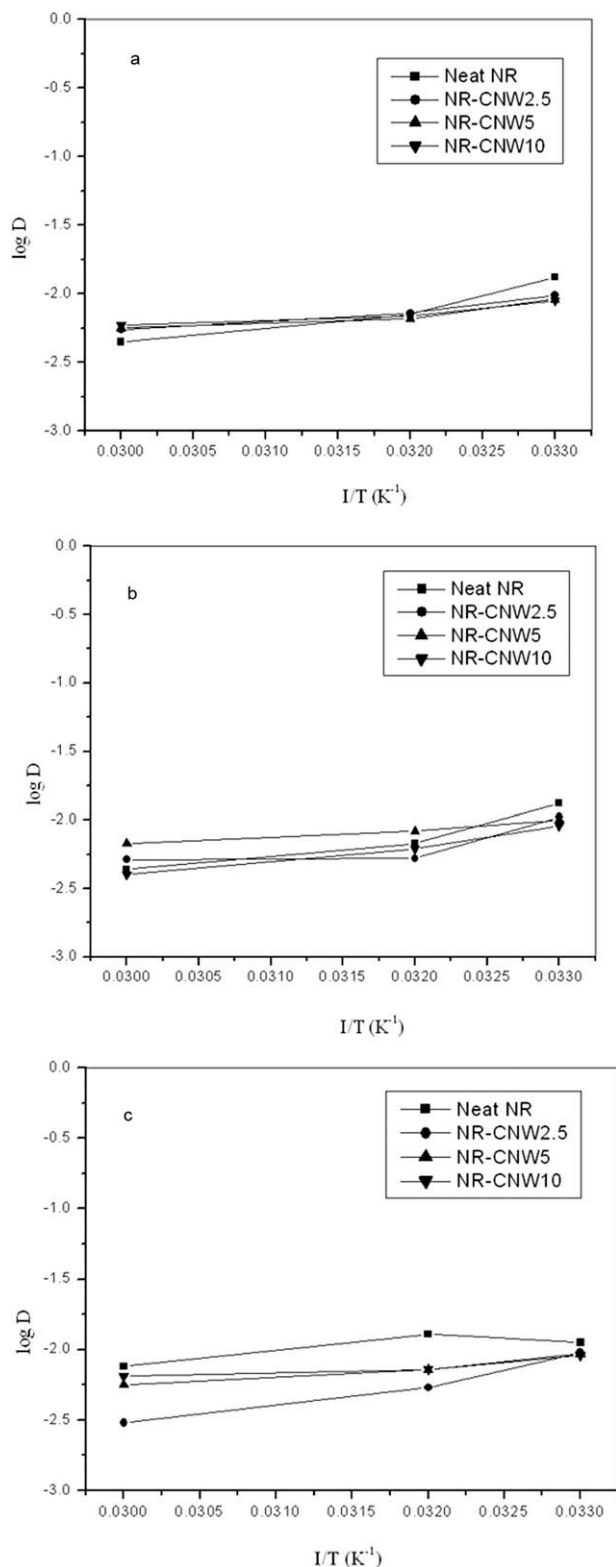


**Figure 6** Arrhenius plots of NR and CNF-based nanocomposites in (a) benzene, (b) toluene, and (c) *p*-xylene.

materials. Arrhenius plots of neat NR and their CNF and CNW nanocomposites, in three different solvents, are shown in Figures 6 and 7, respectively.

The activation energy of diffusion obtained from Arrhenius plots is given in Table VI. In general, the

activation energy is higher for the nanocomposites compared to the neat NR, indicating that the nanocelluloses retard the diffusion process. This can be ascribed to the decreased polymer chain mobility in the presence of nanocelluloses. It was also found



**Figure 7** Arrhenius plots of NR and CNW-based nanocomposites in (a) benzene, (b) toluene, and (c) *p*-xylene.



**TABLE VI**  
**Activation Energy of Diffusion of Solvents Through Neat NR, CNF, and CNW Nanocomposites at Different Solvents and Different Temperature**

Solvents	$-E_D$ (kJ/mol)						
	CNF nanocomposites				CNW nanocomposites		
	NR	NR-CNF <sub>2.5</sub>	NR-CNF <sub>5</sub>	NR-CNF <sub>10</sub>	NR-CNW <sub>2.5</sub>	NR-CNW <sub>5</sub>	NR-CNW <sub>10</sub>
Benzene	2.77	2.43	2.54	2.25	1.53	1.24	1.18
Toluene	2.89	2.98	2.91	2.43	1.71	1.05	1.09
<i>p</i> -Xylene	1.24	1.59	2.2	2.31	1.38	1.35	0.89

