

Uptake of Automobile Fluids by Dynamically Vulcanized Recycled Polyethylene/natural Rubber (rPE/NR) Biocomposites

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Abstract This study presents long term sorption properties of automobile fluids – premium motor spirit (PMS) and automotive gas oil (AGO) in dynamically vulcanized recycled polyethylene/natural rubber (rPE/NR) thermoplastic elastomer biocomposites. The effect of oil palm empty fruit bunch (OPEFB) filler and maleic anhydride graft polyethylene (MAPE) as compatibilizer on the rPE/NR blends were also studied. The automobile fluids uptake trend was observed to reduce with OPEFB incorporation. Uptake of the automobile fluids by the biocomposites increased rapidly within the first 24 hours and subsequently increased gradually within the 7 days period studied. The analysed results also showed that both the uncompatibilized and compatibilized thermoplastic elastomer biocomposites absorbed more PMS than AGO at same OPEFB loading and immersion time. Diffusion, sorption, and permeation coefficients of both PMS and AGO for the compatibilized biocomposites decreased with increasing OPEFB content. The mode of transport of the automobile fluids into the filled rPE/NR blends has been found to be Fickian where the n values ranges from 0.1 to 0.4 for the various systems. This study also revealed greater degree of interaction between the PMS and the biocomposites than the AGO and the biocomposites.

Keywords: polymer composites, recycled polyethylene, natural rubber, automobile fluid, sorption, transport mechanism, thermoplastic elastomers

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1. Introduction

In recent years waste polymer materials have been the biggest threat to the environment. Thermoplastics especially polyethylene constitute bulk of these waste polymer materials. The most effective solution for this problem is to recycle and reuse the polymer products after their useful life [1]. This can be done by several methods which include the blending of the recycled plastic with other classes of polymers. For instance, thermoplastic elastomers can be produced from this process.

Thermoplastic elastomers (TPEs) are a new class of thermoplastic materials that 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 [2]. As a result, many commercial TPEs have been developed for various applications in the automotive, electrical and medical industries [3]. Many literature sources have also

revealed excellent report on the diffusion and sorption processes in elastomer/thermoplastic blends. Obasi et al. [4] investigated the diffusion characteristics of toluene into natural rubber/linear-low density polyethylene. They found that the 75/25 NR/LLDPE blend exhibited the highest amount of molar percentage uptake of toluene at the temperatures studied while noting that the transport of toluene through most of the blends were anomalous.

The presence of solvents in polymers or blends assumes significance since most polymers after swelling in solvent shows reduction in its properties. Thus, the basic transport phenomenon plays a prominent role in many industrial and engineering applications of polymers. The effects of these solvents are believed to be due to localized plasticization that allows the development of craze, and cracks at reduced stress [5]. The diffusion processes in polymers 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 [6].

Reports on the effect of fillers on the diffusion and sorption processes have immersed interest of scientists [7,8,11]. Thus, Onyeagoro and Enyiegbulam [9] studied the sorption characteristics of dynamically vulcanized polypropylene/epoxidized natural rubber blend filled with carbonized Dika nutshell. Ahmed et al. [10] found that the swelling index of filled natural rubber/linear low-density

polyethylene blends in toluene decreased with increase in filler loading and this was attributed to the increase in the crosslink density of the blend.

It is obvious that diffusion study in polymers is very important because of its constant contact with foreign molecules, gases, liquids, or solids. The transport of these molecules in TPEs is also very important since TPEs can be considered for rubber replacement for industrial applications. Therefore, oil resistant TPEs have very serious scientific and economic importance in the automotive industry. Oil resistance is the reciprocal of the degree of swelling in oil and is governed by the competition between the driving force towards dissolution of the thermoplastic elastomer in the oils and the intermolecular forces of the polymer matrix.

In this study, we report the uptake of automobile fluids - automotive gas oil (AGO) and premium motor spirit (PMS) by blends of natural rubber and recycled polyethylene filled with oil palm empty fruit bunch (OPEFB) powder. The effects of maleic anhydride-graft-polyethylene (MAPE) compatibilizer and filler content on the diffusion and sorption processes of the thermoplastic elastomer biocomposites were studied. The present study affords a very good example of how compatibilizers and fillers affect the diffusion of high molecular weight hydrocarbon fluids into polymeric blends. Thus, an understanding of the membrane transport properties, sorption, and diffusion coefficient and penetration rate with respect to automotive gas oil (AGO) and premium motor spirit (PMS) is necessary in order to commercialize the use of the substrate under investigation and other filled TPEs.

2. Materials and Methods

2.1. Materials

The recycled polyethylene (rPE) used in this study was a collection of waste water sachets of Ben-lovers water plant, Awka, Nigeria. The polyethylene water sachets prior to use were washed thoroughly with detergent powder, dried, crushed and pelletized. Its melt flow index was determined to be 2.5 dg/min, while the density and specific gravity are 0.927 g/cm³ and 0.927 respectively. Natural rubber (NR) 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, Nigeria 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 Benin City, Nigeria.

