Diffusion and transport of aromatic hydrocarbons through SBR/chemically modified fly ash composites

V.C. Jasna and M. T. Ramesan*

Department of Chemistry, University of Calicut, Calicut University P.O., Kerala, India 673 635

*Corresponding author: E-Mail: mtramesan@uoc.ac.in

ABSTRACT

Composites based on styrene butadiene rubber (SBR) with chemically modified fly ash particles were prepared by two roll mixing technique. The effect of loading of fly ash (FA) was characterized by optical microscopy and X-ray diffraction analysis (XRD). These composites were prepared by adding different dosage of chemically modified FA with SBR in an open two roll mill and vulcanized by sulphur as vulcanizing agent. Solvent transport of aromatic hydrocarbons through the crosslinked SBR composites containing chemically modified fly ash was investigated using sorption gravimetric analysis in the temperature range of 30-70^{0}C . Optical and XRD studies revealed the ordered arrangement of fly ash particles within the macromolecular chain of SBR. Transport studies revealed that the addition of modified FA particles reduced the swelling considerably and the maximum swelling is obtained for lower loading of fly ash. Benzene shows maximum diffusion with the composite compared to toluene and xylene. The diffusion, sorption and permeation coefficients were calculated and also thermodynamic properties were measured using toluene as the solvent. The estimated Arrhenius activation energy for the diffusion, sorption and permeation were lower for composite containing 40 phr of fly ash.

KEY WORDS: Styrene butadiene rubber, Modified fly ash, Diffusion, Sorption, Permeation.

1. INTRODUCTION

Styrene butadiene rubber (SBR) based composites are used in various engineering and industrial applications due to its high filler loading capacity, abrasion resistance, good flex and crack initiation resistance. However, it has poor gum and green strength as compared to natural rubber. In order to improve these properties, it is important to mix with cheap filler particles. Fly ash is a waste mineral material obtained from coal burning thermal power station, the dumping of this waste material will cause severe environmental pollution to air, land and human beings. Fly ash is important filler having very fine particle size, large surface area, hardness etc. There are about 80-85 thermal power station in India which produces hundreds of million tons of fly ash in a year (Pattil and Anandhan, 2012; Ramesan, 2015 a). Nowadays many conventional methods are used to reduce the effect of fly ash especially in the construction field, agricultural sectors (Sikka and Kansal, 1994). Recently fly ash is used as reinforcing filler in elastomers and thermoplastics (Ramesan, 2014, Chand and Vashishtha, 2000).

The polymer solvent interaction through the filled elastomer composite are affected by various factors such as crystallinity and polarity of fillers, adhesion and compatibility with the polymer matrix, size and nature of penetrants etc. Swelling properties using organic solvents will give an idea about internal structure of polymer (Sareena, 2015). The transport behaviour of various organic solvents and gases through polymers is of great importance (Sareena, 2013). Swelling behaviour of composites is mainly depending on the crosslinking in composites. Crosslinking is mainly depends on the amount of vulcanizing agents, filler rubber interaction and temperature (Asha, 2003). The main objective of the present work is to analyse the transport behaviour of SBR with different loading of chemically modified fly ash composite in different organic solvents such as benzene, toluene and xylene at different temperatures.

2. EXPERIMENTAL

2.1. Materials and methods: SBR (Synaprene, 1501) was collected from Synthetics and Chemicals Ltd., Bareilly, UP., and India. Fly ash containing 63 wt. % of SiO2, 30% Al$_2$O$_3$, 3.5 % MgO, 2.5% CaO, 1% TiO$_2$ and 0.65 % K$_2$O; specific gravity (2.08 g/cm^3) was obtained from thermal power station, Kayamkulam, Kerala. Vulcanizing ingredients such as zinc oxide, stearic acid, processing oil, N-cyclohexyl- 2-benzothiazaol (CBS), 2, 2, 4- trimethyl 1-1, 2- dihydroquinoline (TDQ) and sulfur were commercial grade obtained from local rubber chemical suppliers. The solvents benzene, toluene and xylene used were AR grade supplied by Merck India.

