

Barrier properties of natural rubber/ethylene vinyl acetate/carbon black composites

A. SUJITH, G. UNNIKRISHNAN*

Polymer Science and Technology Laboratory, National Institute of Technology, Calicut, 673601, Kerala, India

E-mail: unnig@nitc.ac.in

Composites based on natural rubber (NR), ethylene vinyl acetate (EVA) and carbon black were prepared. Three types of carbon black viz.; semireinforcing furnace (SRF), high-abrasion furnace (HAF) and intermediate superabrasion furnace (ISAF) were used for reinforcement. The barrier properties of these filled samples were examined in an atmosphere of petrol, kerosene and diesel. Blends loaded with ISAF exhibited the lowest liquid uptake which has been attributed to the higher filler reinforcement and crosslink density of the matrix. Among the three vulcanising systems used, viz.; sulphur (S), dicumyl peroxide (DCP) and mixed (S+DCP), DCP crosslinked samples exhibited high barrier properties to the probe molecules. Diesel showed the lowest interaction with the composites compared to petrol and kerosene. The sorption data were used to estimate the enthalpy, entropy and free energy of the transport process.

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1. Introduction

The mass transport process through filled polymer blends is influenced by factors such as nature of fillers, the degree of adhesion and their compatibility with the polymer matrix, nature of blend components, crosslink density and nature of penetrants. The significant role of fillers on the diffusion process has been identified by several researchers [1–5]. When fillers are incorporated to the blend matrix, a situation may develop in which the filler is unevenly distributed between the two phases, and this distribution affects the compound properties and their swelling behaviour. Compatible, inert fillers will take up the free volume within the polymer blend matrix and create a tortuous path for the permeating molecules. The degree of tortuosity depends on the volume fraction of the filler and the shape and orientation of the filler particles. Lowering in the equilibrium swelling of fibrous filler reinforced samples indicates excellent filler-matrix interaction [6].

Excellent reports on the interaction of filler reinforced polymer blends with solvents exist in literature. For example, the effect of carbon black loading on the cure time (t_{90}) and swelling behaviour of standard Malaysian rubber/epoxidised natural rubber (SMR L/ENR 25) and standard Malaysian rubber/styrene butadiene rubber (SMR L/SBR) blends has been studied by Ismail *et al.* [7] At fixed filler loading, SMR L/ENR 25 blend has been found to exhibit a lower percentage swelling than SMR L/SBR blends. The effect of swelling behaviour in kerosene of a new tri-block rubber based on blends of NR and different

concentration ratios of both SBR and butyl rubber (IIR), all incorporating 40 phr (parts per hundred parts of rubber by weight) of high abrasion furnace (HAF) carbon black, has been investigated by Nasr and Goma [8]. The degree of swelling, in kerosene was found to decrease with both physical ageing and IIR content of the specimen. Segal *et al.* [9] studied the sensing of liquids by electrically conductive immiscible polypropylene/thermoplastic polyurethane (PP/TPU) blends containing carbon black. They found that the interphase region, its quantity, and continuity played a significant role in the liquid-transport process. Narkis *et al.* [10] used carbon black filled immiscible polymer blends with polystyrene (PS) and ethylene vinyl acetate (EVA) for the detection of organic liquid solvents and their vapours. They suggested that the liquid transport principles are an important basis for the interpretation of the sensing behaviour of immiscible blend-based filaments in contact with liquids. Earlier, our research group also reported the transport characteristics of carbon black filled natural rubber and ethylene vinyl acetate composites [11, 12]. Although many other works can also be cited from the literature, the influence of reinforcing fillers on the transport process through polymer blends still needs additional information.

The goal of the present work is to study the influence of three different types of carbon black viz.; semireinforcing furnace (SRF), high-abrasion furnace (HAF) and intermediate superabrasion furnace (ISAF) on the barrier properties of natural rubber/ethylene vinyl acetate blends using petrol, diesel and kerosene as probe

*Author to whom all correspondence should be addressed.

TABLE I Characteristics of the material used

Solvent	Molecular weight (Mn)	Density (g/cm ³)	Boiling point (°C)	Filler type	Grade	Pore density (g/l)	Particle size (nm)
Petrol	100	0.71	95	SRF	N 762	375	60
Kerosene	170	0.81	147	HAF	N 330	375	29
Diesel	326	0.82	300	ISAF	N 220	345	23

molecules. Special stress is being given to the effects of filler loading, nature of fillers, blend-filler interaction, blend ratio, and penetrant size on the transport process.

2. Experimental

2.1. Materials

Natural rubber (NR) used was of ISNR-3L grade, supplied by Rubber Research Institute of India, Kottayam, Kerala, India. Poly (ethylene-*co*-vinyl acetate) (EVA)-1802 was supplied by EXXON Chemical Company, Houston, USA. The fillers used were SRF (semireinforcing furnace), HAF (high-abrasion furnace), and ISAF (intermediate superabrasion furnace) with particle sizes 60, 29 and 23 nm respectively. The aliphatic solvents used viz.; petrol, diesel and kerosene were of reagent grade (99% pure) and were distilled twice before use to ensure purity. The characteristics of the materials are given in Table I.

2.2. Preparation of NR/EVA/carbon black composites

The blends of NR and EVA, with ratios from 0 to 100 percentage reinforced with SRF, HAF and ISAF,

with variable loading and with three crosslink systems viz.; sulphur, dicumyl peroxide (DCP) and a mixture of sulphur and peroxide, were prepared on a two roll mixing mill (150 × 300 mm) with a nip gap of 1.3 mm and at a friction ratio 1:1.4. The compounding recipes are given in Table II. The curing behaviour of the compounded blends was studied by using a Monsanto Rheometer R-100 at a rotational frequency of 100 cycles/min. The samples were cured for their optimum cure time t_{90} , which represents the time to attain 90% of the maximum rheometric torque.

2.3. Solvent diffusion experiments

The NR/EVA blend samples for diffusion experiments were punched out in circular shape of diameter 1.9 cm from tensile sheets (15 × 15 × 0.2 cm³) and were dried in a vacuum desiccator over anhydrous CaCl₂ at room temperature for about 24–28 h. The original weights and thickness of the samples were measured before sorption experiments. They were then immersed in penetrants (15–20 ml) in closed diffusion

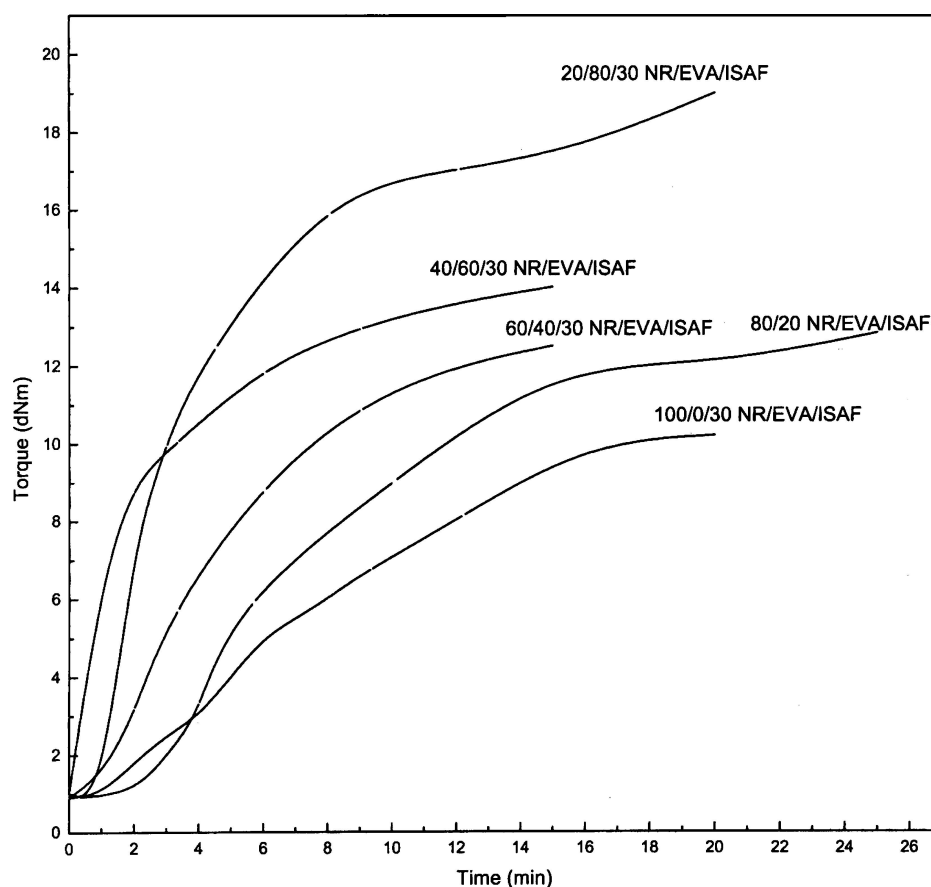


Figure 1 Rheographs of NR/EVA/ISAF composites with different blend ratios (Vulcanising agent: DCP).

TABLE II Formulation of the mixes

Ingredients	Vulcanising systems		
	Sulphur	Mixed	DCP
Polymer	100.0	100.0	100.0
Zinc oxide	4.0	4.0	–
Stearic acid	2.0	2.0	–
MBTS	1.5	1.5	–
Sulphur	2	2	–
DCP	–	4.0	4.0
Carbon black	Variable*	Variable*	Variable*

*10, 20 and 30 phr.

bottles, kept at constant temperature in an air oven. Periodically, the samples were removed from the bottles and weighed immediately using an electronic balance (Shimadzu, Libror AEU-210 Japan) that measured reproducibly within ± 0.0001 g. They were then placed back into the test bottles. The process was continued until equilibrium swelling was achieved. To avoid the possible error due to the removal of samples from the solvents, the weighing was carried out within 40 sec [13]. Similar methodology (ASTM D-471) has been followed by several researcher [14, 15]. The experiments were duplicates or triplicates in most cases. For desorption studies, the blend samples were desorbed quantitatively, after sorption.

These samples were again exposed to solvent for resorption.

The results of sorption experiments have been expressed in terms of mol% uptake Q_t of the liquid by 100 g of the blend as a function of square root of time of immersion.

2.4. Morphological studies

The composite samples for scanning electron micrographs (SEM) were prepared by cryogenically fracturing them in liquid nitrogen. The samples were sputter coated with gold and the photographs were taken using a scanning electron microscope (S-2400, Hitachi).

