Mechanical and transport properties of permanganate treated coconut shell powder – natural rubber composites

T.V. Jinitha, M.P. Sreejith, Aparna K Balan and E. Purushothaman*
Department of Chemistry, University of Calicut, Malappuram (Dt), Kerala 673635, India
*Corresponding author: E-Mail: epurushot@yahoo.com

ABSTRACT

In the present work, modified coconut shell powder has been used as reinforcement material in natural rubber matrix. In order to improve their properties, the coconut shell powder was subjected to chemical treatment using potassium permanganate. Potassium permanganate of two different concentrations was used for chemical treatment. The cure characteristics and mechanical properties of the coconut shell powder (CSP) - natural rubber (NR) vulcanizates were studied at different filler loading of 0, 5, 10, 15 and 20 phr (parts per hundred). The effect of potassium permanganate treatment on the mechanical properties of CSP-NR composites was investigated. The tensile strength of both treated and untreated CSP-NR composites decreased with increase in filler loading. However the values were found to be higher than those of corresponding values of untreated ones. The chemical treatment increases the tensile strength, Youngs modulus, hardness and density. The transport properties of modified CSP-NR composites were studied using aromatic solvents like benzene, toluene and xylene. The effect of filler loading and permanganate treated fibers on the equilibrium swelling was investigated.

KEY WORDS: Composites, modified coconut shell powder, mechanical properties, transport properties.

1. INTRODUCTION

Growing attention is nowadays being paid to natural fiber reinforced composite due to their outstanding properties. Natural filler reinforced materials offer many environmental advantages such as reduced dependence on nonrenewable energy/material sources, lower pollution and green house emission. Natural fibers are hydrophilic in nature as they are derived from lignocelluloses which contain strongly polarized hydroxyl groups. Advantages of natural fillers over traditional ones are their low cost, high toughness, low density, good specific strength properties, reduced tool wear, enhanced energy recovery, CO_2 neutrality when burned and biodegradability (Ismail, 2002). These advantages make natural fibers potential replacement for glass fibers in composite materials.

The drawback of using natural fiber as a reinforcing material is their poor wetability, incompatibility with some polymeric matrices and high moisture absorption (Vazguez, 1999). Treatment of natural fillers is beneficial in order to improve the water resistance of fillers, enhance the wettability of natural filler surface by polymers and promote interfacial adhesion. Chemical modifications of natural fibers aimed at improving the adhesion with a polymer matrix were investigated by a number of researchers (Pual, 1997; Joseph, 1996; Sreekala, 2000; Ray, 2001, Mishra, 2001).

Coconut shell is the one of the most important natural fillers produced in tropical countries like Malaysia, Indonesia, Thailand, Sri Lanka and India. Coconut shell is the nonfood part of coconut, which is hard lignocellulosic agro- waste. Coconut shell is 15-20% of coconut (La Mantia, 2005). Coconut shell powder (*cocos nucifera*) is widely available at very low cost. So it is an ideal filler material in this regard. The utilization of CSP as lignocellulosic fillers in polymer composites becomes more favorable due to their high strength and modulus properties. The present work aims at investigating the prospect of using modified coconut shell powder as reinforcement in natural rubber matrix. The effect of chemical modification and filler loading on the mechanical and transport properties of NR- CSP composites have been studied.

2. EXPERIMENTAL

2.1. Materials: Coconut shell powder (CSP) used as filler obtained from Sip India Exporters Erode. It is reported to contain 29.4% lignin, 27.7% pentosans, 26.6% cellulose, 8% moisture, 0.6% ash, 4.2% solvent extractives and 3.5% uronic anhydride. The NR used was Indian Standard Natural Rubber-5, light colour grade (ISNR-5L). All other rubber chemicals were of reagent grade. Sodium hydroxide and Potassium permanganate used for fiber surface modification were of reagent grade supplied by Merck. The solvents benzene, toluene and xylene used were laboratory reagent grade supplied by Merck.

