

Transport Characteristics of Benzene through Palm Mesocarp Fibre/Low Density Polyethylene Composites

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Abstract- The transport characteristics of benzene through palm mesocarp fibre (PMF)-reinforced low density polyethylene (LDPE) composites have been studied in the temperature range 40–80 °C. The diffusion behavior of benzene through these composite samples was studied, with special reference to the effect of filler content, filler particle size, and temperature. Transport coefficients including diffusion, permeation, and sorption coefficients were estimated. The effect of alkali treatment on the solvent uptake and swelling parameters was also analyzed. All the composites showed a decrease in the uptake of solvent, but the effect was more in the case of alkali-treated composites. The solvent uptake decreased more so with particle size decreasing. The transport mechanism of diffusion was found to be close to Fickian and may be regarded as “less Fickian”. The van’t Hoff’s relationship was used to determine the thermodynamic parameters. The energy of activation and transport kinetics of the composites have been evaluated.

Keywords: palm mesocarp fiber, benzene, transport coefficients, swelling parameters, alkali treatment, transport kinetics

I. INTRODUCTION

Nowadays, polymeric filled systems including natural fiber filled polymer composites are being extensively used in a variety of applications because of their good physical and barrier properties.

Their utilization in composite systems offers several advantages, such as low density, low price, renewability, and biodegradability compared to those of synthetic fibers [1,2]. Natural fibers like coir [3], sisal [4], kenaf [5], jute [6], pineapple leaf fiber [7], oil palm mesocarp [8,9], and oil palm empty fruit bunch [10,11] have

been extensively studied for the fabrication of polymer filled fiber composites. Several authors in the past have reported the blending of palm mesocarp fiber (PMF) with polycaprolactone [12], poly(butylene succinate) [13], epoxy [14], and polypropylene [15], to prepare polymer/fiber composites.

To find suitable application in high-performance areas like coatings, packaging, gas separations, etc., the knowledge of transport of solvents through filled polymers is considered essential. Solvent transport properties such as diffusion, sorption and permeation through polymers and their composites have been used in the design of food packaging materials [16], solvent reservoirs [17], pervaporators [18], and controlled release devices [19].

The study of diffusion, sorption and permeation in blend structures provides valuable means for additional characterization of polymer composites [20]. Transport properties in filled polymers are generally governed by the nature of fillers and the extent of their interaction with the polymer matrix. Obviously, the addition of inert fillers results in the filling of free volume of polymer matrix and creates a tortuous path for the penetrant [21]. The transport mechanisms and properties of natural and synthetic polymers, particulate filled blends and composites have been extensively studied and reported in literature by several researchers [21-26]. Transport of organic fluids through polymer and polymer filled membranes has been the subject of investigations over the past several years, with a view to understanding the internal structure as well as the commercial benefits of these membranes [27,28]. Unnikrishnan and Thomas [29] studied the molecular transport of benzene and methyl-substituted benzenes through filled natural rubber sheets. Ahmed *et al.* [30] have investigated the swelling properties of filled NR/linear low-density polyethylene blends in toluene. On their own, Lawandy and Helaly [31] reported the diffusion of chloroform in neoprene rubber vulcanizates containing different types of carbon black and observed that the penetration rate decreased with increase in the particle size of carbon black. Mesrobian and Ammondson [32]

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reported the diffusion of n-heptane and methyl salicylate through polyethylene/nylon blends. Stephen *et al.* studied the transport properties of nano-structured layered silicates reinforced natural rubber, carboxylated styrene butadiene rubber and their 70/30 blends using solvents, such as benzene, toluene and p-xylene [21]. These nanocomposites exhibited reduced absorption rate. This is because of increased polymer/filler interaction, which resulted in tortuosity of the path and the reduced transport area in polymeric membrane. Mathew and Kuriakose [33] investigated the extent to which the addition of lignin reduced the swelling of conventionally vulcanized natural rubber in aromatic solvents. The swelling behavior of isora/natural rubber composites was investigated by Mathew *et al.* [34]. They reported that solvent uptake in the composites was higher for aromatic solvents compared to that for aliphatic ones. Joseph *et al.* [35] reported that solvent uptake in palm microfiber filled natural rubber composites decreased with fiber content in NR composites. They observed also that the microfibers chemically modified by a silane coupling agent, benzoylation and resorcinol treatments exhibited lower solvent uptake than the unmodified fibers due to the increased interfacial adhesion. The transport coefficients of diffusion, sorption and permeation of PSP/NR composites have been studied by Sereena *et al.* [36] and were found to decrease with increase in PSP content due to increased stiffness imparted to the matrix by the addition of the filler. They also reported that composites containing the modified fibers had lower transport coefficient values. This behavior is obvious from the fact that the untreated PSP-filled NR composites have

-OH groups on the surface which lower the rubber-filler interactions giving rise to higher solvent uptake than their alkali-treated counterparts. Furthermore, Sonia and Dasan [37] have reported a similar behavior as mentioned above when cellulose microfiber was used to reinforce poly(ethylene-co-vinyl acetate) with and without alkali treatment.

In the years past, tremendous efforts have been made to develop, characterize, and utilize bio-based materials owing to their biodegradability, biocompatibility, and environmental friendliness. However, the main problem in the use of these fibers in polymer composites is the fiber-matrix adhesion. The matrix helps to transfer the load to the fibers through shear stresses at the interface. This could be achieved if adequate interfacial bonding exists between the matrix and the fibers. Inadequate interfacial adhesion at the interface means that the resulting composites have poor properties and their advantages cannot be fully utilized. These properties can be enhanced through chemical treatment using maleic anhydride, silanes, isocyanates,

alkali, permanganate and peroxide [38]. The significance of alkali treatment is the alteration of hydrogen bonding, and removal of lignin and other extractives from the fiber surface, resulting in a fiber with improved surface roughness and crystallites exposure [39]. Many researchers had reported on the improved interfacial bonding by the surface modification of the fibers through alkali treatment which enhanced the overall performance of the composites [40-43].

Solvent diffusion through bio-based polymer composites is expected to be influenced by polymer chain entanglement densities, the composition, and morphology of the composite. Another factor that could influence the diffusion process is the free volume of the polymer composite which is a function of the interaction between the polymers matrix and the reinforcement. Cates and White [44-46] were among the foremost to investigate the sorption behavior of water in blends of polyacrylonitrile and cellulose acetate, cellulose and silk, respectively. Angellier *et al.* [47] studied the swelling behavior of natural rubber reinforced with waxy maize starch nanocrystals. They observed that the solvent uptake of natural rubber decreased upon the addition of starch nanocrystals. Gopalan and Dufresne have reported natural rubber-based nanocomposites reinforced with chitin whiskers, produced by the solution casting method [48]. Molecular transport of aromatic solvents through oil palm microfiber-filled natural rubber composites have been investigated by Joseph *et al.* [35]. They reported that the solvent uptake was found to decrease with fiber loading in NR composites and that microfibers treated with the silane coupling agent showed a lower solvent uptake due to strong interfacial adhesion between fibers and silane coupling agent. Understandably, several researchers have reported the diffusion and sorption behavior of solvents in natural filler-filled polymer composites [36,37,49-52]. The influence of these natural fillers on the transport properties through polymeric membranes still needs additional information because of their environmental, industrial, and technological importance. Palm mesocarp fiber is one of oil mill industry wastes and its use as polymer filler will help in the proper management of the wastes.