2.2. Preparation of chemically modified of fly ash: Preparation of chemically modified fly ash was carried out by using the method adopted by (Ramesan, 2015 b) with a slight modification. Fly ash was first purified by froth floatation method, and the powdered fly ash was sieved through 45 μm mesh size to get fine particles. The chemical

modification of FA was done using two different steps; in the first step zinc hydroxide was prepared by stirring zinc chloride and sodium hydroxide in equimolar ratio for about 10 minutes. The precipitate was washed to remove the bye product and unreacted inorganic components. Fly ash was then added to the above precipitate and stirred for 1 hour at 90 °C. The FA/zinc hydroxide weight ratio was maintained as 5:0.7. A coating of zinc silicate was formed on the surface of FA. In the second step calcium hydroxide was added to the above zinc silicate coated FA by maintain the FAZn/calcium hydroxide weight ratio was at 5:1. This slurry was stirred continuously for four hours at 150 rpm and at 100^0C. The zinc silicate and calcium silicate coated FA (FAZnCa)-water mixture was dried in vaccum oven at 70^0 C for 12 hours. The crystalline nature of the modified FA was analyzed by XRD studies.

2.3. Preparation of SBR/chemically modified fly ash composite: SBR/chemically modified fly ash composite with different loading was prepared in a two roll mixing mill. SBR/FA composite was prepared by mixing various amount of fly ash (0, 10, 20, 30 and 40 phr) in a two roll mixing mill. The mixing composition weight percentage (phr) is as follows, SBR 100 phr, stearic acid 2 phr, zinc oxide 5 phr, TDQ 1 phr, processing oil 1 phr, CBS 1.8 phr. Vulcanization of the mixes were done at 150^0C using a hydraulic press according to their respective cure time. The prepared composites were named as S_0 for SBR, S_{10} (SBR + 10 phr FA), S_{20} (SBR + 20 phr FA), S_{30} (SBR +30 phr FA) and S_{40} (SBR+ 40 phr FA).

2.4. Diffusion Studies: Samples of particular diameter and thickness were cut from the sheets obtained after mixing. Thickness and diameter were measured. The solvents of volume 15-20ml were taken in a diffusion bottle. And the samples were weighed initially, and put in the solvent. Samples were weighed in a regular interval by taking samples outside and the adsorbed solvent is removed using a tissue paper, immediately weighed using an electronic balance, and again put the samples in to the bottle and experiment was repeated up to equilibrium weight obtained. The experiment was done in benzene, xylene and toluene at different temperatures. The mole uptake was obtained from the formula (Ramesan, 2015c).

$$Qt(mol\%) = \frac{\text{Mass of solvent absorbed/Molar mass of solvent}}{\text{Mass of polymer}} \times 100 \quad (1)$$

2.5. Diffusion Coefficient (D): Diffusion coefficient is a kinetic parameter, which gives the ability of penetrant molecules to move among the polymers segment.

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

Where h is the initial sample thickness, h the slope of the linear portion of the sorption curve of the plot of % Qt versus √t, and Q∞ is the equilibrium absorption.

2.6. Sorption coefficient(S): The sorption coefficient is related to the equilibrium sorption of the penetrant molecules and is calculated using the formula.

$$S = \frac{M_\infty}{M_P}$$

Where M_∞ is the mass of the solvent at equilibrium swelling and M_p is the mass of polymer sample.

2.7. Permeation coefficient: The permeation process is related to both sorption coefficient and Diffusion coefficient as follows (Harogoppad and Aminabhavi, 1991)

$$P = D \times S$$

Where D is diffusion coefficient and S is the sorption coefficient.

3. RESULTS AND DISCUSSION

3.1. X-Ray Diffraction analysis: The X-ray diffraction of the composite was carried out by using RIGAKU MINIFLEX-600 diffractometer. It gives an idea about the crystallinity and nature of composites. The X-ray diffraction pattern of modified fly ash, SBR and SBR/modified FA composite are shown in Figure 1. SBR exhibit a broad diffraction pattern centered at $2\theta=19.9^0$ indicates its amorphous nature. Zinc and calcium silicate modified fly ash shows different XRD peaks indicating the crystalline nature of the material. The XRD curve of SBR/FA composite showed a sharp crystalline peak of chemically modified fly ash at $2\theta=26.9^0$ indicates the distribution of FA particles in SBR matrix and it is attributed to the interaction between the fly ash and the macromolecular chain of SBR.

3.2. Morphological studies: The morphological study of SBR and SBR /modified FA is obtained from optical microscopy, and is shown in Figure 2. There are so many voids and irregularities seen in SBR, however by the addition of 10 phr of modified fly ash, the surface of composite become more smooth and a uniformity in distribution

is seen is due to the interfacial interaction of filler with the polymer matrix. When the concentration of FA became 30 phr (S_{30}), the agglomeration of filler particles can be clearly evident from the figure.

