

Transport of n-Hexane through Carbonized Oil Palm Empty Fruit Bunch Powder Filled Polypropylene/Natural Rubber Biocomposites

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Abstract The transport behaviour of n-hexane through carbonized oil palm empty fruit bunch powder filled polypropylene/natural rubber has been studied at three different temperatures (313, 333, and 353 K) by gravimetric test method. The effect of MAPP as compatibilizer on the sorption properties of the thermoplastic elastomer biocomposites was also investigated. Diffusion, sorption, and permeation coefficients of the biocomposites showed that the uncompatibilized blends sorbed more n-hexane than the compatibilized blends. Equilibrium sorption was found to decrease with increasing filler loading for both compatibilized and uncompatibilized blends due to the fillers' reinforcing ability. The calculated enthalpies of sorption (ΔH_s), Gibbs free energies of sorption (ΔG_s) and Arrhenius activation energies (E_D and E_P) were all positive. This indicates the non-spontaneity of the solubility of carbonized oil palm empty fruit bunch powder filled polypropylene/natural rubber in n-hexane solvent at 313 K. The mode of transport of n-hexane into filled polypropylene/natural rubber was also found to be Fickian and dominated by Henry's model with endothermic contributions.

Keywords Transport mechanism, n-hexane, Compatibilizer, Polymer blends, Biocomposites

1. Introduction

The study of diffusion, sorption and permeation in polymer blend structures provides a valuable means for additional characterization of polymer blends. These processes are the limiting factors affecting polymer end-use application because these processes may lead to destruction in polymer properties. The diffusion processes in polymer are normally affected by the following factors: the degree of solvent-polymer interactions and solvent properties such as hydrogen bonding, polarity, solubility parameter, nature of additives/fillers among others. The diffusion and transport through polymer blends depend upon its composition, miscibility and phase morphology. The blends may be either homogenous or heterogeneous. In homogeneous blends, the diffusion process is influenced by the interaction between the component polymers[1-3], while in heterogeneous blends interfacial phenomena and the rubbery or glassy nature of the phases are important[4]. The understanding of the transport mechanism of solvents through polymeric blends also helps scientists in the selection of polymer materials and processing considerations to minimize sorption level in

potential barrier polymers. Thus, the basic transport phenomenon plays a prominent role in many industrial and engineering applications of polymers[5-6].

Thermoplastic elastomers (TPEs) are a new class of thermoplastic materials which their properties can be more easily tailored than the block copolymers by simply changing the ratio of the rubber to plastic in the blend. These materials are normally phase separated systems in which one phase is rubbery at room temperature while the other is hard and solid. They possess the elasticity of a rubber and the thermoplasticity of a plastic, yet retain unique features of its components such as better ultraviolet and ozone resistance, solvent resistance and high deformation temperature compared to elastomers[7]. As a result, many commercial TPEs have been developed for various applications in the automotive, electrical and medical industries[8]. The field of TPEs has grown up along two distinctly different product types. The first type consists of a simple blend of the components and in the second type, the rubber phase is dynamically vulcanized which gives rise to a thermoplastic vulcanizate[9]. Many literature sources have revealed excellent report on the diffusion and sorption processes in elastomer/thermoplastic blends. Thus, transport studies have been conducted on blends of polypropylene/nitrile rubber [10], polystyrene/natural rubber[11].

Obasi et al.,[12] investigated the diffusion characteristic of toluene into natural rubber/linearlow density polyethylene

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with the effects of blend ratio on the diffusion, sorption, and permeation coefficients. The 75/25 NR/LLDPE blend exhibited the highest amount of molar percentage uptake of toluene at the temperatures studied. The diffusion co-efficient, and permeation obtained for toluene in 50/50 and 60/40 NR/LLDPE blends were found to increase with an increase in sorption temperature. The transport of toluene through most of the blends was anomalous, although at 35 °C, the transport of toluene through the 60/40 blend was Fickian and at 55°C, pseudo-Fickian. The effects of fillers on the transport characteristics of TPEs have immerse interest to scientist, and report on the effect of fillers on the diffusion and sorption processes exist[13,14]. Fillers are materials that are added to a polymer formulation to lower the compound cost or to improve its properties. Such materials have reinforcing power which enhances the modulus and any failure property. Example of such fillers are the natural fibres e.g. kenaf, jute, coconut shell, oil palm, corn hubs which are eco-friendly[15], carbon black, clay etc. The major disadvantage of incorporating these fillers into a synthetic polymer is their incompatibility[16,17]. Natural fibres are hydrophilic in nature whereas synthetic polymers are hydrophobic. The hydrophilic characteristics of natural fibres leads to a high moisture absorption, causing dimensional change in the fibre and resulting in the swelling of manufactured composites[18].