The objective of the present study deals with the effort to understand the behaviour of the diffusion and transport properties of an aromatic solvent, benzene through palm mesocarp fiber (PMF)-filled polyethylene. The transport phenomenon of PMF/LDPE composites is studied at three different temperatures. The effects of filler content, filler particle size and alkali treatment are also studied. From the swelling data, matrix/solvent interaction parameter, mechanism of swelling, thermodynamic and activation parameters of swelling were estimated.

II. EXPERIMENTAL

A. Materials

Low density polyethylene (LDPE) granules (density: 0.915 g/cm³; melt flow index: 8 g/10 min measured at 190 °C using 2.16 kg standard weight; melting temperature: 110 °C) were purchased from Ceeplast Industries Ltd, Aba, Abia State, Nigeria. Palm mesocarp fiber (PMF) was obtained from Ada Palm Industry, Ohaji, Imo State, Nigeria. The solvent, benzene used in this study was purchased from a chemical vendor at Onitsha Main Market, Anambra State, Nigeria. Benzene was an analytical grade with a density of 0.865 g/cm³, which was used without further purification.

B. Purification/Treatment of Palm Mesocarp Fiber

To get rid of the remaining residual oil from the PMF which was retained after processing, a wet extraction method that uses hot water as described elsewhere, [53] was used. The fibers were thoroughly washed with distilled water to further remove impurities followed by sun drying for five days. The dried fibers were then mercerized with 5% solution of NaOH for about 2 h to avoid fiber degradation. Finally, the fibers were severally washed with distilled water to remove excess NaOH and dried at 80 °C for 12 h. The dried PMF was then pulverized and sieved to obtain different particle sizes.

C. Fabrication of PMF/LDPE Composites

Different mixtures of alkali treated palm mesocarp fiber (APMF) and untreated of palm mesocarp fiber (PMF) and low density polyethylene (LDPE) were melt blended in an injection machine with a screw speed of 50 rpm and at a temperature of 105–130 °C to obtain APMF/LDPE and PMF/LDPE composites. Composites with different fiber contents (10, 20, and 30 wt%) were prepared. After injection molding, the sheets were conditioned for 24 h at 70 °C and stored in a desiccator for further use.

D. Swelling Experiments

The swelling behavior of PMF/LDPE composites for both alkali-treated and untreated, prepared at three different particle sizes of PMF, namely; 425, 500, and 600 μm was studied at three different temperatures (40, 60, and 80 °C). Uniform size cut samples of dimensions 25×25 mm were used in swelling experiments. Initially, the samples were dried in a vacuum oven at room temperature for about 24 h. The original weight and thickness of the samples were measured before the experiments. Then, they were immersed in benzene (20 mL) in closed diffusion bottles, kept at a temperature in a thermostatic water bath. Periodically, the samples were removed from the bottles

and damp dried between filter papers to remove excess solvent on the sample surface. They were then weighed immediately using an electronic balance that measured to the nearest 0.0001 g. The samples were immediately placed back into the test bottles. The process was repeated until equilibrium sorption was reached.

III. RESULTS AND DISCUSSION

A. Swelling Data Analysis

A.1. Determination of Q_t

The equilibrium solvent uptake (Q_t mol %) was calculated using the following equation:

$$Q_t \text{ (mol \%)} = \frac{\text{Mass of solvent sorbed at a given time}}{\text{Molecular mass of the solvent/Initial mass of the polymer sample}} \times 100 \quad (1)$$

The experimental analysis was carried out using benzene and the sorption curves were obtained by plotting the percent solvent uptake, (Q_t %) against the square root of time. The solvent uptake of a polymer composite has been observed to be controlled by many factors, such as segmental mobility of the matrix, availability of free volume in the polymer matrix, the molecular weight of the solvent, nature of the filler, temperature, etc. [54].

B. Effect of Filler Content on Q_t

The effect of filler content on the transport properties of palm mesocarp fibre/low density polyethylene composites has been investigated in aromatic benzene and the results are displayed in Fig. 1. It is observed from the figure that there is a gradual decrease in solvent uptake with an increase in palm pressed fiber content. This may be attributed to the decrease in segmental mobility and reduction in the

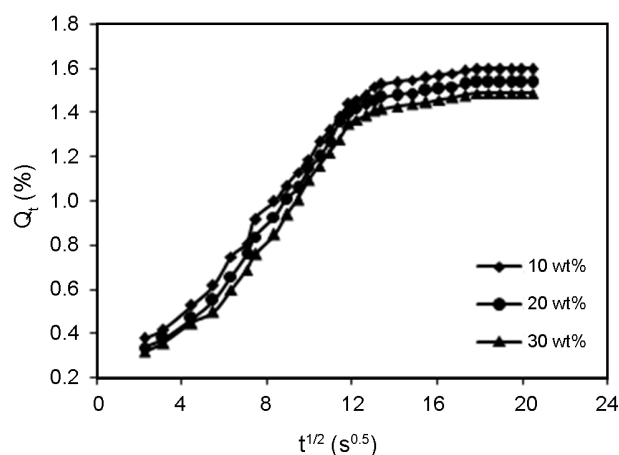


Fig. 1. Effect of filler content on Q_t of PMF/LDPE composites at 80 °C for 425 μm particle size.

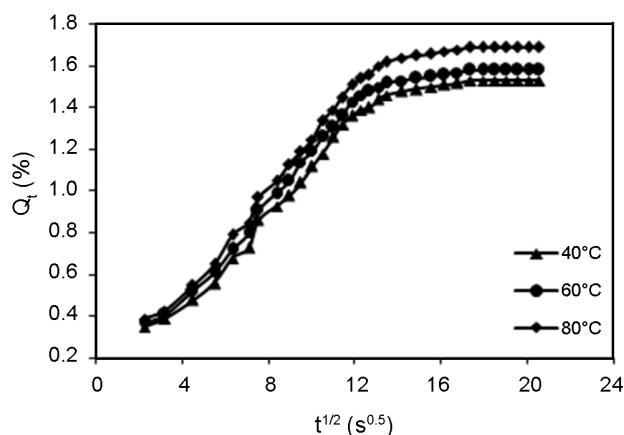


Fig. 2. Effect of temperature on Q_t of PMF/LDPE composites (10 wt%) for 500 μm particle size.

free volume of the matrix because of the addition of filler. With the increase in fibre content, there will be strong interaction between the fiber and matrix thus lowering the solvent penetration rate into the matrix. The decrease in solvent uptake in the filled polymer systems could also be explained in terms of the tortuosity of the path and the reduced transport area in the polymeric membrane in the presence of fillers. The degree of tortuosity is tied to the volume fraction of the filler and the shape and orientation of the particles [26].

C. Effect of Temperature on Q_t

The effect of temperature on the molecular transport through PMF/LDPE composites has been studied using benzene and it is presented in Fig. 2. The sorption experiments were conducted at 40, 60 and 80 °C. The rate of sorption uptake has been found to increase with the increase in temperature. This can be attributed to the increase in free volume because of the increase in segmental motion of the polymer matrix as well as the gain in kinetic energy by the solvent molecules which resulted in an increased number of collisions at the matrix phase.

