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SORPTION CHARACTERISTICS OF DYNAMICALLY VULCANIZED POLYPROPYLENE/EPOXIDIZED NATURAL RUBBER BLENDS FILLED WITH CARBONIZED DIKA NUTSHELL (Irvialgia Gabonensis).

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ABSTRACT

The sorption characteristics of dynamically vulcanized polypropylene/epoxidized natural rubber blends filled with carbonized Dika nutshell have been investigated with special reference to the effects of filler carbonization temperature and dosage of cross-linking agent. Toluene, an aromatic solvent commonly used in the rubber industry, was chosen as the solvent in this investigation. The filled blends were prepared by compression moulding using maleic anhydride-graft-polypropylene as a compatibilizer. The blend morphology was studied using Scanning Electron Microscope (SEM). Both the SEM and dynamic vulcanization studies indicate that the non-compatibilized/ non-vulcanized blends are immiscible and form two-phase structures, accompanied by high solvent (toluene) uptake. Resistance to toluene sorption increased with increase in the dosage of cross-linking agent due to increase in cross-link density as a result of increase in network formation. This behaviour is supported by SEM micrographs of vulcanized and non-vulcanized blends, which reveal restriction to swelling of vulcanized blends due to increase in network formation. Resistance to toluene sorption with increase in filler carbonization temperature was also observed. This is attributed to increase in surface area of the filler due to the elimination of volatile matter that are deleterious to the blend-filler interfacial interaction.

Keywords: sorption characteristics, carbonized Dika nutshell, polypropylene, epoxidized natural rubber, dynamic vulcanization.

INTRODUCTION

One of the most important phenomena in polymer science that has captured great research and industrial interest is the blending of polymers, since blending is a relatively simple way to create materials with significantly improved properties. Different polymers may be blended to obtain a more cost-effective material that combines the properties of both polymers that cannot be obtained from the individual polymers (Sperling, 1997; Datta and Lohse, 1996; Konig *et al.,* 1998). Of all polymer blends, elastomer-thermoplastic blends called thermoplastic elastomers stand out as technologically useful materials, since they have many properties of elastomers and yet process able as thermoplastics (Morris, 1979). Thus, they offer substantial economic advantage with respect to fabrication of finished parts.

The best way to produce elastomer/thermoplastic blend comprising vulcanized elastomer particles in melt process able plastic matrices is by the method called dynamic vulcanization. The improvement in properties resulting from dynamic vulcanization include improved ultimate mechanical properties, greater resistance to attack by fluids, improved high temperature utility, and more reliable thermoplastic fabricatability. Unfortunately, due to relatively low entropy of mixing arising from large differences in surface energy and polarity, most polymer pairs are immiscible, resulting in the formation of a sharp interface between the two polymer phases, coarse phase morphology, and poor mechanical properties (Dilorenzo and Frigione, 1997; Painter and Coleman, 1997).

Very often, copolymers are used as interfacial modifiers in immiscible polymer blends to improve the properties of the blend creating compatibilized blend. Compatibilized blends are not necessarily miscible blends, but blends that satisfy certain useful industrial criteria, such as satisfactory physical

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and chemical properties. Copolymers composed of monomers or segments that are miscible with both phases function as effective compatibilizers, as their presence at the interface may lead to decrease in interfacial tension and increase in interfacial adhesion between the phases and stable phase morphology. The copolymer molecules cross the interface to form stitches which couple the two phases together, thereby compatibilizing the blend. This compatibilization results in improved overall physical and chemical properties (Baker *et al.,* 2001; Hara and Sauer, 1998).

