



Transport Properties of Toluene through Reactive Compatibilized Polyethylene Terephthalate/Natural Rubber using Dikanut shell Powder as Filler

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ABSTRACT

The sorption and diffusion of toluene through dikanut shell powder filled -natural rubber/poly (ethylene terephthalate) bio-composites were studied at 313, 333 and 353k by conventional weight-gain experiments. Samples of dikanut shells were milled and sieved through a mesh size of 150 μ m. The composites were prepared by reactive compatibilization in a two roll mill using maleic anhydride- grafted polyisoprene (MAPI) and hexamethylenediamine (HMDA) as a dual compatibilizer. The effects of (MAPI)/(HMDA) dual compatibilizers, filler loading and temperature on sorption characteristics of the bio-composites were investigated. The amount of toluene absorbed by the composites was substantially decreased on addition of MAPI/HMDA into the composites. Equilibrium sorption values were observed to decrease progressively with increasing content of HMDA in the composites. The sorption, permeation and diffusion coefficient were found to decrease with increase in filler loadings. The calculated enthalpies (ΔH_s), Gibb's free energies (ΔG_s) and Arrhenius activation energies (E_D and E_P) were all positive. The transport characteristics of toluene into the bio-composites was found to be Fickian and dominated by Henry's type sorption with endodermic contribution.

Key words: Bio-composites, natural rubber, poly (ethylene terephthalate), dikanut shell powder, reactive compatibilization; sorption characteristics

1. INTRODUCTION

The effect of fillers on the transport characteristics of polymer composites has been of immense interest to scientist. The diffusion and transport in filled polymers depend upon the nature of the fillers, the degree of adhesion and their compatibility with the polymer matrix. Examples of such fillers are the natural fibres e.g. kenaf, jute, coconut shell, oil palm, corn hubs which are eco-friendly [1], carbon black, clay etc.

Natural fibre-reinforced polymer composites are now a matter of global research interests owing to strong environmental regulations and increased interest in the proper utilization of renewable natural resources to develop eco-friendly components. Benefits of these natural fillers include abundance and low cost, light weight, biodegradability and so on [2, 3]. These advantages led to the use of natural fillers as potential replacement for traditional reinforcement materials such as glass fiber in composite systems [4]. Many literature sources have revealed excellent report on the diffusion and sorption processes in natural fibre-reinforced polymer composites [5-8].

The compatibility or miscibility of natural fillers in polymeric materials is often in doubt due to the non-polar and hydrophobic nature of most polymeric materials when compared with the polar and hydrophilic lignocellulosic filler material due to the presence of hydroxyl groups in cellulose [9]. To address this problem, studies have been conducted on surface modification of natural fibers for the purpose of making the hydrophilic surface more compatible with hydrophobic polymers by using coupling agents [10]. Excellent reports exist in the literature on the use of coupling agents to improve the compatibility between hydrophobic polymer matrices and hydrophilic fillers [10-12].

In a previous study, Oyeagoro et al. [13] revealed that the combination of maleic anhydride-grafted polyisoprene, hexamethylenediamine is an excellent dual compatibilizer for dikanut shell powder filled natural rubber/

polyethylene terephthalate bio-composite as shown by marked improvement in the physico-mechanical and water sorption properties investigated. Obasi et al. [17] investigated the diffusion of toluene onto natural rubber/linear density polyethylene. They concluded that the transport of toluene through 60/40 blend was anomalous, Fickian and at 35⁰C pseudo-Fickian. However, there is no reported literature on the transport of toluene through reactive compatibilized natural rubber/ polyethylene terephthalate filled with dikanut shell powder using a combination of maleic anhydride-grafted polyisoprene and hexamethylenediamine as dual compatibilizer. In the current research, an attempt was made to investigate the transport properties of toluene through reactive compatibilized natural rubber/ polyethylene terephthalate filled with dikanut shell powder using maleic anhydride-grafted polyisoprene and hexamethylenediamine as dual compatibilizer.

2. MATERIALS AND METHODS

2.1 Materials

Poly (ethylene terephthalate) and crumb natural rubber were used. The poly (ethylene terephthalate) of melt flow index of 20g/10min, and compatibilizers, maleic anhydride-grafted-polyisoprene (MAPI) containing 10 wt% maleic anhydride (sigma-Aldrich chemeGmbH.) and hexamethylenediamine (HMDA) (Shell Chemical Co) were purchased from Rovet Chemicals Ltd, Benin City, Nigeria. The crumb natural rubber which conforms to Standard Nigerian Rubber (SNR 10) with Mooney Viscosity of 76 [ML (1+4) @ 100°C] and other compounding ingredients such as zinc oxide, stearic acid, wax MBT, TMTD and sulphur were kindly supplied by Rubber Research Institute of Nigeria (RRIN), Iyanomo, Benin City, Nigeria. The dikanut shells were sourced from different farm yards in Auchi, Nigeria.

The standardized compounding and test equipment were kindly provided by the Department of Polymer Technology, Federal Polytechnic Auchi, Edo State, Nigeria, and the Analytical Laboratory of the Department of Polymer and Textile Engineering, Nnamdi Azikiwe University Awka, Anambra state, Nigeria.

2.2 Preparation of Dikanut Shell Powder

Dikanut shells were washed and dried in air to remove sand particles and moisture. The dried dikanut shells were milled to fine powder and sieved through mesh size 150µm. The fine particles that passed through the mesh were collected, stored in sealed plastic containers and kept in a desiccator until required.

2.3 Preparation of Composite Samples

Blend of poly (ethylene terephthalate) and natural rubber were prepared by melt mixing technique, carried out in a Brabender Plastic order model PLE 331. Poly (ethylene terephthalate) was first melted for 2 minutes at 170°C with a rotational speed of 80 rpm before the addition of natural rubber. Weighed amount of the compounding ingredient with the exception of vulcanizing agent and accelerators were introduced in to the mixer and mixing continued for 8 min. The compound mix produced was transferred to a two-roll mill already preset at 170°C which converted it from an irregularly shaped mass to suitable. The temperature of the mill was reduced from 170°C to 90°C before the introduction of the vulcanizing agent and accelerator to prevent premature curing of the compound mix. The milled samples were then cured into sheets of 2mm thick on a hot press at 10MPa pressure and temperature of 140°C for 15mins. The formulation used in preparing the composites is presented in Table 1.

Table -1 Compounding recipe for NR/PET/DNS bio composites

MAPI: maleic Anhydride grafted polyisoprene, HMD: hexamethylenediamine, MBT: mecaptobenzoylthiazol, TMTD:

Material	Uncompatibilized (pphr)	Compatibilized (pphr)	
Natural rubber	70	70	70
Poly (ethylene terephthalate)	30	30	30
Zinc oxide	5	5	5
Stearic Acid	2	2	2
MAPI/HMDA	0/0	2/0.5	2/0, 2/0.3, 2/0.5, 2/0.5
Sulphur	3	3	3
MBT	1.5	1.5	1.5
TMTD	1	1	1
Wax	4	4	4
Dikanut shell powder	0,10,15,20	0,10,15,20	10

tetramethylthiurandisulphide

2.4 Procedure for Sorption Experiment

Composites 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. 25 ml of toluene were poured into each of the sample bottles. The bottles were then placed in a thermostatically controlled water bath preset at 313K and were equilibrated for different time intervals. At the expiration of the specified time, the composites were removed from the sample bottles, wiped free

of adhering toluene, and weighed using electronic balance. The difference between the dry sample and the wet sample was obtained. The following time intervals were investigated: 5, 10, 15, 20, 30, 60, 90, 140, 180, 230, 300, and 380 minutes. The procedure was further repeated at 333k and 353k. Each weighing was completed in less than 30 seconds, so as to keep the error due to solvent evaporation from the sample surface at a minimum [14].

