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RESEARCH ARTICLE

EFFECT OF POLYMETHYL METHACRYLATE (PMMA) ENCAPSULATED NANO SIZED CALCIUM CARBONATE ON THE TRANSPORT PROPERTIES OF TOLUENE INTO NATURAL RUBBER BASED COMPOSITES

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ABSTRACT

In this work the nano sized calcium carbonate was chemically treated with a synthetic polymer, i.e., polymethyl methacrylate by an in situ polymerization of methyl methacrylate monomer in the presence of filler dispersion in water. The transport properties of a solvent (toluene) through these present composites at different loadings have been investigated at various temperatures. The diffusion coefficient (D), permeation coefficient (P) and sorption coefficient (S) obtained for composites in toluene were found to increase with increasing sorption temperature. It is observed that PMMA coated filler exerts strong influence on the transport parameters. The temperature dependence of transport coefficients have been used to compute the activation parameters from Arrhenius equation. The results were all positive and found to increase with increasing amount of filler. The sorption results have been interpreted in terms of first-order kinetic model.

INTRODUCTION

The solvent absorption process by rubber or any polymer takes place in different steps. The steps are: solvent adsorption onto the contact rubber surface, next penetration through the surface, and lastly absorption into the bulk. The absorption behavior not always similar and depends on many factors. Various patterns are usually as: linear, a slight delay or S-shape with the square root of time and linear with linear time, or increases more rapidly with linear time. The delayed solvent uptake is appeared as a clear "S" shape in a plot of the uptake versus the square root of time. The purpose of the present studies is to point out the factors for solvent diffusion in rubber-filler composites. The performance of nano-filler depends on the nature of the polymer and the dispersion of nano particles in the polymer matrix. Agglomeration of nano particles can not contribute to improved properties of a composite. Poly (propylene carbonate) / nano-$CaCO_3$ composites were reported to show inferior physical properties compared to their micron-sized counterparts (Liet al., 2003) due to agglomeration. Jiang et al. (Ang et al., 2005) studied the SEM micrographs of micron and nano-sized calcium carbonate. For nano sized carbonate particles he observed only agglomerates of different micro sizes with very few nano particles. Some of the agglomerates were as big as 20µm. This agglomeration of nano particles is due to its high surface tension. However, this undesirable tendency of nano particles to agglomerate may be prevented by coating its surface with an organic or polymer (Ott, 2006). There are some reports on the surface modification of inorganic fillers by coating with polymer film (Lee, 1993; et al., 2002; et al., 2001). The *in situ* polymer coating technique includes mini-emulsion, suspension, dispersion and emulsion polymerization. The polymer coated inorganic filler compound is expected to show superior interaction with other polymers in a composite to be used in rubber and other related industries. Based on the above discussion, in the present work several composites were prepared by incorporating varied amounts of nano sized and polymer coated calcium carbonate filler. The nano sized calcium carbonate filler was coated by an *in situ* polymerization of methyl methacrylate monomer on an aqueous dispersion of the filler. The distribution of filler in the rubber matrix is also very important and this can be studied in terms of relative change in surface morphology of the composite using SEM. A good composite should also have excellent solvent resistance properties even when in constant contact with a solvent like water.

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These properties can be studied by transport characteristic of the composites in terms of swelling and diffusion characteristics of the composites. Thus, in the present work the effect of the coated nano sized filler on the transport properties of the composites were discussed.

Experimental

MATERIALS

Table 1 shows the materials used in this study including code, chemical name and manufacturer/supplier of the same. In the present work Natural rubber (NR) of RMA 1X grade with money viscosity ML_{1+4} 72 at 100^0C was used as the rubber material and it was kindly gifted by Kerala Rubber Board, Kerala. Nano sized precipitated calcium carbonate was used as filler. Two types of activator, i.e., zinc oxide and stearic acid were used as supplied. Isopropyl paraphenylenediamine (IPPD) was used as antioxidant. For vulcanization of the composite sulfur and the delayed action, semi ultra sulphenamide type accelerator N-Oxydiethylbenzthiazyl sulphenamide (BSM) were used.

METHODS

In situ polymer coating

Pretreatment of whiting

Required amount of the nano sized precipitated calcium carbonate was dispersed in deionized water in a round bottom flask fitted with a mechanical stirrer. The mixture of whiting and water was stirred for some 10 h in the presence of required amount of sodium lauryl sulfonate till a suspension of whiting is obtained. The whiting was then filtered, dried and heated to 300^0C for 2 h followed by crushing into fine powder with a high speed laboratory crusher (Seul, S.D., Lee, S.R., Kim, Y.H., 2004; Ma et al., 2007; Bourgeat-Lami, E. and Lang, J. 1998).

Polymerization

The aqueous suspension of the heat treated fine purified nano sized precipitated calcium carbonate was taken into a three-necked glass reactor equipped with a condenser, thermometer and a dropping funnel. The mixture was stirred under N_2 atmosphere at 70-80^0C. Small amount of (~0.5% of total reaction volume) polyvinyl alcohol was added. The initiator APS was then added followed by drop wise addition (within 40 min) of methyl methacrylate (MMA) monomer through the dropping funnel. The polymerization was continued for some 4 h with continuous stirring. The slurry was then filtered, repeatedly washed with deionized water and dried at 70-80^0C under vacuum. A small portion of the dried polymer coated nano sized precipitated calcium carbonate was heated at about 300^0C in a muffle furnace for 2 h to remove the unreacted monomer. A small part of the vacuum dried sample was extracted with toluene for 2 days.