Again, at a higher temperature, the viscosity of the solvent is reduced which in turn increases the rate of flow of solvent into the composites. It is reasonable to say that the rate of solvent uptake by the composite is time and temperature dependent. The increase in the solvent uptake by polymers and filled polymers with an increase in temperature had been reported by several researchers [36,55-57]. However, in some cases, there could be an opposite trend, that is, a decrease as the temperature increases. This decrease in equilibrium mol% uptake with increasing temperature could be attributed to the increasing rate of desorption at higher temperatures. Even if, there is an increase in free volume and segmental mobility at

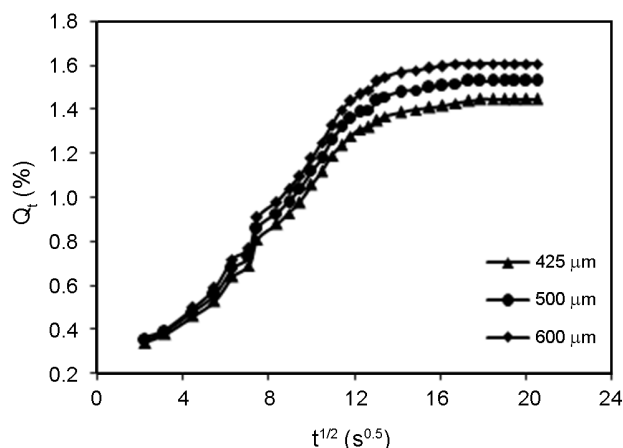


Fig. 3. Effect of particle size on Q_t of PMF/LDPE composites (10 wt%) at 40 °C.

higher temperatures, the rate of desorption overcomes the sorption process as it approaches equilibrium. The high desorption value could also be associated with the leaching out of additives.

D. Effect of Particle Sizes on Q_t

The benzene uptake by the different compositions of PMF/LDPE composites as a function of filler particle sizes is shown in Fig. 3. For the given blend composites, the solvent uptake was found to increase with an increase in particle size in the order: 600 μm > 500 μm > 400 μm . Probably the low viscous polyethylene provided better wetting of the smaller filler particles, which have larger surface area per unit volume, and thus more filler surface area is available for the matrix.

It is obvious that for a given polymer composite, solvent ingression depends on the variation in the interparticle spacing, filler distribution, presence of filler agglomeration and clusters, as well as the quality of filler adhesion to the matrix. Decreased interparticle spacing caused by reduced filler size may lead to a reduction in strain localisation around the filler, and enhanced interfacial adhesion between the polymer and filler is expected due to the strongly increased surface area.

E. Effect of Alkali Treatment on Q_t

The effect on the transport properties due to alkali treatment of the fibers of the composites in benzene is given in Fig. 4. The results show that the composites containing treated fibers has lower solvent uptake. Undoubtedly, alkali treatment improves the filler surface adhesive characteristics by removing natural waxy materials, hemicellulose, and artificial impurities by producing a surface topography [58], thus reducing the rate of transport

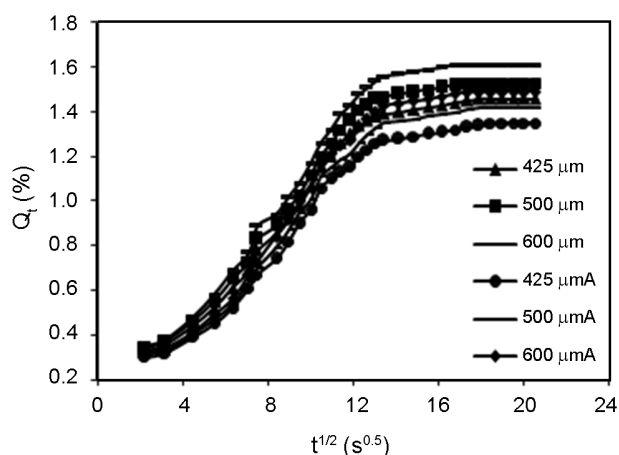


Fig. 4. Effect of filler treatment on Q_t of PMF/LDPE composites (20 wt%) at 60 °C.

of solvent through the interface. In the presence of a strong interface, fewer voids in the interfacial region and tighter packing with in the fiber/matrix network are possible which

make it difficult for solvent ingress. Hence, the distance travelled by the diffusing solvent molecules between two consecutive collisions decreases, resulting in a lowering of solvent uptake.

F. Swelling Properties

The swelling properties of low density polyethylene composites containing alkali treated and untreated oil palm fibers in terms of swelling coefficient and swelling index were determined as a function of benzene uptake using Eqs. (2) and (3), respectively.

$$\text{Swelling coefficient } (\beta) = \frac{\text{Mass of sample at equilibrium} - \text{Initial mass of sample}}{(\text{Initial mass of sample} \times \text{Density of solvent})} \tag{2}$$

$$\text{Swelling Index } (\%) = \frac{\text{Mass of sample at equilibrium} - \text{Initial mass of sample}}{(\text{Initial mass of sample})} \times 100 \tag{3}$$

TABLE I
SWELLING PARAMETERS AND PENETRATION RATE OF PMF/LDPE COMPOSITES AT DIFFERENT TEMPERATURES AND PARTICLE SIZES

Swelling parameters and penetration rate of PMF/LDPE composites													
Temperature (°C)	Filler (wt%)	Swelling index (%)						Swelling coefficient, β					
		425 μm		500 μm		600 μm		425 μm		500 μm		600 μm	
		APMF	PMF	APMF	PMF	APMF	PMF	APMF	PMF	APMF	PMF	APMF	PMF
40	10	10.53	11.31	11.08	11.93	11.70	12.56	1.54	1.65	1.62	1.75	1.71	1.84
	20	10.14	10.92	10.69	11.47	11.31	12.01	1.48	1.60	1.56	1.68	1.65	1.76
	30	09.91	10.69	10.37	11.15	10.92	11.70	1.45	1.56	1.53	1.63	1.60	1.71
60	10	10.92	11.70	11.47	12.32	12.09	13.03	1.60	1.71	1.68	1.80	1.78	1.91
	20	10.53	11.39	11.08	11.93	11.62	12.56	1.54	1.67	1.62	1.75	1.70	1.84
	30	10.14	11.00	10.61	11.51	11.54	12.17	1.48	1.61	1.55	1.69	1.63	1.78
80	10	11.39	12.48	11.93	13.18	12.48	14.04	1.67	1.83	1.75	1.93	1.82	2.05
	20	10.92	12.01	11.47	12.71	11.93	13.57	1.60	1.76	1.68	1.86	1.75	1.99
	30	10.69	11.62	11.15	12.17	11.70	12.79	1.56	1.70	1.63	1.78	1.71	1.87
Penetration rate ($\times 10^{-3} \text{ cm s}^{-0.5}$)													
Temperature (°C)	Filler (wt%)	425 μm		500 μm		600 μm							
		APMF	PMF	APMF	PMF	APMF	PMF						
40	10	2.37	2.45	2.49	2.56	2.62	2.69						
	20	2.33	2.41	2.45	2.51	2.59	2.64						
	30	2.24	2.28	2.37	2.41	2.51	2.55						
60	10	2.32	2.42	2.45	2.54	2.59	2.67						
	20	2.28	2.34	2.41	2.47	2.55	2.60						
	30	2.21	2.23	2.27	2.37	2.49	2.51						
80	10	2.32	2.38	2.46	2.34	2.59	2.65						
	20	2.26	2.32	2.39	2.46	2.51	2.60						
	30	2.20	2.23	2.33	2.37	2.46	2.49						

Table I shows the values of the swelling properties of benzene uptake by PMF/LDPE composites. It is clear from the table that the benzene uptake by the composites decreased as filler content increased in both modified and unmodified fiber systems. However, upon alkali treatment, the degree of swelling is further reduced. This may be linked to enhanced interfacial adhesion between the matrix polymer and the fiber. It is observed also that the swelling parameters are inversely related to decreasing in particle size and are temperature dependent. There is no doubt that small particle sizes offer good composite mix with improved interfacial bonding which promotes diffusion barrier of benzene into the PMF/LDPE composites. On the other hand, the increase in swelling properties with temperature observed is possible because at elevated temperature the cohesive forces of the solvent are reduced and the rate of molecular interchange is increased, leading to high rate of diffusion of solvent molecules into the composites.