3. RESULTS AND DISCUSSION

The sorption data of toluene absorption by compatibilized and uncompatibilized (NR/ PET/ DNS) bio-composites at different temperature (40°C, 60°C, 80°C) were determined and expressed as the molar percentage uptake (Q_t) of toluene per gram of NR /PET/ PET/DNS bio-composites. Q_t was calculated using the following equation [14, 15].

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

The molar percentage uptake (Q_t) at any particular temperature for compatibilized and uncompatibilized bio-composite was plotted against the square root of time (\sqrt{t}) as shown in Figures 1- 9. The Figures show initial increase in mass of toluene absorbed until maximum absorption was reached at which time, the mass of the absorbed toluene remained constant, that is equilibrium absorption was attained.

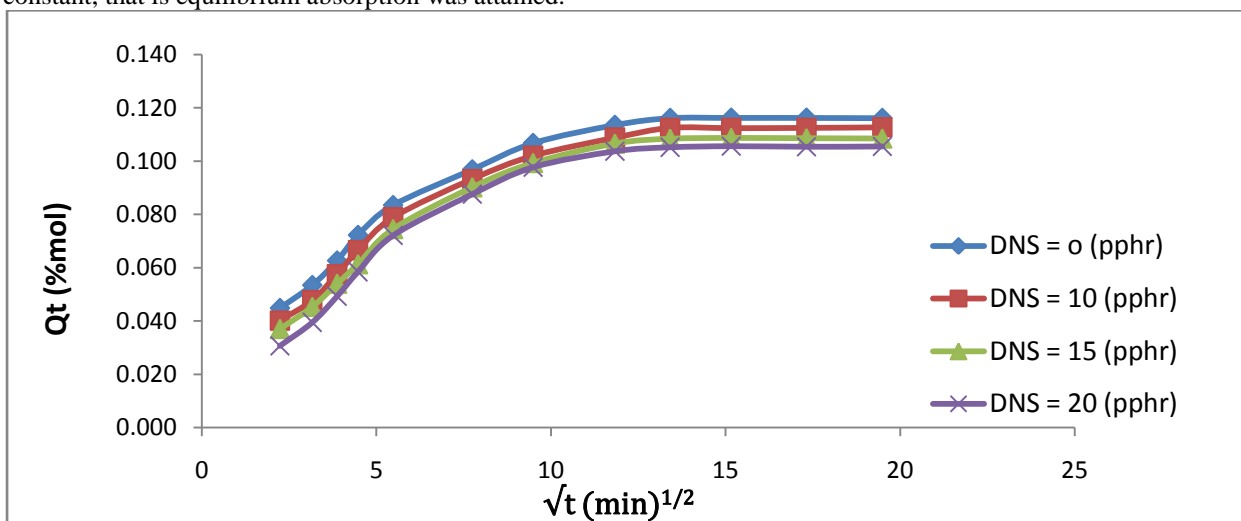


Fig. 1 Plot of molar percentage uptake Q_t (% mol) versus square root of time (\sqrt{t} , $\text{min}^{1/2}$) for uncompatibilized NR/PET/DNS bio-composites filled with different levels of DNS powder at 40°C

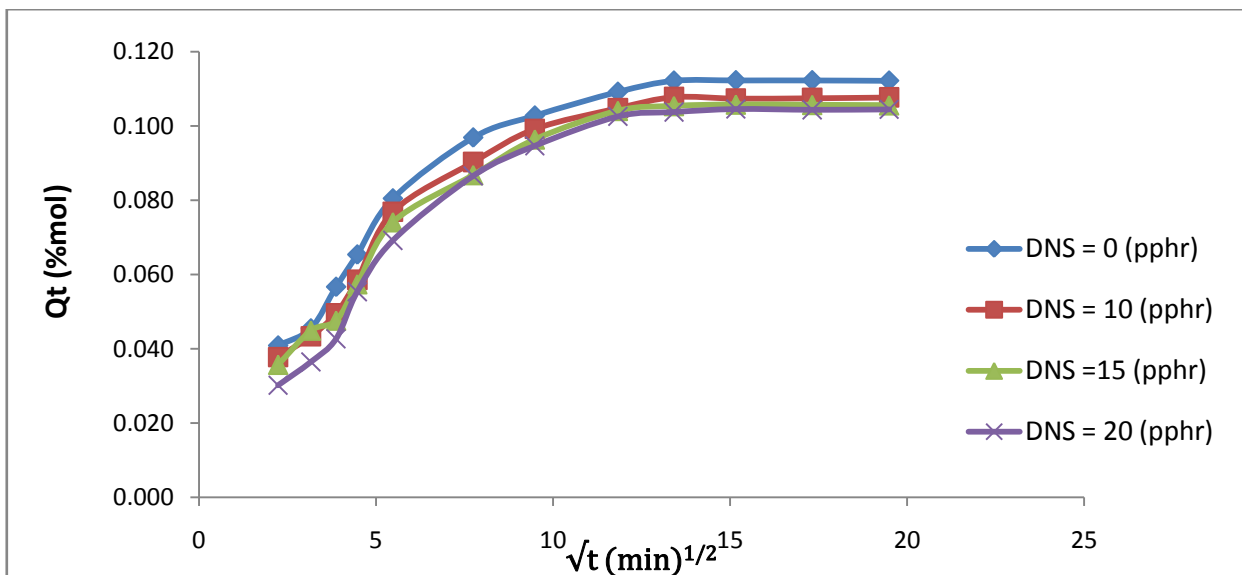


Fig. 2 Plot of molar percentage uptake Q_t (% mol) versus square root of time (\sqrt{t} , $\text{min}^{1/2}$) for compatibilized NR/PET/DNS/MAPI/HMDA bio-composites filled with different levels of DNS powder at 40°C

