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Development and characterization of novel EPDM/NR prophylactic waste composites

G. MATHEW
Department of Chemistry, C.M.S. College, Kottayam 686001, Kerala, India
E-mail: gmathew7@rediffmail.com

R. P. SINGH*
Polymer Chemistry Division, National Chemical Lab, Pune 411008, India
E-mail: singh@poly.ncl.res.in

N. R. NAIR
Rubber Research Institute of India, Kottayam 686009, Kerala, India
E-mail: radhakrishnan@mail.com

S. THOMAS
School of Chemical Sciences, Mahatma Gandhi University, Kottayam 686560, Kerala, India
E-mail: sabut@md4.vsnl.net.in

Ethylene propylene diene rubber (EPDM) is a well-known versatile polymer, which is frequently used in the production of rubber goods based on conventional and specialty polymers. The present paper investigates the role of recycled natural rubber prophylactic waste compared to virgin natural rubber in the development of novel ethylene propylene diene rubber composites. The processing characteristics have been evaluated using a Monsanto rheometer at three different temperatures 150, 160 and 170°C. The cure curves of EPDM compounds have been found to be the resultant of slow curing or marching cure curve of EPDM and that of fast curing 'S' shaped cure curve of natural rubber. The curing properties such as optimum cure time, scorch time and induction time have been found to be decreasing with the loading of prophylactic filler. For most of the cases, the values obtained for compositions with virgin natural rubber (ISNR-5) have been found to be lower than that with prophylactic filler.

The cure activating nature of the prophylactic waste in EPDM is higher at higher temperatures. The unaged tensile strength has been increased with the loading of prophylactic filler up to 30 phr. The aged tensile strength and unaged/aged elongation at break have been found to be a maximum at 20 phr prophylactic filler loading. The tear strength has been found to be a maximum at 40 phr. Better performance has been noted in the case of virgin natural rubber filled samples for unaged/aged tensile strength, elongation break and tear strength except at 40 phr loading. The diffusion process in EPDM vulcanizates is found to be anomalous. Crosslink density values determined using Mooney-Rivlin equation agree with the tensile strength values for most of the cases. An increase in the crosslink density has been noted with the thermal aging of the samples.

1. Introduction

Blending ethylene propylene diene rubber or EPDM with other polymers such as butyl rubber [1], polypropylene [2–7] and NR [8] is an attractive topic of research. This is mainly because of the economic barriers against the development of new elastomers from newly synthesized monomers and the ability to achieve better properties for blends compared to that of component elastomers. EPDM finds use as a component in tire inner tubes together with butyl rubber [1]. This is because of many reasons such as the following.

1. It is cheaper than butyl.
2. A higher proportion of filler and oil can be used in the presence of EPDM. This can substantially reduce the cost of the compound.
3. Better durability due to the retention of physical properties under dynamic conditions.

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*Author to whom all correspondence should be addressed.

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4. If the filler content is not too high, the presence of EPDM can improve aging on long storage.

Toughened polymer blends based on EPDM and polypropylene are also reported extensively [2, 7].

A blend of EPDM and NR exhibits a useful combination of several properties such as good ozone and chemical resistance, better mechanical properties, reduced compression set and improved building tack properties etc. [8]. It is reported [9] that both the building tack and processability of NR/EPDM blends could be improved by the addition of low molecular weight 'liquid like' EPDM. They can give acceptable compromise between the properties of the components, for eg, the NR phase can provide good physical properties without the use of highly reinforcing fillers and expensive coupling agents while the EPDM phase can provide good heat aging and ozone resistance with out the use of antidegradants. Several studies in this area are available in the literature with special reference to the 60:40 ratio of NR:EPDM, which can provide excellent ozone resistance even in the absence of any antiozonant [10]. In addition to this, the influence of physical and chemical modifications to improve the potential properties of EPDM also is studied extensively [11–14]. Natural rubber phase in these blends exhibits strain induced crystallization, which can result in excellent tensile strength, resistance to deformation and stabilise the system by preventing the propagation of the defects. These materials are mainly used in the cable industry for electrical insulation sheathing and in automotive and construction industries as seals.

Apart from property benefits, the blends of EPDM and NR are also attractive from an economic point of view. This is due to the relatively high expense of EPDM. The economic advantage by the partial replacement of an imported elastomer with a locally sourced material in a formulation is very important when the system is to be used in a natural rubber producing country.

It is a known and established fact that industrialization and urbanization resulted in the production of a large quantity of waste materials, the disposal of which is either very difficult or very expensive. The issue of such accumulated waste becomes more severe when the reject rate is in very huge quantities, as high as 10 to 15% of the material consumed. One such a case is the natural rubber latex industry. The unstable nature of the latex compound and strict specifications in the quality of latex dipped products results in the formation of large amount of natural rubber prophylactic waste. This material contains a rubber hydrocarbon of very high quality with a lightly crosslinked network structure. The economic aspects described earlier become much more attractive when the natural rubber component in the EPDM/NR system is a recycled material. This sort of mutual protection system of similar and dissimilar elastomers has attracted much technological interest all over the world. Therefore, recycled natural rubber prophylactic can be considered to be superior to virgin natural rubber in the development of novel EPDM/natural rubber systems.