2.2. Permanganate treatment of coconut shell powder: The coconut shell powder sieved to particle size of 0-53 µm. Here the CSP (1g) was put in a 5% (10mL) NaOH solution for 5h with continuous stirring using a mechanical stirrer and was kept for 24h. The CSP was washed thoroughly with water until the water became neutral. Final washing were carried out with distilled water. The powder was filtered and dried in an air oven at 60^0C. The alkali treated CSP (60g) was soaked with 1L $KMnO_4$ solution in acetone for about 2-3 min. The permanganate solution of concentration 0.01 and 0.05% were used. The treated powder was washed in distilled water and finally dried in air oven at 60^0C.

2.3. Preparation of composites: The composites were prepared by incorporation of filler (untreated and treated CSP) in to NR matrix according to base formulation. The formulation of CSP/NR composites is given in Table 1. Mixing was carried out on a laboratory two roll mixing mill (150x300mm) according to ASTM-D 15-627. Nip gap, mill roll speed ratio, time of mixing and the sequence of addition of ingredients were kept for the same for all the composites. The samples were named as CSP for unmodified coconut shell and permanganate treated CSP were named respectively as P_1CSP and P_2CSP, where P_1 is 0.01% permanganate and P_2 is 0.05% permanganate. Vulcanization of the mixes was done at 160^0C using a hydraulic press having electrically heated plates (150mm x150mm x 2mm) at a pressure of KPa (100psi). The respective cure times at 160^0C were measured using Rheo-Line moving Die Rheometer.

2.4. Filler characterization: The unmodified and modified CSP were characterized using FTIR spectroscopy using JASCO FTIR- 4100 spectrometer using solid KBr pellet. The crystalline structure of CSP was analyzed by X-ray diffractometer RIGAKU MINIFLEX- 600 with Cu Kα (λ = 1.54Å) was recorded between 3^0 to 80^0.

2.5. Testing of composites: Tensile properties: tensile strength indicates the ability of a composites material to withstand forces that pull it apart as well as the capability of the material to stretch prior to failure. Tensile strength, modulus and elongation at break of the composites were examined on a universal testing machine (ASTM D 412) at a cross head speed of 500mm/min after conditioning at 27^0C.

2.6. Hardness and density: Hardness was measured at room temperature by using a shore–A hardness tester according to ASTM D 2240-2004. The relative density of composites was measured by using electron densimeter MD-2005.

2.7. Sorption experiment: Circular sample of diameter 1.94cm were used in sorption experiments that monitored liquid sorption gravimetrically. The original weight and thickness of samples were measured before sorption experiment. They were than immersed in solvents in closed diffusion bottles, kept at room temperature periodically the samples were removed from the bottles and damp dried between filter papers to remove excess solvents on their surface. They were then weighed immediately using an electronic balance (Shimadzu, Libror AEU-210 Japan) that measured reproducibility within ± 0.0001g. The samples were immediately placed back into the test bottles. The process was continued until the equilibrium swelling was achieved.

3. RESULTS AND DISCUSSION

3.1. Filler characterization: The unmodified and chemically modified coconut shell powders were characterized using FTIR spectroscopy. The Figure.1 shows the FTIR spectra of unmodified CSP. The identification reveals lines representing the hydrogen bonded stretching bands of OH groups in the region of 3411 cm^{-1} and in the region of 1024 cm^{-1}, the absorption can be attributed mainly to the carbohydrates including C-O-C and C-O stretch and bonds belongs to the glucoside linkage and possibly to lignin. The peak in the region of 2920 cm^{-1} is due to the aliphatic saturated C-H stretching vibration of lignin /polysaccharides complex. the peak in the region at 1737 cm^{-1} in the fiber are attributed to either the acetyl or uronic ester groups of hemicelluloses or ester linkages of carboxylic groups of lignin (Alemdar, 2008). The chemical treatments removes the waxes, oils and hemicellulose and lignin etc. The removal of these components can observe in FTIR spectra of CSP fiber after permanganate treatment. After modification the intensity of the O-H is reduced due to removal of O-H from cellulose. The peak in the region at 1740 cm^{-1} in the unmodified fiber disappeared in the spectra of permanganate modified fibers, which indicates the complete cleavage of these ester bonds. The schematic representation of the CSP modification is given in the scheme 1.