3. Results and discussion

3.1. Processing characteristics

The cure characteristics and thus the processability of the compounds have been studied from the rheographs. The maximum torque (M_H) indicated in the rheographs is a measure of crosslink density and the stiffness of the composite matrix. The increase in torque observed with time is due to the crosslinking of the composite. The leveling off is an indication of the completion of the curing process. Fig. 1 shows the rheographs of 30 g ISAF loaded NR/EVA with different blend ratios, DCP

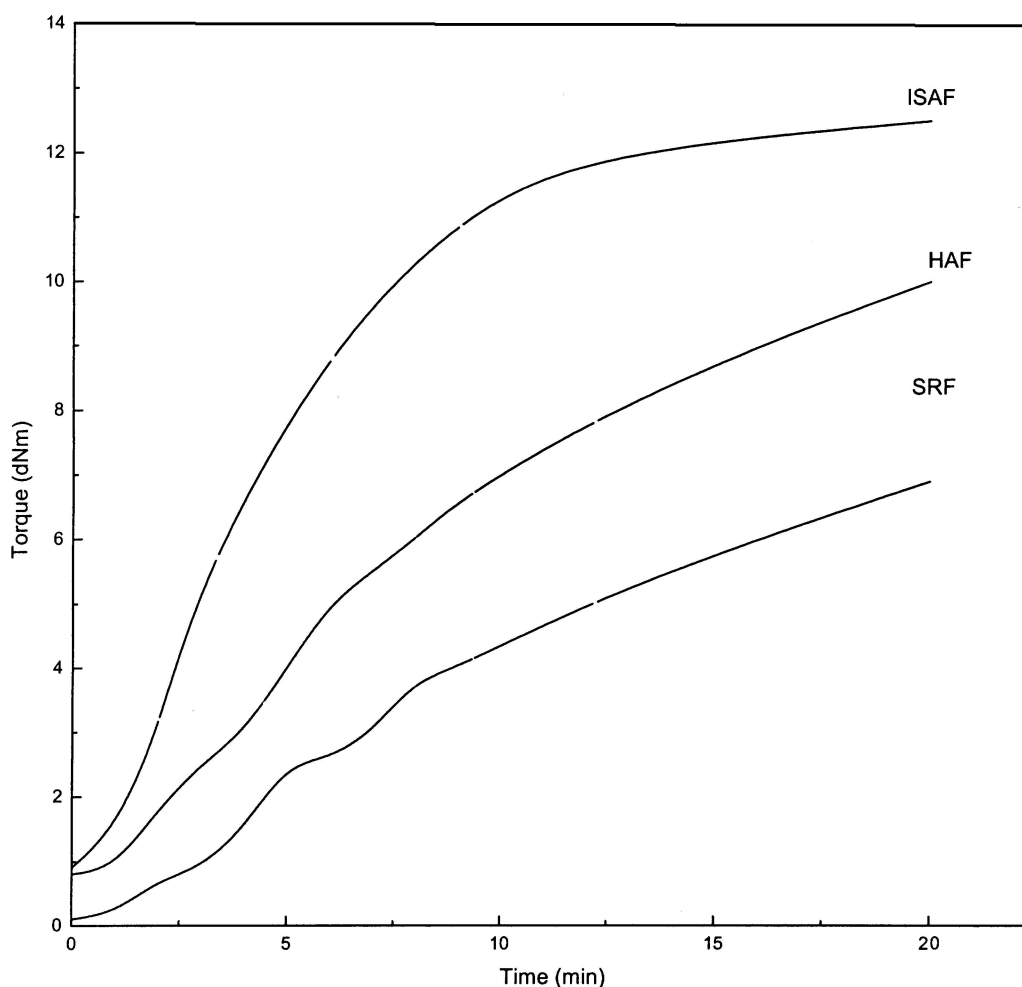


Figure 2 Rheographs of 80/20 NR/EVA reinforced with different carbon blacks (Vulcanising agent: DCP).

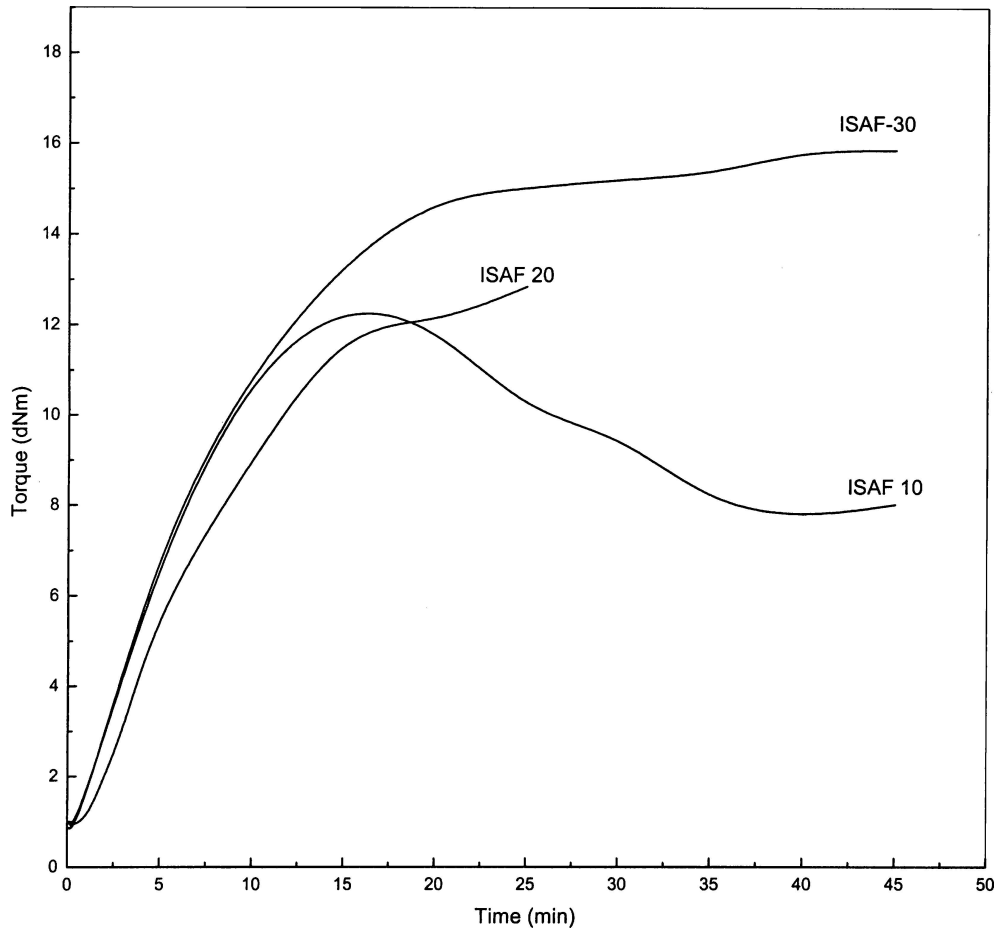


Figure 3 Rheographs of 60/40 NR/EVA reinforced with ISAF at different filler concentrations (Vulcanising agent: DCP).

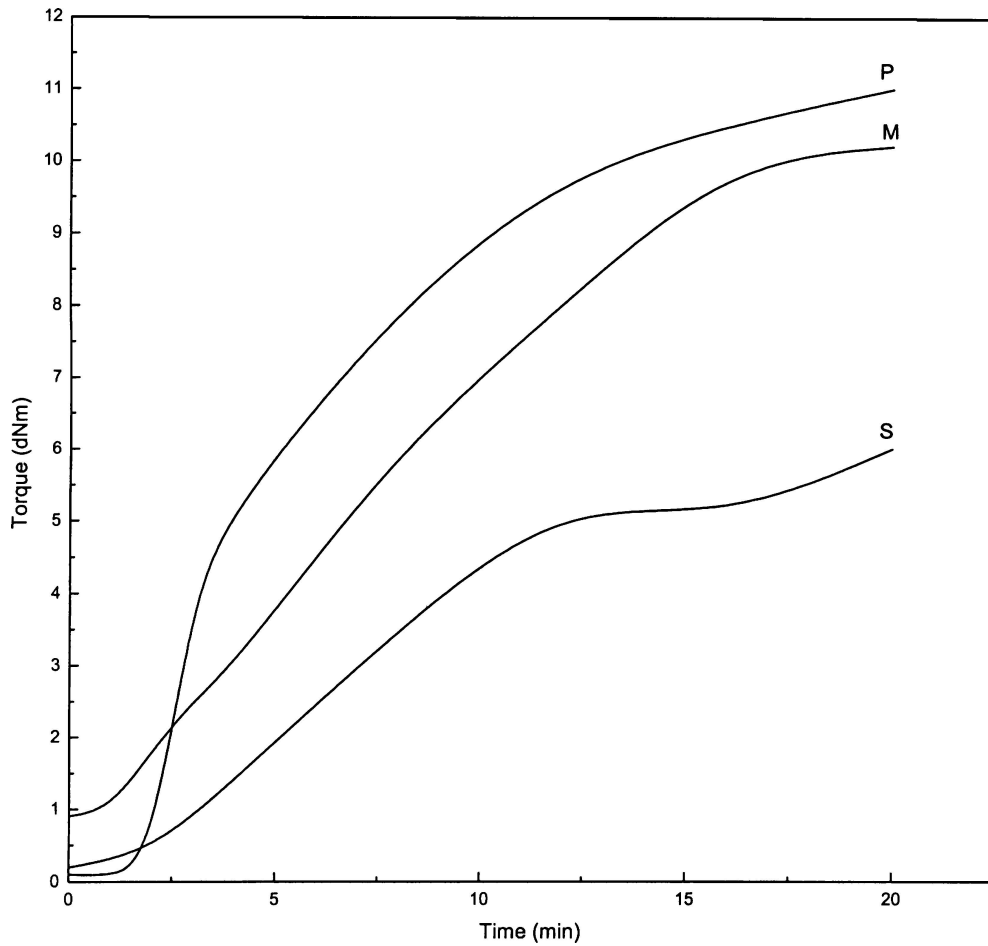


Figure 4 Rheographs of 80/20 NR/EVA reinforced with ISAF crosslinked with different systems.