The preparation of the oil palm empty fruit bunch (OPEFB) powder used as filler has been discussed earlier [11]. Maleic anhydride-graft-polyethylene (MAPE) used as the compatibilizing agent in this study is a product of Sigma-Aldrich Cheme GmbH, Germany and was used as received. The Automotive Gas Oil (AGO) and Premium Motor Spirit (PMS) used in this study are products of Nigerian National Petroleum Commission (NNPC) and were purchased from NNPC mega filling station Awka. The AGO and PMS has densities of 0.835 and 0.745

g/cm³ respectively while their molecular weights are 223.91 and 103.5 g/mol respectively. AGO is composed of about 75% saturated hydrocarbons (primarily paraffins including n, iso, and cycloparaffins), and 25% aromatic hydrocarbons (including naphthalenes and alkylbenzenes). The average chemical formula for common AGO fuel is C₁₂H₂₃, ranging from approximately C₁₀H₂₀ to C₁₅H₂₈. Petrol consists of hydrocarbons with between 5 and 12 carbon atoms per molecule but then it is blended for various uses. Overall a typical petrol sample is predominantly a mixture of paraffins (alkanes), naphthenes (cycloalkanes), aromatics and olefins (alkenes). The ratios vary based on a variety of factors.

2.2. Methods

2.2.1. Preparation of the thermoplastic elastomer biocomposites

The formulation used in preparing the biocomposite blend is presented in Table 1, while the steps taken to blend the thermoplastic elastomer including the incorporation of the OPEFB filler and MAPE compatibilizer is as reported by Ewulonu et al [11]. The oil palm empty fruit bunch was prepared as stated by Ewulonu and Igwe [15]. 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. Two different sets of rPE/NR blend biocomposites were prepared. Firstly, rPE/NR/OPEFB composites were prepared at various filler loadings. Secondly, rPE/NR/OPEFB composites in the presence of a compatibilizer, MAPE were prepared. Blends of rPE and NR were prepared by melt mixing, carried out in a Brabender Plastic order model PLE 331. rPE was first melted for 2 mins at 150°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 into a two-roll mill (set at 150°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 150°C to 80°C before the introduction of the vulcanizing agent and accelerators to prevent premature curing of the compound mix. The blends were compression moulded at 120°C with a pressure of 10MPa for 12 mins. Samples for testing were then punched out from these moulded sheets. The formulation used in preparing the blends is presented in Table 1.

Table 1. Compounding recipe for rPE/NR/OPEFBbiocomposites

Materials	Uncompatibilized (pphr)	Compatibilized (pphr)
Natural rubber	30	30
Recycled polyethylene	70	70
Zinc oxide	5	5
Stearic acid	2	2
OPEFB powder (Filler)	0, 10, 20, 30	10, 20, 30
Sulphur	3	3
MBT	0.5	0.5
TMTD	1	1
Wax	4	4
MAPE	-	5

pphr- Parts per hundred resin

2.2.2. Procedure for sorption test

Blends of uniform thickness (0.38 mm) were cut and weighed on an analytical balance having an accuracy of 0.001 g. The cut samples were put into sample bottles with covers. 20cm³ of PMS was poured into each of the sample bottles. The bottles were placed on a table at room temperature. At the expiration of the specified time, the blends were removed from the sample bottles, wiped free of adhering petrol with filter paper, weighed using the analytical balance and the difference between the dry film and the wet film computed. The following time intervals were investigated: 60, 120, 180, 240, 300, 360, 420, 480, 540, 600, 720, 840, 960, 1080, 1200, 1320, 1440 minutes and 24, 48, 72, 96, 120, 144, 168 hours. 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 using AGO fluid. 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. For each sample, three parallel tests were conducted to ensure accuracy of the results. The sorption data of PMS and AGO into uncompatibilized and compatibilized recycled polyethylene/natural rubber (rPE/NR) blend filled with OPEFB powder were determined and expressed as the molar percentage uptake (Q_t) of automobile fluids per gram of rPE/NR blends. Q_t was calculated using equation (1) [12].

$$Q_t = \frac{\text{Mass of automobile fluid absorbed}}{\left(\frac{\text{Molecular weight of the fluid}}{\text{Initial mass of blend}}\right)} \times 100 \quad (1)$$

3. Results and Discussion

3.1. Sorption Properties

3.1.1. Percentage Molar Uptake

Effect of the oil palm empty fruit bunch (OPEFB) loading on molar percentage uptake of the automobile fluids, AGO and PMS into uncompatibilized and compatibilized rPE/NR blends are illustrated in Figures 1 – 4. Each of the figures shows that there was a gradual decrease in the mol. % AGO and PMS uptake as the OPEFB loading increases. This reduction was distinctive in the uncompatibilized biocomposites (Figure 1 and Figure 3) especially after the first 24 hours of sorption. Billmeyer [13] explains that long-range movements of polymer molecules are restrained by vulcanization leaving their local segmental mobility high. Therefore, reinforcement restricts these local freedoms of movement and thereby improves the fluid resistance. It is clear from all the figures that as the OPEFB loading increased the biocomposites apparent equilibrium fluid uptake decrease. This is evidently due to increased hindrance exerted by OPEFB at higher loadings.