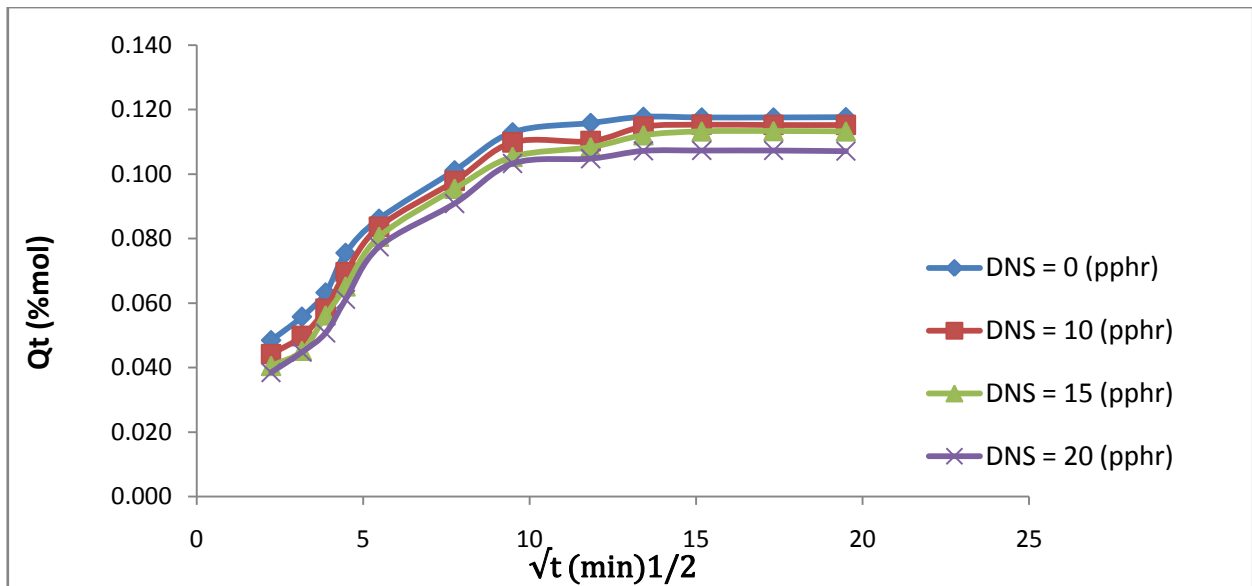


Fig. 3 Plot of molar percentage uptake Q_t (% mol) versus square root of time (\sqrt{t} , $\text{min}^{1/2}$) for uncompatibilized NR/PET/DNS/MAPI/HMDA bio-composites filled with different levels of DNS powder at 60°C

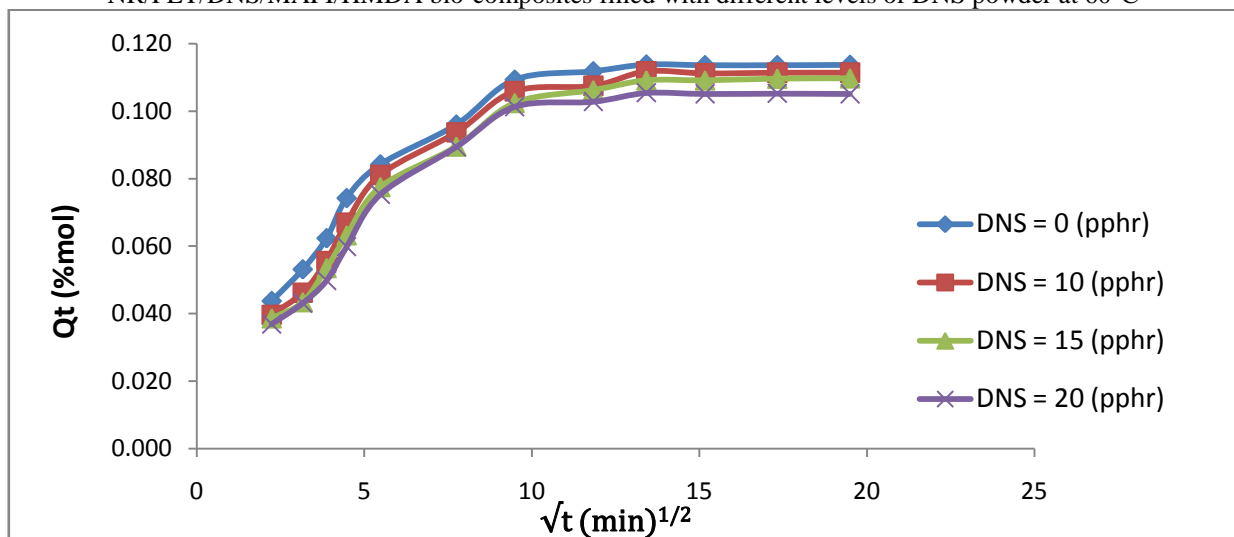


Fig. 4 Plot of molar percentage uptake Q_t (% mol) versus square root of time (\sqrt{t} , $\text{min}^{1/2}$) for compatibilized NR/PET/DNS/MAPI/HMDA bio-composites filled with different levels of DNS powder at 60°C

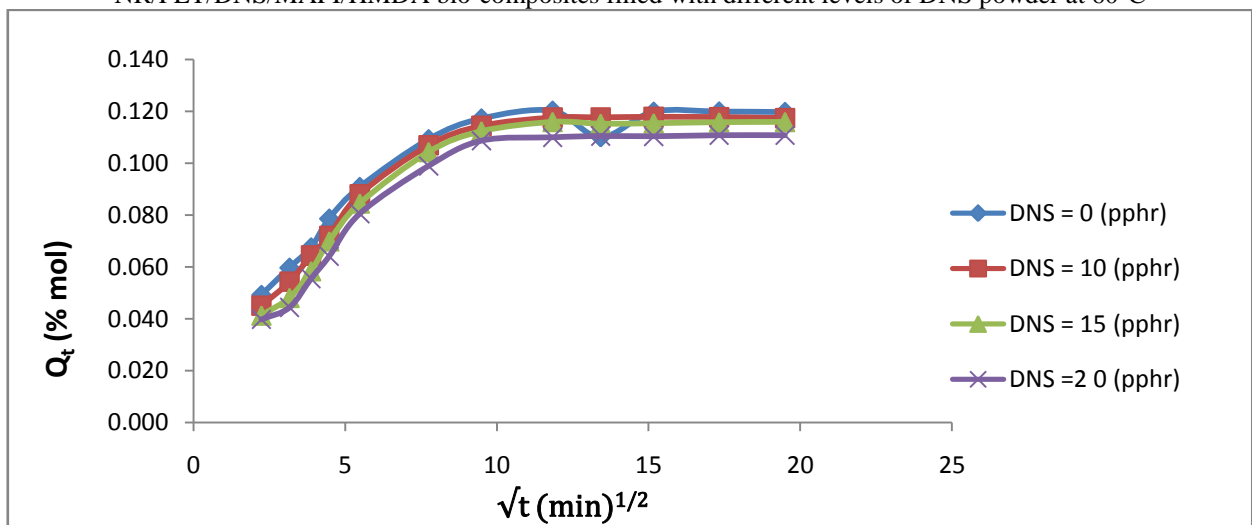


Fig. 5 Plot of molar percentage uptake Q_t (% mol) versus square root of time (\sqrt{t} , $\text{min}^{1/2}$) for uncompatibilized NR/PET/DNS/MAPI/HMDA bio-composites filled with different levels of DNS powder at 80°C