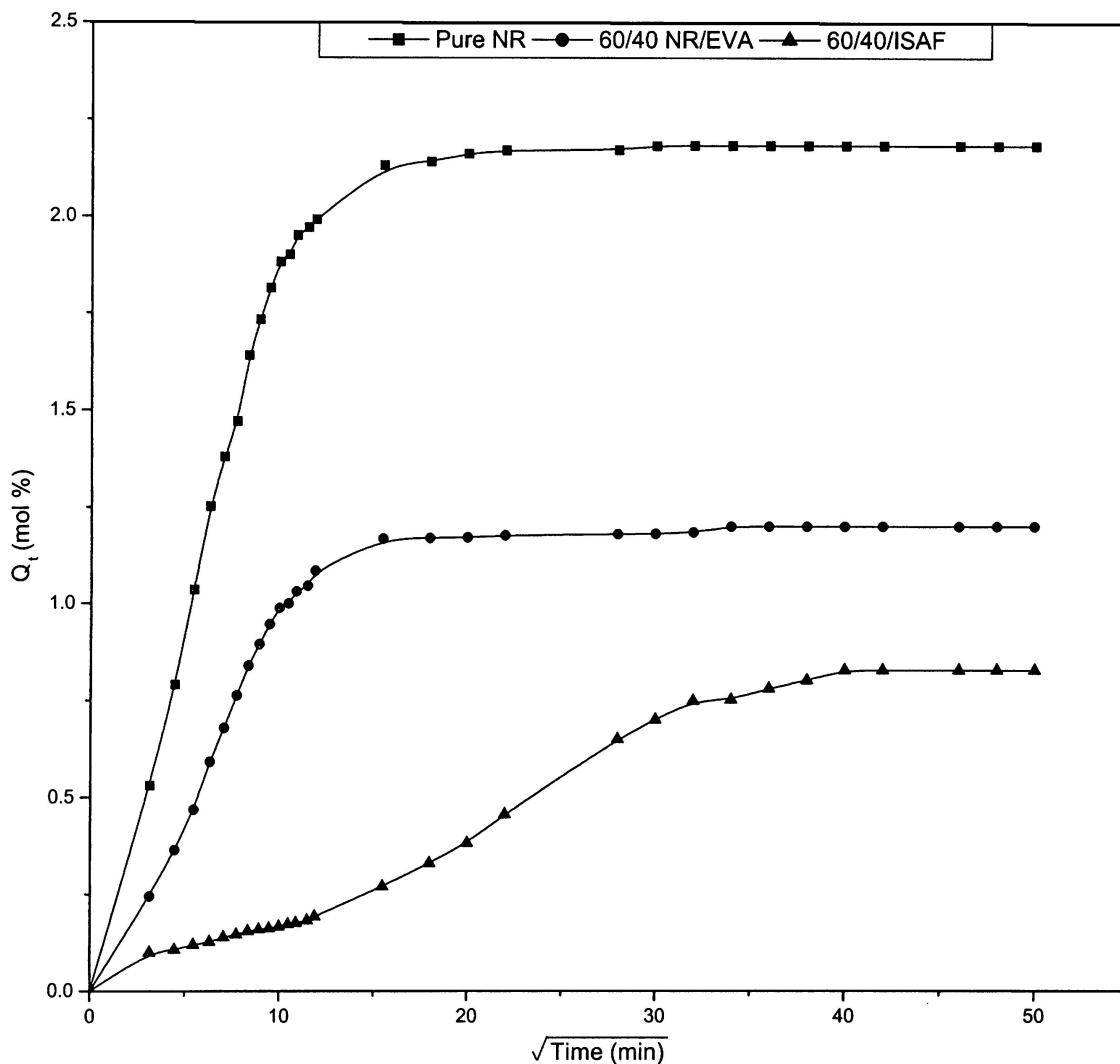


Figure 5 Comparison of mol% petrol uptake of pure NR, NR/EVA and NR/EVA/carbon black.

as vulcanising agent. It is found that higher EVA loaded samples show higher M_H values due to the increased crystallinity in them, EVA being semicrystalline, which causes restriction to the mobility of the macromolecular chains. 100/0 NR/EVA shows the lowest torque. Fig. 2 shows the rheographs of 80/20 NR/EVA mixes with different carbon blacks of 30-phr loading, DCP as vulcanising agent. ISAF black reinforced mix shows highest M_H value due to the increased crosslink density attributed to the maximum reinforcement. Lowest M_H value is observed for SRF filled sample which has minimum reinforcement effect due to the larger particle size of fillers. HAF filled sample shows an intermediate behaviour. Fig. 3 shows the rheographs of the 60/40 NR/EVA mixes reinforced with ISAF black at different loading, DCP as vulcanising agent. The M_H value increases with increase in filler content in all the systems. This may be due to the increase in rigidity of the samples by the increase in filler loading which reduces the mobility of chains. Fig. 4 shows the rheographs of 80/20 NR/EVA/ISAF composites vulcanised with different crosslinking systems. The DCP system has been found to exhibit maximum torque and S system the lowest. This is due to the fact that unlike sulphur and mixed vulcanising systems, DCP can cure both NR and EVA phases uniformly and induce

C-C bonds between the macromolecular chains which makes the matrix more rigid. Sulphur vulcanisation introduces flexible polysulphidic linkages which makes the matrix relatively flexible [16].

3.2. Solvent interaction studies

3.2.1. Comparison of barrier properties

Fig. 5 shows the comparison of mol percent petrol uptake by pure NR, 60/40 NR/EVA and 60/40/30 NR/EVA/ISAF composites crosslinked by DCP. It is clearly seen that pure NR, with flexible chains which easily adjust with the solvent ingress, shows highest solvent uptake. Blending of semicrystalline EVA, with NR introduces rigid regions in the matrix, which reduces the solvent sensitivity of NR. The effect of reinforcement of NR/EVA matrix, which results in improved barrier properties is evident from the sorption curve of the blends loaded with ISAF black. The initial bending of the curve clearly indicates the time lag taken for the carbon black filled samples to interact with petrol. A schematic representation of comparison of NR, NR/EVA and NR/EVA/carbon black is shown in Fig. 6.

Fig. 7a-c show the scanning electron micrographs of pure NR, 60/40 NR/EVA and 60/40/30 NR/EVA/ISAF

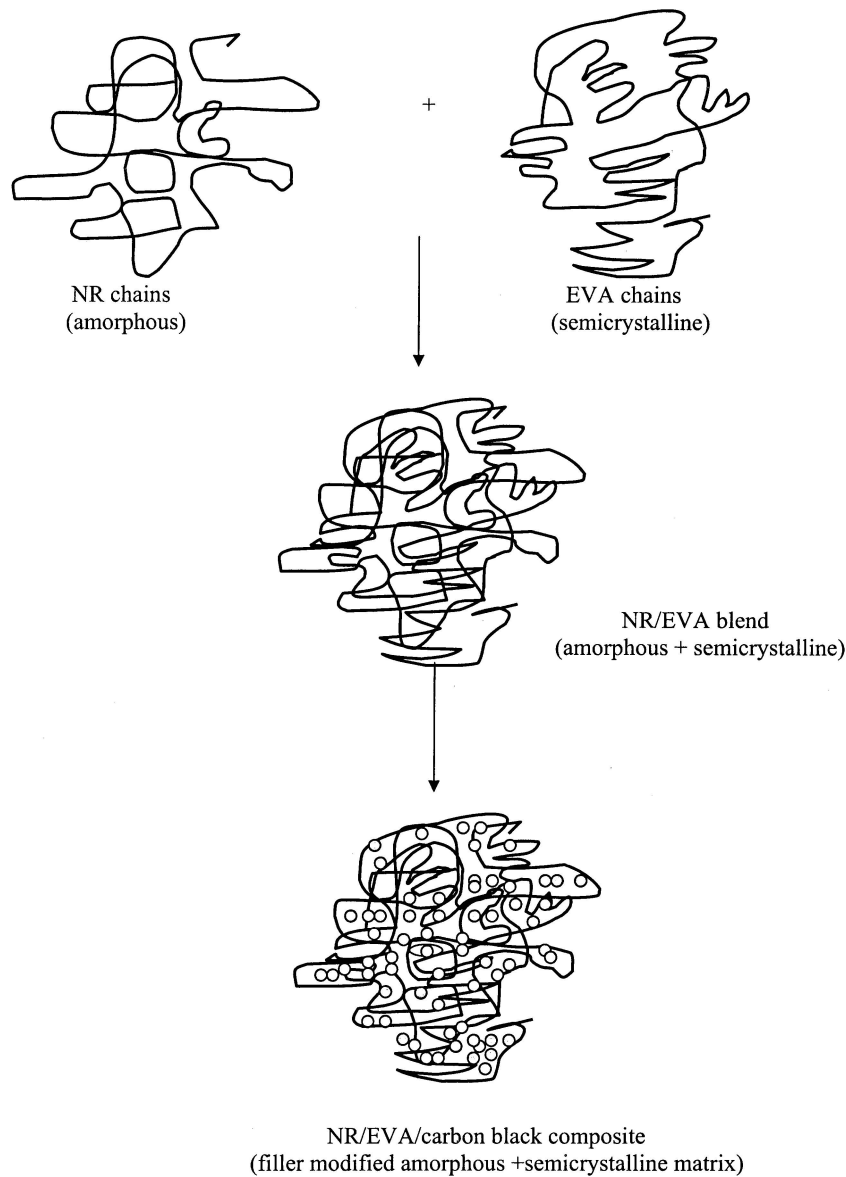


Figure 6 Schematic representation of blending and reinforcement in NR.

samples, respectively, vulcanised by DCP. The EVA domains in the NR matrix (Fig. 7b) fragmented in to smaller size when the filler is incorporated (Fig. 7c). This may probably due to the higher level of mechanical friction experienced during milling, in filler loaded samples compared to the unfilled system [17]. Due to the changes in the morphology of the matrix with blending and filler loading, the solvent uptake decreases in the order NR > NR/EVA > NR/EVA/carbon black.

3.2.2. Effect of blend ratio

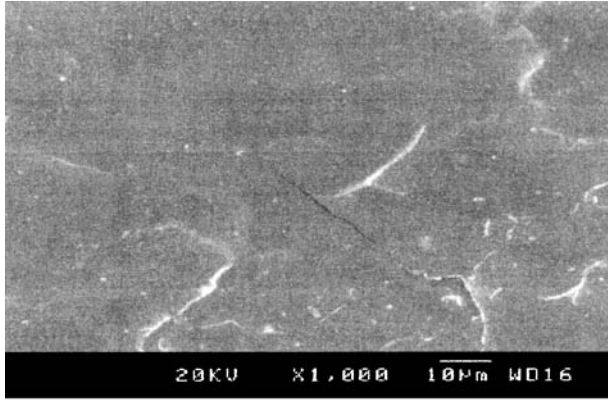
Fig. 8 shows the effect of blend composition on the solvent uptake behaviour of NR/EVA/carbon black (30 phr; ISAF) blends vulcanised by DCP at 28°C. The penetrant used was diesel. It is clear from the figure that the liquid uptake tendency decreases with increase in EVA content in the blends. Upon blending NR with semicrystalline EVA, the crystallinity of blend matrix increases due to the enhanced macromolecular chain rearrangements. This results in lower penetrant ingress into the matrix, which regularly decreases with in-

crease in the weight percent of EVA in the blends. The crystalline regions and relatively close packed structure of EVA put up stiffer resistance to the penetrant molecules leading to a low extent of solvent uptake. Moreover, the interaction between the polar groups present on the surface of the carbon black [18] and the polar EVA chains also increases with the EVA content in the matrix.