Bonstran and Danenberg[19] presented the equilibrium swelling data of filled natural rubber and a number of synthetic rubbers in a variety of solvent. They observed that fillers like carbon black caused a reduction in swelling of the membrane and which commensurate with the volume loading in filler. Investigation on the swelling properties of filled natural rubber/linear low-density polyethylene blends in toluene has been carried out[20]. It was found that the swelling index decreased with increase in filler loading and this was attributed to the increase in the cross – link density of the blend. Studies on the molecular transport of aromatic solvents through microcomposites of natural rubber (NR), carboxylated styrene butadiene rubber (XSBR) and their blends have been carried out[21]. They concluded that the filled samples showed reduced swelling rate owing to the tortuosity of the path. A dramatic decrease in diffusion coefficient of filled samples was also observed. However, blend system exhibited unexpected diffusion behaviour because of the immiscibility of the two components; the activation energy needed for diffusion of penetrant was found to be higher for filled virgin polymers.

Furthermore, the effects of filler loading on properties of polypropylene–natural rubber–recycle rubber powder (PP–NR–RRP) composites have been studied[22]. Carbon black, silica and calcium carbonate were used as fillers in the composites. Carbon black filled PP–NR–RRP composites exhibit lowest resistance toward swelling in ASTM oil No.3 than calcium carbonate and silica filled PP–NR–RRP composites. Onyeagoro and Enyiegbulam[23] studied the sorption characteristics of dynamically vulcanized

polypropylene/epoxidized natural rubber blend filled with carbonized Dika nutshell. They observed that the mass of toluene sorbed by carbonized dika nutshell filled PP/ENR blends showed an initial increasing trend until maximum absorption is reached, after which equilibrium sorption is reached. Non-vulcanized PP/ENR exhibited the least sorption resistance to toluene. Akporhonor et al.[24] studied the equilibrium sorption properties of palm kernel husk and N330 filled natural rubber vulcanizate as a function of filler volume fraction. They observed that unvulcanized rubber dissolved in a suitable solvent while vulcanized rubber can only swell to an extent determined by the crosslinking density. Vulcanizate with higher concentration of palm kernel husk tends to be more soluble in organic solvent than vulcanizate with higher concentration of carbon black.

Filler treatment is the process used to alter the surface chemistry, the energy and the degree of interaction at the filler interface. This leads to enhancement of the mechanical properties. Apart from these benefits, the surface treatment of fillers increases the compatibility, dispersibility and processibility. Many studies have been conducted on the physical and chemical methods to improve the adhesion between the fibre and matrix through a modification of then fibre and/polymer matrix[25]. Effect of treated filler has been found to improve interfacial bonding[26]. In the presence of coupling agent, the water uptake was reduced as better interfacial bonding was established. Transport and mechanical properties were also reported to improve by the use of treated fibres[27].

In the present paper, blends of natural rubber and polypropylene have been prepared using carbonized oil palm empty fruit bunch (OPEFB) powder as filler. The diffusion of n-hexane, an aliphatic solvent, through the blends has been investigated and the mechanism of sorption through the blends was determined. The diffusion, sorption and permeation coefficients were calculated. Also, the effects of maleic anhydride-graft-polypropylene (MAPP) compatibilizer and temperature on the diffusion and sorption processes of the thermoplastic elastomer biocomposites were studied. The analysis of diffusion of n-hexane through carbonized OPEFB powder filled natural rubber/polypropylene thermoplastic elastomer biocomposites has not been reported in the scientific literature to our knowledge. The present study affords a very good example of how compatibilizers affect the diffusion of solvents into polymeric blends. The effects of filler loading on the solvent diffusion parameters are also reported.

2. Experimental

2.1. Materials

The polypropylene used in this study was purchased from Rovet chemicals limited, Benin-city, Nigeria. It has a melt flow index of 3.5 dg/min, density of 0.905 g/cm³ and specific gravity of 0.905. Natural rubber conforming to the Nigeria

Standard Rubber Grade 10 (NSR10) of density 0.92 g/cm³ and specific gravity of 0.92 was used in this study. It was purchased from Iyayi Rubber Factory, Egba, Benin City while other vulcanizing ingredients used such as Zinc Oxide (ZnO), stearic acid, sulphur, MBT (mercaptobenzoylthiazole), TMTD (tetramethylthiuram disulphide) and wax were purchased from a chemical store in Port Harcourt, Nigeria. Oil palm empty fruit bunch (OPEFB) powder was used as filler in the blending of the polypropylene/natural rubber composites. The OPEFB which was collected from Adapalm Nigeria limited, Ohaji, Imo State, Nigeria, is among the waste produced in the processing of palm oil. The oil palm empty fruit bunch was prepared as stated by Ewulonu and Igwe[28]. The prepared fibre was then carbonized at 400°C and sieved through a mesh size of 0.15 mm. The fine powder was collected and used for the blending. Maleic anhydride-graft-polypropylene (MAPP) used as the compatibilizing agent in this study is a product of Sigma-Aldrich Chemie GmbH, Germany and was used as received.