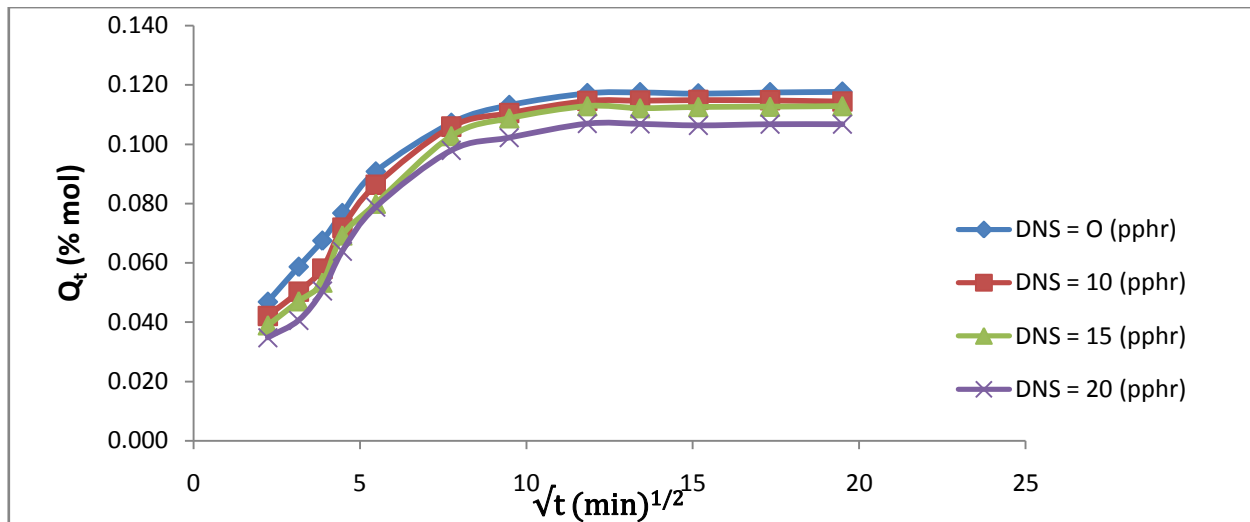


Fig. 6 Plot of molar percentage uptake Q_t (% mol) versus square root of time (\sqrt{t} , $\text{min}^{1/2}$) for compatibilized NR/PET/DNS/MAPI/HMDA bio-composites filled with different levels of DNS powder at 80°C

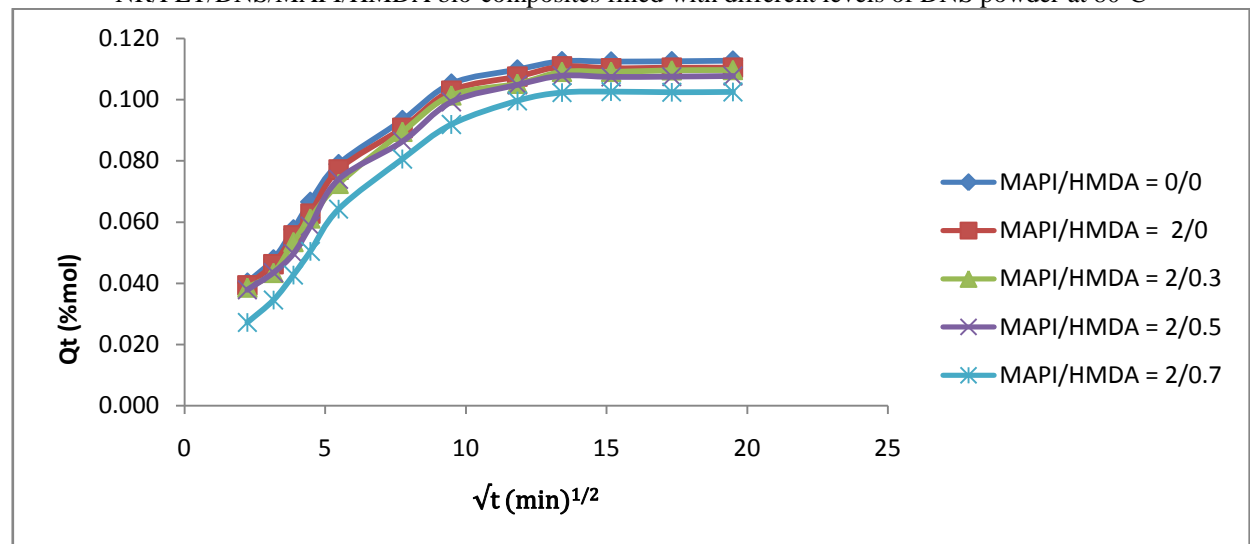


Fig. 7 Plot of molar percentage uptake Q_t (% mol) versus square root of time (\sqrt{t} , $\text{min}^{1/2}$) for compatibilized and uncompatibilized NR/PET/DNS/MAPI/HMDA bio-composites, at different levels of MAPI/HMDA, DNS content = (10 pphr), at temperature of 80°C

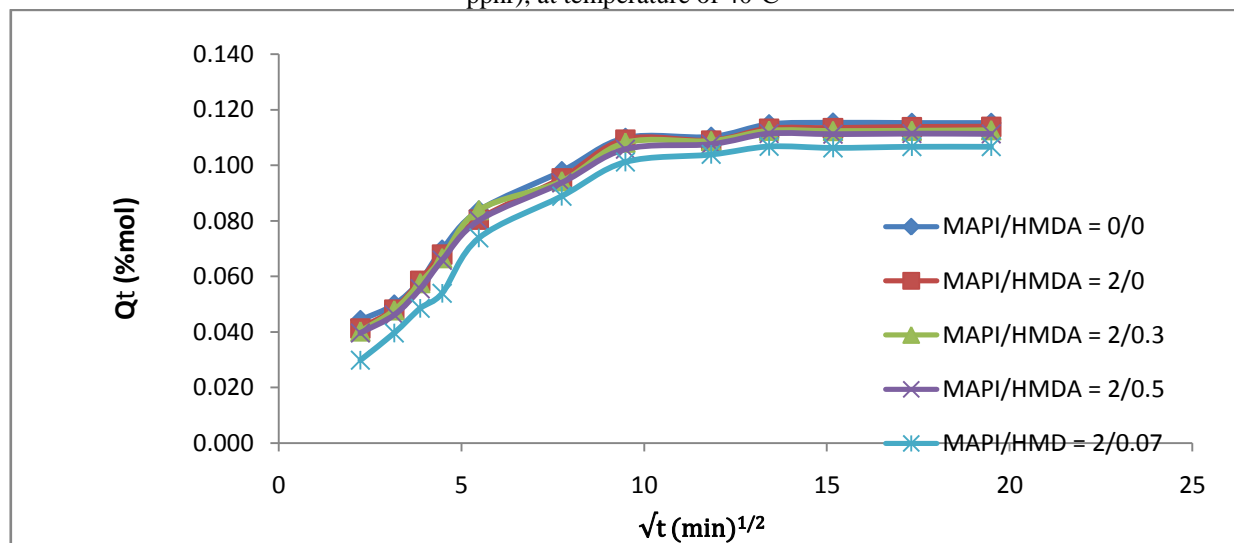


Fig. 8 Plot of molar percentage uptake Q_t (% mol) versus square root of time (\sqrt{t} , $\text{min}^{1/2}$) for compatibilized and uncompatibilized NR/PET/DNS/MAPI/HMDA bio-composites, at different levels of MAPI/HMDA, DNS = content (10 pphr), at temperature of 60°C