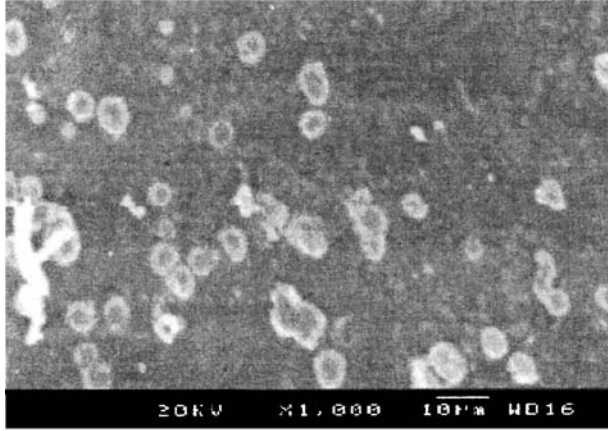
The above observations are complemented by the scanning electron micrographs shown in the Fig. 9a-c. A comparative reduction in the domain size of EVA and the attainment of a relatively uniform morphology is observed with the increase in EVA content in the blend composites. The increased adhesion of carbon black, with the EVA phase in the matrix also contributes to the increase in uniformity with the EVA content.

3.2.3. Effect of different fillers

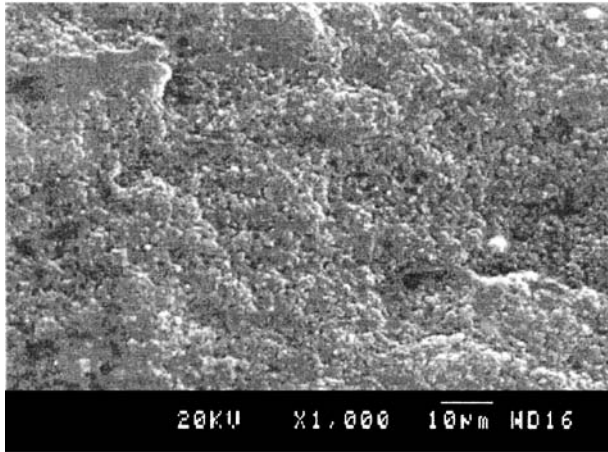
Fig. 10 shows the sorption behaviour of 60/40 NR/EVA blend reinforced with 30 g SRF, HAF and ISAF, vulcanised with DCP, in kerosene. The experiments were done



(a) Natural Rubber



(b) 60/40 NR/EVA



(c) 60/40/30 NR/EVA/ISAF

Figure 7 Scanning Electron Micrographs of DCP vulcanised: (a) NR, (b) 60/40 NR/EVA and (c) 60/40/30 NR/EVA/ISAF.

at 28°C. Among the different fillers used, NR/EVA loaded with ISAF shows the lowest penetrant interaction. The SRF loaded blends shows the highest. The samples reinforced with HAF have been found to exhibit intermediate sorption behaviour. This trend can be explained on the basis of the difference in the particle size of fillers reinforced into the matrix. For maximum reinforcement, the filler particles must be of the same size or smaller than the chain end-to-end distance [18]. The degree of filler reinforcement increases with the decrease in particle size or increase in surface area. The ISAF black, having lower particle size, and hence higher degree of reinforcement, causes much re-

TABLE III Values of M_c

NR/EVA	Carbon black	M_c
100/0	SRF	2710
	HAF	2469
	ISAF	2292
80/20	SRF	2214
	HAF	2066
	ISAF	2002
60/40	SRF	2115
	HAF	1927
	ISAF	1415
40/60	SRF	1051
	HAF	1032
	ISAF	1003
20/80	SRF	772
	HAF	682
	ISAF	649
0/100	SRF	456
	HAF	365
	ISAF	302

sistance to the blend chain relaxation and prevent the diffusion of penetrants compared to the other two carbon blacks. The SRF black, having higher particle size, cannot cause more tortuosity in the path of the penetrants. HAF black which has the particle size in between SRF and ISAF, shows an intermediate sorption behaviour.

Fig. 11a shows the SEM photograph of SRF reinforced 60/40NR/EVA. Fig. 11b and c represent HAF and ISAF filled 60/40 NR/EVA samples. From 11a–c, the domain size of EVA decreases and the filler distribution becomes more uniform. This accounts for the observed solvent uptake behaviour of the blends reinforced with different fillers.

Attempt has been done to apply Kraus equation [19] to find the extent of reinforcement of different fillers in the blend matrix.

$$V_{r0}/V_{rf} = 1 - m[f/1 - f] \quad (1)$$

where V_{r0} and V_{rf} are the volume fraction of the swollen polymer blend in the fully swollen unfilled sample and in the fully swollen filled sample respectively. f is the volume fraction of the filler and the slope m will be a direct measure of the reinforcing ability of the fillers to the blend matrix. Fig. 12 shows the plot of V_{r0}/V_{rf} versus $f/1 - f$ According to Kraus theory, the curves with higher negative slope indicate a better reinforcing effect. From the figure it is clear that the negative value of the slope increases in the order ISAF > HAF > SRF, indicating the degree of reinforcement in the same order. The order of reinforcement is complementary to the observed solvent uptake trend for the different filler loaded matrices used.

3.2.4. Effect of amount of fillers

Fig. 13 shows the sorption curves of 60/40 NR/EVA blends reinforced with ISAF for different filler loadings vulcanised by DCP at 28°C, in kerosene. The solvent uptake decreases in the order 10 phr > 20 phr

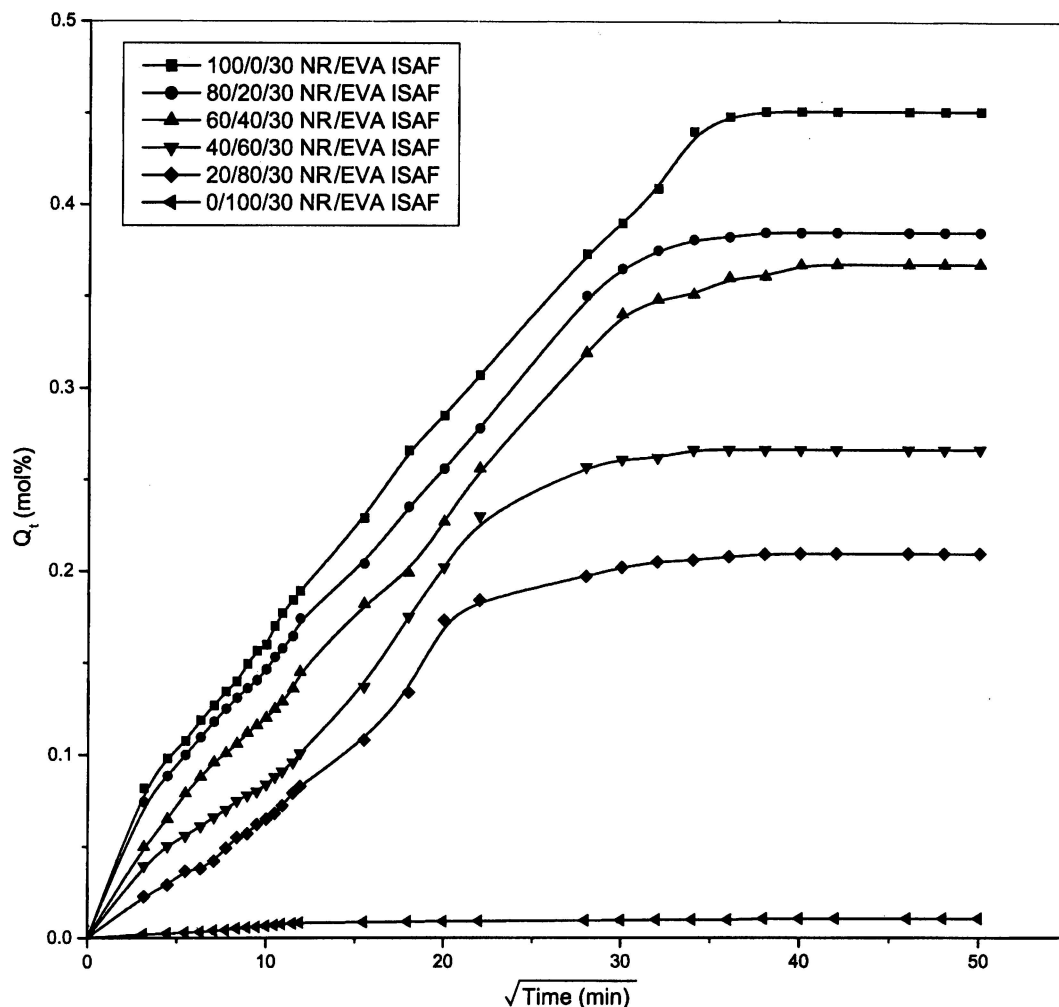


Figure 8 Effect of blend ratio on the mol% diesel uptake of different NR/EVA reinforced with 30-phr ISAF vulcanised with DCP.

> 30 phr ISAF for all the samples. It implies the reduction in free volume or micro voids due to the better filler reinforcement. Increase in filler content also restricts the macromolecular chain mobility resulting in a tortuous path for the diffusion of penetrants.