2.2. Preparation of the Thermoplastic Elastomer Biocomposites

Table 1. Compounding recipe for PP/NR/OPEFB biocomposites

Materials	Uncompatibilized (pphr)	Compatibilized (pphr)
Natural rubber (NR)	40	40
Polypropylene (PP)	60	60
Zinc oxide	5	5
Stearic acid	2	2
OPEFB powder	0, 10, 20, 30	10, 20, 30
Sulphur	3	3
MBT	0.5	0.5
TMTD	1	1
Wax	4	4
MAPP*	-	5

pphr – part per hundred resin
5% of OPEFB powder

Two different sets of polypropylene/natural rubber blend biocomposites were prepared. Firstly, polypropylene/natural rubber/oil palm empty fruit bunch (PP/NR/OPEFB) composites were prepared at various filler loadings. Secondly, PP/NR/OPEFB composites in the presence of a compatibilizer, maleic anhydride – graft – polypropylene (MAPP) were prepared. Blends of PP and NR were prepared by melt mixing, carried out in a Brabender Plastic order model PLE 331. Polypropylene was first melted for 2 mins at 170°C with a rotational speed of 80 rpm, before the addition of natural rubber. The compatibilizer and OPEFB powder were added later and mixing continued for 8 min. The rubber blend produced was then transferred to a two-roll mill (set at 170°C, rotating at 35 rpm with a nip clearance of 2.5 mm) which converted it from an irregularly shaped mass to flat sheets. The temperature of the mill was reduced from 170°C to 90°C before the introduction of the vulcanizing agent and accelerators to prevent premature curing of the compound

mix. The blends were compression moulded at 140°C with a pressure of 10MPa for 12 mins. Samples for testing with 2 mm thickness were then punched out from these moulded sheets. The formulation used in preparing the blends is presented in Table 1.

2.3. Procedure for Sorption Test

Blends of uniform size were cut and weighed on an analytical balance having an accuracy of 0.001g. The cut samples were put into sample bottles with covers. 20 ml of n-hexane was poured into each of the sample bottles. The bottles were then placed in a thermostatically controlled water bath at 313 K and were equilibrated for different time intervals. At the expiration of the specified time, the blends were removed from the sample bottles, wiped free of adhering n-hexane, weighed using the analytical balance and the difference between the dry film and the wet film was obtained. The following time intervals were investigated: 5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 90, 100, 120, 140, 160, 180 minutes. Care was taken to ensure that the solvent molecules absorbed by the film were not removed during the process of wiping using filter paper. The experiments were further repeated at 333 and 353K. Each weighing was completed in less than 40 seconds, so as to keep the error due to solvent evaporation from the sample surface at a minimum[29].

3. Results and Discussion

The uptake of n-hexane by compatibilized and uncompatibilized oil palm empty fruit bunch powder-filled polypropylene/natural rubber vulcanizates have been investigated by gravimetric test method. The sorption data obtained for the filled thermoplastic elastomers at the different temperatures (313, 333, and 353 K) investigated were expressed as the molar percentage uptake (% Q_t) of n-hexane per gram of PP/NR/OPEFB biocomposites. % Q_t was calculated using the following equation[30,31]

$$\%Q_t = \frac{\text{Mass of hexane absorbed}}{\text{Molecular weight of hexane} / \text{Initial mass of the blend}} \times 100 \quad (1)$$

The molar percentage uptake (% Q_t) at any particular temperature and carbonized OPEFB powder loading were plotted against the square root of time (\sqrt{t}) for both compatibilized and uncompatibilized blends. These plots are illustrated in Figures 1 – 6. In all the figures, the mass of hexane sorbed showed an initial increasing trend until maximum absorption was attained, after which equilibrium absorption was reached at which time, the mass of the absorbed hexane remained constant. The results also showed that at any particular sorption temperature and filler loading, the compatibilized blend sorbed less hexane than the uncompatibilized blend. This is as a result of better dispersion of fillers and mixing of blends caused by the presence of maleic anhydride-graft-polypropylene (MAPP) which created a tortuous path for the n-hexane permeating molecules. Lowering of equilibrium swelling in fibre filled

samples indicates excellent fibre-polymer adhesion[32]. Das[33] reported that restricted equilibrium swelling is a true measure of adhesion between short fibres and rubber.

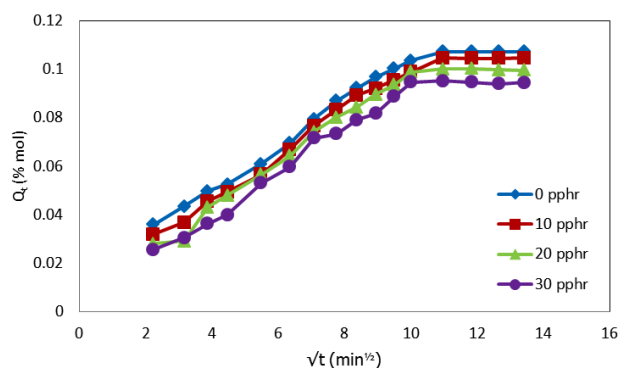


Figure 1. Plot of molar percentage uptake (% Q_t) versus square root of time (\sqrt{t} , $\text{min}^{1/2}$) for uncompatibilized PP/NR blends filled with different levels of carbonized OPEFB powder at 313 K