Polypropylene (PP) is a thermoplastic material with very good physical properties and low cost. It has a high softening temperature of about 230^0C, and is readily steam-sterilized which makes it suitable for use in the manufacture of hospital equipment such as syringes. PP is an excellent electrical insulator with good stress crack resistance. However, pp has low impact resistance, and its methyl side groups are susceptible to thermo-oxidative degradation (Joel, 2005). Although, PP is resistant to aromatic hydrocarbon and chlorinated hydrocarbon solvents, oil and greases, but it is attacked by these solvents at elevated temperatures of 60^0C and above. In order to overcome these drawbacks, PP has been blended with acrylic rubber (Soares *et al.,* 2008), ethylene-propylene-diene rubber (Gupta *et al.*, 2000; Manchado *et al.,* 2002), ethylene-propylene rubber (Chatterjee and Naskar, 2007), nitrile rubber (Zhang *et al.,* 2002; Naderi *et al.,* 1999; George *et al.,* 1999; Soares *et al.,* 2006; Coran and Patel, 1983). These polymer pairs are immiscible, and thus the resultant blends do not attain optimal properties. The non-polar nature of PP and polar character of epoxidized natural rubber (ENR) require that blends of this type be compatibilized in order to obtain a useful material that combines the excellent properties of PP with the impact and oil resistance of ENR (Alex *et al.,* 2003). Maleic anhydride-grafted-polypropylenes (PP-g-MAs) have been successfully used to compatibilize blends of PP with many elastomers such as acrylic rubber (Soares et al, 2008), nitrile rubber (Naderi *et al.,* 1999; Goerge *et al.,* 1999 ; Soares *et al.,* 2006; Zhang *et al.,* 2002; Manchado *et al.,* 2002; Gupta *et al.,* 2000), and natural rubber (Thitihammawong *et al.,* 2007). The presence of maleic anhydride-grafted polypropylene (PP-g-MA) in the blends resulted in improved solvent and impact resistance, and finer phase morphology relative to the non-ncompatibilized blends (Gupta *et al.,* 2000; Naderi *et al.,* 1999; Zhang *et al.,* 2002; Manchado *et al.,* 2002; Soares *et al.,* 2006; Chatterjee and Naskar, 2007).

The presence of solvents in polymers or their blends assumes significance since most polymers after swelling in the solvent show a reduction in their properties. The effect of these solvents is believed to be due to localized plasticization that allows the development of crazes or cracks at reduced stress (Joel, 2005). Therefore, polymers for commercial applications should be chemically resistant and retain their mechanical integrity and dimensional stability on contact with solvents (Henry et al., 2009). It has been pointed out that the study of diffusion, sorption, and permeation in blend structure provides valuable means for additional characterization of polymer blends (Hopffenberg and Paul, 1978). Thus, the basic transport phenomena play a significant role in many industrial and engineering application of polymers (Koszinowoski, 1986; Berens and Hopffenberg, 1982). Many literature sources have revealed excellent reports on the diffusion and sorption processes in elastomer/thermoplastic blends. Thus, transport studies have been conducted on blends of propylene/nitrile rubber (George *et al.,* 2000), nylon/ethylene-propylene rubber (George *et al.,* 2000), polystyrene/natural rubber (Asaletha *et al.,* 1998).

In the present study, blends of polypropylene/epoxidized natural rubber filled with carbonized Dika nutshell (C-DNS) obtained at different carbonization temperatures have been prepared, using maleic anhydride-grafted polypropylene as a compatibilizer. The sorption of toluene, an aromatic solvent, through the blends has been investigated, the sorption coefficient was calculated and the effect of filler (C-DNS) carbonization temperature on the sorption properties of the filled blends was investigated. Also, the extent of cross-linking of the rubber (ENR) phase in the blends using different levels of benzoyl peroxide (BPO) as cure system was studied by measuring the volume fraction (V_r) of the rubber (ENR) in toluene- swollen blends. Furthermore, Scanning Electron Microscopy (SEM) was used to determine the effect of dynamic vulcanization on morphological changes in the blends. Studies on diffusion of toluene through carbonized Dika nutshell powder-filled PP/ENR has not been reported in any accessible scientific literature to our knowledge. However, the preparation of carbonized groundnut shell was reported by Ayo et al, 2011, who investigated the effect of filler carbonization temperature on the mechanical properties of natural rubber composites. Their results revealed that

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tensile strength, modulus, hardness and abrasion resistance increased with increase filler content and filler carbonization temperature, whereas compression set, flex fatigue and elongation showed a decreasing trend with increase in filler content and filler carbonization temperature. This work therefore, seeks to produce a cheap, process able and biodegradable thermoplastic-elastomer blend with improved sorption properties.

Toluene, an aromatic solvent commonly used in the rubber industry, was chosen as the solvent in this work.