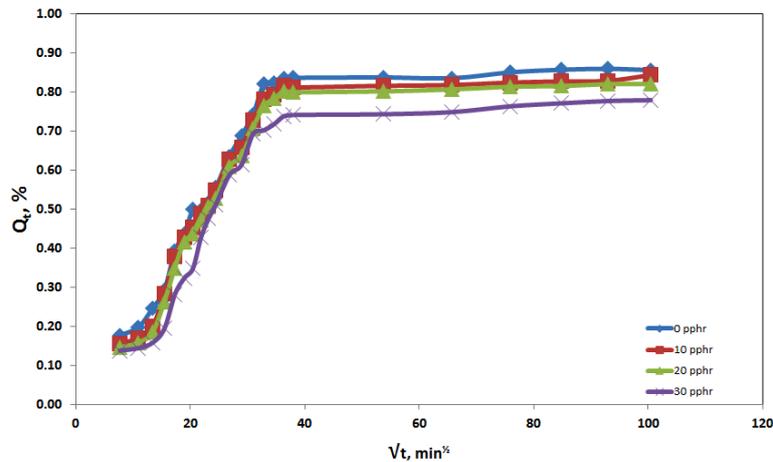


Figure 1. Molar percentage uptake (% Q_t) of AGO sorbed into rPE/NR biocomposites at different OPEFB loadings

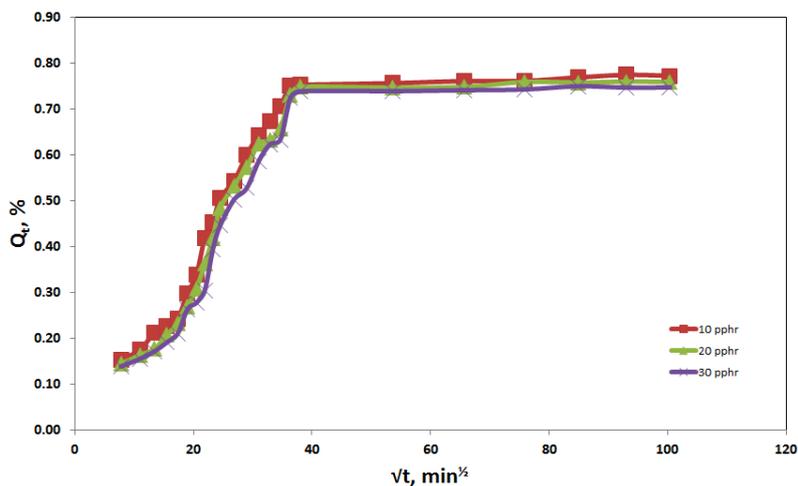


Figure 2. Molar percentage uptake (% Q_t) of AGO sorbed into compatibilized rPE/NR biocomposites at different OPEFB loadings

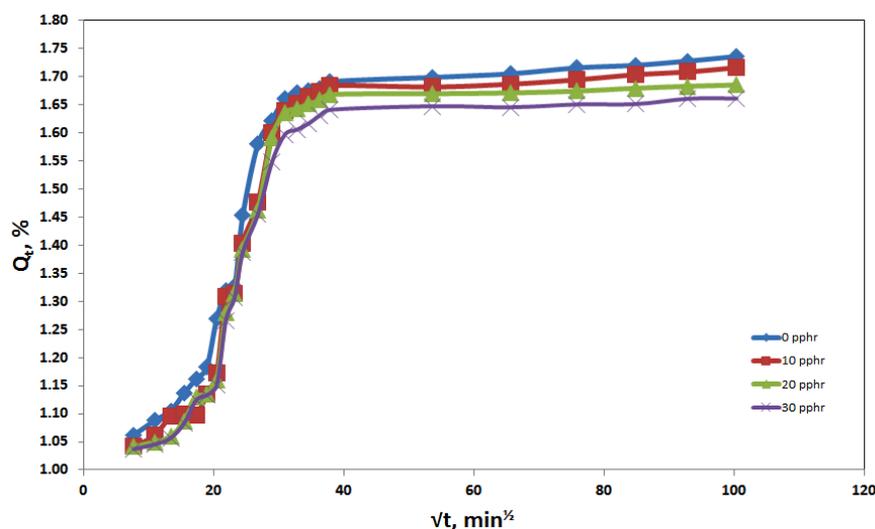


Figure 3. Molar percentage uptake (Q_t) of PMS sorbed into rPE/NR biocomposites at different OPEFB loadings

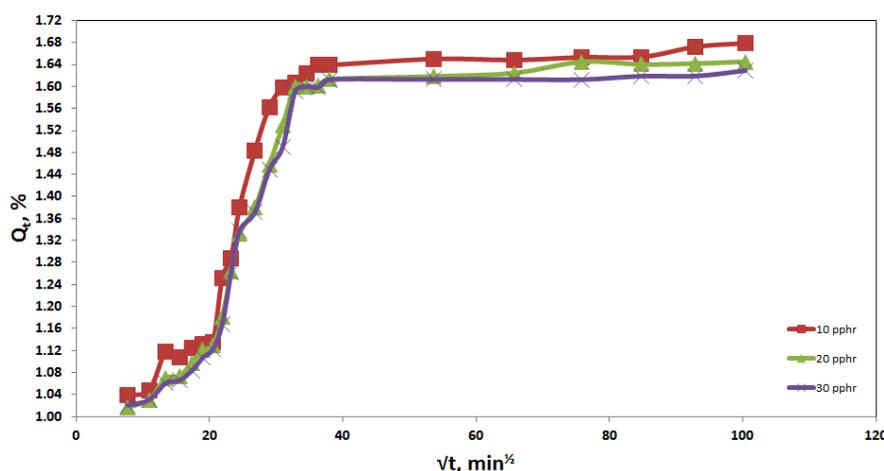


Figure 4. Molar percentage uptake (Q_t) of PMS sorbed into compatibilized rPE/NR biocomposites at different OPEFB loadings

The results also showed that at any particular sorption temperature and filler loading, the compatibilized blend sorbed less AGO and PMS 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-polyethylene (MAPE) which created a tortuous path for the permeating molecules [11]. Since the compatibilizer caused a better bonding between the rPE/NR matrix and OPEFB filler, the strong interface developed restricted the automobile fluid's entrance into the biocomposites leading to a sharp and further decline in the apparent equilibrium uptake. Varghese et al. [14] established that highly bonded systems would exhibit high resistance to swelling compared to the unbounded systems. Ewulonu and Igwe [15] further established that MAPE improves other properties of polyethylene reinforced with OPEFB.