The X- ray diffractograms of untreated and permanganate treated CSP fiber can be seen in the Figure. 2. It can be observed that the major crystalline peaks occurred at 2θ = 22.1^0. Which represent the cellulose crystallographic plane (200). The permanganate treatment cannot significantly effect on the crystalline properties of cellulose. The XRD pattern of permanganate treated CSP shows a well-defined peak in the region 14 - 18^0 compared to untreated CSP. It indicates the removal of hemicelluloses and lignin after permanganate treatment.

3.2. Cure characteristics: Figure.3. shows the reographs of the NR-CSP mixes. The maximum torque is a measure cross link density and stiffness in the rubber. The maximum torque (M_H) value, increases with increasing CSP filler loading. This indicates that as more and more filler dispersed into the rubber matrix, the mobility of the macromolecular chains of the rubber decreased, which ultimately resulted in the rigidity of vulcanizates. This torque values are also increased by permanganate treatment. The Table 2 shows scorch time, t_2 and cure time t_{90} of NR-CSP and NR PCSP composites at different filler loading. Both optimum cure time and scorch time were to show a slight decrease consistently with increasing filler loading. This trend might be due to the longer time the rubber composite remains in the mill during mixing. Similar observation was reported by (Geethamma, 1995). According to these authors, as the filler loading increases, the incorporation time of the filler into rubber matrix also increases and consequently generates more heat due to additional friction.

3.3. Tensile properties: The effect of filler loading and permanganate treatment of CSP on tensile strength of CSP filled NR is presented in Figure.4. The tensile strength shows a maximum at 5 phr of rubber CSP composites. Further increase in filler loading leads to a decrease in tensile strength. Similar trend that is the decrease in tensile strength of rubber composite with increasing filler loading has been reported by (Ismail, 1997; Sareena, 2013; Onyeagoro, 2012). The higher value of tensile strength was exhibited by P_2CSP vulcanizates when compared to P_1CSP. The permanganate treatment (0.05% concentration) of filler can improve the fiber matrix interfacial adhesion, leading to better stress strain transfer efficiency from the matrix to the filler and a consequence improvement in mechanical properties of the composites.

Table.3 shows the effect of filler loading on the elongation at break of CSP-NR composites. The incorporation of filler into the matrix has resulted in a dramatic reduction in the elongation at break. This decrease in elongation at break upon addition of rigid filler arises due to the decreased deformability of rigid interface between filler and rubber. NR composite with permanganate treated CSP at 0.05% concentration (P_2CSP) gives higher elongation at break than untreated CSP and P_1CSP filled NR composites.

Figure.5. shows the variation of Young's modulus of NR with untreated and treated CSP loading. It can be seen that the Young's modulus of CSP–NR composites increases with increase in filler content which is a clear indication of the ability of the CSP to impart greater stiffness to the NR composite. The filler has higher stiffness than the matrix and can increase the modulus of the composite. At given filler loading P_2CSP filled NR gave the highest modulus. Effect of filler loading on the hardness of the CSP-NR composites was shown in the Figure.6. The incorporation of filler content into the NR matrix reduces the mobility of the polymer chain and increases the cross linking density, hardness also increases. The treated CSP composites have better hardness compared to untreated ones. This could be attributed to both better dispersion of the fiber into the matrix with minimum voids and stronger interfacial adhesion between the matrix and the filler. At given filler loading P_2CSP– NR gives highest hardness than untreated CSP and P_1CSP filled NR composite.

Figure.7. shows the effect of filler loading on the density of the CSP-NR composites. The incorporation of both untreated and treated CSP into the NR matrix has increased the density of the composite. The density of composite is found to increase with an increase in the filler loading. At a given filler loading P_2CSP filled NR gave the highest density.