G. Kinetic Parameters

Diffusion coefficient (D). The diffusion process is a kinetic phenomenon related to many other factors, such as size and shape of the solvent, the segmental mobility of the polymer, temperature, etc. The diffusion coefficient of a polymer sample kept in an excess amount of solvent can be calculated using Eq. (4), [21]:

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

where D is the diffusion coefficient, h is the thickness of the sample, t is the time and n is an integer. For short period of swelling a modified short-time equation can be used as shown below [59]:

$$Q_t / Q_\infty = (4/h)(Dt/\pi)^{1/2} \quad (5)$$

A plot of Q_t vs. $t^{1/2}$ gives a curve with the initial linear portion. Thus, D can be calculated on the rearrangement of Eq. (5) as shown in Eq. (6):

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

where h is the initial sample thickness, θ is the slope of the linear portion of the sorption curve of the plot of Q_t against $t^{1/2}$ and Q_∞ is the equilibrium absorption. The variation of diffusion coefficient for the different fiber contents at all the temperatures studied is given in Table II. The diffusion coefficient generally decreases as the temperature and fiber content increase. A small diffusion coefficient indicates that only a small amount of solvent

can be absorbed by the sample. The diffusion coefficient is lower for treated fiber and is the lowest for 400 μm particle size reinforced composites. The low diffusion coefficient values have been attributed to the low void content and high fiber/matrix adhesion. It is reasonable to state that there is no interaction between hydrophilic fibers and non-polar solvents, but fiber resistance, and hence low diffusion can be observed at high fiber contents. Diffusion coefficient is also related to penetration rate as shown in Eq. (7). The penetration rate may be expressed by the rate of the advancing swollen fronts which could be calculated from the linear portion of the sorption curve.

$$P_r = 2 \times \sqrt{\frac{D}{\pi}} \quad (7)$$

The penetration rate of the solvent benzene decreases with the increase in filler content as given in Table I. This is similar to the results obtained for diffusion coefficients calculated for the composites at various filler contents. However, penetration rate did not show any temperature dependence. This might be attributed to the fact that with increasing filler content and alkali treatment the penetration of solvent among macromolecular chains is prevented.

The variations of the diffusion and permeation with filler content and particle sizes in the composite were also evaluated and are presented in Figs. 5 and 6, respectively. The 10 wt% content has the highest diffusion and permeation values. This may be attributed to the difference in polarity between the solvent and filler used, which favored diffusion rate at low filler content (Fig. 5). The diffusion and permeation values were highest for 600 μm particle size (Fig. 6).

Sorption Coefficient (S). The sorption coefficient, which is the maximum saturation sorption value, is calculated using the equation [59,60]:

$$S = \frac{M_\infty}{M_p} \quad (8)$$

where S is the sorption coefficient, M_∞ is the mass of polymer sample at equilibrium, and M_p is the initial mass of polymer sample.

The sorption coefficient (S) values were obtained from the plateau regions of the equilibrium sorption plots and are presented in Table II. From the table, it is evident that the sorption coefficient increases with fiber content, filler particle size and temperature in the composite but decreases with treatment, indicating that sorption is somewhat restricted by the alkali treatment of filler. This observation agrees with the findings of Michaels *et al.* [61] who reported that the solubility of solvents in polymers

TABLE II
SORPTION VALUES OF PMF/LDPE COMPOSITES AT DIFFERENT TEMPERATURES AND MESH SIZES

		Kinetic parameters of PMF/LDPE composites at different temperatures and particle sizes											
Temperature (°C)	Filler (wt%)	Diffusion coefficient ($\times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$)						Sorption, S (%)					
		425 μm		500 μm		600 μm		425 μm		500 μm		600 μm	
		APMF	PMF	APMF	PMF	APMF	PMF	APMF	PMF	APMF	PMF	APMF	PMF
40	10	4.42	4.71	4.88	5.16	5.40	5.67	3.51	3.79	3.68	3.95	3.87	4.15
	20	4.26	4.46	4.72	4.93	5.27	5.47	3.59	3.87	3.79	4.06	4.01	4.26
	30	3.94	4.09	4.43	4.57	4.95	5.10	3.73	4.01	3.93	4.23	4.15	4.45
60	10	4.24	4.59	4.72	5.07	5.26	5.60	3.59	3.90	3.76	4.09	3.95	4.31
	20	4.08	4.31	4.56	4.79	5.09	5.31	3.73	4.04	3.93	4.23	4.12	4.45
	30	3.84	3.92	4.32	4.41	4.86	4.94	3.87	4.15	4.06	4.37	4.28	4.62
80	10	4.23	4.46	4.74	4.95	5.29	5.51	3.79	4.12	3.95	4.31	4.15	4.53
	20	4.02	4.23	4.48	4.77	4.97	5.33	3.87	4.26	4.06	4.51	4.23	4.81
	30	3.79	3.94	4.25	4.42	4.77	4.88	4.04	4.42	4.23	4.67	4.42	4.98

		Permeation coefficient, P ($10^{-6} \text{ cm}^2 \text{ s}^{-1}$)					
Temperature (°C)	Filler (wt%)	425 μm		500 μm		600 μm	
		APMF	PMF	APMF	PMF	APMF	PMF
40	10	15.51	17.85	17.96	20.38	20.90	23.53
	20	15.29	17.26	17.89	20.02	21.13	23.30
	30	14.70	16.40	17.41	19.33	20.54	22.69
60	10	15.22	17.90	17.75	20.74	20.78	24.14
	20	15.22	17.41	17.92	20.26	20.97	23.63
	30	14.86	16.27	17.54	19.27	20.80	22.82
80	10	16.03	18.37	18.72	21.33	21.95	24.96
	20	15.56	18.02	18.19	21.52	21.02	25.64
	30	15.31	17.41	17.98	20.64	21.08	24.30

increases with an increase in sorption temperature. Johnson and Thomas [57], also in their sorption studies reported that the sorption coefficient increased with increase in sorption temperature and in filler particle size too.

Permeation Coefficient (P). The permeation coefficient of a permeant in a polymer membrane depends on the diffusivity as well as solubility or sorption of the penetrant

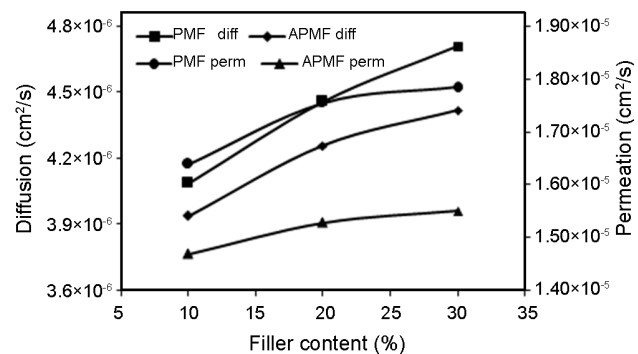


Fig. 5. Variation of diffusion and permeation with filler content.

in the polymer membrane. The permeation coefficient, P, can be evaluated using Eq. (9) [62]:

$$P = D \times S \tag{9}$$

where D is the diffusion coefficient and S is the sorption coefficient. The values of permeation coefficient are presented in Table II. The table indicates that as fiber

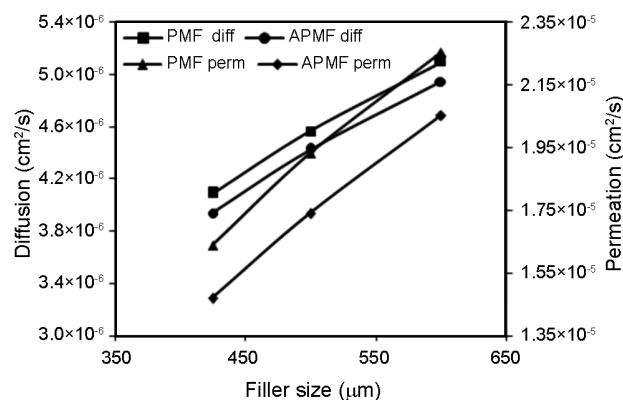


Fig. 6. Variation of diffusion and permeation with filler particle sizes.

content increases there is a corresponding decrease in the permeation coefficient values, showing that fibers restrict the movement of solvent into the matrix.