It is interesting to note that both the uncompatibilized and compatibilized thermoplastic elastomer biocomposites absorbed more PMS than AGO at same OPEFB loading and immersion time. This may be attributed to the molecular weight of the hydrocarbon fluids. Mathew et al. [16] stated that larger size of solvent molecules hinders the molecule from penetrating voids or solvent pockets present in composites. Therefore, the low molecular weight hydrocarbons present in premium motor

spirit can easily penetrate into the biocomposites than those present in automotive gas oil. It is important to note that the molecular weight of AGO (223.91g/mol) is higher than that of PMS (103.5 g/mol).

3.1.2. Effect of OPEFB and MAPE on long term sorption

Figure 5 and Figure 6 show the long termsorption effects on the thermoplastic elastomer biocomposites at different OPEFB loadings for uncompatibilized and compatibilized blends. It is obvious from the figures that loading the thermoplastic elastomers with OPEFB slightly reduced the percentage molar uptake. This effect was studied between 12 hours and 168 hours (7 days). It is important to state that though the OPEFB loading reduced the AGO uptake as shown in Figure 5, there was also a gradual increase in the quantity sorbed as the time of sorption increased. The compatibilized blends did not deviate from this trend though slightly lower values were observed. The long term sorption behaviour is represented as follows: AGO99UC or AGO99C; PMS99UC or PMS99C. Where AGO is automotive gas oil, PMS is premium motor spirit, 99 is the period of sorption in hours, UC represents the uncompatibilized blends while C is for the compatibilized blends.

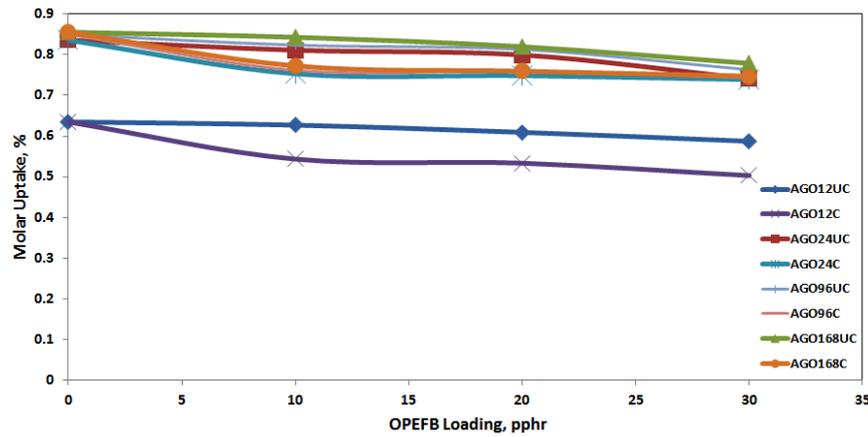


Figure 5. Effect of OPEFB loading on the molar percentage uptake of AGO by compartibilized and uncompartibilized rPE/NR biocomposites at different time intervals

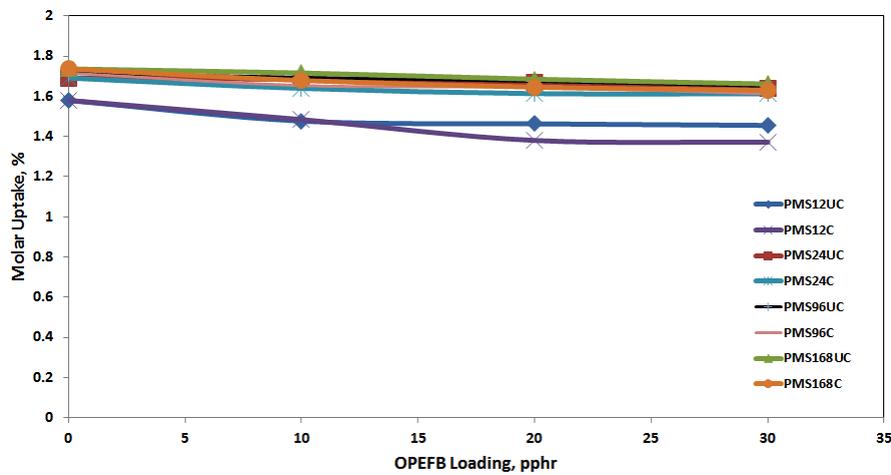


Figure 6. Effect of OPEFB loading on the molar percentage uptake of PMS by compartibilized and uncompartibilized rPE/NR biocomposites at different time intervals

However, the quantity of PMS sorbed by both the uncompartibilized and compartibilized biocomposites were much higher than the quantity of AGO sorbed within the same time and OPEFB loading. From Figure 6, it is obvious that after the first 24 hours of immersion for both the uncompartibilized (PMS24UC) and compartibilized (PMS24C) blends, there was no further uptake of PMS rather there was a very slight decline in uptake as OPEFB loading increased. This evidently shows that for PMS uptake, MAPE has little or no effect on the biocomposite's ability to reach equilibrium but greatly affects the quantity of fluid sorbed before equilibrium in the case of AGO.