The present paper reports some of the results on the development and characterization of composite materials based on EPDM. The matrix EPDM is filled with two other elastomer inclusions such as natural rubber prophylactic waste and virgin natural rubber (ISNR-5). The curing behavior of the rubber compounds, physical properties and swelling behavior of the vulcanizates are analyzed giving emphasis to the influence of changes in temperature.

2. Experimental

2.1. Materials

The basic materials used in this work are given below.

1. EPDM, ethylene propylene diene rubber (Royalene® 521, manufactured and supplied by Uniroyal, USA. The general characteristics of EPDM [15] are given in Table I.

2. ISNR-5 was obtained from Rubber Research Institute of India, Kottayam, Kerala, India. The general characteristics of ISNR-5 [15] also are given in Table I.

3. NR prophylactic filler was prepared from waste rubber rejects supplied by Hindustan Latex Ltd, Thiruvananthapuram, Kerala, India.

4. Other compounding ingredients such as zinc oxide, stearic acid, CBS (N-cyclohexyl benzthiazyl sulfenamide), MBTS (mercapto benzo dithiazole disulphide), DPG (Diphenyl guanidine), DCP (Dicumyl peroxide), etc. were of reagent grade and obtained from local rubber chemical suppliers. Toluene (reagent grade) was used for carrying out swelling studies.

TABLE I General characteristics [15] of EPDM and ISNR-5

Properties	EPDM	ISNR-5
Specific gravity (gm/cc)	0.86	0.93
Glass transition temperature (°C)	−58	−75
Solubility parameter ($\mathrm{cal}^{1/2}/\mathrm{cm}^{3/2}$)	8	8.25
IRHD hardness	40–95	25–95
Resilience, at 20°C	3	4
at 100°C	3	4
Tensile strength, gum	1	3
Reinforced	3	4
Dielectric properties	3	3
Bonding to substrates	2	3
Resistance to gas permeation	2	2
Abrasion resistance	2/3	3/4
Tear resistance	2	3
Resistance to cutting and cut growth	2	3
Resistance to flexing and fatigue	3	3
Heat resistance	3	2/3
Flame resistance	2	2
Light resistance (staining and discolouration)	2/3	2/3
Ozone resistance	4	1
Environmental resistance	4	2/3
Resistance to acids	3	2
Aqueous	3	3
Aliphatic	1	1
Aromatic	1	1
Animal and vegetable oils	3	1
Oxygenated organics	3	2/3

1, poor; 2, moderate; 3, good; 4, outstanding.

TABLE II Basic formulation

	Loading (phr)						
Material	A0	A1a	A1b	A2	A3	A4a	A4b
EPDM	100	100	100	100	100	100	100
NR Prophylactics filler	0	10	0	20	30	40	
ISNR-5	0		10				40

2.2. Methods

2.2.1. Preparation of powdered rubber

The details of the powdering and characterization of prophylactics has been reported earlier [16]. Powdered prophylactic filler with fraction size between 0.6 to 0.9 mm was selected for this study.

2.2.2. Mixing

Mixing of ENR and filler was carried out using a laboratory size two roll mill having a friction ratio 1:1.4, as per ASTM D 15-627. The recipe used is given in Table II. The compositions such as A1a & A1b and A4a & A4b are included in order to analyze the substitution effect of natural rubber (ISNR-5) with prophylactic waste. In all the mixes, the loading of zinc oxide used is 5 phr, stearic acid – 2 phr, MBTS – 0.5 phr, DPG – 0.4 phr, DCP – 2.25 phr and sulfur – 1.5 phr.

2.2.3. Rheometry

The processing characteristics such as initial (M_i), minimum (M_n) and maximum viscosities (M_h) and cure characteristics such as optimum cure time (t_{90}), scorch time (t_2) and induction time (t_1) of the rubber compounds were determined using rheographs obtained using a Monsanto Rheometer model R-100. The instrument recorded the variation of torque (with time) developed in the rotation of a disc in a chamber containing a certain quantity of rubber compound. Rheographs at different temperatures (150, 160 and 170°C) were analyzed for this purpose.

All the above parameters are indicated in Fig. 1 which presents typical rheographs of EPDM and virgin natural rubber, focusing the difference in their curing behaviors. Fig. 1a is the typical rheograph of EPDM, 'b' is that of NR and 'c' the resultant rheograph of a blend of EPDM and NR. The minimum torque in rheograph is taken as the minimum viscosity (M_n). The maximum torque in rheographs is presented as the maximum viscosity (M_h) and is a direct measure of the crosslink density in the cured sample.