3.2.5. Effect of penetrants

The effect of molecular weight of the solvents on the mole percent uptake by the 40/60/30 NR/EVA/ISAF composite crosslinked with DCP is shown in Fig. 14. There is a systematic trend in the sorption behaviour of liquids of different molecular size. With an increase

TABLE IV Values of diffusion and permeation coefficients of DCP vulcanised samples at 28°C

NR/EVA/carbon black	$D^* \times 10^9$ (cm ² /sec)			$P \times 10^8$ (cm ² /sec)		
	Petrol	Kerosene	Diesel	Petrol	Kerosene	Diesel
100/0/30 SRF	9.3	7.6	5.4	16.4	9.5	6.8
100/0/30 HAF	7.6	6.4	4.6	14.2	8.2	5.9
100/0/30 ISAF	5.8	5.0	3.6	11.3	6.4	5.0
80/20/30 SRF	5.3	4.6	2.0	14.0	7.4	6.2
80/20/30 HAF	3.9	2.6	1.5	12.6	5.6	5.8
80/20/30 ISAF	3.2	2.3	1.3	12.0	4.5	4.6
60/40/30 SRF	4.4	3.5	2.0	6.1	5.3	4.0
60/40/30 HAF	3.6	2.9	1.6	5.3	3.5	3.5
60/40/30 ISAF	3.1	2.2	0.9	4.0	3.0	2.1
40/60/30 SRF	3.2	2.8	1.6	4.6	2.6	2.2
40/60/30 HAF	2.6	2.0	1.5	3.9	2.2	1.6
40/60/30 ISAF	1.5	1.3	1.1	3.0	1.8	1.4
20/80/30 SRF	2.7	1.6	1.2	3.3	2.2	1.9
20/80/30 HAF	1.9	1.6	0.9	2.6	1.9	1.3
20/80/30 ISAF	1.2	1.2	0.5	2.1	1.8	1.2
0/100/30 SRF	1.5	1.1	0.9	1.8	1.2	0.9
0/100/30 HAF	1.0	0.8	0.7	1.2	1.1	0.8
0/100/30 ISAF	0.9	0.6	0.4	0.8	0.7	0.5

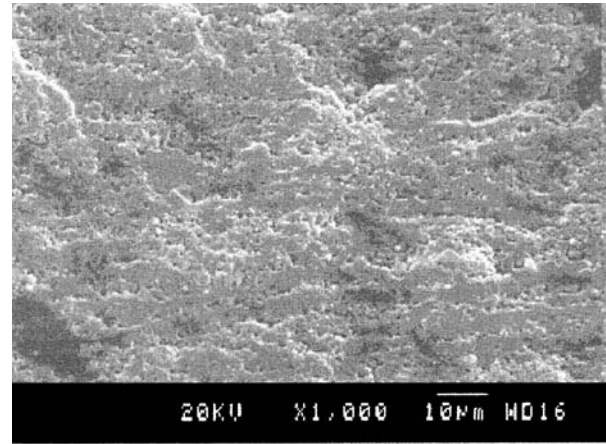
TABLE V Van't Hoff's parameters-entropy, enthalpy and free energy (Penetrant–Petrol).

NR/EVA/carbon black	Thermodynamic parameters		
	ΔS (J/mol/K)	$-\Delta H$ (J/mol)	$-\Delta G$ (J/mol)
100/0/0	12.38	1808.25	5534.63
100/0/30 SRF	9.35	1232.56	4046.91
100/0/30 HAF	7.56	1155.62	3431.18
100/0/30 ISAF	6.02	1032.86	2844.88
80/20/0	9.98	1384.25	4388.23
80/20/30 SRF	9.01	967.35	3679.36
80/20/30 HAF	6.30	862.24	2758.54
80/20/30 ISAF	4.90	522.31	1997.21
60/40/0	8.84	1308.81	3969.65
60/40/30 SRF	7.69	735.25	3049.94
60/40/30 HAF	5.80	456.53	2202.33
60/40/30 ISAF	3.50	396.12	1449.62
40/60/0	8.01	1245.23	3656.24
40/60/30 SRF	6.23	453.84	2379.07
40/60/30 HAF	3.89	401.56	1572.45
40/60/30 ISAF	3.05	268.35	1186.40
20/80/0	6.99	1202.24	3306.23
20/80/30 SRF	4.93	356.21	1840.14
20/80/30 HAF	2.56	245.32	1015.88
20/80/30 ISAF	1.41	221.51	645.92
0/100/0	4.39	995.35	2316.74
0/100/30 SRF	2.68	185.62	952.30
0/100/30 HAF	1.12	103.26	440.38
0/100/30 ISAF	0.92	98.65	375.57

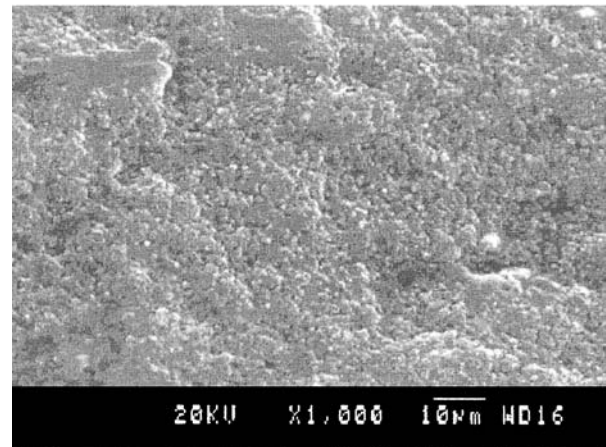
in molecular weight of the solvent molecules, there is a decrease in the values of Q_t in all the systems. Petrol shows the maximum value of Q_t and diesel the minimum, among the solvents used in the work. Kerosene takes an intermediate position. An exactly similar trend is observed for all the compositions. This can be explained on the basis of free volume theory [20], according to which the diffusion rate of a molecule depends primarily on the ease with which the polymer chain segments exchange their positions with penetrant molecules. As the penetrant size increases, the ease of exchange becomes less, particularly in the case of filled matrices leading to a decrease in the values of diffusion coefficient.

3.2.6. Effect crosslinking systems and crosslink density

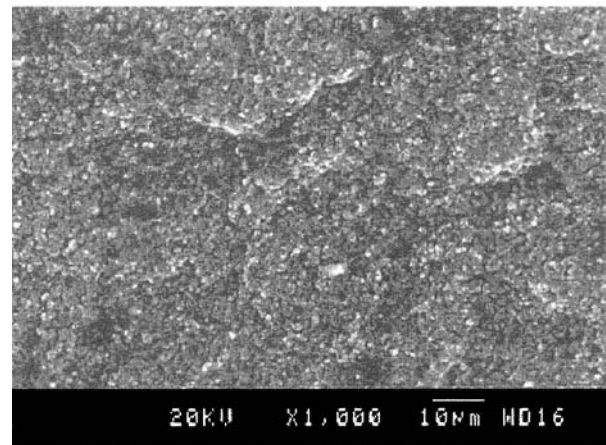
Fig. 15 shows that the sorption curves of 80/20 NR/EVA blends, loaded with 30 phr ISAF, but crosslinked by three vulcanising modes viz., sulphur, DCP and a mixed system comprising sulphur and peroxide, with kerosene as the probe molecule. It has been found that the liquid sorption behaviour decreases in the order sulphur > mixed > DCP. The differences in the transport behaviour through the matrices with different vulcanising agents arises due to the types of crosslinks formed during vulcanization and also due to the difference in the distribution of crosslinks. The sulphur vulcanization leads to the formation of flexible S-S linkages between the macromolecular chains, which easily rearrange under solvent stress to permit the penetrants to permeate relatively easily, while DCP vulcanization produces rigid C-C linkages. In mixed systems,



(a) 80/20/30 NR/EVA/ISAF



(b) 60/40/30 NR/EVA/ISAF



(c) 40/60/30 NR/EVA/ISAF

Figure 9 Scanning Electron Micrographs of DCP vulcanised: (a) 80/20/30 NR/EVA/ISAF, (b) 60/40/30 NR/EVA/ISAF and (c) 40/20/30 NR/EVA/ISAF.

intermediate sorption behaviour is observed, since it contains both C-C and S-S linkages.

In order to test how well the observed solvent uptake behaviour correlates with the crosslink distribution in the matrix, the molecular mass between crosslinks M_c has been calculated using Flory-Rehner equation [21]

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

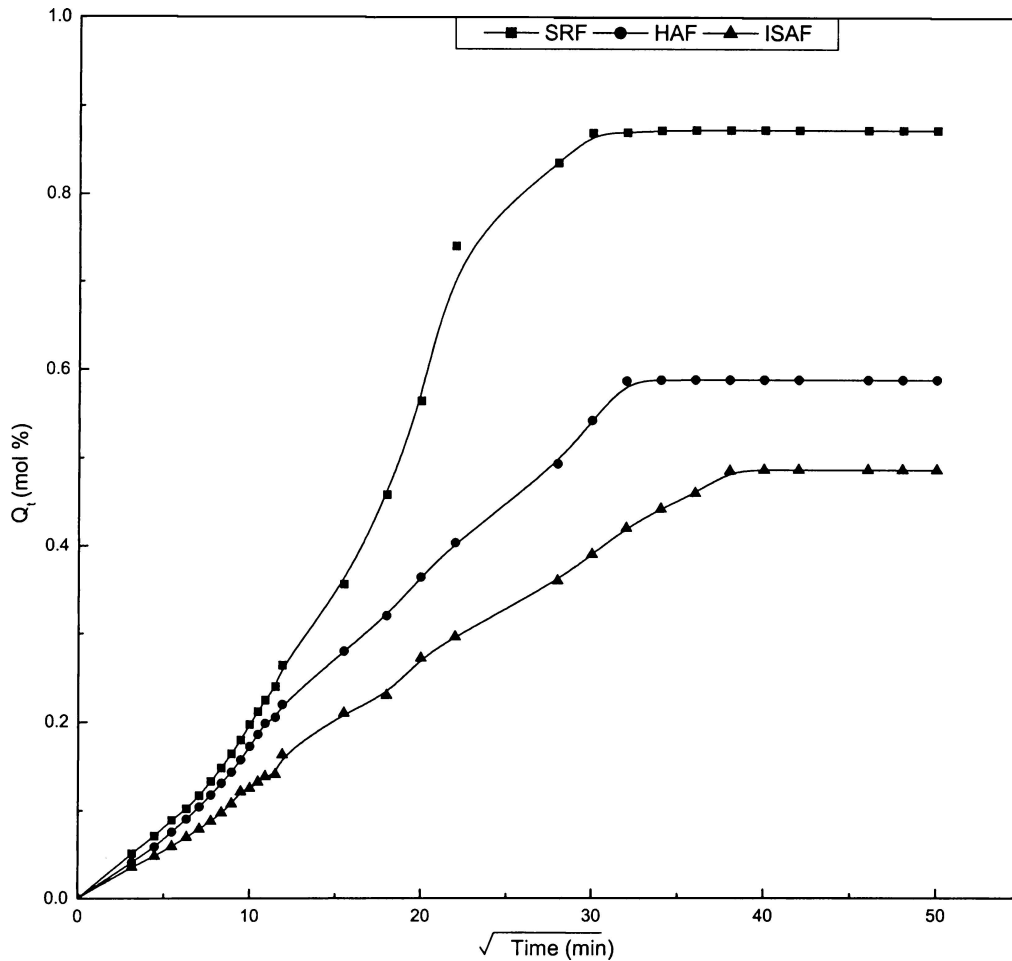


Figure 10 Effect of different carbon black fillers on the mol% kerocene uptake of 60/40 NR/EVA, vulcanised with DCP.

where ρ_p is the density of the matrix, V is the molar volume of the solvent, ϕ is the volume fraction of the amorphous component on the polymer blend in the fully swollen state, and χ is the blend-solvent interaction parameter determined as suggested by several researchers [22, 23]. The estimated values of M_c are given in Table III. It is seen that the M_c values decrease with increase in the EVA content in the blends, for a given filler in accordance with the solvent uptake behaviour. The semicrystalline EVA phase could induce physical crosslinks in addition to the permanent chemical crosslinks, formed during vulcanization, in the matrix. The values for different fillers are in the order SRF > HAF > ISAF, for a given blend ratio. As the value of M_c increases, the available free volume between the adjacent crosslinks increases. Hence more solvents can easily be accommodated between the crosslinks within the matrix. This result supports the observed highest solvent uptake in SRF loaded samples and the lowest in ISAF systems.