3.1.3. Effect of OPEFB and MAPE on crosslinking density

The plot of apparent crosslink density of the present systems which represents the average molecular weight between crosslinks is illustrated in Figures 7 and 8. The swelling data was estimated using Equation (2).

$$\text{Crosslinking Density} = \frac{1}{Q} \quad (2)$$

Where

$$Q = \frac{\text{Swelling Percentage}}{\text{Molecular Weight of the Automobile Fluid}} \quad (3)$$

The extent of crosslinking can be established by determining the reciprocal swelling values, $1/Q$, where Q is defined as the amount of fluid absorbed by the biocomposite [17,18].

From the figures, the apparent crosslinking density increased as the OPEFB loading increased but decreased as the time of sorption increased. The addition of the MAPE lead to a slight increase in the crosslinking density of the biocomposites as the OPEFB loading and time of sorption increased. It is important to note that the crosslinking density was studied after long term sorption (12 hours to 7 days).

The crosslinking density is a representation of the molecular interaction between the automobile fluids, MAPE, OPEFB and the thermoplastic elastomer matrix. This interaction explains the bonding strength of the above variables. The increase observed as the OPEFB loading increased can be attributed to restriction to molecular mobility caused by blockage and increased network formation created by OPEFB preventing the automobile fluids from penetrating the matrix. It was obvious that as time increased, bonds are been broken by the fluids granting free energy to the molecules of the matrix for movement, thereby reducing the crosslinking density.

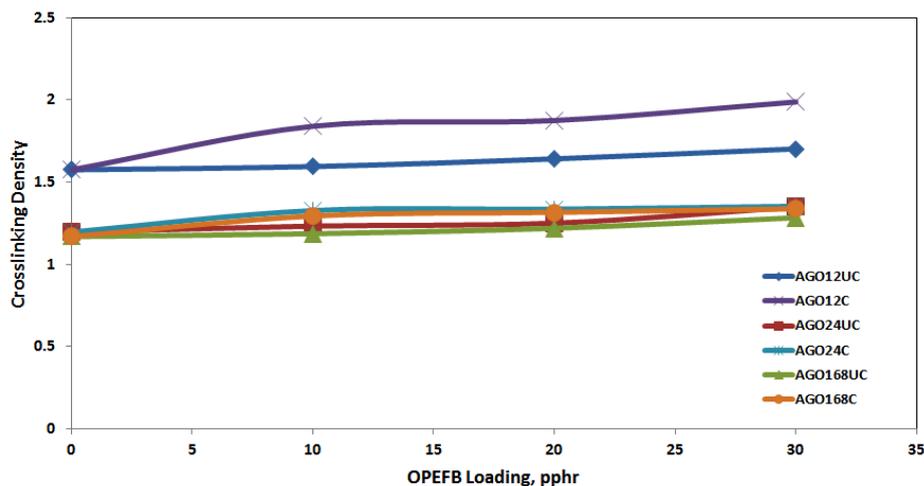


Figure 7. Effect of OPEFB loading on the crosslinking density of compatibilized and uncompatibilized rPE/NR biocomposites immersed in AGO at different time intervals

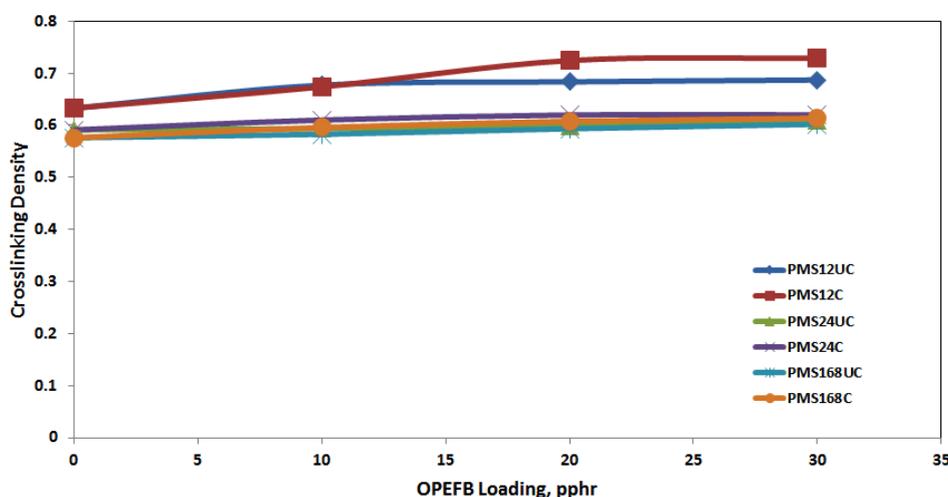


Figure 8. Effect of OPEFB loading on the crosslinking density of compatibilized and uncompatibilized rPE/NR biocomposites immersed in PMS at different time intervals

3.2. Analysis of Diffusion, Sorption and Permeation Coefficients

3.2.1. Diffusion Coefficient

The diffusion coefficient (D) of a solvent molecule in a polymer network is a kinetic parameter that relates polymer segmental mobility and penetrant nature to the different crosslinks present in the polymer matrix. Diffusion coefficient can be calculated using Equation (4) [19].