Filler-rubber composites chips preparation

The mixing and compounding of natural rubber with other additives was same as described in previous chapters. One 'control' mix STNC0 was prepared which did not contain any filler . Six filled composites noted as STNC5, STNC10, STNC15, STNC20, STNC25 and STNC30 containing 5, 10, 15, 20, 25 and 30 phr, respectively of the PMMA coated or 'treated' nano sized calcium carbonate fillers were prepared. The composition of these composites is presented in Table 2. All components were mixed together step by step in a two-roll mixing mill ($150\times300mm^2$) with a nip gap of 1.3mm and a friction ratio 1:1:4 at initial temperature of 60^0C. First, natural rubber was masticated in the two-roll mill for 6 min,then filler was added and continued mixing for 5 min. Subsequently, stearic acid, IPPD and zinc oxide were added and mixed for 2-3 min, this was followed by addition of BSM and mixinng for another 2 min. Finally sulfur (as the curing agent) was added and mixed for 2 min. The compound was taken out in sheet form and tested with a Monsanto ODR 100 instrument to obtain optimum cure time at curing temperature of 140^0, 150^0 and 160^0C with a micro die and 3^0 arc of oscillation. After curing in a compression mould for a period of 90% cure time using a hydraulic press having electrically heated platens under a pressure of $45Kg/m^2$, cure sheets of different thickness (1.5mm,0.75mm,0.35mm) was obtained. All seven types of chips with different formula and different three thickness were cut into small pieces. The sample thickness was measured at several points with an accuracy of $\pm$ 0.01mm using a micrometer screw gauge. An average of several values were taken as the initial thickness of the polymer samples. Initial length and width of the small piece of test samples were noted. All test sample were dried in a vacuum desiccator over anhydrous $CaCl_2$ at room temperature for about 24 h. The chips were tested in the following experiments.

Evaluation of transport properties

The solvent used was reagent grade toluene. Original weight and thickness of the samples were noted before sorption experiments. The cured composite samples were allowed to swell in 20 mL of toluene (solvent) taken in stoppered glass bottles kept in a constant temperature bath. The samples were taken out at different time intervals and weighed after wiping out the excess solvents from the sample with a tissue paper. The process was continued till its equilibrium swelling. After equilibrium was attained, there was no more change of sample weight. The sorption experiments were carried out in triplicate and the results were averaged. The sorption experiments were carried out at three different temperatures of 28^0 50^0 and 70^0C.

Morphology of the composite

Scanning electron microscopic (SEM) studies of the four composite samples were carried out in a S3400N Scanning electron microscope (Hitachi, Japan). The samples were coated with Gold and subjected to a voltage of 10-15 kV at varied magnifications till a good image is observed.

RESULTS AND DISCUSSION

Chain Mobility (Crosslink Density) of the Networks in Vulcanized composites he degree of mobility of the rubber chains in the macromolecular networks, which plays an active role in the diffusion process, was determined by swelling data (Unnikrishnan, 1994). For each vulcanized composite sheet the molar mass between the crosslinks (M_c) was determined by Flory-Rehner model Eq.1 (Begum et al., 2008).

Table 1. Rubber and compounding ingredients used in this study

Raw material	Code	Chemical name/ formula	Manufacturer
Natural rubber	RMA 1X	cis-1,4-polyisoprene	Kerala Rubber Board, India
Activator	AR grade Zinc Oxide	ZnO	Loba cheme Ltd., India
	Extra pure Stearic acid, saturated fatty acid	$CH_3(CH_2)_{16}CO_2H$; Octadecanoic acid (IUPAC)	E. Merck Ltd.
Antioxidant/ Antiozonate	IPPD	Isopropyl paraphenylenediamine,	Bayer India Ltd
Accelerator	BSM	2- Morpholinothiobenzothiazole / N-Oxydiethylbenzthiazylsulphenamide	ACCI Ltd., India
Vulcanizer	S	Sulphur	E. Merck
Filler	precipitated calcium carbonate	Nano Calcium Carbonate	Chemical and Mineral Industries Pvt. Ltd., Rajasthan, India

Table 2. Composition of the composites

Ingredient	STNC0	STNC5	STNC10	STNC15	STNC20	STNC25	STNC30
Natural rubber (RMA-IX)	100	100	100	100	100	100	100
Zinc oxide	4.5	4.5	4.5	4.5	4.5	4.5	4.5
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5	1.5
IPPD	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Sulfur	2.0	2.0	2.0	2.0	2.0	2.0	2.0
BSM	2.0	2.0	2.0	2.0	2.0	2.0	2.0
PPt $CaCO_3^C$	0	5	10	15	20	25	30

c…..PMMA coated nano $CaCO_3$.