MATERIALS ND METHOD

Materials

Polypropylene of density 0.9g/cm^3 and melt flow index of 3.5g/10min at 230^{0}C/2.16kg, and maleic anhydride-modified polypropylene (PP-g-MA) (Polybond 3200) melt flow index = 115g/10min at 190^{0}C/2.16kg ; 1 wt.% of maleic anhydride) were purchased from Rovet Chemicals Ltd, Benin City, Nigeria. Epoxidized natural rubber of density 0.95g/cm^3 and epoxide content of 33%, was obtained from a chemical store in Lagos, Nigeria. Rubber grade additives used were Zinc Oxide (ZnO), stearic acid, and benzoyl peroxide (BPO).

Preparation of Carbonized Dika Nutshell Powder (C-DNS)

Dika nutshells were washed and dried in air to remove sand particles and moisture. The dried Dika nutshells were milled to fine powder and sieved through a mesh size of 150µm. The fine particles that passed through the mesh were collected and divided into four portions. The four portions were then carbonized for 3hours (Ishak and Baker, 1995) at different temperatures of 200^{0}C, 400^{0}C, 600^{0}C, and 700^{0}C, respectively. Each carbonized portion was kept in a desiccator and allowed to cool to room temperature until required.

Preparation of Blend Samples

Blends of PP and ENR were prepared by melt mixing, carried out in a Brabender Plastic order model PLE 331. PP was first melted for 2min at 230^{0}C followed by the addition of ENR. Mixing continued for 6min. In dynamically vulcanized samples, the curatives and compatibilizer were added 2min after the rubber (ENR) had been introduced, followed by the addition of C-DNS filler. Mixing was stopped after 10min. The formulation used in preparing the blends is given in Table 1. Four different blends were prepared and are designated as P50, P50B1, P50B2, and P50B3. In this designation, P and B represent PP and BPO, respectively. The figures following P and B indicate the corresponding concentrations of PP and BPO in each blend. The amounts of the curatives are based on the rubber phase only. The blend formulations were compression moulded at 230^{0}C. Samples for testing were then punched out from these moulded sheets.

Table 1. Compounding recipe for PP/ENR blend

	Designation			
Ingredients (by weight)	**P50**	**P50B1**	**P50B2**	**P50B3**
PP	50	50	50	50
ENR	50	50	50	50
PP-g-MA	0	1.5	2.5	3.5
Stearic acid	0	2.0	2.0	2.0
sZnO	0	5.0	5.0	5.0
BPO	0	1.0	2.0	3.0
C-DNS	0	10	10	10

Sorption Test

Blends of uniform size were cut and weighed on an electronic balance having an accuracy of 0.001g. The cut samples were put into sample bottles with covers. 25ml of toluene were poured into each of the sample bottles. The bottles were placed in a thermostatically controlled water bath at 30^0C 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 toluene, and weighed using the electronic balance (Henry et al, 2009). The weighing was continued till equilibrium swelling was attained. The experiments were further repeated with blends containing C-DNS filler obtained at four different filler carbonization temperatures of 200^0C, 400^0C, 600^0C, and 700^0C. 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 (Danwanichakul et al, 2006).

Measurement of Crosslink Density

The crosslink density of an elastomer or its blends can be determined from swelling or mechanical measurements (Al-Gahtani, 2011). In this study, the crosslink density which is a measure of the extent of cross-linking was measured by determining the volume fraction, V_r of the rubber (ENR) in toluene swollen blend samples after 48 hours using the relation (Soares et al, 2008):

$$V_r = \frac{(D - f\,T)P_r^{-1}}{(D - f\,T)P_r^{-1} + A_0 P_S^{-1}} \quad \text{---------------------------------------(1)}$$

Where D is the weight after drying, f is the fraction of insoluble components, T is the weight of the sample, A_0 is the weight of the absorbed solvent, P_r is the density of the rubber, and P_s is the density of the solvent.

Scanning Electron Microscopy (SEM) Studies.

The morphology of P50 and P50B3 samples were analyzed using liquid nitrogen fractured samples. The SEM micrographs were obtained using a JEOL Model 5610 LV Scanning electron microscope after sputter coating the surface with gold/palladium alloy.