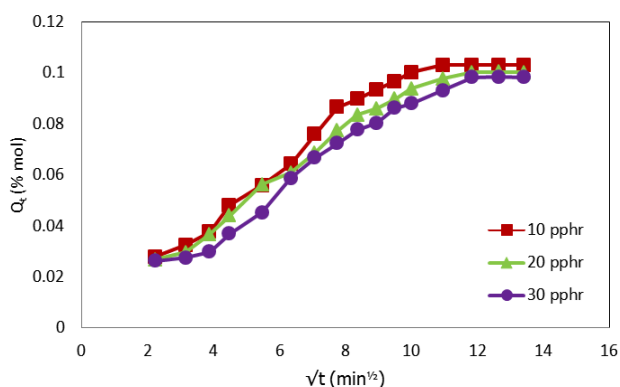


Figure 2. Plot of molar percentage uptake (% Q_t) versus square root of time (\sqrt{t} , $\text{min}^{1/2}$) for compatibilized PP/NR blends filled with different levels of carbonized OPEFB powder at 313 K

Careful observation of Figures 1 – 6 also reveals that the values of equilibrium sorption decreased with increase in filler loading. The decreasing equilibrium sorption value of the carbonized OPEFB powder filled PP/NR (for both compatibilized and uncompatibilized) blends with increasing filler loading indicates the fillers' reinforcing ability and suggests a swelling restriction of the rubber matrix due to the presence of the filler. The decrease in sorption with increasing filler concentration observed in the blends may be accounted on the basis of the fact that each filler particles behaves as an obstacle to the diffusing molecules. As concentration of filler increases in the thermoplastic elastomer matrix, more and more obstacles are created to diffusing molecules which ultimately reduce the amount of penetrant solvent. For the two blends investigated at different sorption temperature, equilibrium sorption decreases with increases in filler loading. It is important to note that the solvent – filler interaction can be a barrier to the sorption properties of the biocomposites. Ewulonu and Igwe[28] reported that OPEFB filled high density polyethylene composite showed an increase in water absorption as the filler content increased as a result of the hydrophilic nature of OPEFB. Therefore, the solvent – filler

interaction between n-hexane and carbonized OPEFB is poor and expectedly, the decrease in sorption as the filler loading increased for all the biocomposites at all temperatures studied.

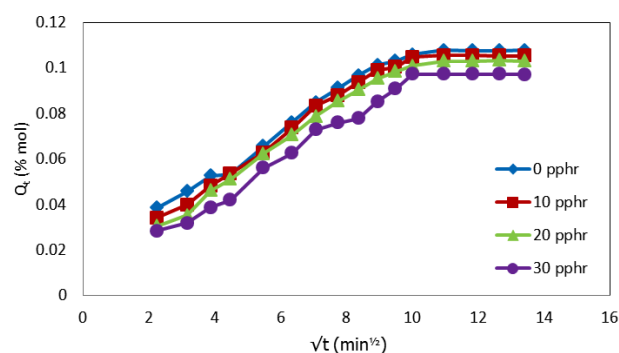


Figure 3. Plot of molar percentage uptake (% Q_t) versus square root of time (\sqrt{t} , $\text{min}^{1/2}$) for uncompatibilized PP/NR blends filled with different levels of carbonized OPEFB powder at 333 K

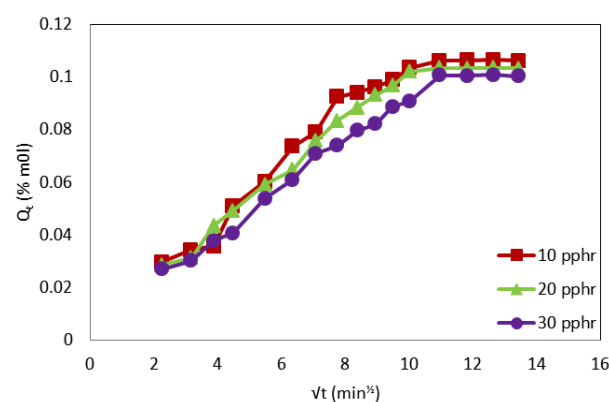


Figure 4. Plot of molar percentage uptake (% Q_t) versus square root of time (\sqrt{t} , $\text{min}^{1/2}$) for compatibilized PP/NR blends filled with different levels of carbonized OPEFB powder at 333 K