3.4. Sorption studies: From the diffusion data, the mol% uptake of solvent/g of polymer, Q_t was determined using the equation (1) (Thomas, 1986).

$$Qt(mol\%) = \frac{\left(\text{Mass of solvent absorbed} \middle/ \text{Molar mass of the solvent} \right)}{\text{Mass of polymer}} \times 100 \qquad (1)$$

The Q_t becomes Q_∞ when equilibrium reached. The effect of chemical treatment of fiber on equilibrium swelling of the composites is given in Figure. 8. It is observed that in composites containing treated fibers, the solvent uptake is reduced further, which is due to the enhanced interfacial bonding between the fiber and rubber. This prevents the transport of solvent to some extent through the interface. The permanganate treatment has resulted in lowering of solvent uptake when compared to the untreated composites. With an increase in the molecular size of the solvent molecules, there is a decrease in the value of Q_t in all the systems shown in Figure. 9. Benzene shows the maximum value of Q_t and xylene the minimum, among the solvents used in this study. The solvent uptake increases in the order xylene <toluene <benzene. As the size of the penetrant increases, the resistance offered by the polymer to the transport of the solvents through the matrix is enhanced. The decrease in sorption with increasing filler concentration in NR –CSP composites is shown in the Figure. 10. The trend may be that each particle behaves as an obstacle to the diffusing molecule. As the concentration of filler increase in the rubber matrix more and more obstacles are created to the diffusing molecule and thus reduce the amount of penetrant solvents.

3.5. Diffusion coefficient (D): Diffusion coefficient is a kinetic parameter, is the ability of the penetrant to move among the polymers segment. Diffusion coefficient was calculated from the equation eq. (2) (Southern, 1967).

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

Where h is the initial sample thickness, θ is the slope of the linear portion of the sorption curve of the plot of Qt verses $\sqrt{t}$ and $Q\infty$ is the equilibrium absorption.

The 'D' values decrease with increasing filler loading as show in the Table 4. As the filler loading increasing the crosslinking increases, it reduces the mobility of the penetrant in the composite which ultimately resulting decrease in diffusion with increasing filler content. The size of penetrant also affects the D value. As penetrant size increases, the D value decreases. A decrease in the diffusion coefficient of same polymers with increases in molecular mass of penetrant has already been reported (Mathew, 2007; Dasan, 2008). The permanganate treated CSP –NR composites shows minimum lowest D value compared to untreated CSP-NR composites

3.6. Sorption coefficient (S): Sorption is a surface phenomenon and it is an indication of the tendency of the penetrant to dissolve into the polymer. The sorption coefficient was calculated using the eq. (3) (Igwe, 2007)

$$S = W_\infty/W_p \qquad (3)$$

The Table 4 shows that the sorption coefficient of NR- CSP composites. The sorption coefficient is found to be decrease with increase coconut shell powder content in the rubber vulcanizate. The sorption coefficient was highest in benzene, followed by toluene, and then xylene for any set of composite is considered in the table. It indicates that as size of the penetrant increases the sorption coefficient is decreased similar to that of diffusion coefficient. The permanganate treated (P_2CSP) composite shows lower sorption coefficient than untreated CSP-NR composites.

3.7. Permeation coefficient (P): Permeation can be considered as the combined effect of sorption and diffusion process. The permeability or permeation coefficient of a penetrant in a polymer membrane depends on the diffusivity as well as solubility or sorption of the penetrant in the polymer membrane. The permeability coefficient of the aromatic solvents in the rubber vulcanizates was obtained using the eq. (4) (Aminabhavi, 1995).

$$P = D \times S \qquad (4)$$

Where D is diffusion coefficient and S is the sorption coefficient. The values of P are given in Table.4. The permeability coefficients were generally observed to decrease with increase in filler loading. The permeability coefficients were generally observed to decrease with increase in penetrant molecular mass.