3.3. Mole % uptake of solvent (Q_t): The swelling characteristics of SBR/modified FA with various compositions are studied in aromatic solvents like benzene, xylene and toluene. The sorption of composite with increasing filler concentration in toluene is given in Figure 3. In all concentrations there is an initial increase in the mass of the solvent absorbed, then the solvent absorption remains constant, and equilibrium absorption is attained. The mole % uptake of solvent (Qt) is plotted against square root of time to study the diffusion, sorption and kinetics of the systems. At room temperature as the filler loading increases the sorption value is found to be decreasing. SBR/modified FA composite containing 10 phr of modified FA shows maximum sorption and composite having 40 phr of modified FA shows minimum sorption. Similar trend is also observed in benzene and xylene as solvents.

3.4. Effect of penetrant size or Nature of solvent on Q_t: Aromatic solvents such as benzene, xylene and toluene are used to study the effect of solvent on mole uptake; the effect of molecular weight of solvents on mole uptake at room temperature is given in the Figure 4. The Qt values are decreasing with increase in molecular weight of the aromatic solvents. And the variation is in the order benzene > toluene > xylene. This trend is explained using free volume theory, i.e., the diffusion rate of molecule depends mainly on the ease with which the polymer chains exchange their position with penetrant molecules. The mobility of polymer depends on the free volume inside the polymer matrix, on increasing the penetrant size, the exchangeability decreases and thus sorption also decreases. The above nature of SBR-modified FA composite with 30 wt % of modified FA (i.e., S_{30}) in benzene, xylene and toluene are shown below.

3.5. Effect of Temperature on sorption: The effect of temperature on the diffusion of SBR FA composite is done using benzene, xylene and toluene as the solvents. All the solvents show similar trend, sorption in toluene at 30, 50 and 70 °C are given in the Figure 5.The rate of diffusion and the solvent uptake increases with increase in temperature. It reveals the rate of diffusion of solvent into the composite is time and temperature dependent. It is due to the increased segmental mobility and free volume inside the matrix on increasing the temperature. The kinetic energy and transport coefficient of penetrant is also increases with increase in temperature.

3.6. Diffusion (D), Sorption coefficient (S) and Permeability coefficients (P): It can be seen from Table 1 that the value of diffusion coefficient (D) decreases with increase in molecular weight of solvent and this is due to increase in volume, dipole moment, density of solvents and solubility parameter of solvents used. The highest D values are shown in benzene whereas the lowest D value is obtained for xylene. Further the diffusion coefficient decreases with increase in filler loading is also seen from the Table 1. The diffusion is very less at high filler loading and maximum at lower filler loading. The sorption coefficient (S) values also decreases with increase in filler content. SBR-modified FA with 40 wt% (S_{40}) shows minimum S value. Permeation coefficient (P) also show similar trend because it depends on diffusion and sorption. From the table it is clear that P value is maximum for composite in benzene and minimum for xylene.

3.7. Transport mechanisms: The mechanism of transport can be computed from the swelling data using the Equation

Log Qt/Q∞ = log k + n log t

Where Qt and Q∞ are the mol % sorption at time t, and at equilibrium respectively, *k* indicates the interaction between the penetrant and the polymer and *n* represents the mode of transport The value of *n* suggests the mode of transport. For the normal 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, the transport approaches non- Fickian behaviour, where chain relaxation is slower than the liquid diffusion. If the value of *n* is in between 0.5 and 1, the mode of transport is classified as anomalous (Sareena, 2012), *k* is a constant depending on the interaction between the rubber and solvent. The estimated values of *n* and *k* of different systems in aromatic solvents at room temperature are given in Table 2. From the table it is clear that the n values obtained in toluene at room temperature are anomalous transport behaviour. In benzene and toluene n values are higher than xylene. In xylene it is somewhat close to Fickian. Also we can see that n values are closing to non- Fickian on increasing filler loading. The k values show similar trend, ie., benzene have higher k value and xylene have the lowest.