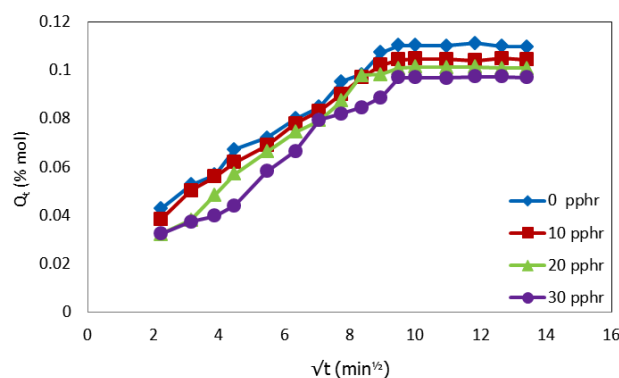


Figure 5. Plot of molar percentage uptake (% Q_t) versus square root of time (\sqrt{t} , $\text{min}^{1/2}$) for uncompatibilized PP/NR blends filled with different levels of carbonized OPEFB powder at 353 K

Furthermore, analysis of the dependence of equilibrium absorption on temperature and time, illustrated in Figure 7 and 8 shows that sorption values at 313K had the least mass of n-hexane sorbed with much longer equilibrium absorption time while 353K had the highest mass of n-hexane sorbed at faster equilibrium absorption time. The decrease in equilibrium absorption time with increase in temperature is

because temperature significantly affects the rate of chemical reaction. Increase in temperature increases the rate at which the solvent penetrates through the blends. Thus, higher equilibrium values at closer time intervals. This phenomenon can also be attributed to the fact that most common polymers tend to be more unstable at higher temperatures, as a result, build up tendency to swell easily or even dissolve.

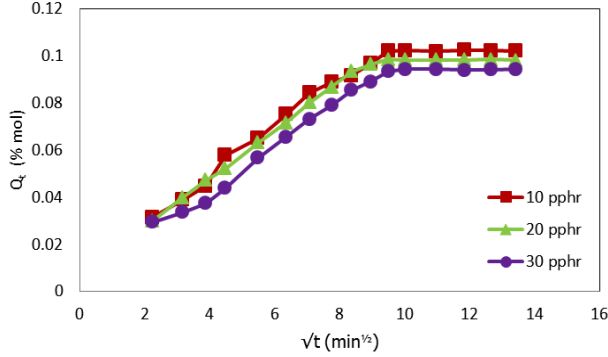


Figure 6. Plot of molar percentage uptake (% Q_t) versus square root of time (\sqrt{t} , min^{1/2}) for compatibilized PP/NR blends filled with different levels of carbonized OPEFB powder at 353 K

3.1. Diffusion Coefficient (D)

The diffusion coefficient of a solvent molecule through a polymer membrane can be obtained using Fickian's second law of diffusion[31].

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

where h is the blend thickness, θ is the slope of the initial linear portion of the plot of Q_t against \sqrt{t} , and Q_∞ is the equilibrium absorption. The diffusion coefficient values (D) are given in Table 2 along with other sorption parameters. From Table 2, it is evident that the D values for the uncompatibilized blends decreased with increase in filler concentration. Contrarily, the compatibilized blends showed an increase in the diffusion coefficient as the filler content increased for all temperatures studied. This can be attributed to the increased heterogeneity occasioned by the increasing filler content in the compatibilized blends. Note that diffusion process is influenced by interfacial phenomenon and the rubbery or glassy nature of phases for heterogeneous blends[4] and the diffusion and transport through polymer blends depend upon its composition, miscibility and phase morphology. However, it is significant to note that the values of diffusion coefficient for the compatibilized blends are much lower than that of the uncompatibilized blends. For the temperatures studied, the D values for both compatibilized and uncompatibilized blends were found to have the least value at 333K. The same order was not observed for 30 pphr uncompatibilized, where D increased with increases in temperature. This is an indication that there was no strong dependence of D values on temperature at any filler concentration. This is in agreement with the findings of Obasi *et al.*[12], who reported that no dependence of diffusion coefficient, D on temperature for the amount of NR

and LLDPE in their blends was observed. Contrary to this, Igwe *et al.*[34] found that the diffusion coefficients of solvents (benzene, toluene, and xylene) into polypropylene film increased with increases in sorption temperature. While Igwe and Ezeani,[35] reported that D values generally decrease with increase in sorption temperature of snail shell powder filled natural rubber for any particular solvent and filler particle size. It is important to note that diffusivity in a given polymer system whether it is rubbery or glassy polymers, polymer blends, graft polymers, polymer composites or thermoplastic elastomers varies from one polymer system to another.