RESULTS AND DISCUSSION

The sorption data of toluene into PP/ENR blends filled with C-DNS obtained at different filler carbonization temperatures of 200^0C, 400^0C, 600^0C, and 700^0C were determined and expressed as the molar percentage uptake (Qt) of toluene per gram of PP/ENR blends. Qt was calculated using (1) (Danwanichakul et al, 2006).

$$Qt = \frac{\text{Mass of toluene absorbed}}{\text{Molecular weight of toluene/Initial mass of the blend}} \times 100 \quad \text{------------------------------(2)}$$

The molar percentage uptake (Qt) of the blends filled with C-DNS obtained at any particular filler carbonization temperature was plotted against the square root of time (√t) as shown in Figures 1, 2, 3, 4, and 5. The results show initial increasing trend in the mass of toluene sorbed until maximum absorption was attained, after which equilibrium absorption was reached at which time, the mass of the absorbed toluene remained constant. The results also show that at any particular filler carbonization temperature, the non- vulcanized blend (P50) sorbed more toluene than the vulcanized blends. This is consistent with the results of the SEM micrographs of the blends (Figure 7), which reveal better dispersion and mixing, and less solvent uptake caused by dynamic vulcanization. The order in the amount of toluene (Qt) sorbed by the blends at the four filler carbonization temperatures studied is P50 > P50B1 > P50B2 > P50B3 blend.

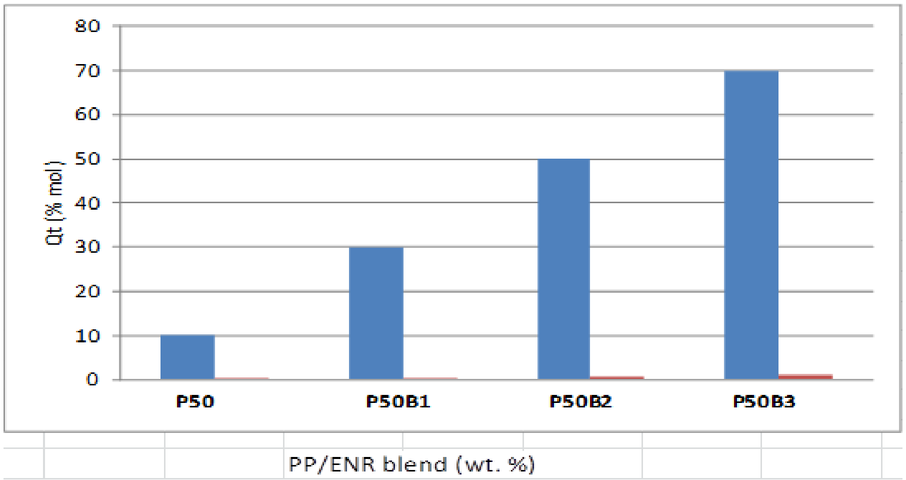

Figure 1. Dependence of equilibrium toluene uptake Qt (% mol) on blend compositions of PP/ENR blends filled with C-DNS obtained at 600˚C carbonization temperature.

Crosslink Density

The extent of cross-linking of the rubber phase in the blends containing different levels of BPO was studied by measuring V_r values. The variation of V_r values with BPO concentration is presented in Figure 6. The result shows that V_r values increase with extent of cross-linking due to restriction to swelling which increases with increase in network formation. Thus, crosslink density increased with increase in BPO content.

Morphological Changes

The SEM micrographs of non-vulcanized (P50) and dynamically vulcanized (P50B3) samples are presented in Figure 7 (a) and (b), respectively. The results show that due to the incompatibility of PP and ENR a few number of coarsely distributed ENR particles can be observed in the non-vulcanized (P50) sample. Dynamic vulcanization results in cross-linking of the rubber (ENR) phase, thereby causing particles break-up and more efficient dispersion and mixing as observed in Figure 7(b).