The permeation coefficient of the composites was also found to increase with increasing temperature and filler particle size. This may be due to the development of micro-cracks on the surface and in the bulk of the material at elevated temperatures. The permeation coefficient is lower for the alkali treated compared to the untreated and decreases as a function of filler content. This is because the presence of alkali-treated filler offers a better adhesion of filler and matrix which restricts the polymer chain mobility and the movement of solvent molecules between the polymer composites. The equilibrium solvent uptake has been found to closely follow the trend of diffusion, sorption, and permeation coefficients, indicating that the transport phenomenon is controlled by these three parameters [52,63].

G. Transport Mechanisms

In order to evaluate the mechanism of sorption, a fickian model is adopted, which is the most common and the easiest model for analysis. To investigate its applicability to this study, the results have been subjected to a time power law equation [64]:

$$Q_t/Q_\infty = kt^n \quad (10)$$

where Q_t and Q_∞ are the mol% sorption at time t , and equilibrium, respectively. k is a constant that depends upon the structural characteristics of the polymer, as well as its interaction with the solvent. The value of the exponent, n , indicates the nature of the transport mechanism. 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 $n=1$, it 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 rate of relaxation process. The n value of 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. Super-case II transport occurs when $n>1.0$; in that case, the release rate is time-dependent and it is pseudo-Fickian (less Fickian behavior) when $n<0.5$. Eq. (11) can be linearized by taking logarithms of both sides such that:

$$\text{Log}\left(\frac{Q_t}{Q_\infty}\right) = \log k + n \log t \quad (11)$$

The values of n and k , calculated by the regression analysis of the plot of $\log(Q_t/Q_\infty)$ against $\log t$, for the PMF/LDPE composites in benzene are shown in Table III. The values of n for treated and untreated samples in benzene are more close to 0.5 and may be regarded as less-Fickian [65]. The values of k , which decrease with increase in filler content, are higher for the untreated composites but show no dependence on particle size and temperature. This may be due to the higher interfacial adhesion between the treated fibers and the matrix.

H. Energy of Activation

The activation energy of diffusion was calculated from the Arrhenius Eq. (12) [66] based on diffusion studies of the composites at three different temperatures of 40, 60, and 80 °C:

TABLE III
VALUES OF n AND k (g/g/min⁻ⁿ) OF PMF/LDPE COMPOSITES.

Temperature (°C)	Filler (wt%)	Transport mechanism											
		n						k					
		425 μm		500 μm		600 μm		425 μm		500 μm		600 μm	
APMF	PMF	APMF	PMF	APMF	PMF	APMF	PMF	APMF	PMF	APMF	PMF	APMF	PMF
40	10	0.43	0.42	0.45	0.43	0.46	0.45	0.092	0.102	0.086	0.097	0.080	0.092
	20	0.46	0.45	0.47	0.46	0.46	0.47	0.080	0.088	0.076	0.085	0.080	0.081
	30	0.47	0.47	0.48	0.48	0.49	0.49	0.074	0.077	0.071	0.075	0.067	0.073
60	10	0.42	0.41	0.44	0.42	0.45	0.44	0.098	0.109	0.092	0.103	0.086	0.097
	20	0.44	0.44	0.45	0.45	0.47	0.46	0.089	0.093	0.083	0.090	0.079	0.085
	30	0.46	0.46	0.47	0.47	0.48	0.48	0.081	0.083	0.077	0.081	0.074	0.077
80	10	0.42	0.41	0.43	0.42	0.45	0.44	0.102	0.108	0.096	0.102	0.090	0.095
	20	0.43	0.44	0.45	0.45	0.46	0.47	0.092	0.094	0.087	0.088	0.083	0.082
	30	0.46	0.45	0.47	0.46	0.48	0.47	0.082	0.088	0.077	0.084	0.073	0.080

TABLE IV
VALUES OF ACTIVATION ENERGY (E_D AND E_p) OF PMF/LDPE COMPOSITES

Filler (wt%)	Energy of activation											
	$-E_D (\times 10^3 \text{kJ/mol})$						$E_p (\times 10^3 \text{kJ/mol})$					
	425 μm		500 μm		600 μm		425 μm		500 μm		600 μm	
	APMF	PMF	APMF	PMF	APMF	PMF	APMF	PMF	APMF	PMF	APMF	PMF
10	1.08	0.56	1.06	0.56	1.06	1.08	1.03	1.01	1.03	1.55	0.54	1.03
20	1.59	1.06	1.57	0.54	1.06	0.54	0.50	1.03	0.52	1.57	0.50	2.07
30	1.08	1.06	0.56	0.52	0.54	0.52	1.01	0.47	1.57	1.06	1.03	1.57

$$\text{Log } X = \text{Log} X_0 - \frac{E_x}{2.303RT} \quad (12)$$

where, X is P or D and X_0 represents P_0 or D_0 , which are constants; E_x is the activation energy, R, the universal gas constant and T, the absolute temperature. From the slopes of the Arrhenius plots of Log D and Log P against $1/T$, E_D , and E_p can be calculated by linear regression analysis. The values of E_D and E_p are given in Table IV. The activation energy of permeation, E_p , is greater than the activation energy of diffusion, E_D , for all compositions. The negative value of the activation energy suggests that the rise in the solution temperature does not favor benzene absorption into PMF/LDPE composites.

The negative value also indicates an exothermic reaction and the low value of the activation energy indicates that the absorption process of benzene adsorption into LDPE-filled composites may be by a physical absorption. It means that the rate-limiting step of benzene absorption into PMF/LDPE composites involved predominantly a physical process.

I. Thermodynamic Parameters

The thermodynamic parameters for diffusion, ΔH_0 and ΔS_0 , can be calculated using van't Hoff's equation:

$$\text{Log} K_s = \frac{\Delta S_0}{2.303R} - \frac{\Delta H_0}{2.303RT} \quad (13)$$

where K_s is the equilibrium sorption constant given by:

$$K_s = \frac{\text{(Number of moles of the solvent absorbed at equilibrium)}}{\text{(Mass of the composite sample)}} \quad (14)$$

The values of ΔH_0 and ΔS_0 were calculated by the regression analysis of the plots of Log K_s versus $1/T$ and are given in Table V. It can be seen from the table that the composites have positive values of ΔH_0 , indicating that the sorption is dominated by Henry's mode, that is, sorption proceeds through the creation of new sites or pores in the polymer [67]. All the ΔS_0 values are found to be negative and lie

in the range -34.49 to -39.94 J/mol/K. From this result, we know that solvent molecule is in the liquid state, even in the sorbed state within the polymer matrix. ΔS_s in this study did not show any relationship to the alkali treatment, filler content, and particle size. The negative entropy values indicate the orderliness of the sorbed molecule in the matrix [68].