Table .1. Mixing formulation of CSP-NR composites

Ingredients	Parts per hundred of rubber (Phr)
Natural rubber (NR)	100
Zinc oxide	5
Stearic acid	2
TDQ[a]	1
Processing oil	1/20th of filler
Filler[b]	0,5,10,15 and 20
CBS[c]	0.8
Sulphur	2.8
[a]2, 2, 4 - Trimethyl -1, 2- dihydroquinoline	
[b]Coconut shell powder (CSP)	
[c] N –cyclo hexyl -2-benzothiazyl sulphenamid	

**Table.2.Effect of filler loading on scorch time and cure time of CSP-NR composites**

Sample name	NR	CSP				P_1CSP				P_2CSP			
Filler loading (phr)	0	5	10	15	20	5	10	15	20	5	10	15	20
Scorch time (min)	2.38	2.2	2.13	1.83	1.86	2.11	1.97	1.88	1.85	2.07	1.84	1.82	1.77
Cure time (min)	5.01	5.73	5.44	5.2	4.72	4.99	4.96	4.95	4.59	4.84	4.82	4.72	4.42

Table.3. Effect of filler loading on the elongation at break

Sample name	NR	CSP				P_1CSP				P_2CSP			
Filler loading(phr)	0	5	10	15	20	5	10	15	20	5	10	15	20
Elongation @ break(%)	622	658.1	643.8	631.7	629.4	705.8	666.5	669	620.9	706	670.5	649.4	625

Table. 4. Diffusion, sorption and permeation coefficient of CSP- NR Composites

Sample Name	Diffusion Coefficient $D \times 10^{-7}$ (cm^2/s)			Sorption Coefficient S (mol %)			Permeation Coefficient $P \times 10^{-7}$ (cm^2/s)		
	Benzene	Toluene	Xylene	Benzene	Toluene	Xylene	Benzene	Toluene	Xylene
NR	0.655	0.645	0.615	3.839	3.810	3.798	2.514	2.457	2.336
CSP	0.635	0.610	0.598	3.538	3.501	3.455	2.247	2.135	2.067
	0.596	0.588	0.578	3.360	3.358	3.342	2.005	1.975	1.933
	0.540	0.536	0.515	3.261	3.259	3.185	1.761	1.749	1.640
	0.438	0.420	0.403	3.180	3.137	3.112	1.393	1.317	1.254
P$_1$CSP	0.648	0.593	0.580	3.510	3.497	3.474	2.275	2.075	2.015
	0.580	0.578	0.563	3.333	3.321	3.329	1.933	1.921	1.875
	0.483	0.525	0.530	3.259	3.251	3.178	1.574	1.706	1.684
	0.463	0.435	0.431	3.165	3.166	3.107	1.466	1.377	1.341
P$_2$CSP	0.640	0.598	0.570	3.520	3.415	3.253	2.252	2.043	1.854
	0.558	0.540	0.538	3.335	3.241	3.194	1.862	1.750	1.719
	0.526	0.521	0.530	3.213	3.219	3.144	1.692	1.679	1.666
	0.436	0.445	0.430	3.192	3.116	3.123	1.394	1.386	1.342
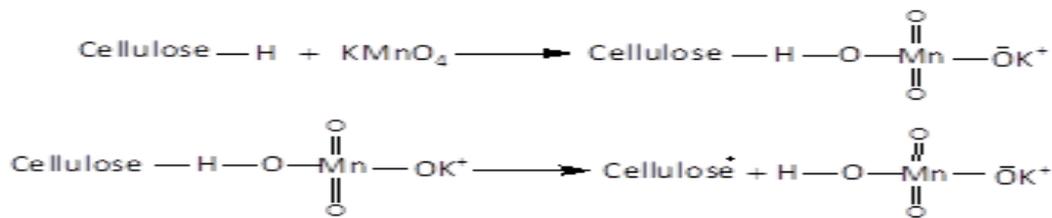
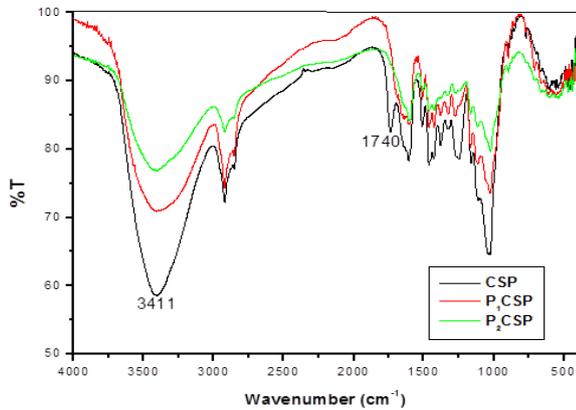**Scheme 1. Modification of CSP using potassium permanganate**