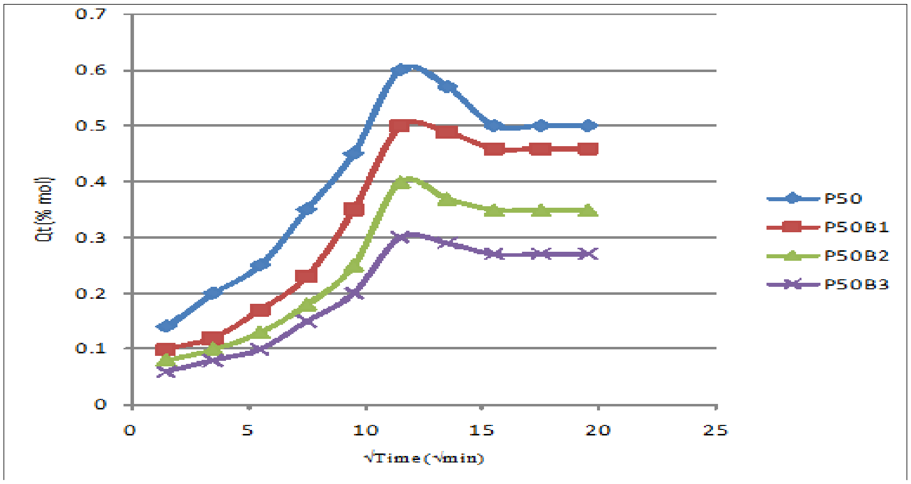

Figure 2. Plot of Molar percentage uptake (Qt) versus square root of Time of PP/ENR blends filled with C-DNS obtained at 200˚C carbonization temperature.

Determination of Sorption Coefficient (S)

The sorption coefficient (S) of the carbonized Dika nutshell filled-PP/ENR blends was evaluated using the relation (Danwanichakul et al, 2006):

$$S = \frac{M_e}{M_O} \quad \text{---(3)}$$

Where M_e is the mass of toluene sorbed at equilibrium and M_O is the initial mass of the blend. M_e is given as

$$M_e = Z \text{ x molecular weight of toluene} \quad \text{---(4)}$$

Where Z denotes moles of toluene sorbed at equilibrium swelling. The calculated values of the sorption coefficient (S) are presented in Table 2. As shown in Table 2, the non-vulcanized blend (P50) is least resistant to toluene sorption, irrespective of the carbonization temperature of the filler (C-DNS) used. However, resistance to toluene sorption increased on dynamic vulcanization and with increase in filler carbonization temperature, except the blend filled with 700^{0}C temperature- carbonized C-DNS, which did not show any definite order in the variation of S. The increase in toluene sorption with dynamic vulcanization is attributed to increase in cross-link density due to increase in network formation. Similarly, the observed increase in toluene sorption with increase in filler carbonization temperature is caused by increase in surface area of the filler (C-DNS) due to the elimination of volatile matter that are deleterious to blend-filler interfacial interaction. The order in the variation of S with filler carbonization temperature is P50 > P50B1 > P50B2 > P50B3 blend.

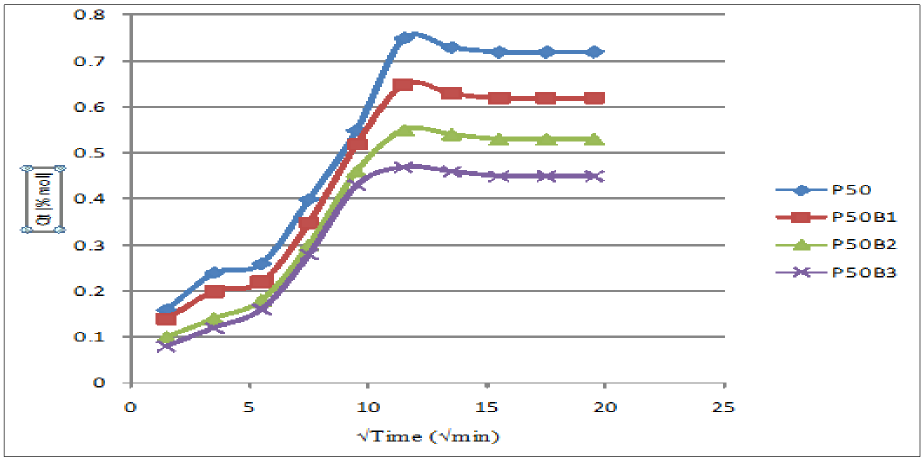

Figure 3. Plot of Molar percentage uptake (Qt) versus square root of Time of PP/ENR blends filled with C-DNS obtained at 400˚C carbonization temperature.