Table 3 Equilibrium toluene up take (Q_∞) (mol %) of the composites

Solvent	Temp (C^0)	STNC0	STNC5	STNC10	STNC15	STNC20	STNC25	STNC30
Toluene	28	3.88	3.77	3.37	3.25	3.12	2.87	2.66
	50	3.81	3.72	3.28	3.15	3.05	2.75	2.59
	70	3.68	3.61	3.18	3.11	2.98	2.67	2.55

Table 4. Transport parameters of the composites based on its sorption in toluene

Sample	T(^{0} C)	h_a(cm/s)	D_a(cm^2/s)	B_a (-)	D_c(cm^2/s)	B_c(-)	S (g/g)	P(cm2/s)
STNC0	28	$1.07x10^{-4}$	$5.65x10^{-7}$	28	$3.34x10^{-7}$	48	3.28	$1.09x10^{-6}$
	50	$2.01x10^{-4}$	$11.5x10^{-7}$	26	$5.79x10^{-7}$	51	3.38	$1.96x10^{-6}$
	70	$2.08x10^{-4}$	$14.7x10^{-7}$	20	$8.77x10^{-7}$	34	3.24	$2.84x10^{-6}$
STNC5	28	$1.64x10^{-4}$	$6.93x10^{-7}$	35	$3.31x10^{-7}$	74	3.40	$1.12x10^{-6}$
	50	$2.5x10^{-4}$	$10.5x10^{-7}$	36	$5.16x10^{-7}$	73	3.32	$1.72x10^{-6}$
	70	$2.47x10^{-4}$	$16.7x10^{-7}$	22	$7.83x10^{-7}$	47	3.33	$2.60x10^{-6}$
STNC10	28	$1.66x10^{-4}$	$6.76x10^{-7}$	36	$3.30x10^{-7}$	75	3.09	$1.02x10^{-6}$
	50	$2.58x10^{-4}$	$11.8x10^{-7}$	32	$5.64x10^{-7}$	66	3.12	$1.76x10^{-6}$
	70	$2.98x10^{-4}$	$14.7x10^{-7}$	30	$7.41x10^{-7}$	60	2.48	$1.83x10^{-6}$
STNC15	28	$1.65x10^{-4}$	$6.68x10^{-7}$	37	$3.14x10^{-7}$	79	2.97	$0.93x10^{-6}$
	50	$2.36x10^{-4}$	$12.25x10^{-7}$	29	$5.30x10^{-7}$	67	2.91	$1.54x10^{-6}$
	70	$2.85x10^{-4}$	$16.7x10^{-7}$	25	$7.35x10^{-7}$	58	2.89	$2.12x10^{-6}$
STNC20	28	$1.82x10^{-4}$	$7.37x10^{-7}$	37	$3.12x10^{-7}$	87	2.79	$0.87x10^{-6}$
	50	$2.28x10^{-4}$	$12.25x10^{-7}$	28	$5.63x10^{-7}$	61	2.80	$1.58x10^{-6}$
	70	$2.52x10^{-4}$	$15.97x10^{-7}$	24	$6.99x10^{-7}$	54	2.79	$1.95x10^{-6}$
STNC25	28	$1.37x10^{-4}$	$6.33x10^{-7}$	32	$3.10x10^{-7}$	65	2.62	$0.81x10^{-6}$
	50	$2.58x10^{-4}$	$12.25x10^{-7}$	31	$5.23x10^{-7}$	74	2.53	$1.32x10^{-6}$
	70	$2.34x10^{-4}$	$14.7x10^{-7}$	24	$6.91x10^{-7}$	51	2.61	$1.80x10^{-6}$
STNC30	28	$1.89x10^{-4}$	$7.06x10^{-7}$	40	$3.06x10^{-7}$	92	2.45	$0.75x10^{-6}$
	50	$2.70x10^{-4}$	$13.61x10^{-7}$	30	$5.40x10^{-7}$	75	2.39	$1.29x10^{-6}$
	70	$2.81x10^{-4}$	$15.9x10^{-7}$	26	$6.74x10^{-7}$	62	2.38	$1.61x10^{-6}$

Table5. Thermodynamic parameters, crosslink density and molecular weight between crosslinks of the composites

Composite	E_D (KJ/mol)	E_P (JK/mol)	Ln(D_0)	ΔH_S (KJ/mol)	M_C	$\nu = (1/2M_C)x10^{-5}$
STNC0	19.5329	19.4706	-7.09	0.0623	850745	5.8772
STNC5	17.3540	16.9572	-7.99	0.3968	9736.15	5.1355
STNC10	16.4898	12.1743	-8.30	4.3155	6889.76	7.2571
STNC15	17.3385	16.7292	-8.02	0.6094	8722.08	5.7325
STNC20	16.5349	16.4962	-8.32	0.0387	9028.33	5.5381
STNC25	16.2596	16.2112	-8.45	0.0483	8146.83	6.1373
STNC30	16.1704	15.6318	-8.49	0.5386	7588.66	6.5888

$$M_c = \frac{-\rho_p v_s v_r^{\frac{1}{3}}}{[\ln(1-v_r)+v_r+\chi v_r^2]} \quad (1)$$

where ρ_p is the density of the composite, v_s is the molar volume of the solvent, v_r is the volume fraction of the composite in the fully swollen sample and χ is the polymer-solvent interaction parameter.