The solvent uptake behaviour has been further supported by finding out the crosslink density n_1 by the equation [24]

$$n_1 = 1/(2M_c) \quad (3)$$

Fig. 16 shows the effect of different fillers on the crosslink density. It is seen that the trend is in the order

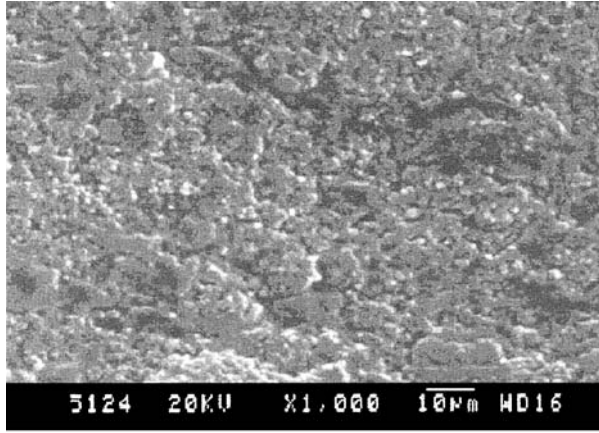
ISAF > HAF > SRF. Solvent uptake has been found to be inversely proportional to the crosslink density. Figure also shows the change in the crosslink density values with respect to the EVA content in the matrix. The values are varying complimentary to the Q_t values discussed earlier.

3.2.7. Effect of temperature

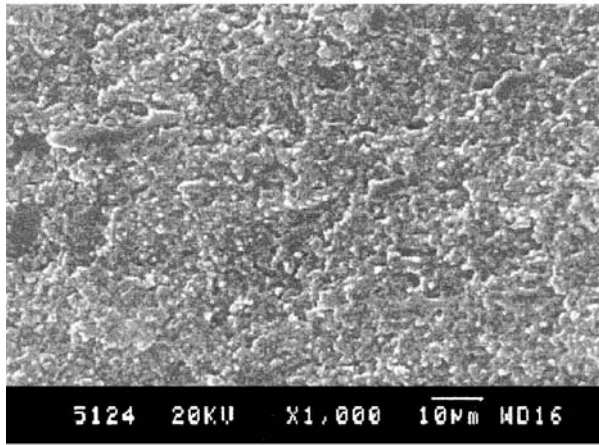
The dependence of diffusion behaviour of NR/EVA/carbon black composites on temperature was studied by doing the experiments at 28, 38, 48°C. The sorption curves of 60/40/30 NR/EVA/HAF composites vulcanised by DCP in diesel at different temperatures are given in the Fig. 17. The rate of diffusion and the maximum solvent uptake has been found to increase with temperature. This is due to the increased segmental mobility and free volume within the matrix at higher temperature. The kinetic energy of the penetrants also increases with increasing temperature. The disruptions of crystalline regions of EVA in the matrix at higher temperature can also contribute to the enhanced segmental motions and the subsequent higher solvent uptake.

3.2.8. Diffusion and permeation coefficients

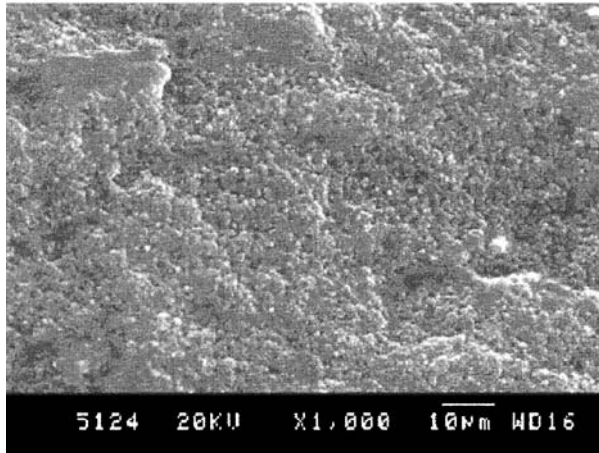
The kinetic parameter, diffusion coefficient D for the different systems, under investigation was estimated as



(a) 60/40/30 NR/EVA/SRF



(b) 60/40/30 NR/EVA/HAF



(c) 60/40/30 NR/EVA/ISAF

Figure 11 Scanning Electron Micrographs of DCP vulcanised: (a) 60/40/30 NR/EVA/SRF, (b) 60/40/30 NR/EVA/HAF and (c) 60/40/30 NR/EVA/ISAF.

[25]

$$D = \pi(h\theta/4Q_{\infty})^2 \quad (4)$$

where h is the sample thickness, θ is the slope of the linear portion of the sorption curves before attaining 50% of equilibrium, and Q_{∞} is the equilibrium sorption value. Since significant swelling was observed during sorption experiments in all solvents, corrections to diffusion coefficients under swollen conditions were

essential. This was done by calculating the intrinsic diffusion coefficient D^* from the volume fraction ϕ of the blends in the swollen sample using the relation [26]

$$D^* = \frac{D}{\phi^{7/3}} \quad (5)$$

The values of D^* are given in Table IV. It can be seen that the D^* values regularly decrease with decrease in particle size of the fillers and increase in EVA content in the composites, in a given solvent. It is also found that the D^* values are highest for SRF filled samples for a given blend ratio and solvent. The D^* values are found to be lower for the blend-diesel system compared to the corresponding petrol and kerosene systems.

The permeation process through any matrix is a combination of sorption and diffusion and hence the permeation coefficient depends on sorption coefficient and diffusion coefficient. The permeation coefficient P for all the systems under investigation was computed as [25]

$$P = D^*S \quad (6)$$

where D^* is the intrinsic diffusion coefficient and S is the sorption coefficient, which is the ratio of the mass of the penetrant molecule at equilibrium swelling to the mass of the polymer sample. The calculated values of P are also given in Table IV. It is observed that the P values of the composite-solvent systems follow the same trend as that of intrinsic diffusion coefficient, in terms of blend ratio, fillers and penetrant size.

3.2.9. Thermodynamic parameters

From the amount of penetrant sorbed by a given mass of the composite, the equilibrium sorption constant K_s for the composite samples at different temperature has been computed as

$$K_s = \frac{\text{No. of moles of penetrant sorbed}}{\text{Unit mass of the composite}} \quad (7)$$

From the values of K_s , enthalpy ΔH and entropy ΔS of sorption have been determined using the Van't Hoff relation [11]

$$\log K_s = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \quad (8)$$

The computed values of ΔH and ΔS are given in Table V. The ΔH values are negative for all the NR/EVA/carbon black samples, which become more negative from ISAF to SRF reinforced blends. The ΔS values also show a regular trend, which decrease with increase in the EVA content and decrease in the particle size of carbon black fillers in the composites.

From ΔH and ΔS , the free energy of sorption process has been obtained using the relation

$$\Delta G = \Delta H - T\Delta S \quad (9)$$

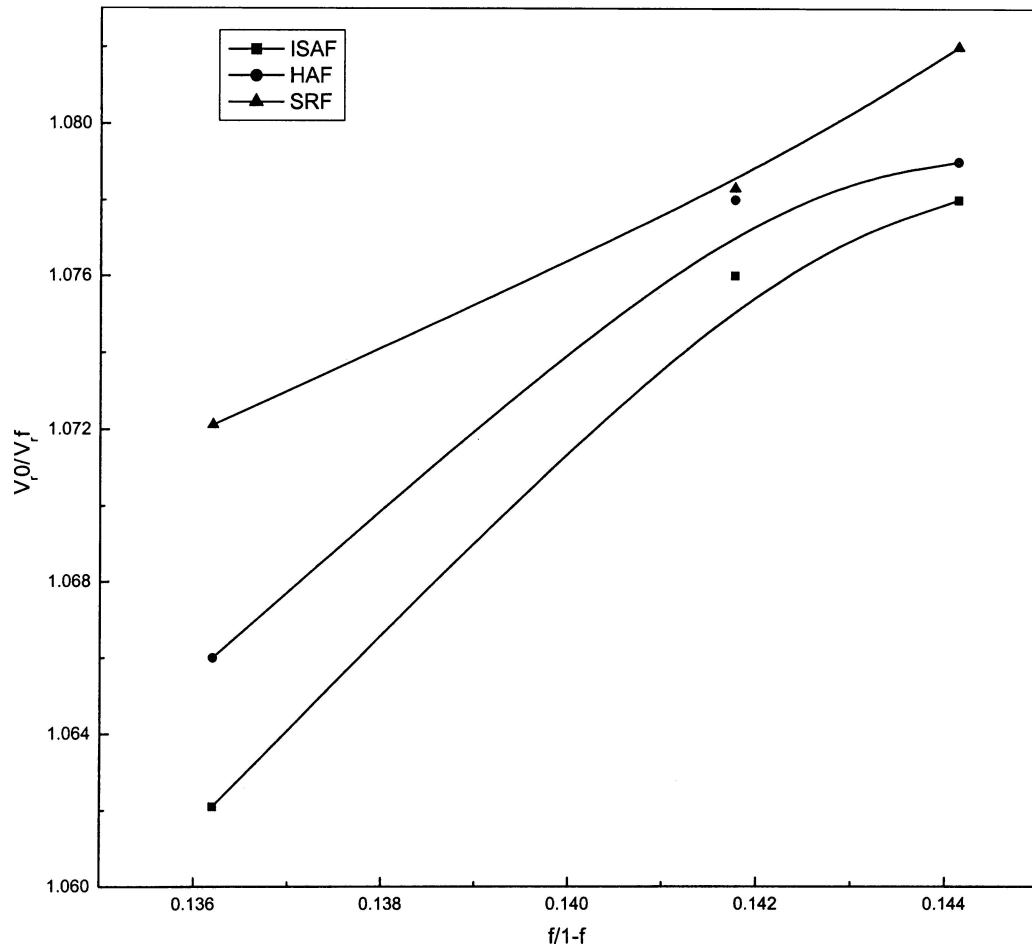


Figure 12 V_0/V_f versus $f/1-f$ curve of 60/40/30 NR/EVA/ISAF vulcanised with DCP.