J. Gibbs Free Energy of Sorption (ΔG_0)

The change in ΔG_0 for the aromatic solvent, benzene in filled LDPE composites was calculated using the equation:

$$\Delta G_0 = \Delta H_s - T\Delta S_s \quad (15)$$

The values of ΔH_0 and ΔS_0 earlier determined for the solvents were substituted into Eq. (15), and the calculated values of ΔG_0 are also shown in Table V. The calculated ΔG_0 was found to show a direct relationship to the filler content, particle size, and alkali treatment. The positive values of free energy is an indication of the spontaneity of the solubility of filled LDPE in the aromatic solvent calculated at 313 K.

K. Transport Kinetics

Polymer membrane undergoes a structural rearrangement during the process of diffusion and sorption of solvent molecules. This rearrangement induces a kinetic behavior which is dependent on the segmental mobility and availability of free volume within the polymer matrix. Hence, the transport of liquids through a polymer membrane is a rate-controlled kinetic process, which can be studied by first-order kinetic rate equation [26,69]:

$$\frac{dC}{dt} = K_1(C_\infty - C_t) \quad (16)$$

where K_1 is the first order rate constant, C_t and C_∞ are the concentrations at time t and at equilibrium time, respectively.

The above equation on integration gives:

TABLE V
VALUES OF ENTHALPY OF ABSORPTION (ΔH_0), THE ENTROPY OF ABSORPTION (ΔS_0), AND GIBBS FREE ENERGY (ΔG_0) OF PMF/LDPE COMPOSITES

Thermodynamic parameters of the PMF/LDPE composites												
Filler (wt%)	ΔH_0 ($\times 10^3$ kJ/mol)						$-\Delta S_0$ (J/mol/K)					
	425 μm		500 μm		600 μm		425 μm		500 μm		600 μm	
	APMF	PMF	APMF	PMF	APMF	PMF	APMF	PMF	APMF	PMF	APMF	PMF
10	1.74	2.26	1.70	2.25	1.48	2.57	38.65	36.66	38.62	36.23	38.82	34.81
20	1.69	2.16	1.64	2.36	1.22	2.78	39.33	37.23	39.07	36.20	39.94	34.49
30	1.73	1.94	1.68	2.00	1.57	2.00	39.44	38.14	39.24	37.59	39.13	37.16
Filler (wt%)	ΔG_0 ($\times 10^3$ kJ/mol)											
	425 μm		500 μm		600 μm							
	APMF	PMF	APMF	PMF	APMF	PMF						
10	13.84	13.73	13.78	13.60	13.63	13.47						
20	14.00	13.81	13.87	13.70	13.72	13.57						
30	14.08	13.88	13.96	13.76	13.82	13.63						

TABLE VI
VALUES OF KINETIC DATA ($K' \times 10^3 \text{ min}^{-1}$) OF PMF/LDPE COMPOSITES.

Temperature ($^{\circ}\text{C}$)	Filler (wt%)	First-order kinetic rate constants					
		425 μm		500 μm		600 μm	
		APMF	PMF	APMF	PMF	APMF	PMF
40	10	3.49	3.54	3.69	3.84	3.77	4.13
	20	3.78	4.05	3.96	4.19	4.18	4.57
	30	4.11	4.21	4.38	4.46	4.63	4.71
60	10	3.93	4.10	4.15	4.27	4.31	4.42
	20	4.21	4.50	4.44	4.80	4.84	5.16
	30	4.42	4.94	4.87	5.09	4.99	5.38
80	10	4.34	4.48	4.48	4.74	4.70	4.97
	20	4.73	5.27	5.26	5.41	5.42	5.75
	30	4.98	5.42	5.34	5.58	5.54	5.92

$$\text{Log}(C_{\infty} - C_t) = \text{Log}C_{\infty} - \frac{K_1 t}{2.303} \quad (17)$$

The plot of $\text{Log}(C_{\infty} - C_t)$ versus t gives a straight line with slope equal to $-K_1/2.303$. From the slope, the value of rate constant is determined and is presented in Table VI. The values were found to increase with the increase of fiber content, particle size and temperature, however, they were lower for modified composites. The rate constant values are a quantitative measure of the rate with which polymer composite absorbs the solvent. The increase of rate constant with temperature supports the fact that the rate of transport is favored by increasing temperature.

IV. CONCLUSION

The transport studies of anaromatic solvent, benzene through palm mesocarp fiber were carried out. Also, the influences of filler content, filler particle size and alkali treatment on the diffusion process were investigated. The diffusion coefficient was found to decrease with increase in palm mesocarp fiber content. Solvent transport mechanism was studied and in all cases mechanism of sorption followed the pseudo-Fickian trend. The swelling parameters and penetration rate were also evaluated and were found to be dependent on the filler concentration and treatment. Entropy, enthalpy, and free energy of sorption were estimated. It was found that the first-order rate equation

fitted the experimental data for PMF/LDPE composites/solvent system. It was found that temperature activated the diffusion process, which was supported by higher values of diffusion properties. However, the decrease in equilibrium solvent uptake at higher temperatures suggested the greater rate of desorption.

CONFLICT OF INTEREST

Authors declare that there is no conflict of interest.