Figure 1. FTIR spectra of unmodified CSP and permanganate treated CSP
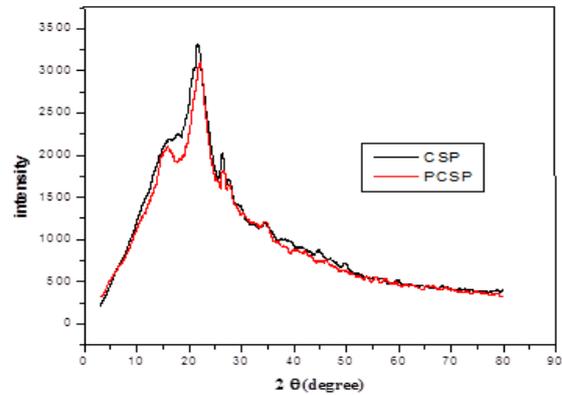

Figure.2. XRD of unmodified and permanganate modified CSP
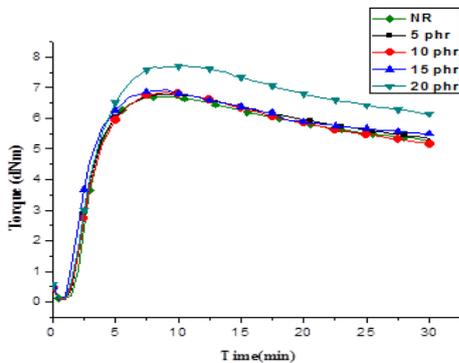

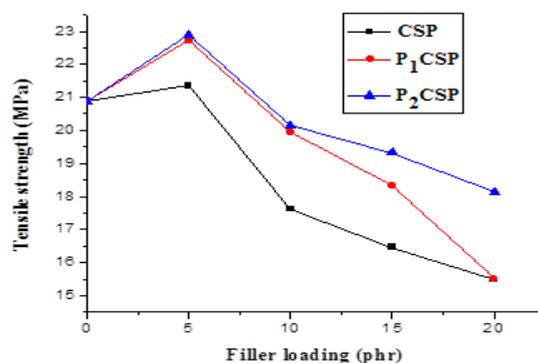**Figure. 3. Reograph of CSP-NR composites**

Figure.4. Effect of filler loading on the tensile strength of CSP- NR composite
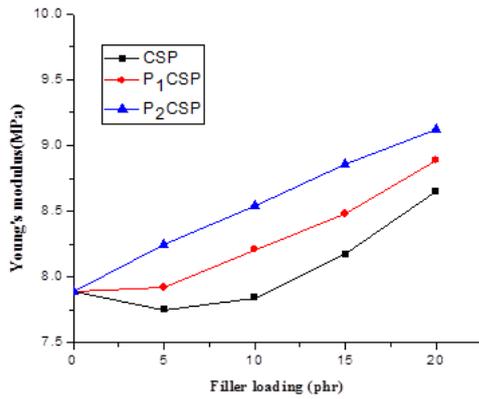
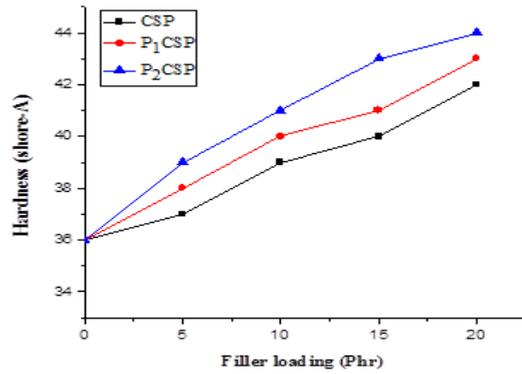**Figure.5.Effect of filler loading on the Young's modulus of CSP- NR composites**