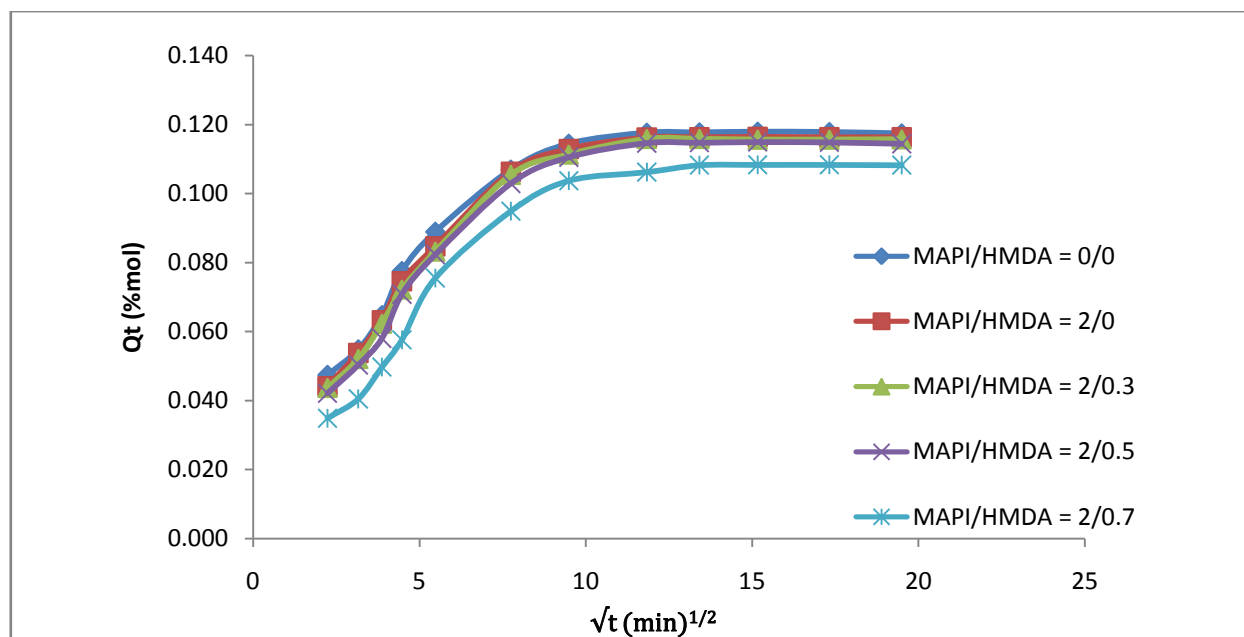


Fig. 9 Plot of molar percentage uptake Q_t (% mol) versus square root of time (\sqrt{t} , $\text{min}^{1/2}$) for compatibilized and uncompatibilized NR/PET/DNS/MAPI/HMDA bio-composites, at different levels of MAPI/HMDA, at fixed DNS content (10 pphr), at temperature of 80°C

Figures 1- 6, show that at any particular temperature and filler loading the compatibilized composites absorbed less toluene than the uncompatibilized composites.

The effect of DNS filler loading on the equilibrium sorption values of the compatibilized and uncompatibilized bio-composites is shown in Fig 1- 6. The result showed that at any temperature investigated, equilibrium sorption values decreased with increase in filler loading. The decreasing equilibrium sorption values of the composites (compatibilized and uncompatibilized) with increasing filler loading indicate the filler's reinforcing ability and suggest a swelling restriction of the rubber matrix due to the presence of the filler. This observation is in agreement with the work of Mathew et al. [15] who reported decrease in equilibrium oil uptake of Isora fiber filled natural rubber composites with increasing filler loading. The authors attributed this observation to increased hindrance exerted by the polar fibre at higher fibre loading.

The effect of MAPI and HMDA content on the equilibrium sorption values of the compatibilized and uncompatibilized composites is presented Figures 7- 9. The equilibrium sorption value of the uncompatibilized sample was noticeably high due to poor compatibility between NR and PET. Clearly, the incompatibility of the composite phases has improved significantly through compatibilization as shown by marked reduction in the equilibrium sorption values in the presence of the MAPI/HMDA dual compatibilizer.

It can be seen (Figures 7-9) that compatibilization by MAPI alone leads to insignificant reduction in the equilibrium sorption values. This can be attributed to insignificant reaction between PET and MAPI during melt compounding. However, compatibilization by MAPI/HMDA dual compatibilizer produced greater degree of reduction in the equilibrium sorption values of the composites. This result indicates that portion of the HMDA was able to effectively couple with MAPI and PET simultaneously to produce the desirable PET-co-HMDA-co-MAPI copolymer which intended to anchor along the interface, which also provides adequate interfacial adhesion at phase boundaries.

Figures 7- 9, also showed the effect of HMDA content on the values of equilibrium sorption. Equilibrium sorption values were observed to decrease progressively with increasing content of HMDA in the composites at any temperature considered. This is an indication that HMDA enhance the filler-matrix interaction at the interface, thus decreasing the amount of equilibrium toluene uptake by the composites. The effect of sorption temperature and time on the equilibrium absorption of toluene by the compatibilized and uncompatibilized bio-composites is presented in Figures 10-12.

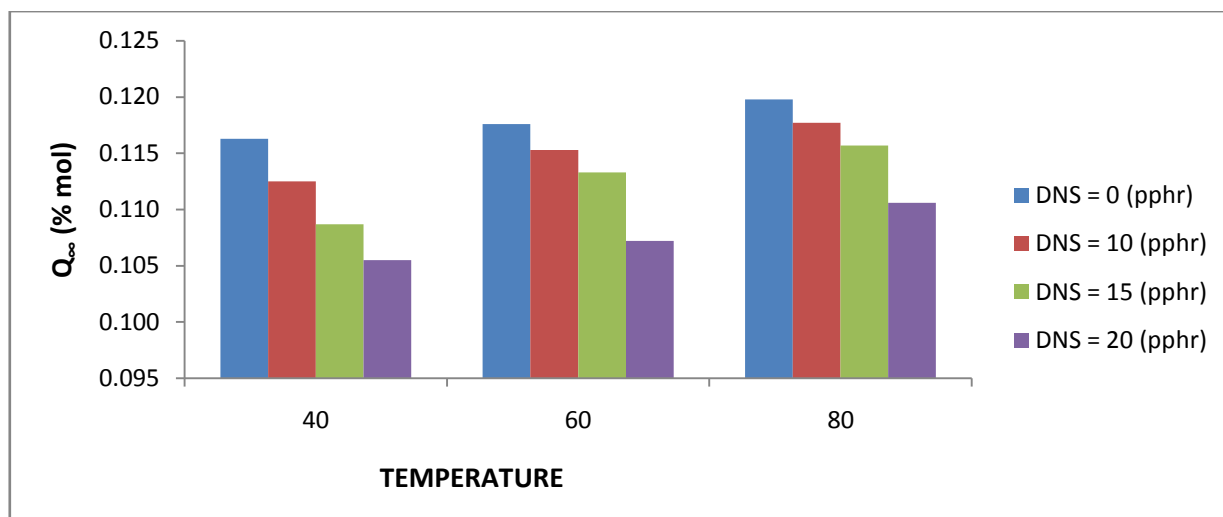


Fig. 10 Dependence of Equilibrium toluene uptake Q (% mol) on sorption temperature for uncompatibilized NR/PET/MAPI/HMD, at different level of DNS (pphr) content, at different temperature (40°C, 60°C, 80°C)