$$\frac{Q_t}{Q_\infty} = 1 - \frac{8}{\pi^2} \sum_{m=0}^{\infty} \left[\frac{1}{(2m+1)^2} \right] e^{-(2m+1)^2 \pi^2 \frac{D.t}{h^2}} \quad (4)$$

where Q_t and Q_∞ are the mol. % uptake at time t and at equilibrium respectively and m is an integer. D is the diffusion coefficient and h is the initial thickness of the sample. Equation (4) can be solved for short time limiting as:

$$\frac{Q_t}{Q_\infty} = 4 \left[\frac{D.t}{\pi h} \right]^{\frac{1}{2}} \quad (5)$$

Since the plot of Q_t versus \sqrt{t} is linear at short times, Equation (5) can be rearranged to give the overall diffusion coefficient thus:

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

Where θ is the slope of the initial linear portion of the plot of Q_t against \sqrt{t} .

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 in AGO increased with increase in filler concentration. This can be attributed to the increased heterogeneity occasioned by the increasing filler content in the uncompatibilized blends. On the other hand, the diffusion coefficient of the compatibilized blends in both AGO and PMS decreased as the OPEFB content increased. The diffusion mechanisms in polymers are essentially connected with the ability of the polymer to provide pathways for the solvent to progress in the form of randomly generated voids. As the void formation decreases with increased homogeneity occasioned by improved interfacial adhesion caused by the

compatibilizer addition, the fluid uptake also decreases leading to a decline in the D values.

Note that diffusion process is influenced by interfacial phenomenon and the rubbery or glassy nature of phases for heterogeneous blends [20]. 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. Furthermore, very low D values were observed for both the uncompatibilized and compatibilized blends in PMS than in AGO.

Table 2. Values of sorption properties, n and k for the AGO and PMS in the uncompatibilized and compatibilized blends

Sorption/Transport Properties	OPEFB CONTENT (pphr)	Uncompatibilized Blends		Compatibilized Blends	
		AGO	PMS	AGO	PMS
Diffusion Coefficient (mm ² /min) X 10 ⁻⁵	0	2.8621	0.82260	-	-
	10	3.0432	0.80629	2.7360	0.73555
	20	3.1160	0.82183	2.6637	0.65933
	30	3.5807	0.76179	2.4456	0.62284
Sorption Coefficient (mol. %)	0	1.8676	7.7918	-	-
	10	1.8248	6.7096	1.6867	1.6964
	20	1.7899	8.2580	1.6729	1.6696
	30	1.6635	7.1043	1.6544	1.6690
Permeation Coefficient (mm ² min ⁻¹ mol. %) X 10 ⁻⁵	0	5.3452	6.4095	-	-
	10	5.5534	5.4099	4.6147	1.2478
	20	5.5772	6.7867	4.4560	1.1008
	30	5.9558	5.4120	4.0459	1.0395
n	0	0.3181	0.1167	-	-
	10	0.3380	0.1223	0.3506	0.1163
	20	0.3507	0.1206	0.3719	0.1198
	30	0.3742	0.1175	0.3861	0.1178
k	0	0.0770	0.3882	-	-
	10	0.06557	0.3669	0.0576	0.3867
	20	0.0593	0.3718	0.0475	0.3739
	30	0.0492	0.3814	0.0416	0.3764

3.2.2. Solubility

The sorption coefficient (S) of the oil palm empty fruit bunch powder filled rPE/NR blends in AGO and PMS was evaluated using Equation (7) [12].

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

where M_{∞} is the mass of automobile fluids sorbed at equilibrium and M_o is the initial mass of rPE/NR/OPEFB blend. M_{∞} is given as:

$$M_{\infty} = Z * \text{molecular weight of the automobile fluids} \quad (8)$$

where Z denotes number of moles of automobile fluids orbbed at equilibrium swelling.

The calculated values of the sorption coefficient (S) are also presented in Table 2. It is evidently clear from the table that the S values of the biocomposites decreased with increase in OPEFB loading except for the uncompatibilized blends sorbing PMS which did not show any clear pattern. This justifies the sorption process since the solvent molecules have to penetrate into the tightly packed network and hence the rate of penetration process will be low [21].

Interestingly, PMS showed a very high solubility in the uncompatibilized blends when compared to the behaviour of AGO in either the compatibilized and uncompatibilized blends or PMS in the compatibilized blends. The higher solubility coefficient observed could be due to the closeness of compatibilized blend's solubility parameter to that of PMS. Solubility parameter is a measure of intermolecular attraction and it is a very important factor that affects solubility of polymers in solvents. Thus, similarity in the solubility parameters of polymers and solvents increases their chances of absorption and dissolution [11].

3.2.3. Permeability Coefficient (P)

The permeability or permeation coefficient (P) of a penetrant in a polymer membrane depends on the diffusivity as well as solubility or sorption of the penetrant in the polymer membrane [22]. Therefore, the permeability coefficient (P) of the automobile fluids in the thermoplastic elastomer (TPE) biocomposites was obtained using the following expression [23].

$$P = D * S \quad (9)$$

where D id the diffusion coefficient and S is the sorption coefficient.