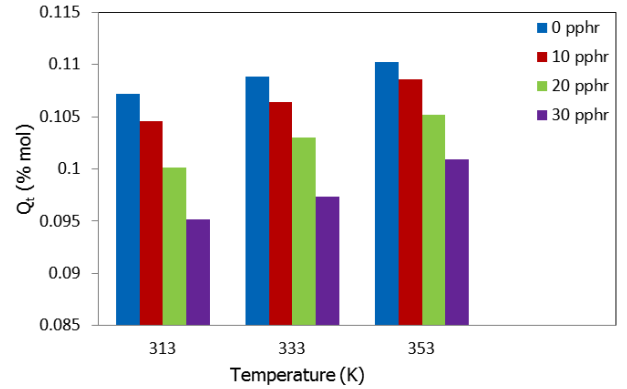


Figure 7. Dependence of equilibrium n-hexane uptake Q_t (% mol) on sorption temperature (K) for uncompatibilized PP/NR blends filled with different levels of carbonized OPEFB powder

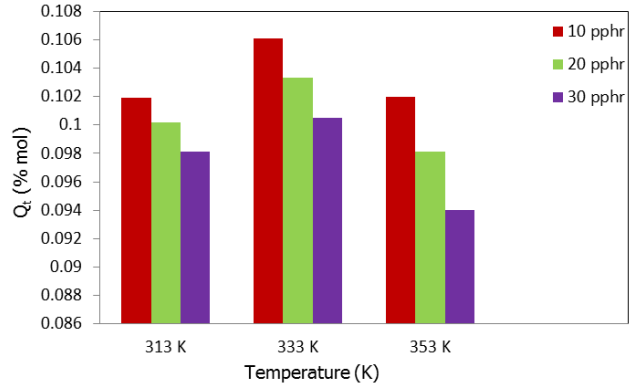


Figure 8. Dependence of equilibrium n-hexane uptake Q_t (% mol) on sorption temperature (K) for compatibilized PP/NR blends filled with different levels of carbonized OPEFB powder

3.2. Sorption Coefficient (S)

The sorption coefficient (S) of the carbonized oil palm empty fruit bunch powder filled PP/NR blends was evaluated using Equation 3[31].

$$S = \frac{M_\infty}{M_o} \quad (3)$$

where M_∞ is the mass of n-hexane sorbed at equilibrium and M_o is the initial mass of PP/NR/OPEFB blend. M_∞ is given as:

$$M_\infty = Z \times \text{molecular weight of n-hexane}, \quad (4)$$

Table 2. Values of sorption parameters for carbonized OPEFB powder filled PP/NR (compatibilized and uncompatibilized) blends at different temperatures

Sorption Properties	Filler Content (pphr)	Uncompatibilized Blends			Compatibilized Blends		
		313 K	333 K	353 K	313 K	333 K	353 K
Diffusion Coefficient (mm ² /min) x 10 ⁻⁵	0	5.690	5.675	7.287	-	-	-
	10	5.588	5.519	7.154	4.979	4.809	6.427
	20	5.454	5.408	7.072	5.347	4.908	6.713
	30	5.331	5.357	6.926	5.607	5.166	6.923
Sorption Coefficient (mol %)	0	0.993	0.998	1.022	-	-	-
	10	0.980	0.987	1.012	0.960	0.987	1.003
	20	0.954	0.977	0.990	0.927	0.967	0.983
	30	0.944	0.957	0.974	0.891	0.944	0.964
Permeability Coefficient (mm ² min ⁻¹ mol %) x 10 ⁻⁵	0	5.604	5.621	7.328	-	-	-
	10	5.476	5.409	7.240	4.780	4.703	6.446
	20	5.203	5.284	7.001	4.957	4.746	6.599
	30	5.032	5.127	6.746	4.996	4.877	6.674

Table 3. Values of n and k for carbonized OPEFB powder filled PP/NR (compatibilized and uncompatibilized) blends at different temperatures

Filler Content(pphr)	n for Uncompatibilized Blends			n for Compatibilized Blends			k for Uncompatibilized Blends			k for Compatibilized Blends		
	313 K	333 K	353 K	313 K	333 K	353 K	313 K	333 K	353 K	313 K	333 K	353 K
0	0.3445	0.3274	0.3139	----	-----	-----	0.1867	0.2064	0.2222	-----	-----	-----
10	0.3760	0.3561	0.2771	0.4201	0.4175	0.3609	0.1601	0.1813	0.2655	0.1334	0.1356	0.1804
20	0.4077	0.3804	0.3502	0.4245	0.4103	0.3511	0.1420	0.1617	0.1912	0.1260	0.1338	0.1922
30	0.4174	0.4000	0.3657	0.4508	0.4227	0.3902	0.1322	0.1438	0.1735	0.1079	0.1251	0.1551

where Z denotes number of moles of n-hexane sorbed at equilibrium swelling. The calculated values of the sorption coefficient (S) are presented in Table 2. The table shows that the sorption coefficient increased with increase in temperature at any carbonized OPEFB powder content in the polypropylene/natural rubber blend for both compatibilized and uncompatibilized blends. However, the sorption coefficient decreased with increases in carbonized OPEFB powder content in the polypropylene/natural rubber blend at any temperature for both compatibilized and uncompatibilized blends. The higher solubility coefficient observed for least filled blends could be due to the closeness of its solubility parameter to that of n-hexane. The solubility parameter, which is a measure of intermolecular attraction, is a very important factor that affects solubility of polymers in solvents. Thus, polymers and solvent absorbs or dissolves if they have similar solubility parameter values.