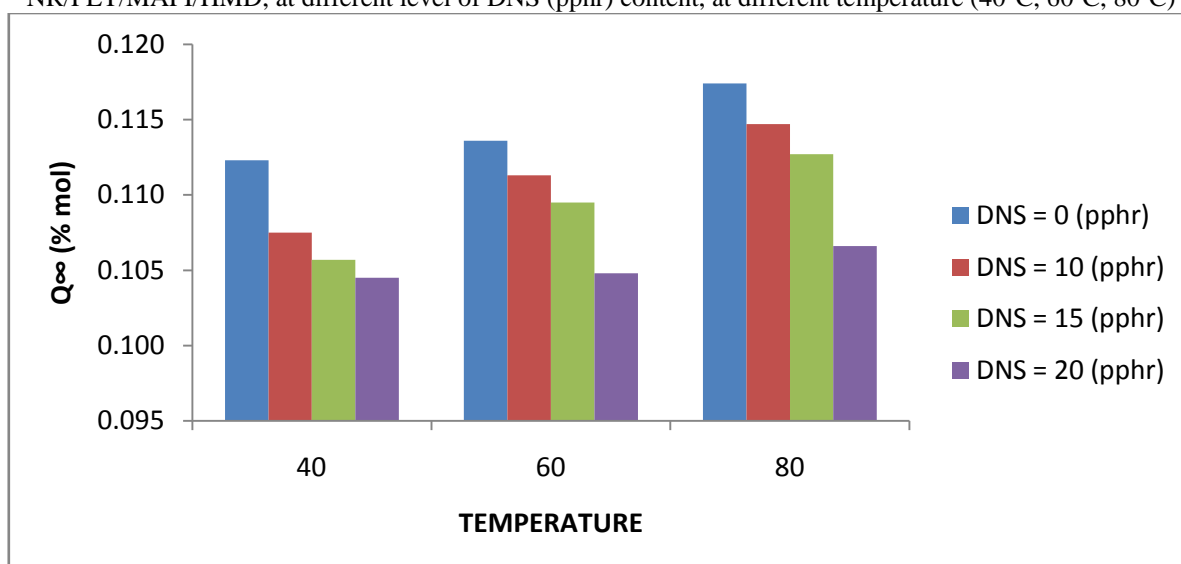


Fig. 11 Dependence of Equilibrium toluene uptake Q (% mol) on sorption temperature for compatibilized NR/PET/MAPI/HMDA, at different level of DNS (pphr) content, at different temperature (40°C, 60°C, 80°C)

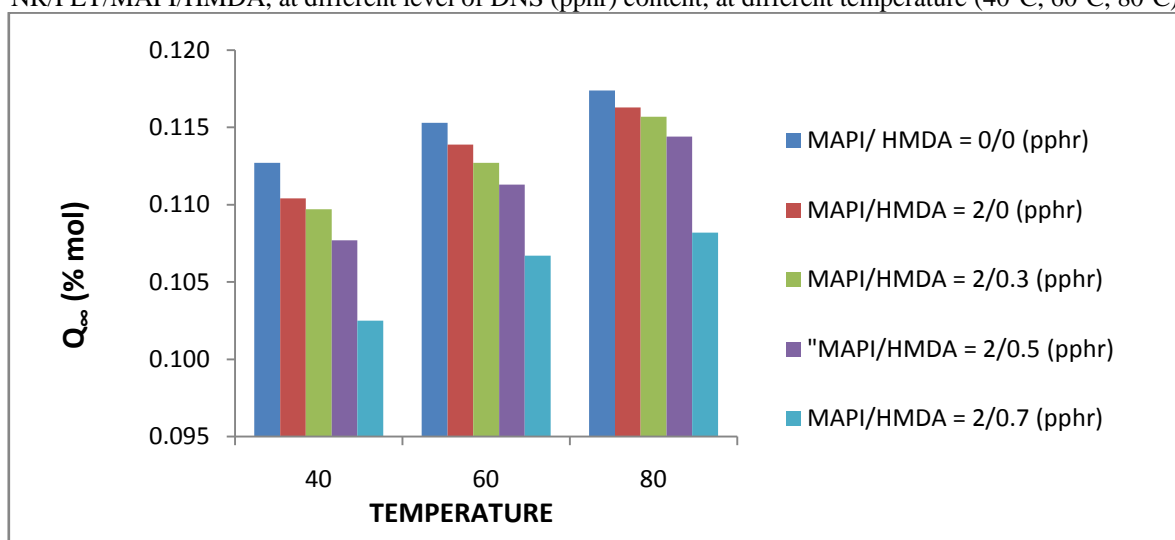


Fig. 12: Dependence of Equilibrium toluene uptake Q (% mol) on sorption temperature for compatibilized and uncompatibilized NR/PET/MAPI/HMDA, at different level MAPI/HMDA content, DNS = 10 (pphr), at different temperature (40°C, 60°C, 80°C).

Figures 10-12 showed that sorption values at 40°C had the lowest mass of toluene absorbed with much longer equilibrium absorption time, while 80°C had the highest mass of toluene absorbed at faster equilibrium adsorption time. The decrease in equilibrium absorption time with increase in temperature is due to the fact that temperatures significantly affect the rate of chemical reaction. Increase in temperature increases the rate at which the solvent penetrate the bio-composite.

Figures 10-12 also showed that at any particular filler loading and HMDA content (compatibilized and uncompatibilized), equilibrium sorption values increased in 1.157% - 3.44% range after increasing the sorption temperature by 20°C. This occurs because the diffusing solvent molecule is facilitated by the higher thermal energies at increasing temperature. This result is an indication of subsequent reduction in the viscosity of the solvent, and a further increase in the segmental mobility of the polymer. The increase in the mass of solvent absorbed by polymer with increase in temperature had been reported in the scientific literature. Igwe et al [16] who studied the transport of aromatic solvents (benzene, toluene, xylene) through filled natural rubber reported that for any particular solvent at the filler particle sizes investigated (0.075 and 0.030µm), solvent uptake generally increased with increase in sorption temperature.

3.1 Determination of Sorption Coefficient (S)

The sorption coefficient (S) of the dika nutshell composite (comptibilized and uncompatibilized) was calculated using the following equation [14, 17]

$$S = \frac{M_{\infty}}{M_0} \quad (2)$$

Where M_{∞} is the mass of toluene absorbed at equilibrium and M_0 is the initial mass of the composites.

M_{∞} is obtained using the following equation:

$$M_{\infty} = Z \times \text{molecularweightoftoluene} \quad (3)$$

Where Z, denotes the number of moles of toluene absorbed at equilibrium.