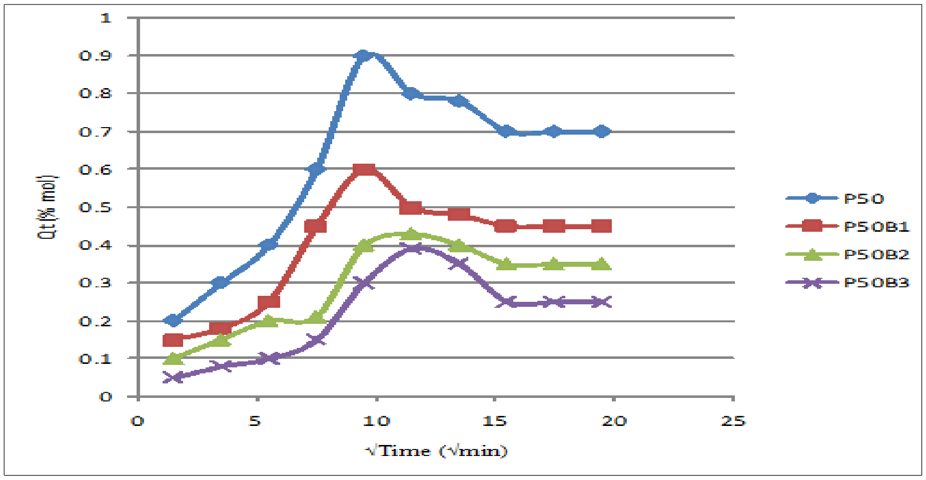

Figure 4. Plot of Molar percentage uptake (Qt) versus square root of Time for PP/ENR blends filled with C-DNS obtained at 600˚C carbonization temperature.

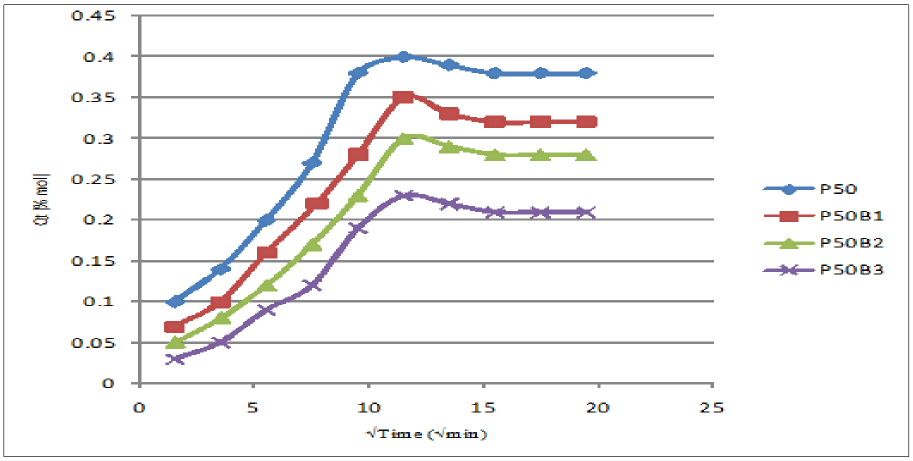

Figure 5. Plot of Molar percentage uptake (Qt) versus square root of Time of PP/ENR blends filled with C-DNS obtained at 700˚C carbonization temperature.

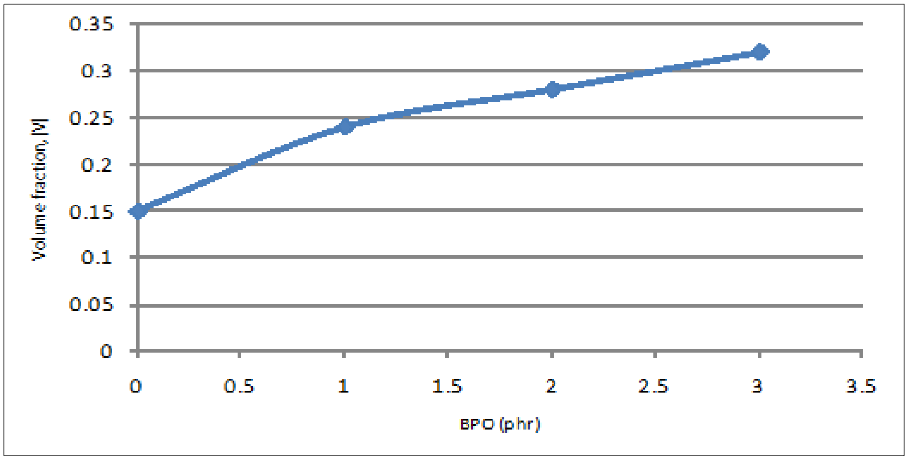

Fig. 6. Dependence of Volume fraction (Vr) on BPO concentration showing the influence of extent of crosslinking on Vr values of blend samples.