3.3. Permeability Coefficient (P)

The permeability coefficient of n-hexane in the carbonized oil palm empty fruit bunch powder filled PP/NR biocomposite was obtained as follows[31]:

$$P = D \times S \quad (5)$$

where D is the diffusion coefficient and S is the sorption coefficient. The values of permeation coefficients are given in Table 2. The result obtained for both compatibilized and uncompatibilized blends indicate an increase in P values as

the filler content increase for all temperatures studied. It is interesting to note that the P values for both compatibilized and uncompatibilized blend did not show any definite trend in relation to temperature for all filler concentration studied. This pattern practically followed the path of diffusion coefficient, hence, it may be inferred that the diffusion process controls the permeability of the solvent in the biocomposites.

3.4. Transport Mechanism

The mechanism of diffusion of n-hexane into carbonized OPEFB powder filled PP/NR was analysed by fitting the sorption data into the following empirical relation[36]:

$$\log \frac{Q_t}{Q_\infty} = \log k + n \log t \quad (6)$$

where Q_t and Q_∞ are the mol % sorption at time t and equilibrium, respectively. k is a constant which depends on the polymer morphology and the polymer-solvent interaction. The value of n determines the mode of transport of n-hexane through the thermoplastic elastomer biocomposites. For a Fickian transport, $n = 0.5$, When $n = 1.0$, it indicates Case II (relaxation controlled) transport, and when n lies between 0.5 and 1.0, it indicates anomalous transport behaviour. The values of n and k for the biocomposites were obtained by regression analysis of $\log (Q_t/Q_\infty)$ against $\log t$, and the results are shown in Table 3.

It is evident from Table 3 that the values of n obtained for

the thermoplastic elastomer biocomposites both for compatibilized and uncompatibilized at different temperatures are Fickian. This is in agreement with the work of Igwe and Ezeani[35] who studied the transport of aromatic solvents through snail shell powder filled rubber vulcanizates. The values of n did not show any relationship with the amount of carbonized OPEFB incorporated into the polypropylene/natural rubber blends at high temperature for the compatibilized blends. However, n values increased as filler content increase for the uncompatibilized blends at all temperatures studied. The computed values of n on Table 3 were also found to decrease as the sorption temperature increase for both the compatibilized and uncompatibilized blends at all filler loadings studied.

The values of k obtained in this study were observed to decrease with increases in the carbonized OPEFB content of the thermoplastic elastomers. This pattern was observed for both the compatibilized and uncompatibilized blends at all the temperatures studied except for 353 K of the compatibilized blends where 20 pphr filler content had the highest k value of 0.1922. For all the filler loadings studied, the values of k were found to increase as the sorption temperature increase in both the compatibilized and uncompatibilized blends. This is an indication of the degree of interaction between the thermoplastic elastomer biocomposites and the n-hexane. Therefore, it can be inferred that at higher temperature or lower filler loadings, there was a higher sorption of n-hexane by the carbonized OPEFB powder filled thermoplastic elastomers.

3.4.1. Activation Energy Parameters

The temperature dependence of transport properties was used to evaluate the activation energy for the diffusion, and permeation processes using the Arrhenius relation[37]:

$$D = D_0 \exp\left(-\frac{E_D}{RT}\right) \quad (7)$$

where E_D is the activation energy of diffusion, which is a function of the intra- and interchain forces that must be overcome to create the space for a diffusional jump of the n-hexane molecule, D_0 is a pre-exponential factor, and RT is gas constant and temperature in kelvin respectively. Plots of $\log D$ against $1/T$ were used to calculate the activation energy parameters of diffusion (E_D) and permeation (E_P) as presented in Table 4. From Table 4, it is seen that as the amount of carbonized OPEFB powder increased in the

biocomposites, the values of E_D also increased, and vice versa for the uncompatibilized biocomposites. Conversely, the compatibilized blends showed an increase in the values of E_D as the filler content decreased. No definite order in the variation of E_P for both the compatibilized and uncompatibilized blends was noticed. Generally, the direction of increase of E_D and E_P values indicates the direction of increasing solvent resistance of the blends, and vice versa. In essence therefore, and in agreement with our earlier observation on the molar percentage uptake (Q_t) of n-hexane by the compatibilized and uncompatibilized biocomposites.