The values of P presented in Table 2 shows that there was a reduction in P values as the OPEFB content increased in the compatibilized blends both for AGO and PMS. Inversely, the P values for AGO in the uncompatibilized blends increased with increase in filler loading whereas that of PMS in uncompatibilized blends did not show any clear pattern of relationship to the amount of OPEFB incorporated. In Figure 9, it was further observed that the P values of PMS in the uncompatibilized blends where much higher than P values of PMS in compatibilized blends and AGO in both uncompatibilized and compatibilized blends. This pattern practically followed the path of diffusion coefficient, hence, it may be inferred that the diffusion process controls the permeability of the automobile fluids in the biocomposites. This is also in agreement with the works of Unnikrishnan et al, [24] and Ewulonu et al, [11] who found that the permeability values of filled NR-penetrant and TPE-penetrant systems respectively followed the same trend as that of diffusivity. This behaviour further explains the closeness of the solubility parameters of PMS and the compatibilized biocomposites.

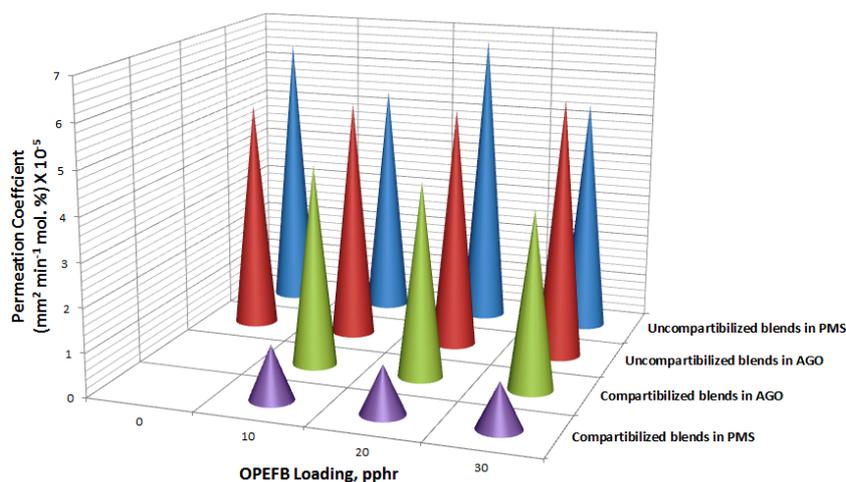


Figure 9. Effect of OPEFB loading on the permeation coefficient of compartmentalized and uncompartmentalized rPE/NR biocomposites immersed in PMS and AGO

3.3. Mode of Transport

The mechanism of transport was analysed by fitting the sorption data into the following empirical relation [25]:

$$\log \frac{Q_t}{Q_\infty} = \log k + n \log t \quad (10)$$

where k indicates the interaction between the penetrant and the polymer and n represents the mode of transport.

For a Fickian mode of transport, where the rate of polymer chain relaxation is higher compared to the diffusion rate of the penetrant, the value of n is 0.5. When $n = 1.0$, it indicates Case II (relaxation controlled) transport, that is the transport approaches non-Fickian behaviour, where chain relaxation is slower than the liquid diffusion. When n lies between 0.5 and 1.0, it indicates anomalous transport behaviour. The values of n and k for the different systems are presented in Table 2. It is evident from the table that the n values obtained for all the different systems studied are Fickian. The values of n for both the uncompartmentalized and compartmentalized OPEFB powder filled rPE/NR did not show any relationship to the amount of OPEFB powder incorporated in the case of PMS whereas in AGO, the n values increased with increase in OPEFB loading.

The values of k obtained in this study were observed to decrease with increases in the OPEFB content of the thermoplastic elastomers. This pattern was observed for both the compatibilized and uncompatibilized blends in AGO. The values of k for sorption of PMS exhibited no relationship with the quantity of OPEFB in the biocomposites for both the uncompartmentalized and compartmentalized blends. The values of n obtained in PMS for both the uncompartmentalized and compartmentalized blends are lower than that obtained for AGO in the blends whereas the values of k in AGO are lower than the k values in PMS for both the uncompartmentalized and compartmentalized TPE biocomposites. This is an indication that there is a greater degree of interaction between the thermoplastic elastomer biocomposites and PMS than AGO. This could be as a result of the lower molecular size of PMS when compared to AGO which gave PMS easier access into the TPE biocomposite structure.

4. Conclusions

The sorption of automobile fluids (AGO and PMS) into rPE/NR blend filled with OPEFB powder has been investigated. The effect of OPEFB content (0 to 30 pphr), and MAPE on the sorption properties of the TPE biocomposites was also evaluated within 7 days sorption period. The automobile fluids uptake trend has been observed to be reduced by OPEFB incorporation. It is interesting to note that both the uncompartmentalized and compartmentalized thermoplastic elastomer biocomposites absorbed more PMS than AGO at same OPEFB loading and immersion time. Diffusion, sorption, and permeation coefficients of both PMS and AGO for the compatibilized biocomposites decreased with increasing OPEFB content. The mode of transport of the automobile fluids into the filled recycled polyethylene/natural rubber blends has been found to be Fickian with greater degree of interaction between the PMS and the biocomposites.