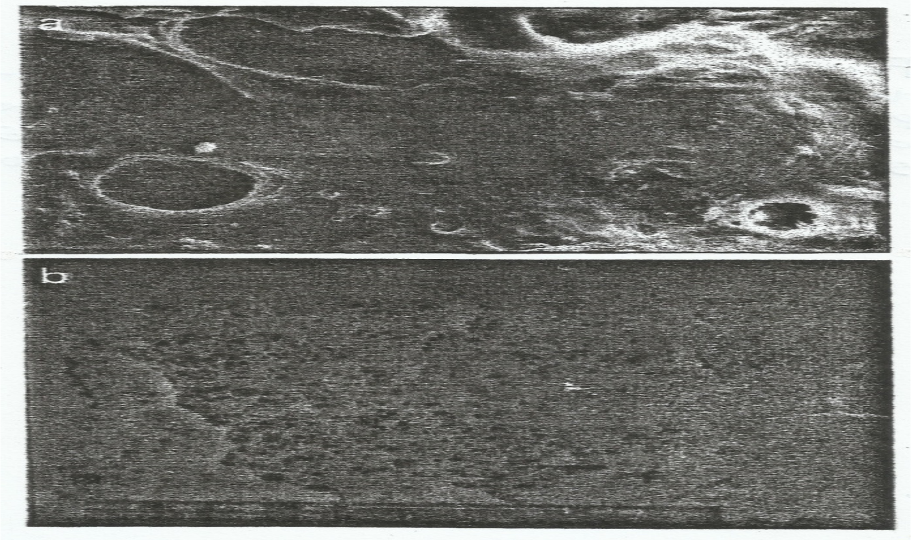

Figure 7. SEM micrographs showing the degree of dispersion of the rubber (ENR) phase of (a) non-vulcanized (P50) and (b) dynamically vulcanized (P50B3) 50/50 blends of PP and ENR.

Table 2. Sorption Properties of dynamically vulcanized PP/ENR Blends filled with C-DNS carbonized at different temperatures.

Temp (^{0}C)	Blend Designation	Sorption Coefficient	Q_t (mol %)	n	K
200	P50	0.35	0.75	0.75	0.0345
	P50B1	0.29	0.54	0.60	0.0424
	P50B2	0.24	0.42	0.80	0.0523
	P50B3	0.18	0.31	0.60	0.0655
400	P50	0.44	0.63	0.80	0.0421
	P50B1	0.38	0.44	0.75	0.0525
	P50B2	0.30	0.39	0.65	0.0622
	P50B3	0.21	0.25	0.60	0.0731
600	P50	0.52	0.51	0.85	0.0532
	P50B1	0.45	0.39	0.70	0.0624
	P50B2	0.39	0.31	0.80	0.0715
	P50B3	0.26	0.18	0.50	0.0855
700	P50	0.15	0.34	0.90	0.0354
	P50B1	0.22	0.66	0.70	0.0735
	P50B2	0.18	0.45	0.60	0.0526
	P50B3	0.23	0.76	0.70	0.0855

Transport Mechanism of Toluene through PP/ENR Blends

In a study by Lutch and Peppas, 1987 on transport of penetrants in the macromolecular structure of coal, sorption data were fitted into the relation:

$$\text{Log}\left[\frac{Q_t}{Q_e}\right] = \log k + n \log t \qquad \text{--(5)}$$