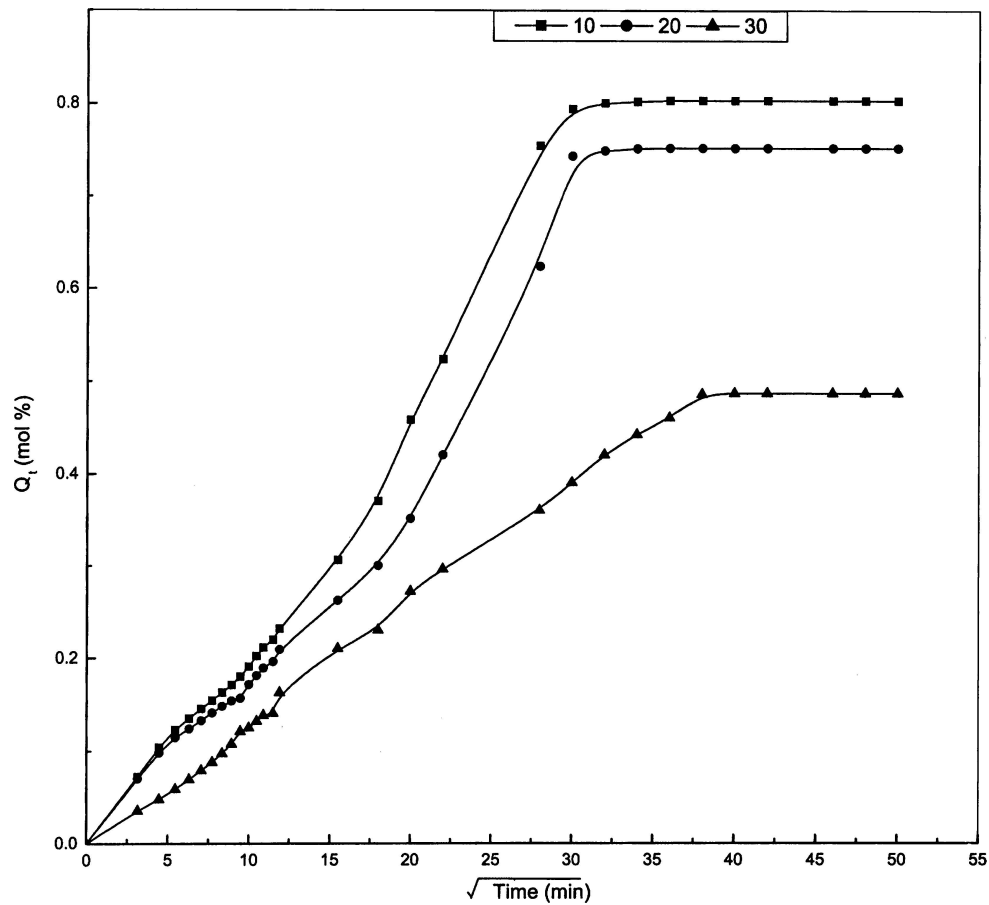


Figure 13 Mol% kerosene uptake of 60/40 NR/EVA with different ISAF concentration, vulcanised with DCP.

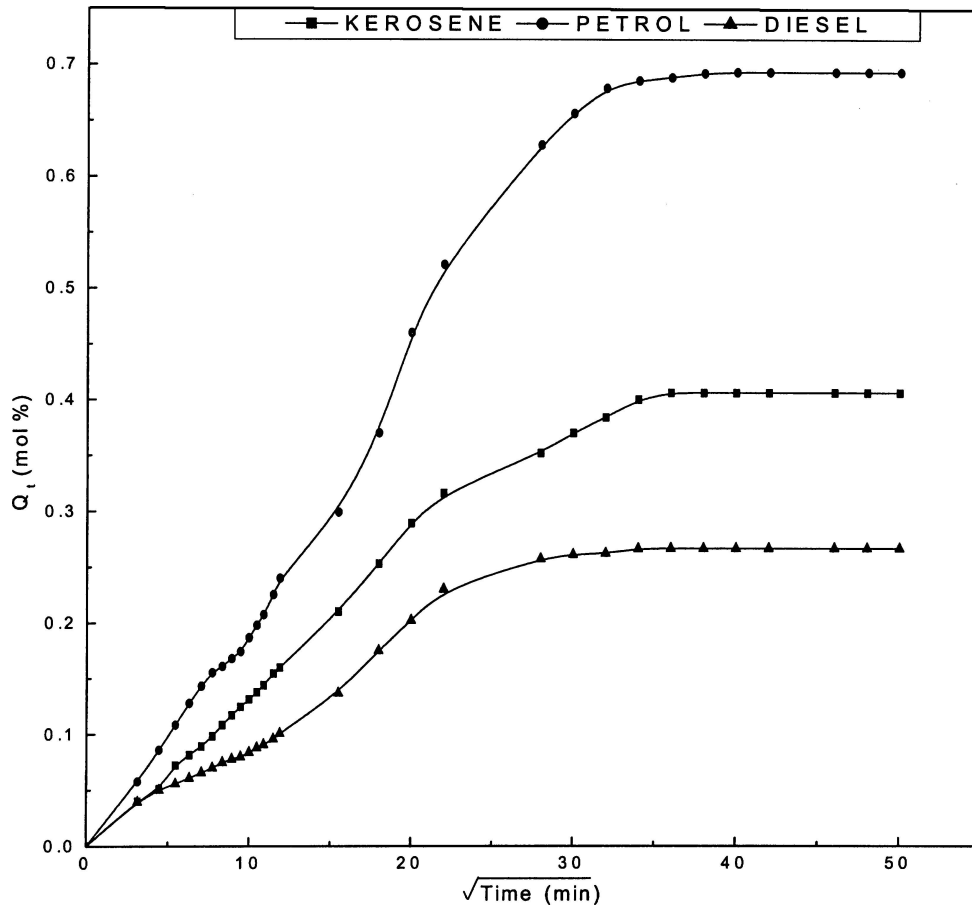


Figure 14 Mol% uptake of 40/60/30 NR/EVA/ISAF composites, vulcanised with DCP in different solvents.

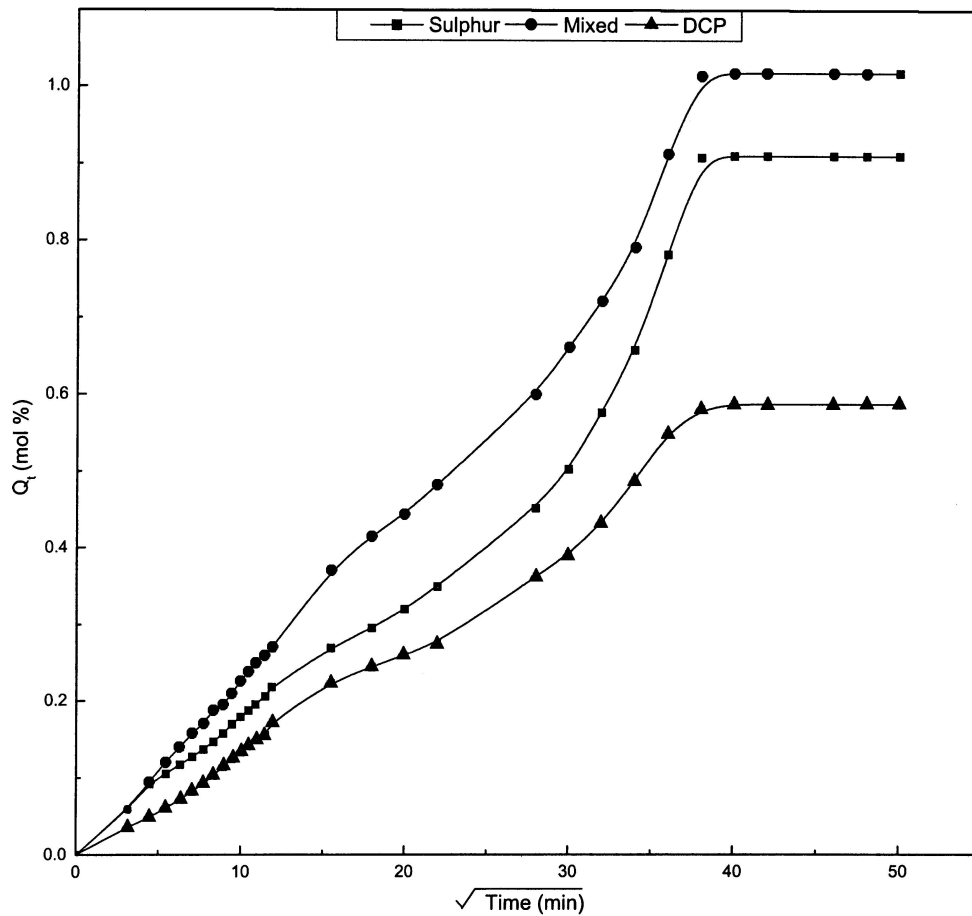


Figure 15 Effect of crosslink systems on the mol% kerosene uptake of 80/20 NR/EVA reinforced with 30-phr ISAF.

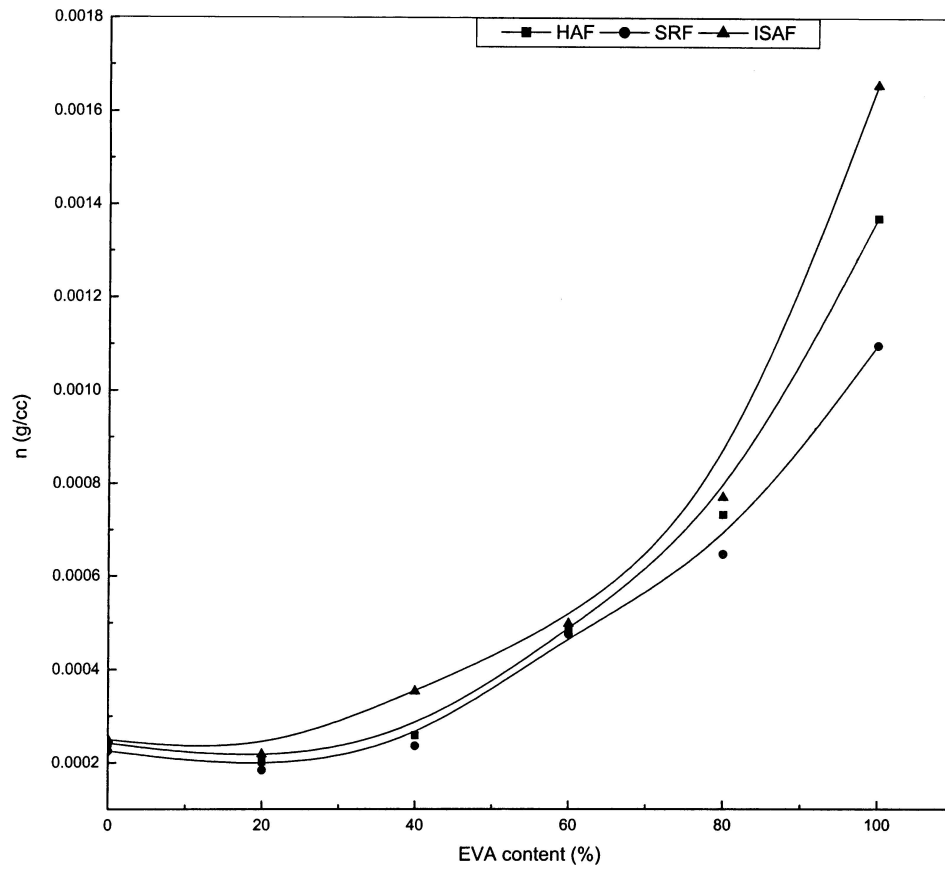


Figure 16 Variation of crosslink density with the EVA content.