References

- [1] S. Rajalekshmia and R. Josepha. Studies on thermoplastic elastomer based on linear low-density polyethylene and latex product waste modified with thiocarbonyl. *International journal of polymeric materials and polymeric biomaterials*, 54(10), (2005).
- [2] S. H. Zhu, C. M. Chan and Y. X. Zhang. Nitrile rubber/natural rubber thermoplastic composites. *Journal of applied polymer science*, 58, (2005).
- [3] F. Cai and N. Isayev. Studies on the mechanical and morphological properties of nitrile rubber/polystyrene blend. *Journal of elastomer and plastics*, 25, 249-260(2003).
- [4] H. C. Obasi, O. Ogbobe and I. O. Igwe. Diffusion characteristics of toluene into natural rubber/linear low density polyethylene blends. *International journal of polymer science*, 54(4), 765-771(2009).
- [5] R. F. Jeol, *Polymer science and technology*, second edition, New Delhi: Prentice-Hall, 2005.
- [6] I. O. Igwe, C. M. Ewulonu and I. Igboanugo. Studies on the diffusion characteristics of some aromatic solvent into polypropylene films. *Journal of applied polymer science*, 102(2), 1985-1989, (2006).
- [7] F. Candia, L. Gargani, and A. Renzulli. Transport properties of filled elastomeric networks. *Journal of applied polymer science*, 41(5-6), 955-964, (1990).

- [8] S. N. Lawandy and S. H. Botros. Effect of type and amount of carbon black on the interaction between polychloroprene rubber and motor oil. *Journal of applied polymer science*, 42 (1), 137–141, (2001).
- [9] G. N. Onyeagoro and M. E. Enyiegbulam. Sorption characteristics of dynamically vulcanized PP/epoxidized NR blends filled with carbonized dika nutshell. *Academic research intimation*, 3 (2), (2012).
- [10] A. Ahmed, D. H. Mohd and I. Abdullah. Mechanical properties of filled natural rubber/linear low density polyethylene blends. *Iranian polymer journal*, 13 (3), 73-178, (2004).
- [11] C. M. Ewulonu, G. N. Onyeagoro and I. C. Chukwujike. Transport of n-hexane through carbonized oil palm empty fruit bunch powder filled polypropylene/natural rubber biocomposites. *International journal of composite materials*, 4(1), 4-13, (2014).
- [12] D. Danwanichakul, S. Jaroenkarn, P. Jumpathi and D. Dechojarassri. Sorption and desorption of toluene, m-xylene, p-cresol and water by natural rubber chips. *Songklanakarinn journal of science and technology*, 28(5), 1071-1082, (2006).
- [13] F. W. Billmeyer. *Text book of polymer science*. WileyInterscience, Singapore (1994).
- [14] H. Varghese, S. S. Bhagawan and S. Thomas. Transport properties of crosslinked acrylonitrile butadiene rubber/poly (ethylene-co-vinyl acetate) blends. *Journal of polymer science part B: polymer physics*, 37(15), 1815-1831, (2009).
- [15] C. M. Ewulonu and I. O. Igwe. Properties of oil palm empty fruit bunch fibre filled high density polyethylene. *International journal of engineering and technology*, 3(6), 458-471, (2012).
- [16] A. P. Mathew, S. Packirisamy, R. Stephen and S. Thomas. Transport of aromatic solvents through natural rubber/ polystyrene (NR/PS) interpenetrating polymer network membranes. *Journal of membrane science*, 201(1-2), 213-227, (2002).
- [17] I. C. Chukwujike, C. M. Ewulonu and M. Chukwu. Sorption properties of carbonized/uncarbonizedcornhub powder filled natural rubber/acrylonitrilebutadiene rubber biocomposite. *International journal of multidisciplinary research and development*, 2 (8), 154-160, (2015).
- [18] J. W. M. Noordermeer, R. N. Datta, W. K. Dierkes, R. Guo, T. Mathew, A. G. Talma, M. Tiwari and W. van Ooij. Surface modification of fillers and curatives by plasma polymerization for enhanced performance of single rubbers and dissimilar rubber/rubber blends. *Advanced polymer science* 239, 167-218, (2011).
- [19] J. Crank. *The mathematics of diffusion*. Clarendon – Oxford university press, Oxford, UK (1975).
- [20] H. Odani, M. Uchikura, Y. Ogino, M. Kurata. Diffusion and solution of methanol vapor in poly (2-vinylpyridine)- block-polyisoprene and poly(2-vinylpyridine)-block-polystyrene. *Journal of membrane science*, 15(2), 193-208, (1983).
- [21] K. P. Dasan, G. Unnikrishnan and E. Purushothaman. Solvent transport through carbon black filledpoly (ethylene-co-vinyl acetate) composites. *eXPRESS polymer letters*, 2(5),382-390,(2008).
- [22] I. O. Igwe, and O. E. Ezeani, Studies on the transport of aromatic solvents through filled natural rubber. *International journal of polymer science*, vol. 2012, 1-11, (2012).
- [23] C. Kumnuantip and N. Sombatsompop. Dynamic mechanicalproperties and swelling behaviour of NR/reclaimed rubberblends. *Materials letters*, 57(21), 3167-3174, (2003).
- [24] G. Unnikrishnan, and S. Thomas. Diffusion and transport of aromatic hydrocarbons through natural rubber. *Polymer*, 35(25), 5504-5510 (2004).
- [25] T. M. Aminabhavi and H. T. S. Phayde. Molecular transportof alkanes through thermoplastic miscible blends of ethylenepropylenerandom copolymer and isotactic polypropylene. *Journal of applied polymer science*, 55, 1335-1352, (1995).