Swelling (sorption) curves

The sorption of the composite is expressed in terms of the percentage of the moles of solvent uptake by 100 g of sample; Q_t is the mol%, which can be calculated using the following Eq.2 (Danwanichakul et al., 2006).

$$Q_{tmol\%} = \frac{\left(\dfrac{\textit{Mass of the solvent sorbed}}{\textit{Molar mass of solvent}}\right)}{\textit{Initial mass of the sample}(g)} \times 100(g) \quad (2)$$

The variation of $Q_{mol\%}$ with time (t) in toluene as solvent at three different experimental swelling temperatures of 28^0, 50^0 and 70^0C is shown in Fig. 1. a-g for one unfilled (composite without filler) and 6 filled composites while the swelling of the composites at the same temperature is compared in Fig. 2 a-c. The trends of these swelling curves are more or less same, i.e., initially swelling of the composites in toluene increases rapidly with an almost linear trends up to a ~40% of the total swelling which is followed by its delayed saturation at higher values with a 'S' type trends indicating time lag due to a mass transfer resistance from the surface of the composites. In fact, after saturation a dynamic equilibrium is attained when the rate of solvent absorption equals the rate of solvent desorption from the composites. The equilibrium swelling values ($Q_{\alpha,}$ mol%) of the composites at the three temperatures are presented in Table 3. It is observed from Table 3. that the equilibrium swelling decreases at higher temperature indicating its exothermic nature. However, the rate of increase of swelling (slope of the swelling curves) increases with temperature as observed in Fig.1.

The increasing swelling rate may be attributed to the increase of osmotic stress and no effective leaching of the additives (Mathai and Thomas, 1996) at higher temperature. The decrease in equilibrium swelling at higher temperature may also be due to the induced crystallinity in the presence of the solvent which reduces the free energy of mixing and hence also solvent uptake at higher temperature (Barr-Howell, B.D, Peppas and Squires, 1986). It is also observed that with an increase in the filler content for the same amount of the composite, as the amount of polymer (rubber fraction) decreases, swelling in toluene also decreases from STNC0 to STNC30, i.e., incorporation of the polymer coated filler makes the composite more solvent resistant than the composite without any filler (STNC0). The polymer coated filler fills the rubber network of the cross linked (vulcanized) composites and also reduces the mobility of the rubber chains due to strong filler-rubber interaction resulting in a decrease in swelling with an increase in the filler content in the rubber composites.

Mass transfer and transport Coefficients

For a Case II sorption, if C_s and C_∞ are concentration (g/cm^3) at surface and at equilibrium, respectively, then the mass flux, F_s (g/cm^2.s) in a composite sample exposed on both sides can be expressed in *x* direction as (Hansen, 2010)

$$F_s = -D\frac{dC}{dx} = h(C_\alpha - C_s) \quad (3)$$

Here *D* is diffusion coefficient (cm^2 /s), *h* is surface mass transfer coefficient (cm/s). For a generalized solution to the diffusion Eq. 3, a dimensionless time parameter, *T*, is used as

$$T = \frac{Dt}{L^2} \quad (4)$$

Here *t* or time is in *s* and *L*, the thickness of the sample is in *cm*. Another dimensionless surface parameter *B* is defined as

$$B = \frac{R_d}{R_s} = \frac{L/D}{1/h} \quad (5)$$

Table 6 Diffusion characteristics of the composites

Temperature	Sample	n	K(mol/mol sec)x10^4
28^0 C	STNC0	0.6652	33.07
	STNC5	0.5867	74.69
	STNC10	0.6360	44.99
	STNC15	0.5970	69.52
	STNC20	0.5921	80.66
	STNC25	0.5791	75.92
	STNC30	0.5832	88.66
50^0 C	STNC0	0.6228	88.91
	STNC5	0.5952	93.09
	STNC10	0.5961	115.10
	STNC15	0.5742	114.73
	STNC20	0.6248	87.65
	STNC25	0.5901	112.04
	STNC30	0.5906	124.15
70^0 C	STNC0	0.6645	62.64
	STNC5	0.5813	125.00
	STNC10	0.5977	130.88
	STNC15	0.5867	137.05
	STNC20	0.6112	99.63
	STNC25	0.6264	97.53
	STNC30	0.5924	133.39

Here R_d and R_s corresponds to the resistance to overall transport from diffusion and surface, respectively. Now Eq.3 may be rewritten as

$$h = \left(\frac{F}{(C_\alpha - C_s)}\right)_{t=0} \quad (6)$$

The mass transfer coefficient, *h* may be determined from the slope of the plot of mass flux (*F*) versus time (*t*) by extrapolating to zero time (t =0). Considering zero surface resistance and a value of dimensionless time parameter, *T* =0.049 at the half time of absorption ($t_{1/2}$), the constant diffusion coefficient D_c is obtained by rearranging Eq.4 as

$$T = \frac{D_c t_{1/2}}{L^2} = 0.049 \quad \text{or} \quad D_c = \frac{L^2 0.049}{t_{1/2}} \quad (7)$$

If there is a significant surface resistance with diffusion from the sides of the samples, an apparent diffusion coefficient, D_a is corrected in an isotropic media (Marom, 1985) as

$$D_c = \frac{D_a}{(1+\frac{L}{l}+\frac{L}{w})^2} \quad (8)$$

Here *l* and *w* are length and width, respectively of the sample of thickness *L*.

The values of the apparent diffusion parameters, i.e., h_a, B_a, D_a, B_c, D_c (considering surface resistance) and F_∞ (∞ for swelling or sorption equilibrium) for the seven composites at three experimental temperatures are shown in Table 4. The surface resistance before penetration of the solvent (toluene) in the interior of the composite network is evident in terms of delayed sorption with a pseudo time lag in Fig.1. From the values of diffusion parameters given in Table 4 it is observed that the values of apparent mass transfer coefficient (h_a) increases with an increase in the filler loading from STNC0 (0% filler) to STNC30 (30% polymer coated nano filler) at the three experimental temperatures of 28, 50 and 70°C signifying increased mass transfer resistance in the filled composites due to heterogeneous surface morphology which causes hindered entry of the solvent molecules in the composites.