3.8. Arrhenius parameters Ep, E_D and ΔH (KJ mol^{-1}) in Toluene as the Solvent: The temperature dependence of and transport properties can be calculated from Arrhenius equation.

$$X = X_0 \, exp\left(\frac{-E_X}{RT}\right)$$

Where X is either D or P, and X_0 is D_0 or P_0. E_x is the activation energy, from the plots of log D or log P against 1/T drawn and from the slopes of curves the activation energy for diffusion (E_D) and activation energy for permeation (E_P) were calculated from linear regression analysis (Ramesan, 2015) and are given in the Table 3. It is clear that the values of E_D and E_P decreases with increase in filler loading and also the values of E_P are greater than that of E_D. The enthalpy of sorption (ΔH) is related with E_P and E_D as follows,

$$\Delta H = E_P - E_D$$

And ΔH values are increase with increase in filler loading. The positive ΔH values are obtained for all composition in toluene reveal that sorption in this composite is endothermic.
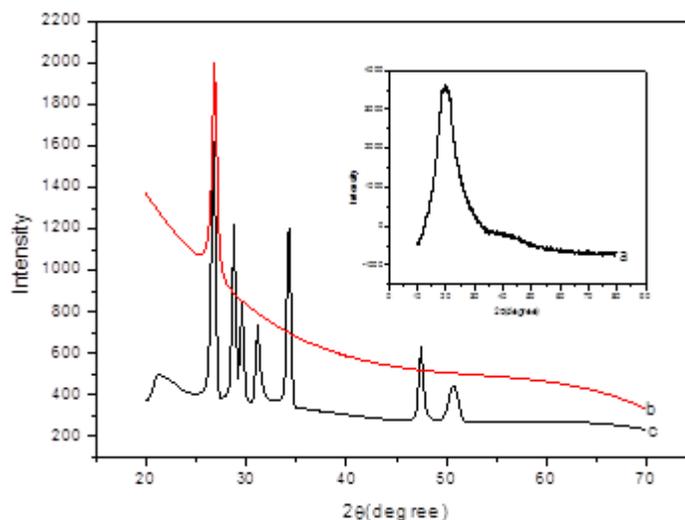

Figure.1.XRD of (a) SBR, (b) SBR with 20 phr of modified FA and (c) modified FA
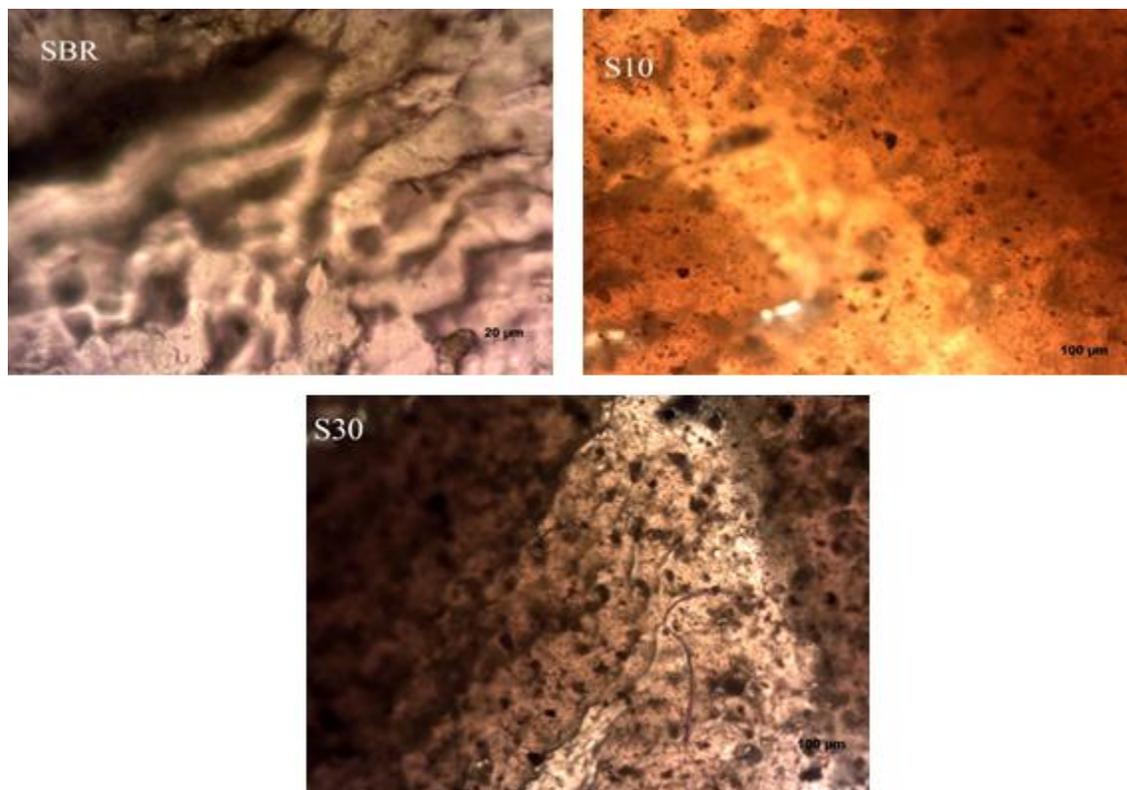