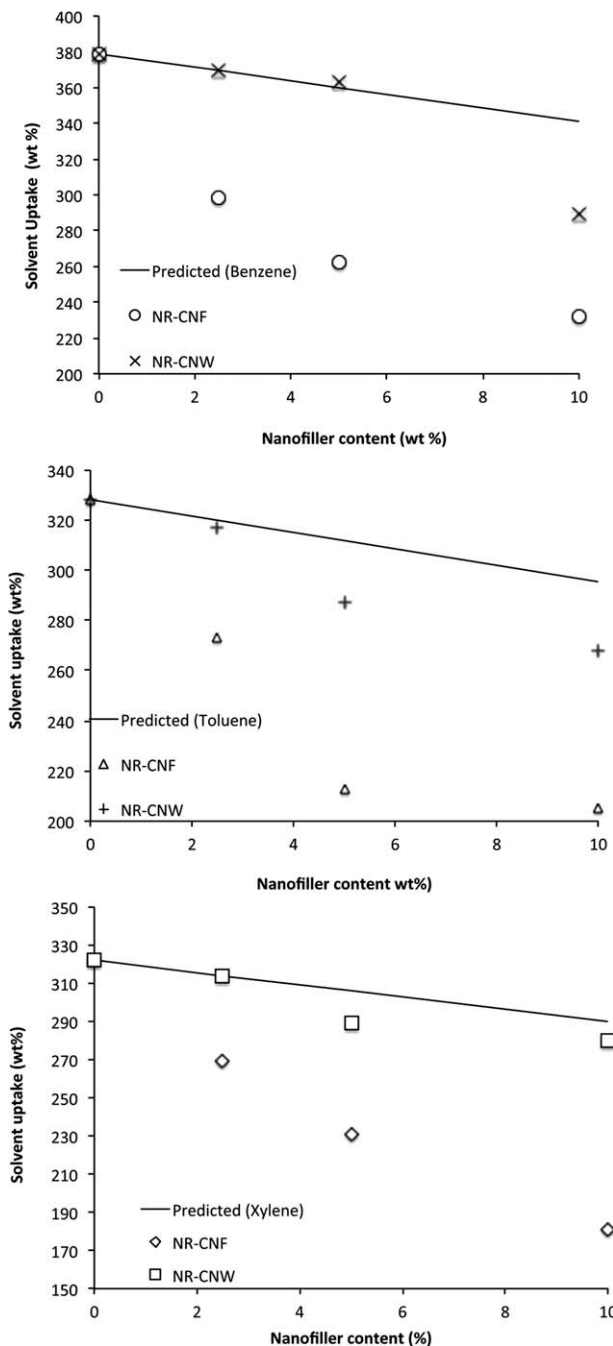
that the activation energy increases with nanocellulose concentration. The penetrant size also had an impact on activation energy and increased with increased penetrant size. However, the activation energy of the CNW-based nanocomposites was found to be higher than that of CNF-based ones, which was an unexpected trend. The CNW composites have shown higher solvent uptake in spite of higher activation energies.

In general, it can be seen that the uptake of the three studied organic solvents through NR matrix decreased with the addition of CNFs and CNWs, and the uptake depended on the nanocellulose content, the nature of the nanocellulose used, and the molecular weight or size of the penetrant molecule.

CNWs and CNFs do not have the affinity to the used with organic solvents or do not take organic solvents. Therefore, the addition of these nanomaterials is expected to decrease solvent uptake of NR matrix. The NR phase being vulcanized in all the studied materials has chemical crosslinks between the NR polymer chains, and networks of nanocelluloses in the matrix act as physical crosslinks or entanglements which restrict the polymer chain mobility. Furthermore, the results show that both the nanocelluloses have a positive impact in reducing the solvent uptake, even at concentrations as low as 2.5 wt %, which is attributed to the large interfacial area between the matrix and the nanocelluloses with restricted chain mobility.

### Theoretical prediction

The solvent transport may be used as a probe to understand the influence of nanocelluloses on the internal structure, a simple theoretical prediction was carried out and compared with the experimental data in Figure 8. The predicted values were calculated as a linear combination of the data for the pure components, that is by assuming additivity.<sup>34</sup> To determine the predicted values, it is assumed that there is no interaction between the matrix and the reinforcement and the nanocelluloses have no affinity to the solvent, and the solvent uptake decreases as a function of addition of nanocellulose. For, e.g., the uptake value at 10 wt % CNW or CNF should be 90% of the uptake by NR matrix.



**Figure 8** Comparison of predicted values of solvent uptake with the experimental values of the nanocomposites with different filler content. (Data based on benzene, toluene, and xylene are shown).

On comparing the predicted uptake values thus obtained with that of the experimental values, it can be seen that the experimental values are significantly lower in most cases. This leads to the conclusion that there are specific interaction between the matrix and the nanocellulose in the case of both the CNFs and CNWs. It is also obvious that CNF nanocomposites have larger deviations from the predicted values at all concentrations where as CNW nanocomposites showed significant deviations only at higher CNW contents. This also suggests that the dispersion is not adversely affected even at 10 wt % nanocellulose. It may be noted that CNFs are more efficient in decreasing the uptake than CNWs, probably due to the tangling effect of nanofibres combined with restricted chain mobility at the interphase and the resultant higher degree of tortuosity induced by the CNFs compared to the CNWs.

### CONCLUSIONS

Transport properties of aromatic solvents such as benzene, toluene, and *p*-xylene through NR-based nanocomposite membranes containing varying amounts of CNFs or CNWs were investigated. Generally, the study showed that CNWs as well as CNFs, being in nanoscale, have the ability to restrict the molecular mobility and the polymer chain relaxation and thereby decrease the solvent uptake of NR membranes. The uptake for a given solvent and the diffusion coefficient, sorption coefficient, and permeation coefficients were found to decrease with increasing nanocellulose content. In all the studied materials the solvent uptake of polymer decreased in the order benzene > toluene > *p*-xylene, which is attributed to the difference in molecular weight and bulkiness between the three solvents. It was found that, the higher the molecular weight or bulkiness of the solvent molecule, the lower the solvent uptake.

The study shows that transport of the solvent molecules through neat NR was found to be successfully manipulated or tailored by selecting the appropriate nanocellulose that act as functional additive. A comparison with theoretically predicted solvent uptake with the experimental values indicates that both the nanocelluloses interacts with the matrix and restricts the solvent uptake probably by decreasing the polymer chain mobility at the interphase. Though the two types of nanocelluloses have effectively reduced the molecular transport, CNFs are more efficient than CNWs in decreasing the solvent uptake, probably due to the tangling effect of nanofibres.

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