3.4.2. Enthalpy of Absorption (ΔH_s) and Entropy of Absorption (ΔS_s)

The enthalpy of absorption (ΔH_s) and entropy of absorption (ΔS_s) in the MAPP compatibilized and uncompatibilized biocomposites were calculated from the sorption data by first determining the values of the equilibrium absorption constant (K_s) of n-hexane using the following formula[38]:

$$K_s = \frac{\text{Number of moles of n-hexane absorbed at equilibrium}}{\text{Mass of the PP/NR/OPEFB biocomposite}} \quad (8)$$

The values of K_s obtained were substituted into Van't Hoff's equation[39]:

$$\log K_s = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \quad (9)$$

and plots of Van'thoff's equations made were used in calculating ΔH_s and ΔS_s . The obtained values are presented in Table 5. The calculated ΔH_s for both the compatibilized and uncompatibilized blends are generally positive and showed no relationship to the amount of carbonized OPEFB in the both blends. ΔH_s is a composite parameter involving contributions from Henry's law, which is needed for the formation of a site and the dissolution of the species into that site (the formation of the site involves an endothermic contribution). It also involves the contribution of Langmuir's (hole-filling) sorption mechanism, in which case, the site already exists in the polymer matrix and sorption by hole filling gives exothermic heat of sorption. The positive ΔH_s values obtained for the n-hexane suggest that sorption in this case is dominated by Henry's mode with endothermic contributions.

Table 4. Values of activation energy of diffusion (E_D) and permeation (E_P) for carbonized OPEFB powder filled polypropylene/natural rubber (compatibilized and uncompatibilized) blends

Filler content (pphr)	E_D (KJ/mol)		E_P (KJ/mol)	
	Uncompatibilized blends	Compatibilized blends	Uncompatibilized blends	Compatibilized blends
0	24.14×10^2	-	26.20×10^2	-
10	24.07×10^2	24.78×10^2	27.21×10^2	29.13×10^2
20	25.32×10^2	21.87×10^2	29.04×10^2	27.76×10^2
30	25.57×10^2	20.26×10^2	28.69×10^2	28.17×10^2

Table 5. Values of enthalpy of absorption (ΔH_s), entropy of absorption (ΔS_s) and Gibbs free energy of sorption (ΔG_s) for carbonized OPEFB powder filled polypropylene/natural rubber (compatibilized and uncompatibilized) blends

Filler Content (pphr)	ΔH_s		ΔS_s		ΔG_s	
	Uncompatibilized blends	Compatibilized blends	Uncompatibilized blends	Compatibilized blends	Uncompatibilized blends	Compatibilized blends
0	12.45×10^2	-	-33.4596	-	12.56×10^2	
10	9.60×10^2	11.27×10^2	-34.4266	-34.0953	9.70×10^2	11.37×10^2
20	7.23×10^2	10.76×10^2	-35.4777	-34.5070	7.34×10^2	10.87×10^2
30	20.36×10^2	14.26×10^2	-31.4607	-41.9016	20.46×10^2	14.39×10^2

3.4.3. Gibbs Free Energy of Sorption (ΔG_s)

The change in ΔG_s for the n-hexane in carbonized OPEFB filled polypropylene/natural rubber blends were obtained using the following expression:

$$\Delta G_s = \Delta H_s - T\Delta S_s, \quad (10)$$

where T is the temperature in Kelvin. The values of ΔH_s and ΔS_s earlier determined for n-hexane were substituted into the expression (10), and the calculated values of ΔG_s are also shown in Tables 5. The calculated ΔG_s values were all positive, and this was an indication of the non-spontaneity of the solubility of carbonized OPEFB filled polypropylene/natural rubber blends in the n-hexane at 313 K. The calculated ΔG_s did not show any reasonable relationship to the carbonized OPEFB powder content for both the compatibilized and uncompatibilized blends. Igwe[40] who studied the uptake of aromatic solvents (benzene, toluene, and xylene) by polyethylene films found that the solvents showed similar ΔG_s values, which indicated that the change in ΔG_s of the aromatic solvents in polyethylene films might be independent of the solvent properties.

4. Conclusions

The transport behaviour of n-hexane through carbonized oil palm empty fruit bunch powder filled polypropylene / natural rubber has been studied at three different temperatures (313, 333, and 353 K) by gravimetric test method. The effect of MAPP as compatibilizer on the sorption properties of the thermoplastic elastomer biocomposites was also investigated. Diffusion, sorption, and permeation coefficients of the biocomposites showed that the uncompatibilized blends sorbed more n-hexane than the compatibilized blends. Equilibrium sorption was found to decrease with increasing filler loading for both compatibilized and uncompatibilized blends due to the fillers' reinforcing ability.

The calculated enthalpies of sorption (ΔH_s), and Gibbs free energies of sorption (ΔG_s) were all positive also the Arrhenius activation energies (E_D and E_p) were all positive. The positive ΔG_s obtained in this study is an indication of non-spontaneity of the solubility of carbonized oil palm empty fruit bunch powder filled polypropylene/natural rubber in n-hexane solvent at 313 K. The mode of transport of n-hexane into filled polypropylene/natural rubber has been found to be Fickian and dominated by Henry's model

with endothermic contributions. The transport parameters presented in this study have not only provided additional characterization of the oil palm empty fruit bunch powder filled polypropylene/natural rubber blends but gave an insight into the behaviour of the thermoplastic elastomer biocomposites in external liquid environment which is essential for their successful applications. The data obtained could be of importance in problem solving like designing a barrier material, gaskets or tubes for transporting liquids.

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