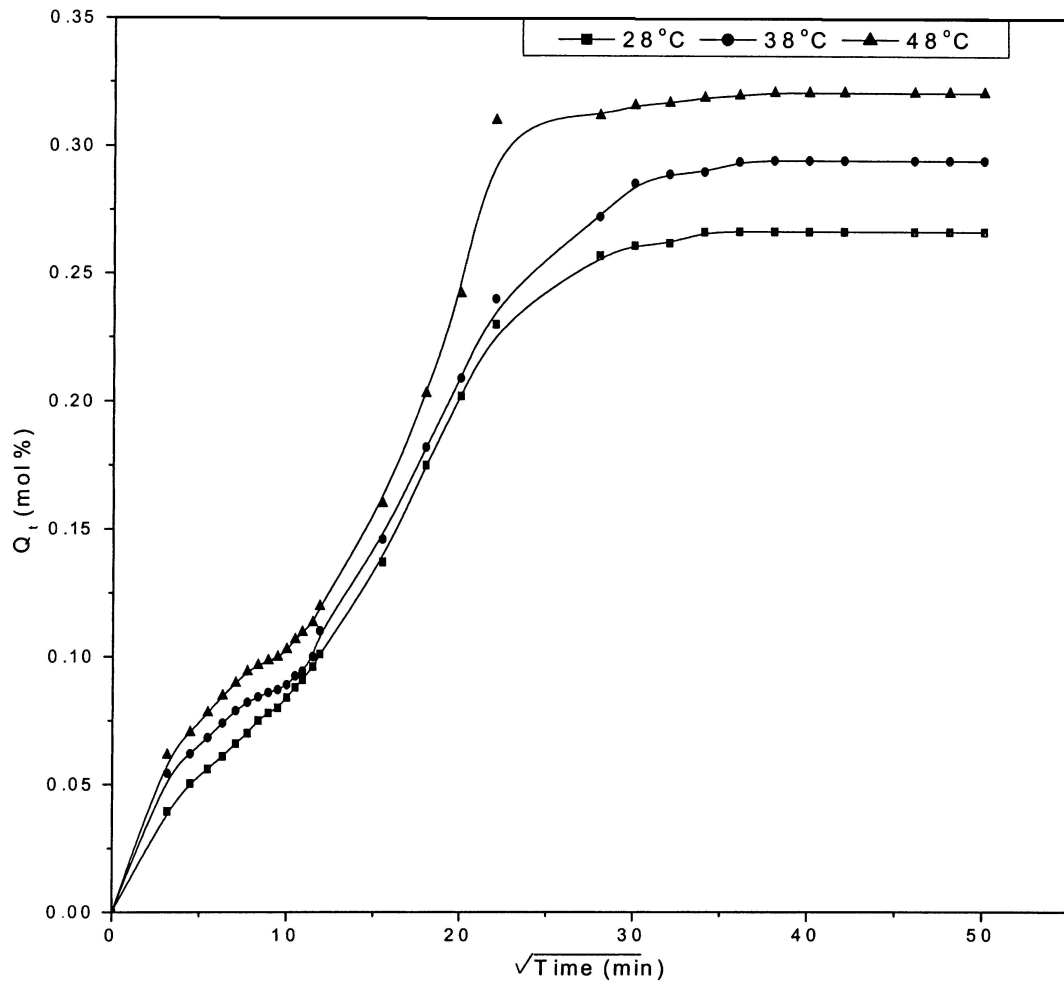


Figure 17 Mol Percent diesel uptake of 40/60/30 NR/EVA/ISAF, vulcanised with DCP at different temperature.

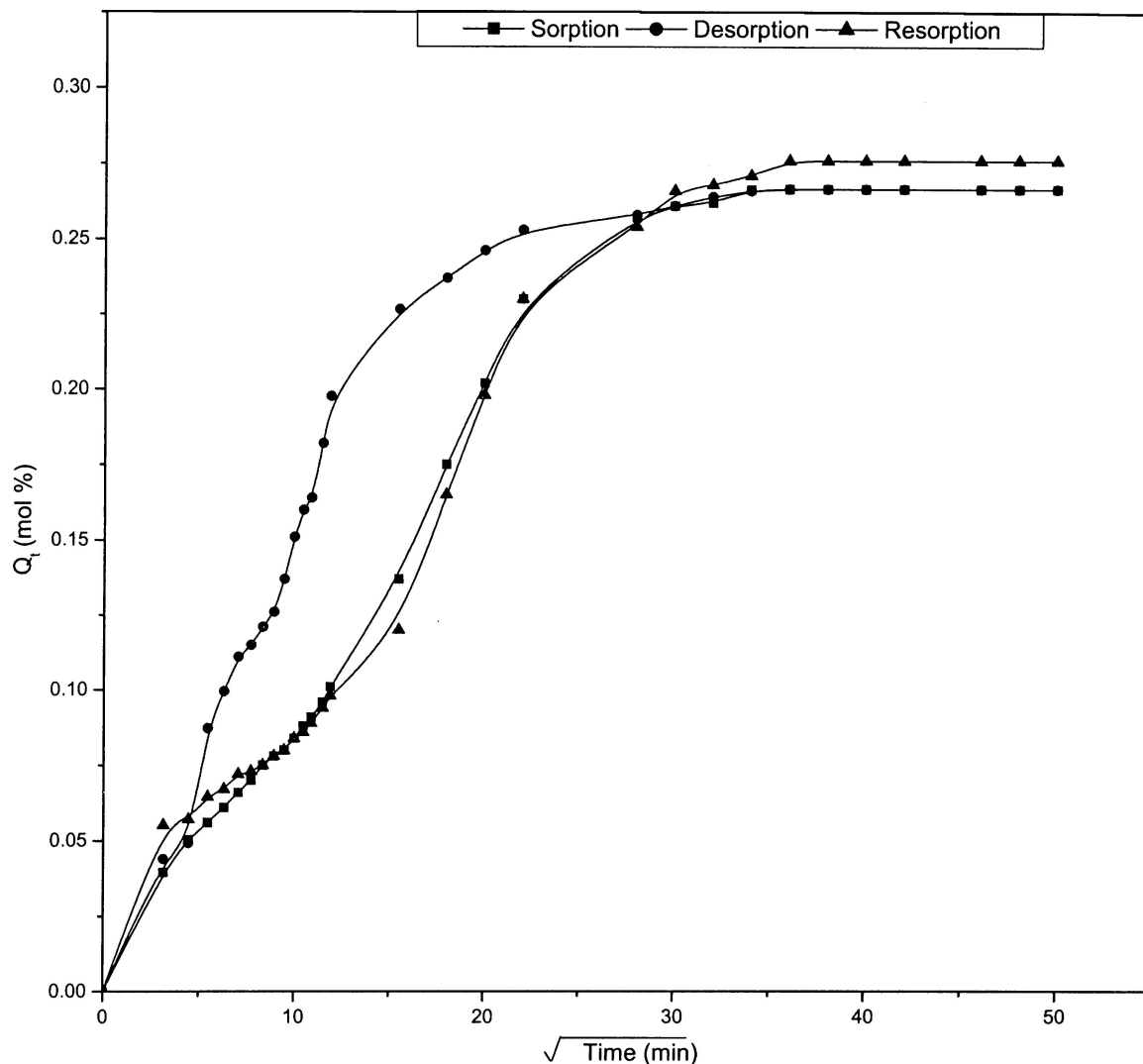


Figure 18 S-D-RS curves of 40/60/30 NR/EVA/ISAF, vulcanised with DCP in diesel.

The ΔG values, given in Table V, become more negative from ISAF to SRF filled composites and with a decrease in EVA content in the matrix. These values indicate the increase in tortuosity of diffusion process through the composites with the decrease in the particle size of fillers and increase in the percentage of EVA in the composites.

3.2.10. S-D-RS experiments

The physical changes associated with the diffusion of the penetrants through the composite has been analysed by sorption-desorption-resorption (S-D-RS) studies. The solvent saturated sample was desorbed completely, allowed to sorb the solvent again and then desorbed. The S-D-RS curves of 40/60/30 NR/EVA/ISAF composites vulcanised by DCP in diesel are shown in Fig. 18. The resorption curves show that the equilibrium uptake values and the time taken to attain equilibrium are not much higher compared to the first sorption process. This indicates that the available free volume within the matrix is not much increased by solvent ingress. The samples showed consistency in their mechanical properties when tested after a sorption-desorption-resorption-

redesorption cycle. These results will be included in our following paper.

4. Conclusion

The barrier properties of NR/EVA blends reinforced with carbon black, have been studied using petrol, kerosene and diesel as penetrants with special reference to the effects of EVA content, different types of carbon blacks, crosslinking systems and penetrant size. The regular reduction in solvent uptake by the blends with increase in EVA content in majority of the composites has been attributed to the semicrystalline nature of EVA. Among the carbon black fillers used, SRF loaded samples showed the highest solvent uptake and ISAF loaded samples, the lowest. HAF showed an intermediate behaviour. The reason for this trend has been attributed to the increased restriction to the overall mobility and flexibility of the polymeric chains with decrease in the size of carbon particles. The sample crosslinked by DCP showed the lowest equilibrium uptake in all penetrants compared to the samples with sulphur and mixed vulcanization modes for a given type of filler. This has been explained in terms of the differences in the nature and distribution of crosslinks in the network. Solvent uptake follows the order petrol

> kerosene > diesel for a given matrix according to the reverse trend of their molecular weight. Thermodynamics of the system has also been studied by the calculation of enthalpy, entropy and free energy. From the sorption-desorption-resorption cycles it has been found that all the samples show good mechanical stability after the liquid interaction. Experiments are in progress on the use of these membranes as barriers to hazardous liquids.

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