Diffusion coefficient

From Table 4 it is observed that the apparent or true diffusion coefficient (D_a or D_c) decreases with an increase in filler loading while for the same filler loading it increases with temperature. The diffusion of a solvent through a polymer depends on the exchange capacity of its chain segments with the penetrating solvent molecules which increases with an increase in chain mobility of the polymer. However, the mobility of the rubber (polymer) chain segment in the composite decreases with an increase in filler loading because of a decrease in free volume available in the rubber matrix (Mathai et al., 2003). Accordingly, the diffusion coefficient of the solvents decreases with an increase in filler loading. At higher temperature, the mobility of the chain segments of the rubber increases. Thus, for the same filler loading the transient free volume in the composite also increases at elevated temperature with an increase in diffusion coefficient.

B Values

From the same Table 4 it is also observed that the dimensionless *B* values increase at higher temperature. In fact, the *B* values reveal the sorption mechanism, i.e. if it is mass transfer or diffusion controlled. For *B*-values < 1, surface resistance dominates while for *B* = 1 diffusional resistance equals surface resistance. For *B* values < 10 the values of the diffusion coefficient should be further corrected for surface resistance and concentration dependence factors. The variation of B-values of the composites at the three sorption temperatures is shown in Fig. 4. In this work, all the B-values are observed to be higher than 10 but less than 100 indicating the dominance of surface resistance to the transport of the solvent molecules. At lower B values the S shape curvature of the sorption curves become more pronounced.

Solvent volume fraction (V_f) and Sorption coefficient (S)

The equilibrium volume fraction of the solvent (toluene) in the composites, V_f and the sorption coefficient, S which is the ratio of the mass of the equilibrium solvent content (m_e) and the initial mass (m_s) of the composite sample ($S = m_e/m_s$, g/g) for the seven composites at three sorption temperatures are also presented in Table 4.

It is observed that like D or B values, V_f or S also decreases with an increase in filler loading while at higher temperature both V_f or S increases for all the composites with few exception (composite containing 5 wt% filler giving higher V_f or S than the composite without filler at 28 and 70°C. This trend may also be explained with similar reason as in the case of diffusion coefficient.

Permeation coefficient (P)

The values of P of the seven composites for toluene at the three sorption temperatures are also presented in Table 4. It is observed that the values of P also follow the similar trend like V_f or S. Overall, from the values of the transport characteristics with respect to toluene for the seven composites at three experimental temperatures clearly indicates that because of strong interaction between rubber and polymer coated filler, the filled composite shows excellent solvent resistance properties.

Crosslink Density and molecular weight between crosslink of the Composites

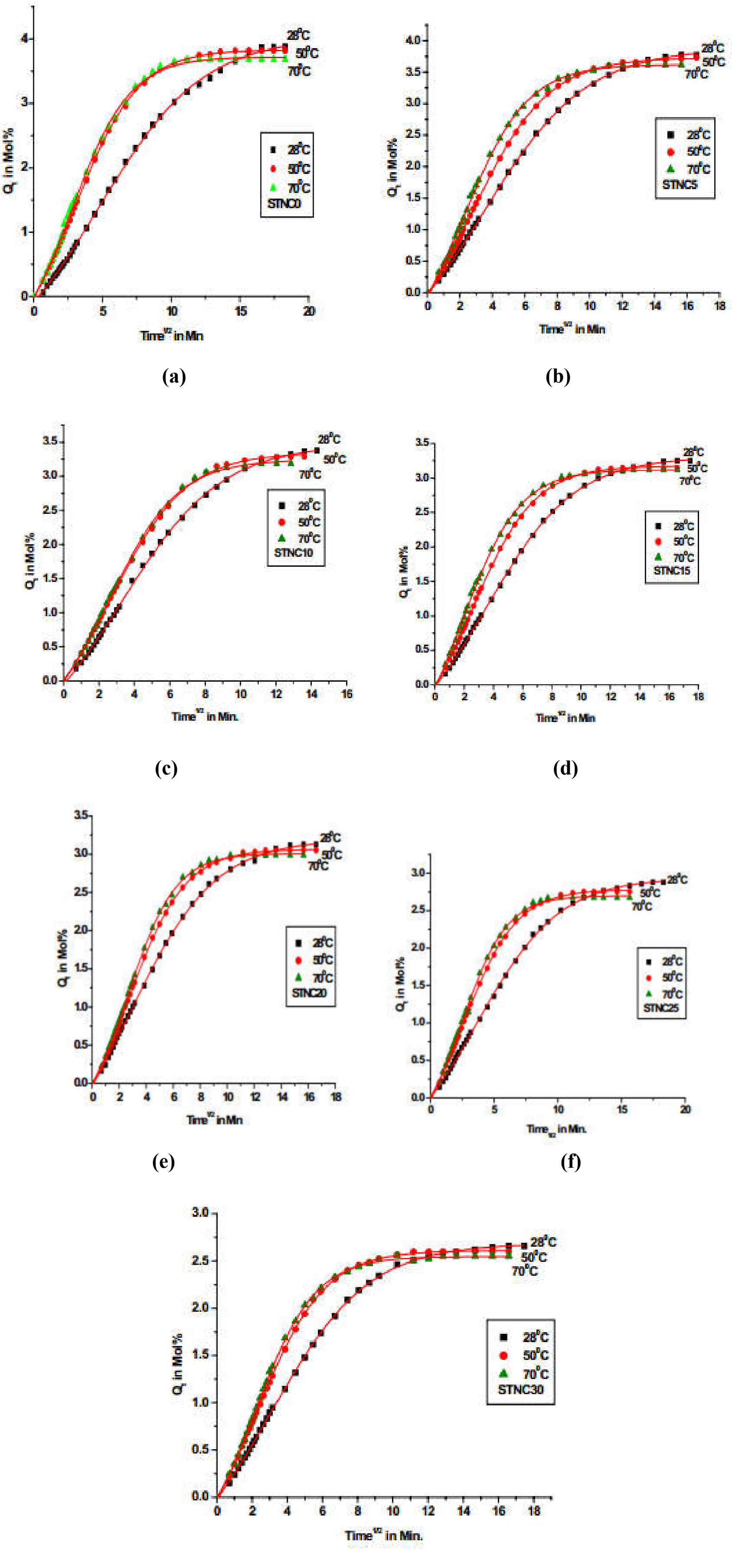
The crosslink density and the molecular weight between crosslink of the composites were calculated using Eq. 1. and are shown in Table 5. The order of crosslink density (ν) was observed to be STNC10 > STNC30 > STNC25> STNC0 > STNC15 > STNC20 >STNC5, i.e., the highest and the lowest *ν* was observed for STNC10 and STNC5, respectively. The composite with high crosslink density will offer more resistance to the transport of the solvents. This is because highly crosslink rubber chains are more tightly bound together and resist the formation of voids capable of accommodating diffusing molecules. Therefore, the energy necessary to create such voids will be large (Mathai et al., 2003) **.**