The calculated values of the sorption coefficient are presented in Tables 2 and 3. It is evident from Table 2 that the sorption coefficient decreased with increase in Dikanut shell (DNS) powder content in the composites (uncompatibilized and compatibilized) at all temperatures investigated. This result is in agreement with the finding of Ewulonu et al. [5], who reported decreases in sorption coefficient with increase in carbonized OPEFB powder content in the polypropylene / natural rubber blend at all temperatures considered for both compatibilized and uncompatibilized blends. Similarly, Igwe et al. [16] in their studies reported that sorption coefficient decreased with increase in snail shell powder content in the rubber vulcanizate at any particular temperature, solvent and filler particle size considered.

Again, the sorption coefficient values increased with increase in sorption temperature. Johnson and Thomas, (2000) and Igwe (2006) [16, 18] in their studies reported that sorption coefficient increased with increase in sorption temperature. It is evident from Table 3 that sorption coefficient values decreased with increase in HMDA content for the temperature and filler content investigated. The presence of HMDA promoted a decrease in the interfacial tension, an improvement in both the interfacial adhesion and cross- linking of the rubber particles which resulted to the observed decrease in the toluene sorption with increase in HMDA content.

Table -2 Values of sorption Parameters for NR / PET / DNS bio-composite (Uncompatibilized and Compatibilized), at different DNS content, at different temperatures (313k, 333k and 353k)

Sorption Properties	Filler Content (pphr)	Uncompatibilized			Compatibilized		
		313K	333K	353K	313K	333K	353K
Diffusion Coefficient (cm ² min ⁻¹) x10 ⁻⁵	0	5.807	5.969	6.925	4.768	4.966	5.698
	10	5.454	5.633	6.552	4.625	4.831	5.531
	15	5.384	5.535	6.468	4.499	4.603	5.435
	20	5.249	5.384	6.261	4.319	4.516	5.292
Sorption Coefficient (mol %)	0	0.615	0.658	0.672	0.627	0.637	0.657
	10	0.631	0.643	0.659	0.603	0.624	0.643
	15	0.611	0.635	0.647	0.592	0.613	0.631
	20	0.591	0.601	0.619	0.586	0.589	0.597
Permeability Coefficient Px10 ⁻⁵ (cm ² min ⁻¹ mol %)	0	3.781	3.937	4.652	2.989	3.159	3.746
	10	3.444	3.623	4.319	2.789	3.015	3.554
	15	3.287	3.500	4.187	2.664	2.823	3.431
	20	3.103	3.235	3.878	2.530	2.684	3.161

Table -3 Values of sorption Parameters for NR / PET / DNS bio-composites (compatibilized), at different MAPI / HMDA content, DNS =10(pphr), at different temperatures (313k, 333k and 353k)

Properties	MAPI / HMDA	313K	333K	353K
Diffusion Coefficient (cm ² min ⁻¹) x10 ⁻⁵	2/0	5.375	5.538	6.205
	2/0.3	5.306	5.427	6.025
	2/0.5	4.625	4.831	5.531
	2/0.7	4.405	4.687	5.375
Sorption Coefficient (mol %)	2/0	0.618	0.637	0.652
	2/0.3	0.612	0.631	0.648
	2/0.5	0.601	0.624	0.643
	2/0.7	0.572	0.597	0.606
Permeability Coefficient P x10 ⁻⁵ (Cm ² min ⁻¹ mol %)	2/0	3.322	3.530	4.048
	2/0.3	3.248	3.423	3.903
	2/0.5	2.782	3.013	3.556
	2/0.7	2.518	2.799	3.259

3.2. Determination Diffusion Coefficient (D)

The kinetic parameter, the diffusion coefficient (D), for the filled poly (ethylene terephthalate)/ natural rubber penetrant systems was obtained using the following expression [17, 19]

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

Where h is the initial composite thickness, θ is the slope of the first linear portion of the sorption curve of the plot of Q_t versus \sqrt{t} , and Q_{∞} is the equilibrium absorption. The values of (D) for the different composites (compatibilized and uncompatibilized) system are given in Tables 2 and 3 along with other sorption parameters.

Tables 2 and 3, show that (D) values generally increase with increase in the sorption temperature. Johnson and Thomas, [18] had reported an increase in diffusion coefficient (D) with increase in sorption temperature. This is in contrast to the finding of author [20] who reported that D values generally decreased with increase in sorption temperature of snail shell powder filled natural rubber for the solvent and filler particle size investigated. It is important to note that diffusivity in a given polymer system, whether it is rubbery or glassy polymers, blends, graft polymer, polymer composites or thermoplastic elastomer varies from one polymer system to another.

Table 2, also shows that the (D) values generally decreased with increase in dikanut shell (DNS) powder content at any temperature considered. The decrease in the diffusion coefficient with increasing filler concentration observed in the composites may be due to each filler particle behaving as an obstacle to the diffusing molecules. As the concentration of filler increases in the thermoplastic elastomer matrix, more and more obstacles are created to the diffusing molecules which ultimately reduce the amount of penetrant solvent.

Table 3 also shows strong dependence of (D) on the HMDA content at any filler content and temperature of investigation. The (D) values generally decreased with increase in HMDA content. As expected, higher level of HMDA caused increased cross-linking of the NR/PET/DNS composite and resulted in decrease in the diffusion coefficient. Johnson and Thomas [18] in their studies found that D values decreased with increasing level of epoxidation in the rubber system investigated. It is significant to not that the values of diffusion coefficient for compatibilized composite are lower than that of uncompatibilized composite.

3.3 Determination of Permeability Coefficient (P)

The permeability coefficient (P) of toluene in the composites was obtained using the following expression [21, 22]:

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

The values of permeability coefficients (P) are given in Tables 2 and 3. The values were generally observed to increase with increase in the sorption temperature. This result is in agreement with the finding of Obasi et al, [17] who reported that the permeability coefficient of 50/50 and 60/40 NR/LLDPE blends were observed to increase with increase in sorption temperature. The same trend was also observed for the diffusion coefficient (D). Similarly, Johnson and Thomas, [18] who studied the transport of some n - alkanes through epoxidized natural rubber, found that the permeability coefficient increased with increase in temperature.

However, from Table 3 it is clear that permeability coefficient decreased with increase in HMDA content for all temperatures investigated. This result is an indication of the enhancement of compatibility of the composites with increase in HMDA content.

3.3 Determination of Transport Mechanism

In a study by Igwe and Ezeani, [6] on transport of aromatic solvents through filled natural rubber, sorption data were fitted into the relation:

$$\log \frac{Q_t}{Q_\infty} = \log k + n \log t \tag{6}$$

Where Q_t and Q_∞ are the mol % sorption at time t and equilibrium, respectively
 K , is a constant that depend on the structural characteristics of the composites and gives information about the interaction between the composite and the solvent, The value of $n = 0.5$ indicates a Fickian mode of transport while $n = 1$ indicates case II (relaxation controlled) transport. When the value of n , lies between 0.5 and 1 it indicates anomalous transport behaviour. The values of n and k for the composites were obtained by regression analysis of $\log (Q_t / Q_\infty)$ versus $\log t$, and the results are given in Table 4

It can be seen in Tables 4 that the values of n obtained for the bio-composites (compatibilized and uncompatibilized) at different temperatures and dikanut shell contents considered are Fickian.