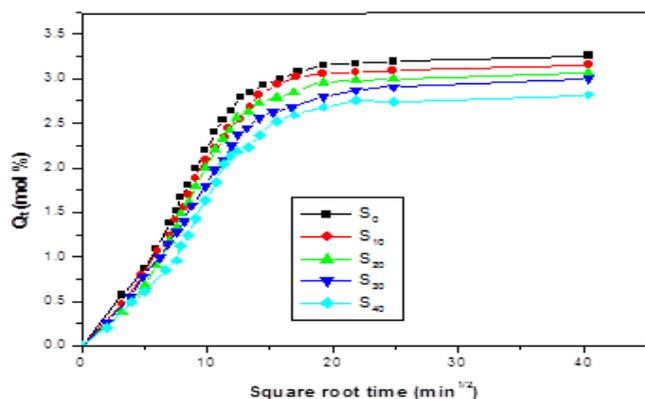**Figure 2. Optical images SBR and SBR with different content of modified FA**

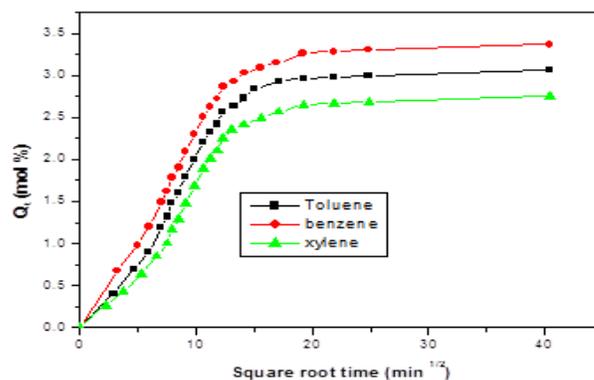**Figure.3.Effect of filler loading on diffusion at room temperature**

Figure.4.Effect of Solvent on diffusion at room temperature
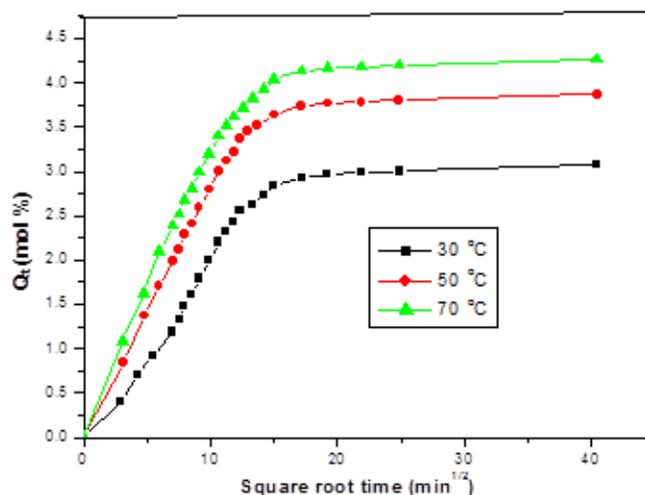

Figure.5.Effect of temperature on mole uptake of solvent (Toluene)

Table.1.Diffusion, sorption and permeation values of SBR/ FA composites in aromatic solvents

Samples	Diffusion coefficient $D \times 10^5$ (cm^2/s)			Sorption coefficient S (mol %)			Permeation coefficient $P \times 10^5$(cm^2/s)		
	Benzene	**Toluene**	**Xylene**	**Benzene**	**Toluene**	**Xylene**	**Benzene**	**Toluene**	**Xylene**
S_0	2.58	2.22	1.84	4.23	4.01	3.81	11.02	9.11	7.23
S_{10}	2.41	2.04	1.69	4.10	3.92	3.74	7.57	7.04	6.48
S_{20}	2.26	1.89	1.51	3.98	3.81	3.61	7.20	6.38	5.52
S_{30}	2.15	1.81	1.34	3.74	3.42	3.06	6.61	5.65	4.56
S_{40}	2.01	1.73	1.13	3.29	3.03	2.84	5.97	4.82	3.60