Sorption mechanism and activation energy

According to Henry's model of sorption, it involves an endothermic process of forming sorption sites followed by dissolution of the penetrants in to these sites. In contrast, Langmuir's hole filling theory suggests that the sorption sites are not generated since these are already available on the polymer matrix and filling of the penetrants in these sites generates exothermic heat of sorption. The effect of temperature on sorption may be expressed with an Arrhenius type relation as (Mathai, 1996)

$$\ln X = \ln X_o - \left(\frac{E_x}{RT}\right) \quad (9)$$

Here X represents the diffusivity (D) or permeation coefficient (P) and X_o is a constant representing D_o or P_o. Plot of ln X (X = D or P) against 1/T was used to calculate the activation energies of diffusion (E_D) and permeation (E_P). The plots are shown in Figs. 5. and 6, respectively. The values of E_D and E_P are presented in Table 5.. E_D is the activation energy required to create an opening between polymer chains which is large enough to allow the solvent molecules to penetrate. Thus, E_D is a function of inter- and intra- chain forces that must be overcome to create the space required for a unit differential jump of the penetrant (Harogoppad, 1991). However, no definite trend of E_D values of the composites is observed in Table 5.. Heats of sorption impart important information regarding the transport process. The derived ΔH_S ($\Delta H_S = E_P - E_D$) values are also listed in Table 5.



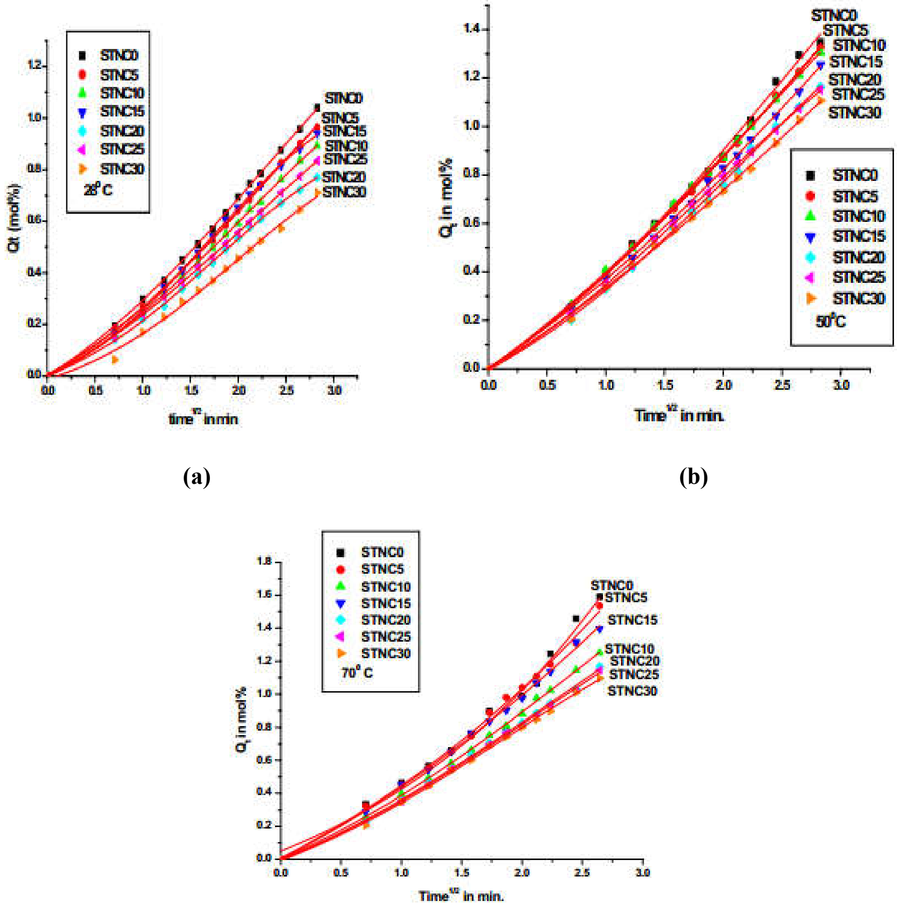
(a) (b)