Table -4 Values of n and K for NR/PET/DNS bio-composites (Uncompatibilized and Compatibilized), at different DNS content, at different temperatures (313k, 333k and 353k)

Filler (pphr)	n for Uncompatibilized			k for Uncompatibilized			n for compatibilized			k for compatibilized		
	313k	333K	353K	313K	333K	353K	313K	333K	353K	313K	333K	353
0	0.338	0.318	0.306	0.197	0.216	0.219	0.351	0.334	0.311	0.164	0.208	0.2115
10	0.348	0.338	0.329	0.166	0.182	0.199	0.364	0.350	0.341	0.146	0.173	0.185
15	0.359	0.355	0.351	0.152	0.177	0.182	0.384	0.359	0.357	0.129	0.154	0.171
20	0.390	0.385	0.355	0.116	0.158	0.162	0.406	0.360	0.359	0.116	0.147	0.160

It is evident from Tables 4 that the values of n obtained for the thermoplastic elastomer (compatibilized and uncompatibilized) decreased with increase in the sorption temperature. Ewulonu et al [5] in their studies of transport of n - hexane through carbonized oil palm empty fruit bunch powder filled polypropylene/ natural rubber bio-composite found that n values for compatibilized and uncompatibilized bio-composites decreased with increase in sorption temperature. The values of n were also observed to increase with increasing filler loading at any temperature considered. The values of k obtained in this study were observed to increase with increase in sorption temperature for compatibilized and uncompatibilized bio-composites for all filler loading studied. The values of k in Table 4 were found to decrease with increasing filler content.

3.4 Determination of Activation Energy Parameters.

The temperature dependence of transport properties was used to evaluate the activation energy for diffusion, and permeation processes using the Arrhenius relation [18, 23]:

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

Where E_D is the activation energy of diffusion, which is a function of the intra- and inter- chain forces that must be overcome to create the space for a diffusional jump of the toluene molecule, D_0 is the pre-exponential factor, and R and T are the 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 5

Table -5 Values of activation energy of diffusion (E_D) and permeation (E_P) for NR/PET/DNS bio-composites (Uncompatibilized and Compatibilized), at different DNS content

Filler (pphr)	E_D (KJ/mol)		E_P (KJ/mol)	
	Uncompatibilized	Compatibilized	Uncompatibilized	Compatibilized
0	13.155x10 ²	17.012x10 ²	20.275x10 ²	22.068x10 ²
10	14.597x10 ²	17.222x10 ²	22.1677x10 ²	23.652x10 ²
15	17.139x10 ²	18.237x10 ²	23.669x10 ²	24.645x10 ²
20	17.845x10 ²	19.716x10 ²	23.81710 ²	25.667x10 ²

Table 5 shows that as amount of Dikanut shell (DNS) increased, the values of E_D also increased for both compatibilized and uncompatibilized bio-composites. Again, the values of E_D for compatibilized composites are generally higher than that of the uncompatibilized composites.

3.5 Determination of Enthalpy (ΔH_s) of Absorption and Entropy (ΔS_s) of Absorption

In order to determine enthalpy of absorption (ΔH_s) and entropy of absorption (ΔS_s) for the solvent in the filled poly (ethylene terephthalate)/ natural rubber, the equilibrium absorption constant (K_s) of the solvent was first toluene using the following Equation [24]:

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

The values of k_s obtained were substituted into Van't Hoff's equation [19]:

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

The plots of Van't Hoff's equation were used in calculating ΔH_s and ΔS_s . The values of ΔH_s and ΔS_s obtained are given in Tables 8 and 9

Table -6 Values of Enthalpy of absorption (ΔH_s), Entropy of absorption (ΔS_s) and Gibbs free energy of sorption (ΔG_s) for NR/PET/DNS bio-composites (Uncompatibilized and Compatibilized), at different DNS content.

Filler (pphr)	ΔH_s (KJ/mol)		ΔS_s (KJ/mol)		ΔG_s (KJ/mol)	
	Uncompatibilized	Compatibilized	Uncompatibilized	Compatibilized	Uncompatibilized	Compatibilized
0.	9.022×10^2	15.671×10^2	-38.490x9	-36.762	9.4069×10^2	16.0770×10^2
10	8.134×10^2	13.850×10^2	-37.7802	-37.338	8.7040×10^2	14.2237×10^2
15	9.559×10^2	22.241×10^2	-38.6445	-35.264	9.9458×10^2	22.5944×10^2
20	14.462×10^2	18.494×10^2	-37.6265	-39.605	14.7945×10^2	8.8875×10^2

Table 6 shows that the calculated values of ΔH_s for both compatibilized and uncompatibilized bio-composites are generally positive. No definite order in variation of ΔH_s with filler loading investigated was observed. This result is in agreement with the finding of author [20] who reported that for rubber vulcanizates of snail shell powder (0.075Nm), the calculated ΔH_s was observed to be generally positive and showed no relationship with the penetrant (solvent) size, the dipole moment, filler, content, or filler particle size.

Enthalpy of absorption (ΔH_s) is a composite parameter involving contribution from (1) 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) and (2) 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. In this study, the positive Enthalpy of absorption (ΔH_s) values obtained for the aromatic solvent (toluene) suggest that sorption, in this case, is dominated by Henry's mode with endothermic contribution.

3.6 Determination of Gibbs free energy of Sorption (ΔG_s)

The change in Gibbs free energy (ΔG_s) for the aromatic solvent (toluene) in the NR/PET/DNS composite was obtained using following expression [5]:

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

Where, T is the temperature in Kelvin. The calculated values of ΔG_s are presented in Table 6, The values of ΔH_s and ΔS_s earlier determined for the solvent were substituted into equation 10. The calculated values of ΔG_s were all positive, and this is an indication of the non-spontaneity of the solubility of composites at 313K. The calculated values of ΔG_s did not show any relationship to the dikant shell (DNS) content.

4. CONCLUSION

The transport behaviour of toluene through dikant shell powder filled natural rubber/ poly (ethylene terephthalate) has been studied at three different temperatures (313, 333, and 353 K) by conventional weight-gain experiments. The effects of maleated polyisoprene (MAPI)/hexamethylenediamine (HMDA) as dual compatibilizers and filler loading on the sorption properties of the bio-composites was also investigated. The result showed that at any particular sorption temperature and filler loading, the compatibilized composites absorbed less toluene than uncompatibilized composites. Equilibrium sorption values were observed to decrease progressively with increasing content of HMDA in the compatibilized composites at any temperature considered. Equilibrium sorption was also found to decrease with increasing dikant shell powder loading for both compatibilized and uncompatibilized composites. 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 mode of transport of toluene into filled natural rubber/ poly (ethylene terephthalate) 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 dikant shell powder filled natural rubber poly (ethylene terephthalate) bio-composites but gave an insight into the behaviour of the bio-composites in external liquid environment which is essential for their successful applications.

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