Table 2. n and k values of SBR /FA with different filler loading in aromatic solvents at 30 ^{0}C

Samples	Benzene		Toluene		Xylene	
	n	$Kx10^2(min^{-1})$	n	$kx10^2(min^{-1})$	n	$Kx10^2(min^{-1})$
S_0	0.64	1.59	0.62	1.48	0.59	1.41
S_{10}	0.68	1.53	0.66	1.47	0.61	1.39
S_{20}	0.71	1.44	0.69	1.31	0.66	1.30
S_{30}	0.74	1.33	0.71	1.25	0.70	1.22
S_{40}	0.73	1.31	0.70	1.20	0.69	1.19

Table.3. E_D, ΔH and E_P values of SBR/FA composites in Toluene

Samples	E_D(KJ/mol)	ΔH(KJ/mol)	E_P(KJ/mol)
S_0	4.83	0.89	5.72
S_{10}	5.61	1.15	6.76
S_{20}	6.42	1.47	7.89
S_{30}	3.89	1.79	5.68
S_{40}	2.75	1.6	4.35

4. CONCLUSIONS

SBR/FA composites were prepared by dispersing different loading of fly ash particles in polymer by a two roll mixing technique. The optical and XRD studies revealed the occurrence of fly ash particles within the polymer matrix. The transport properties of SBR/FA composites had been studied using benzene, xylene and toluene as penetrants with respect to the loading of fly ash particles at different temperature. The equilibrium swelling decreased with increase in concentration of filler, temperature and solvent density. The diffusion, sorption and permeation coefficients are also found to be decrease with increasing filler concentration. The transport mechanism of the composite was closer to a non-fickian mode. The values of E_P and E_D showed the similar trend of diffusion.

5. ACKNOWLEDGMENTS

REFERENCES

Asha EM, Singh RP, Thomas S, Transport of Aromatic Solvents through Nitrile Rubber/Epoxidized Natural Rubber Blend Membranes, Polymer Engineering and Science, 43, 2003, 704-715.

Chand N, Vashishtha SR, Development, structure and strength properties of PP/PMMA/FA blends, Bulletin of Material Science, 23, 2000, 103-107.

Harogoppad SB, Aminabhavi TM, Diffusion and sorption of organic liquids through polymer membranes. 5. Neoprene, styrene-butadiene-rubber, ethylene-propylene-diene terpolymer, and natural rubber versus hydrocarbons (C8-C16), Macromolecules, 24, 1991, 2598-2605

Pattil AG, Anandhan S, Ball milling of class- F Indian fly ash obtained from a thermal power station, Journal of Energy Engineering, 2, 2012, 57-62.

Ramesan MT, Processing characteristics and mechanical and electrical properties of chlorinated Styrene butadiene rubber/ fly ash composites, Journal of Thermoplastic Composite Materials, 28, 2015 a, 1286-1300.

Ramesan MT, Jasna VC, Francis J, Abdu Raheem VP, Subburaj M, Preparation of Zinc and Calcium Silicate Modified Fly Ash/ Styrene Butadiene Rubber, Chemist, 88, 2015 b, 1-6.

Ramesan MT, Poly (ethylene-co-vinyl acetate)/ Magnetite Nanocomposites: Interaction of Some Liquid Fuels, Thermal and Oil Resistance Studies, Polymer and Polymer Composite 23, 2015 c, 85-92.

Ramesan MT, Flammability, oil resistance and interaction of petroleum fuels with dichlorocarbene modified styrene butadiene rubber/fly ash composites, Petroleum Science and Technology, 32, 2014, 1775-1783.

Sareena C, Sreejith MP, Ramesan MT, Purushothaman E, Transport properties of coconut shell powder (CSP) reinforced natural rubber composites in aromatic solvents, Polymer Bulletin,72, 2015, 1683-1702.

Sareena C, Ramesan MT, Purushothaman E, Transport Studies of Peanut Shell Powder Reinforced Natural Rubber Composites in Chlorinated Solvents, Fibers and Polymers, 14, 2013, 1674-1687.

Sareena C, Ramesan MT, Purushothaman E, Transport Studies of Peanut Shell Powder Reinforced Natural Rubber Composites in Aromatic Solvents, Polymer Composites, 33, 2012, 1678-1692.

Sikka R, Kansal BD, Characterization of thermal power-plant fly ash for agronomic purposes and to identify pollution hazards, Bioresource Technology, 50, 1994, 269-273.