(c) (d)

(e) (f)

(g)

Fig.1.Swelling curves of the composites at 28, 50 and 70oC (a) STNC0 (b) STNC5 (c) STNC10, (d) STNC15, (e) STNC20, (f) STNC25 & (g) STNC30



(a)

(b)

(c)

Figure 2. Qt vs t$^{1/2}$ plot (initial portion) of the composites at a) 280 C, (b) temp 500 C and (c) 700C

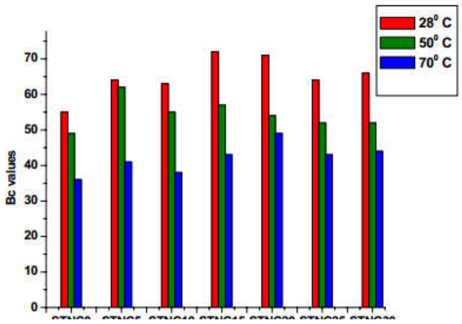


Fig. 3 .Variation of equilibrium toluene take up ($Q\infty$) of the composites

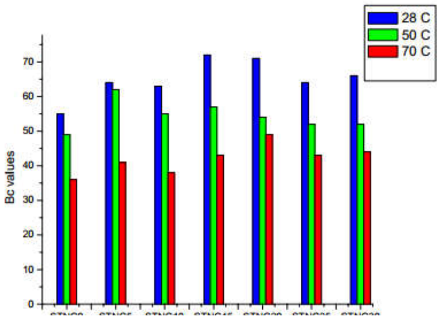


Fig 4 Variation of “B” values of the composites at various temperature

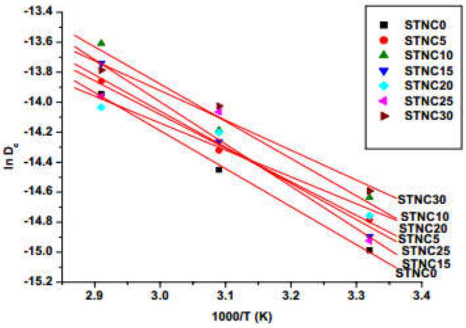


FIG .5. Arrhenius plots of diffusivity for composites in toluene

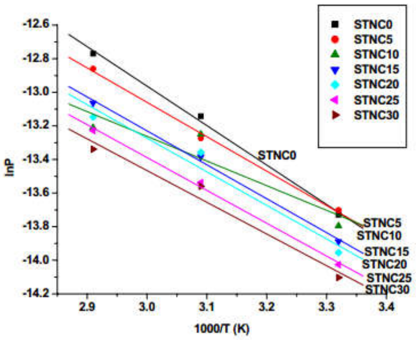


Fig .6. Arrhenius plots of permeability for composites in toluene

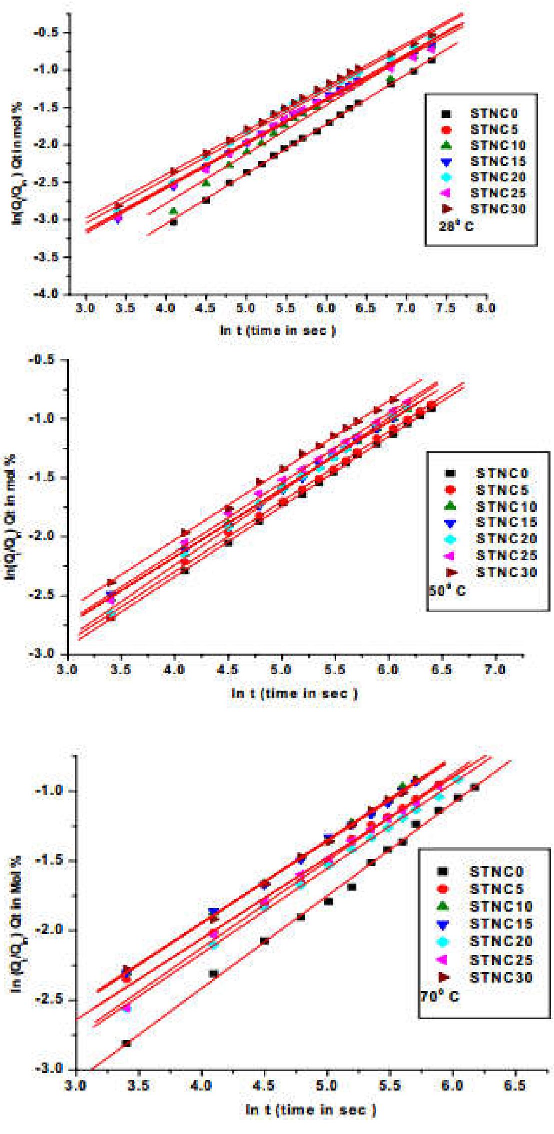


Fig 7. Plots of ln(Qt/Qin) vs time of the composites in toluene at a) 280C b) 500C and c) 700C

Activation energy of diffusion (E_D) is less than the activation energy of permeation (E_P). The values of ΔH_S appear to be positive indicating endothermic nature of sorption isotherms. It also suggests that E_D is less than E_P. This is because E_P depends on the transport of penetrant molecules along the boundary lines of the polydomain heterogeneous morphology of the composites. High positive ΔH_S value of the unfilled and filled composites indicate that it is dominated by Henry's law of dissolution process.