REFERENCES

- [1] V. Tserki, P. Matzinos, and C. Panayiotou, "Novel biodegradable composites based on treated lignocellulosic waste flour as filler. part II. development of biodegradable composites using treated and compatibilized waste flour", *Compos., Part A: Appl. Sci. Manufact.*, vol. 37, no. 9, pp. 1231-1238, 2006.
- [2] A. Jahan, M.M. Rahman, H. Kabir, M.A. Kabir, F. Ahmed, M.A. Hossain, and M.A. Gafur, "Comparative study of physical and elastic properties of jute and glass fiber reinforced LDPE composites", *Int. J. Sci. Technol. Res.*, vol. 1, no. 10, pp. 68-72, 2012.
- [3] Z.H. Xu and Z.N. Kong, "Mechanical and thermal properties of short-coirfiber-reinforced natural rubber/polyethylene composites", *Mech. Compos. Mater.*, vol. 50, no. 3, pp. 353-358, 2014.
- [4] K. Joseph, S. Thomas, C. Pavithran, and M. Brahmakumar, "Tensile properties of short sisal fiber-reinforced polyethylene composites", *J. Appl. Polym. Sci.*, vol. 47, no. 10, pp. 1731-1739, 1993.
- [5] K. Joseph, S. Thomas, and C. Pavithran, "Effect of chemical treatment on the tensile properties of short sisal fibre-reinforced polyethylene composites", *Polymer*, vol. 37, no. 23, pp. 5139-5149, 1996.
- [6] S. Mohanty, S.K. Verma, and S.K. Nayak, "Dynamic mechanical and thermal properties of MAPE treated jute/HDPE composites", *Compos. Sci. Technol.*, vol. 66, no. 3, pp. 538-547, 2006.
- [7] J. George, S. Bhagawan, and S. Thomas, "Effects of environment on the properties of low-density polyethylene composites reinforced with pineapple-leaf fibre", *Compos. Sci. Technol.*, vol. 58, no. 9, pp. 1471-1485, 1998.
- [8] C.C. Teh, N.A. Ibrahim, and W.M.Z.W. Yunus, "Response surface methodology for the optimization and characterization of oil palm mesocarp fiber-graft-poly(butyl acrylate)", *Bioresources*, vol. 8, no. 4, pp. 5244-5260, 2013.
- [9] Y.Y. Then, N.A. Ibrahim, N. Zainuddin, H. Ariffin, and W.M.Z.W. Yunus, "Oil palm mesocarp fiber as new lignocellulosic material for fabrication of polymer/fiber biocomposites", *Int. J. Polym. Sci.*, vol. 2013, 2013.
- [10] H.D. Rozman, H. Ismail, R.M. Jaffri, A. Aminullah, and Z.A. Mohd Ishak, "Mechanical properties of polyethylene-oil palm empty fruit bunch composites", *Polym.-Plast. Technol. Eng.*, vol. 37, no. 4, pp. 495-507, 1998.
- [11] M. Rayung, N.A. Ibrahim, N. Zainuddin, W.Z. Saad, N.I.A. Razak, and B.W. Chieng, "The effect of fiber bleaching treatment on the properties of poly(lactic acid)/oil palm empty fruit bunch fiber composites", *Int. J. Mol. Sci.*, vol. 15, no. 8, pp. 14728-14742, 2014.
- [12] C.C. Eng, N.A. Ibrahim, N. Zainuddin, H. Ariffin, W.M.Z.W. Yunus, and Y.Y. Then, "Enhancement of mechanical and dynamic mechanical properties of hydrophilic nanoclay reinforced polylactic acid/polycaprolactone/oil palm mesocarp fiber hybrid composites", *Int. J. Polym. Sci.*, vol. 2014, 2014.
- [13] Y. Then, N. Ibrahim, N. Zainuddin, H. Ariffin, W.W. Yunus, and M.A. Rahman, "Effect of electron beam irradiation on the tensile properties of oil palm mesocarp fibre/poly(butylene succinate) biocomposites", *Int. J. Automot. Mechanic. Eng.*, vol. 10, pp. 2070, 2014.
- [14] H. Obasi, N. Iheaturu, F. Onuoha, C. Chike-Onyegbula, M. Akanbi, and V. Eze, "Influence of alkali treatment and fibre content on the properties of oil palm press fibre reinforced epoxy biocomposites", *Am. J. Eng. Res.*, vol. 3, no. 2, pp. 117-123, 2014.
- [15] N. Nordin, H. Ariffin, M. Hassan, N. Ibrahim, Y. Shirai, and Y. Andou, "Effects of milling methods on tensile properties of polypropylene/oil palm mesocarp fibre biocomposite", *Pertanika J. Sci. Technol.*, vol. 23, no. 2, pp. 325-337, 2015.
- [16] J. Landois-Garza and J. Hotchkiss, "Permeation of high-barrier films by ethyl esters. effect of permeant molecular weight, relative humidity, and concentration", *J. Plast. Film Sheeting*, 1993.
- [17] R.B. Seymour, *Engineering Polymer Sourcebook*, Texas: McGraw-Hill, 1990.
- [18] R.Y. Huang, *Pervaporation Membrane Separation Processes*, Amsterdam: Elsevier Science, 1991.
- [19] P. Kulkarni, S. Rajur, P. Antich, T. Aminabhavi, and M. Aralaguppi, "Transport studies on macromolecules used as drug carriers", *J. Macromol. Sci.-Rev. Macromol. Chem. Phys.*, vol. 30, no. 3-4, pp. 441-490, 1990.
- [20] H. Hopfenberg and D. Paul, "Transport phenomena in polymer blends", *Polym. blends*, vol. 1, pp. 445-487,

- 1978.
- [21] R. Stephen, S. Varghese, K. Joseph, Z. Oommen, and S. Thomas, "Diffusion and transport through nanocomposites of natural rubber (NR), carboxylated styrene butadiene rubber (XSBR) and their blends", *J. Membr. Sci.*, vol. 282, no. 1, pp. 162-170, 2006.
- [22] J. Wang and W. Wu, "Swelling behaviors, tensile properties and thermodynamic studies of water sorption of 2-hydroxyethyl methacrylate/epoxy methacrylate copolymeric hydrogels", *Eur. Polym. J.*, vol. 41, no. 5, pp. 1143-1151, 2005.
- [23] R.P. Kumar and S. Thomas, "Interfacial adhesion in sisal fiber/SBR composites: an investigation by the restricted equilibrium swelling technique", *J. Adhes. Sci. Technol.*, vol. 15, no. 6, pp. 633-652, 2001.
- [24] A.E. Mathai, R. Singh, and S. Thomas, "Transport of substituted benzenes through nitrile rubber/natural rubber blend membranes", *J. Membr. Sci.*, vol. 202, no. 1, pp. 35-54, 2002.
- [25] T. Johnson and S. Thomas, "Natural rubber/epoxidised natural rubber-25 blends: morphology, transport phenomena and mechanical properties", *J. Mater. Sci.*, vol. 34, no. 13, pp. 3221-3239, 1999.
- [26] S.C. George, S. Thomas, and K. Ninan, "Molecular transport of aromatic hydrocarbons through crosslinked styrene-butadiene rubber membranes", *Polymer*, vol. 37, no. 26, pp. 5839-5848, 1996.
- [27] H.B. Hopfenberg, *Permeability of Plastic Films and Coatings*, Springer, 1974.
- [28] R. McGregor, *Diffusion and Sorption in Fibers and Films*, London: Academic Press, 1974.
- [29] G. Unnikrishnan and S. Thomas, "Molecular transport of benzene and methyl-substituted benzenes into filled natural rubber sheets", *J. Appl. Polym. Sci.*, vol. 60, no. 7, pp. 963-970, 1996.
- [30] A. Ahmad, D.H. Mohd, and I. Abdullah, "Mechanical properties of filled NR/LLDPE blends", *Iran. Polym. J.*, vol. 13, pp. 173-178, 2004.
- [31] S. Lawandy and F. Helaly, "Diffusion of a volatile liquid in polychloroprene rubber", *J. Appl. Polym. Sci.*, vol. 32, no. 6, pp. 5279-5286, 1986.
- [32] R.B. Mesrobian and C.J. Ammondson, "Method of preparing mixtures of hydrocarbon polymer resins and linear polyamide resins and product thereof", Google Patents, 1963.
- [33] T.V. Mathew and S. Kuriakose, "Molecular transport of aromatic hydrocarbons through lignin-filled natural rubber composites", *Polym. Compos.*, vol. 28, no. 1, pp. 15-22, 2007.
- [34] L. Mathew, K. Joseph, and R. Joseph, "Swelling behaviour of isora/natural rubber composites in oils used in automobiles", *Bull. Mater. Sci.*, vol. 29, no. 1, pp. 91-99, 2006.
- [35] S. Joseph, S. Thomas, K. Joseph, U. Cvelbar, P. Panja, and M. Ceh, "Molecular transport of aromatic solvents through oil palm micro fiber filled natural rubber composites: role of fiber content and interface adhesion on transport", *J. Adhes. Sci. Technol.*, vol. 26, no. 1-3, pp. 271-288, 2012.
- [36] C. Sareena, M.T. Ramesan, and E. Purushothaman, "Transport studies of peanut shell powder reinforced natural rubber composites in aromatic solvents", *Polym. Compos.*, vol. 33, no. 10, pp. 1678-1692, 2012.
- [37] A. Sonia and K. Priya Dasan, "Solvent transport phenomenon of cellulose microfibril (CMF) reinforced poly(ethylene-co-vinyl acetate) (EVA) composites", *Fibers Polym.*, vol. 14, no. 11, pp. 1886-1893, 2013.
- [38] P. Wambua, J. Ivens, and I. Verpoest, "Natural fibres: can they replace glass in fibre reinforced plastics?," *Compos. Sci. Technol.*, vol. 63, no. 9, pp. 1259-1264, 2003.
- [39] A. Mohanty, M. Misra, and L.T. Drzal, "Surface modifications of natural fibers and performance of the resulting biocomposites: an overview", *Compos. Interfaces*, vol. 8, no. 5, pp. 313-343, 2001.
- [40] E. Sinha and S. Rout, "Influence of fibre-surface treatment on structural, thermal and mechanical properties of jute fibre and its composite", *Bull. Mater. Sci.*, vol. 32, no. 1, pp. 65-76, 2009.
- [41] M.S. Huda, L.T. Drzal, A.K. Mohanty, and M. Misra, "Effect of fiber surface-treatments on the properties of laminated biocomposites from poly(lactic acid) (PLA) and kenaf fibers", *Compos. Sci. Technol.*, vol. 68, no. 2, pp. 424-432, 2008.
- [42] M.Z. Rong, M.Q. Zhang, Y. Liu, G.C. Yang, and H.M. Zeng, "The effect of fiber treatment on the mechanical properties of unidirectional sisal-reinforced epoxy composites", *Compos. Sci. Technol.*, vol. 61, no. 10, pp. 1437-1447, 2001.
- [43] J. Rout, M. Misra, S. Tripathy, S. Nayak, and A. Mohanty, "The influence of fibre treatment on the performance of coir-polyester composites", *Compos. Sci. Technol.*, vol. 61, no. 9, pp. 1303-1310, 2001.
- [44] D.M. Cates and H.J. White, "Preparation and properties of fibers containing mixed polymers. I. polyacrylonitrile-cellulose acetate fibers", *J. Polym. Sci.*, vol. 20, no. 94, pp. 155-180, 1956.
- [45] D.M. Cates and H.J. White, "Preparation and properties of fibers containing mixed polymers. II. polyacrylonitrile-cellulose fibers", *J. Polym. Sci.*, vol. 20, no. 94, pp. 181-195, 1956.