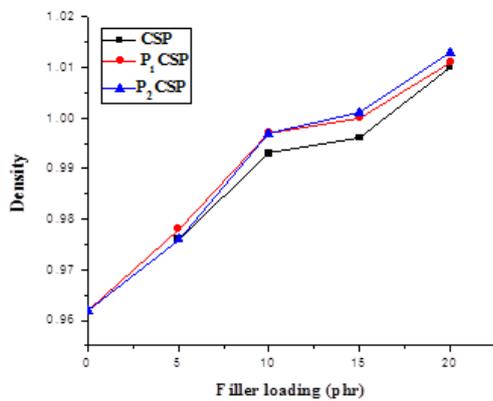**Figure.6.Effect of filler loading on the hardness of CSP-NR composites**

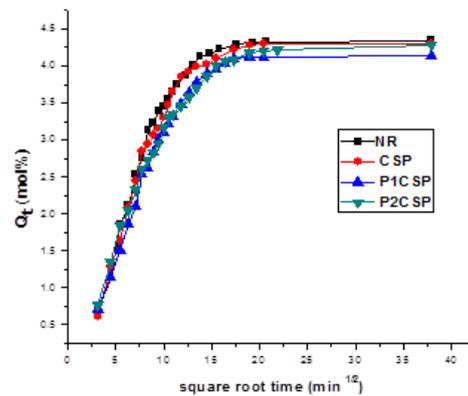**Figure.7.Effect of filler loading on the density of CSP-NR composites**

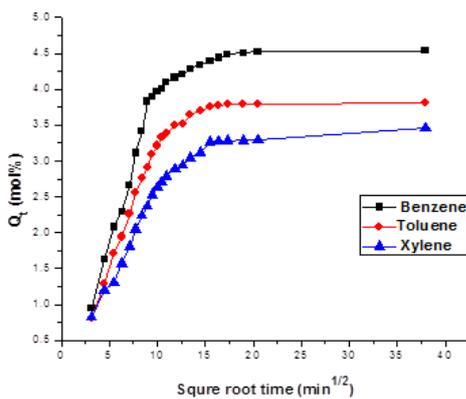**Figure.8.Effect of modification on Q_t of CSP- NR composites in benzene**

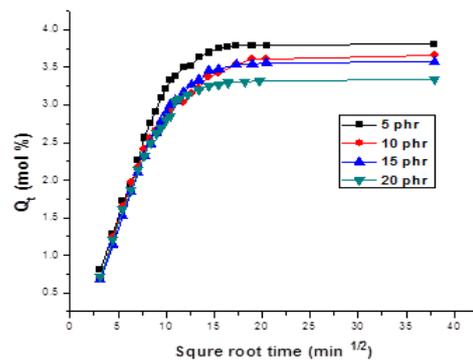**Figure.9.Effect of penetrant size on the Q_t of CSP-NR composites**

Figure.10.Effect of filler loading on Q_t of the CSP-NR composites

4. CONCLUSIONS

The processability characteristics, mechanical properties and transport properties of coconut shell powder reinforced natural rubber composites have been investigated as a function of chemical modifications (permanganate) and filler loading. It was observed that upon chemical treatment the torque values increased indicating greater crosslinking. Permanganate treatment increased the tensile strength of the composites and the maximum tensile strength was observed for composites prepared with 0.05% $KMnO_4$ treated CSP. Addition of coconut shell powder increased modulus of composites. Mechanical properties such as tensile strength and elongation at break show a decreasing trend with increase in filler loading and the greater the CSP loading, poorer the mechanical properties. The order of solvent uptake of composites is benzene › toluene › xylene. The surface

modification of fibers reduces the equilibrium swelling. The concentration filler content effects equilibrium swelling of composites, minimum concentration shows maximum swelling. The kinetic parameters like diffusion coefficient, sorption coefficient and permeation coefficients are decreased with increasing filler loading.

5. ACKNOWLEDGEMENT

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