Where Q_t is the swelling quotient at time, t, and Q_e, the equilibrium swelling, and 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 toluene through the blends. When n = 0.5, the mode of transport is Fickian. For relaxation controlled transport, n = 1.0, whereas for anomalous transport behavior, n lies between 0.5 and 1.0. The values of n and k were obtained from the plot of log [Q_t/Q_e] against log t and are presented in Table 2. The results show that for all blends studied, the non-vulcanized blend showed the highest value of equilibrium toluene uptake Q_t. For blends filled with C-DNS obtained at 200^{0}C, 400^{0}C and 600^{0}C carbonization temperature, Q_t decreased with dynamic vulcanization, but showed an anomalous behaviour for the blend filled with C-DNS carbonized at 700^{0}C. This behavior was noted for the sorption coefficient (S) of the filled blends. The order observed in the value of Q_t for blends filled with C-DNS carbonized at 200^{0}C, 400^{0}C and 600^{0}C is P50 > P50B1 > P50B2 > P50B3 blend. Table 3 also shows that with the exception of the P50B3 blend filled with C-DNS carbonized at 600^{0}C, which showed a Fickian transport behaviour (n = 0.5), other C-DNS filled blends are non-Fickian (n lies between 0.5 and 1.0) and may be described as anomalous. The k values obtained for the blends in this study are an indication of the degree of blend-toluene interaction. The k values were observed to increase with dynamic vulcanization, and also with increases in carbonization temperature of C-DNS, except for the blend filled with C-DNS carbonized at 700^{0}C, where there is no definite trend in the variation of k values with vulcanized and non-vulcanized blends. The order observed in the variation of k values with blends filled with C-DNS carbonized at 200^{0}C, 400^{0}C and 600^{0}C is P50 > P50B1 > P50B2 > P50B3, indicating an increase in interfacial interaction between PP and ENR due to the compatibilizing effect of maleates PP, and also an increase in crosslink density due to dynamic vulcanization. This is consistent with the result of the SEM micrographs of non-vulcanized and vulcanized blends (Figure7), which shows poor morphological structures of the blends (Figure7a) due to coarsely distributed ENR particles in the non-vulcanized blend (P50). There was significant improvement in the blend morphology on dynamic vulcanization (Figure7b) due to cross-linking of the rubber (ENR) phase which causes effective dispersion and mixing resulting in less solvent uptake.

Determination of Activation Energy of Sorption

The dependence of carbonization temperature of C-DNS on sorption characteristics of blends was used to evaluate the activation energy for the sorption processes using the relation (Mathai and Thomas, 1996):

$$\text{Log } S = \log S_0 - (E_s/2.303RT) \quad \text{---(5)}$$

Where S represents sorption coefficient (S), S_0 is a constant, E_s is the activation energy of sorption. Plots of S against 1/T were used to calculate the activation energy of sorption (E_s). The calculated values of E_s are shown in Table 3.

Table 3. Calculated values of Activation Energies of Sorption (E_s) for PP/ENR Blends

Blend Designation	E_s (KJ/mol)
P50	5.4
P50B1	7.6
P50B2	10.5
P50B3	20.8

Table 3 shows that the non-vulcanized blend (P50) with the lowest E_s is the least resistant to toluene sorption. Table 3 also shows that the resistance to toluene sorption increased with dynamic vulcanization of blends, reaching a maximum at P50B3 blend which has the highest E_s value of 20.8KJ/mol. This behavior is consistent with the result of the effect of cross-linking on toluene uptake, which shows that the volume fraction, V_r of the rubber (ENR) phase increased with extent of crosslinking due to restriction to swelling which increases with increase in network formation.

CONCLUSION

The following conclusions can be drawn from this work:

1. The mass of toluene sorbed by carbonized Dika nutshell (C-DNS) filled-PP/ENR blends showed an initial increasing trend until maximum absorption was reached, after which equilibrium absorption was attained, at which time the mass of the absorbed toluene remained constant.
2. The non-vulcanized PP/ENR filled blend (P50) exhibited the least resistance to toluene sorption. Resistance to toluene sorption increased with dynamic vulcanization of the blends, reaching a maximum at P50B3 blend which has the highest crosslink density. This behaviour is supported by SEM micrographs of vulcanized and non-vulcanized blends, which reveals restriction to swelling of vulcanized blends due to increase in network formation.
3. Except for the P50B3 blend filled with C-DNS carbonized at 600^0C, which showed Fickian transport behaviour, other filled blends are non-Fickian and may be described as anomalous.
4. The k values of the filled blends, which is an indication of the degree of blend-toluene interaction increased with dynamic vulcanization, and also with increase in carbonization temperature of the Dika nutshell (C-DNS) used as filler, except for the blend filled with C-DNS carbonized at 700^0C, which did not have any definite trend in the variation of k values.
5. Dika nutshell used as filler in the present study is a biodegradable agricultural by-product and thus, confers biodegradability to the PP/ENR blends. This will help to reduce the impact of non-biodegradable materials on our solid waste stream, which is already a global environmental problem compounded by the ever decreasing availability of landfill space as well as increasing cost of municipal solid waste disposal. This is in addition to the production cost reduction advantage of this filler over the use of conventional, but costly petroleum-based reinforcing fillers such as carbon black.

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