Transport Mechanism

In order to understand the mechanism of transport of toluene (solvent) through the composites, the results of solvent uptake were analyses using the following Eq. 10

$$\ln\left(\frac{Q_t}{Q_\infty}\right) = \ln k + n \ln t \qquad (10)$$

Here Q_t and Q_∞ are the moles % of the solvent up take by the composite samples at time t and at equilibrium, respectively; k is a constant which depends upon the structural characteristics (morphology of the composite) of the sample and its interaction with the solvent.

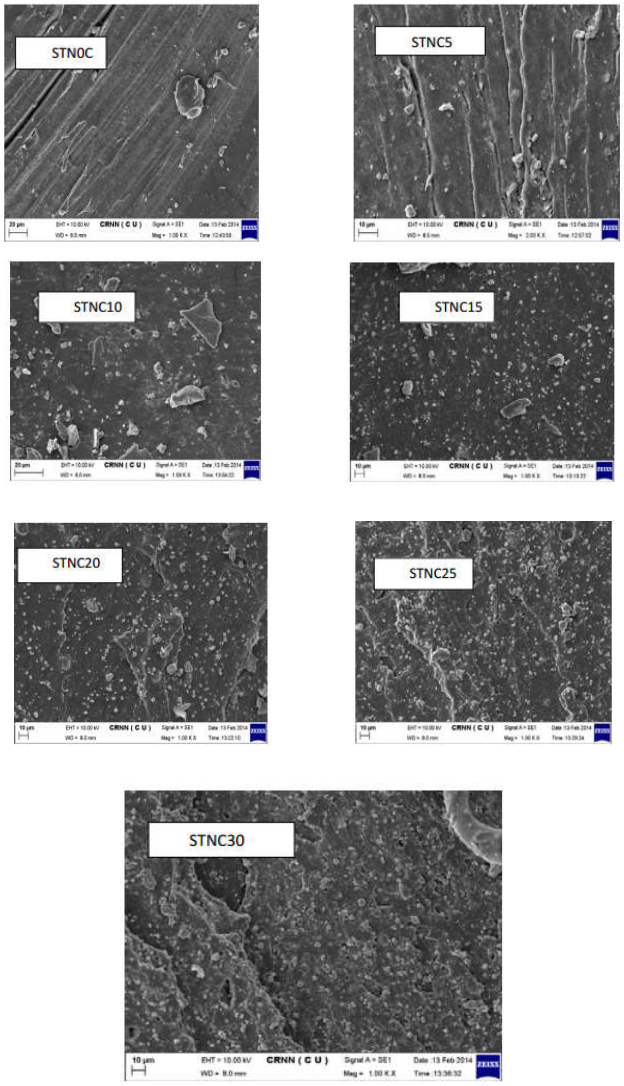


Figure 8. SEM observation of the surface NR/ treated nano CaCO3 composite (1000X)

The values of *n* give an idea about the mechanism of solvent transport. For Fickian case-I transport, n= 0.5 and in this case the rate of diffusion of permeant molecules is much less than the polymer segment mobility. It is also called case I transport mechanism. For non- Fickian case-II transport, n = 1.0 and the rate of diffusion of permeant molecules is much greater than the polymer segment mobility. When 0.5 < n < 1.0, it is called anomalous transport and in this case the rate of diffusion of permeant molecules equals the relaxation rate of the polymer chain. Similarly, for n values exceeding unity (1), the sorption is termed as super case –II (Vieth, 1991).

For the sorption of the present seven composites the plots of $\ln(Q_t/Q_\alpha)$ versus ln t are shown in Fig. 7. a ,b and c. In these linear regressions, the initial data points up to 40% of total sorption were used. The values of n and k for these composites are given in Table 6. The values of *n* of the composites are higher than 0.5 and less than 1 at all temperature, suggesting anomalous mode of transport.

Morphological properties rubber composites by SEM

The morphology of the composites filled with varied amounts of the polymer coated nano fillers were studied with SEM at 1000x magnification as shown in Fig. 8. It is observed that the filler networks are well dispersed within the rubber matrix in the filled composites. The surface roughness is observed to increase with an increase in filler loading. The better mechanical properties of the filled composites with respect to the unfilled one (SNTC0) may be due to this surface roughness as also reported elsewhere (Teh, et al., 2004). Some agglomeration of the nano filler is also observed at higher % of filler loading (>20 wt%).

Conclusion

The effect of polymethyl methacrylate (PMMA) encapsulated nano sized calcium carbonate on the properties of NR based composites prepared with varied phr of this filler were studied in term of transport characteristics. The transport properties of a solvent (toluene) through these composites were also studied at three experimental temperatures. The equilibrium solvent up take (Q_∞) of filled composites was less than the same of the unfilled composites. High crosslink density may be the cause for high rubber filler interaction. The solvent absorptions also increased at higher temperature indicating no leaching of the other additives. The diffusion coefficient (D), permeation coefficient (P) and sorption coefficient (S) obtained for the present composites in toluene were found to increase with an increase in sorption temperature. It is observed that PMMA coated filler exerts strong influence on the transport parameters.

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