- [46] D.M. Cates and H.J. White, "Preparation and properties of fibers containing mixed polymers. III. polyacrylonitrile-silk fibers", *J. Polym. Sci.*, vol. 21, no. 97, pp. 125-138, 1956.
- [47] H. Angellier, S. Molina-Boisseau, L. Lebrun, and A. Dufresne, "Processing and structural properties of waxy maize starch nanocrystals reinforced natural rubber", *Macromolecules*, vol. 38, no. 9, pp. 3783-3792, 2005.
- [48] K. Gopalan Nair and A. Dufresne, "Crab shell chitin whisker reinforced natural rubber nanocomposites. 2. mechanical behavior", *Biomacromolecules*, vol. 4, no. 3, pp. 666-674, 2003.
- [49] M. Jacob, K. Varughese, and S. Thomas, "A study on the moisture sorption characteristics in woven sisal fabric reinforced natural rubber biocomposites", *J. Appl. Polym. Sci.*, vol. 102, no. 1, pp. 416-423, 2006.
- [50] T.V. Mathew and S. Kuriakose, "Molecular transport of aromatic hydrocarbons through lignin-filled natural rubber composites", *Polym. Compos.*, vol. 28, no. 1, pp. 15-22, 2007.
- [51] M. Jacob, K. Varughese, and S. Thomas, "Water sorption studies of hybrid biofiber-reinforced natural rubber biocomposites", *Biomacromolecules*, vol. 6, no. 6, pp. 2969-2979, 2005.
- [52] C. Sareena, M. Sreejith, M. Ramesan, and E. Purushothaman, "Transport properties of coconut shell powder (CSP)-reinforced natural rubber composites in aromatic solvents", *Polym. Bull.*, vol. 72, no. 7, pp. 1683-1702, 2015.
- [53] V. Subramaniam, N.R. Menon, H. Sin, and C.Y. May, "The development of a residual oil recovery system to increase the revenue of a palm oil mill", *J. Oil Palm Res.*, vol. 25, no. 1, pp. 116-122, 2013.
- [54] J. Manikath, B. Francis, M. Jacob, R. Stephen, S. Joseph, S. Jose, and S. Thomas, "Interaction of n-alkanes with crosslinked cis-1, 4-polybutadiene", *J. Appl. Polym. Sci.*, vol. 82, no. 10, pp. 2404-2413, 2001.
- [55] I.O. Igwe and O.E. Ezeani, "Studies on the transport of aromatic solvents through filled natural rubber", *Int. J. Polym. Sci.*, vol. 2012, pp. 1-11, 2012.
- [56] H.C. Obasi, O. Ogbobe, and I.O. Igwe, "Diffusion characteristics of toluene into natural rubber/linear low density polyethylene blends", *Int. J. Polym. Sci.*, vol. 2009, pp. 1-6, 2009.
- [57] T. Johnson and S. Thomas, "Effect of epoxidation on the transport behaviour and mechanical properties of natural rubber", *Polym.*, vol. 41, no. 20, pp. 7511-7522, 2000.
- [58] A. Bledzki and J. Gassan, "Composites reinforced with cellulose based fibres", *Prog. Polym. Sci.*, vol. 24, pp. 54, 1999.
- [59] J. Crank, *The Mathematics of Diffusion*, 2d Ed: Clarendon Press, 1975.
- [60] G. Unnikrishnan, S. Thomas, and S. Varghese, "Sorption and diffusion of aromatic hydrocarbons through filled natural rubber", *Polymer*, vol. 37, no. 13, pp. 2687-2693, 1996.
- [61] A.S. Michaels, W. Vieth, A.S. Hoffman, and H.A. Alcalay, "Structure-property relationships for liquid transport in modified polypropylene membranes", *J. Appl. Polym. Sci.*, vol. 13, no. 4, pp. 577-598, 1969.
- [62] T.M. Aminabhavi and H.T. Phayde, "Molecular transport of alkanes through thermoplastic miscible blends of ethylene-propylene random copolymer and isotactic polypropylene", *J. Appl. Polym. Sci.*, vol. 55, no. 9, pp. 1335-1352, 1995.
- [63] P. Visakh, S. Thomas, K. Oksman, and A.P. Mathew, "Cellulose nanofibres and cellulose nanowhiskers based natural rubber composites: diffusion, sorption, and permeation of aromatic organic solvents", *J. Appl. Polym. Sci.*, vol. 124, no. 2, pp. 1614-1623, 2012.
- [64] L.M. Lucht and N.A. Peppas, "Transport of penetrants in the macromolecular structure of coals. V. Anomalous transport in pretreated coal particles", *J. Appl. Polym. Sci.*, vol. 33, no. 5, pp. 1557-1566, 1987.
- [65] J. Wang, W. Wu, and Z. Lin, "Kinetics and thermodynamics of the water sorption of 2-hydroxyethyl methacrylate/styrene copolymer hydrogels", *J. Appl. Polym. Sci.*, vol. 109, no. 5, pp. 3018-3023, 2008.
- [66] U. Aithal, T. Aminabhavi, and P. Cassidy, "Barrier Polymer and Structures", CS Publications, vol. 423, 1990.
- [67] K. Manjula, "Sorption and diffusion of substituted aromatic organic penetrants into carboxylic acid-based chain extended polyurethane membranes", *J. Chem. Eng. Data*, vol. 55, no. 6, pp. 2271-2278, 2010.
- [68] S. Harogoppad and T. Aminabhavi, "Diffusion and sorption of organic liquids through polymer membranes. II. neoprene, SBR, EPDM, NBR, and natural rubber versus n-alkanes", *J. Appl. Polym. Sci.*, vol. 42, no. 8, pp. 2329-2336, 1991.
- [69] S.B. Harogoppad, T.M. Aminabhavi, and R.H. Balundgi, "Sorption and transport of aqueous salt solution in polyurethane membrane at 25, 44, and 60 °C", *J. Appl. Polym. Sci.*, vol. 42, no. 5, pp. 1297-1306, 1991.