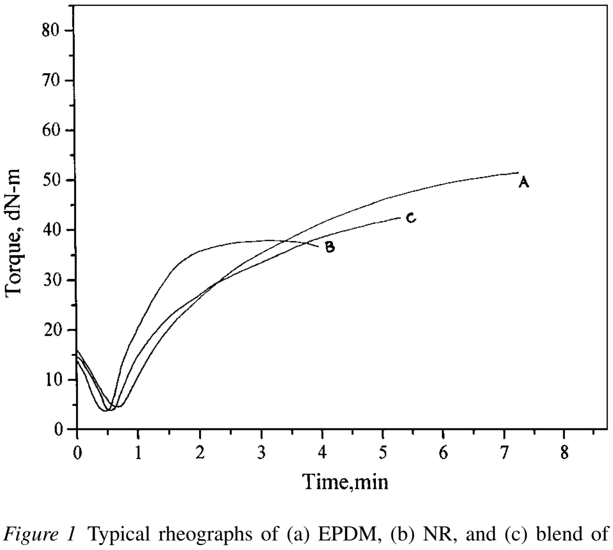

Figure 1 Typical rheographs of (a) EPDM, (b) NR, and (c) blend of EPDM and NR.

Optimum cure time (t_{90}) is the time corresponding to the development of 90% of maximum torque (T_{90}). The correct value of t_{90} was calculated using the equation,

$$T_{90} = \frac{(M_h - M_t) \times 90}{100} + M_n \qquad (1)$$

where M_h and M_n were the maximum and minimum rheometric torques respectively. Rheometric scorch time (t_2) is the time required for the torque value to increase by two units above the minimum torque. It is a measure of the scorch safety of the rubber compound. Rheometric induction time (t_1) is the time required for the torque value to increase by one unit above the minimum torque. It indicates the minimum time required to start the cure reaction.

2.2.3.1. Cure reaction kinetics. The fastness of the curing reaction was analyzed by measuring two parameters, cure rate index (CRI) and cure reaction rate constant.

$$\mathrm{CRI} = \frac{100}{t_{90} - t_2} \qquad (2)$$

The kinetics of vulcanization was studied from the rheographs by the method [17] given below.

The general equation for the kinetics of a first order chemical reaction is

$$\ln(a - x) = -kt + \ln a \qquad (3)$$

where, a = initial reactant concentration, x = reacted quantity of reactant at time t, and k = first order rate constant.

For the vulcanization of rubber, the rate of crosslink formation is monitored by measuring the torque developed during vulcanization. The torque obtained is proportional to the modulus of rubber. So following substitutions can be made

$$(a - x) = M_h - M_t, \qquad (4)$$

$$a = M_h - M_0 \qquad (5)$$

M_h = Maximum rheometric toque, M_0 = Minimum rheometric torque, and M_t = Rheometric torque at time t.

So the equation is

$$\ln(M_h - M_t) = -kt + \ln(M_h - M_0) \qquad (6)$$

This equation is of the general form of a straight line. Therefore, if a plot of ln ($M_h - M_t$) Vs. time t is a straight line graph, it means that the cure reaction follows first order kinetics. The cure reaction rate constant (k) was directly obtained from the slope of the respective straight lines.

The energy of activation E_{act} of curing was determined using the Arrhenius equations given below

$$k = A\exp(-E_{\mathrm{act}}/RT) \tag{7}$$

$$\log\ k = \log\ A - \frac{E_{\mathrm{act}}}{2.303\,RT} \tag{8}$$

where, A is the Arrhenius constant, E_{act}, the activation energy, R, the universal gas constant and T, the absolute temperature.

2.2.4. Preparation of test samples

The compounds were compression molded to optimum cure at 150°C using an electrically heated hydraulic press to their respective optimum cure times (t_{90}) at a pressure of 45 Kg/cm^2 on the mold. Dumbbell shaped tensile and angular tear specimens were punched out from the compression-molded slabs along the mill grain direction.

2.2.5. Physico-mechanical testing of the samples

Stress-strain data were determined on an Instron Universal Testing Machine (UTM), using C-type dumbbell specimen, according to ASTM D 412-80. The tear strength was determined as per ASTM D 624-81 using angular tear specimens. Both the tests were done at 28°C and at a crosshead speed of 500 mm/min.

2.2.6. Thermal aging

The resistance to thermal aging of the samples was analyzed by keeping the samples in an air oven at 100°C for 72 hrs according to ASTM D 573 procedure. The retained values of tensile strength, elongation at break and young's modulus etc. were calculated.

2.2.7. Swelling studies

In order to analyze the interaction between the components of the system, equilibrium swelling [18] studies were carried out in toluene. Circular samples of 2 cm diameter were punched from the vulcanized elastomer sheet and were allowed to swell in toluene at room temperature and 40°C. During the swelling time, the amount of solvent entering the sample is assessed gravimetrically until equilibrium was reached, as evidenced by the constant weight of the sample.

2.2.7.1. Diffusion, sorption and permeation coefficients. The mole% uptake was calculated using the equation;

$$Q_{\mathrm{t}} = \frac{M_{\mathrm{c}}(\mathrm{m})/M_{\mathrm{r}}(\mathrm{m}) \times 100}{M_{\mathrm{i}}(s)} \tag{9}$$

where, M_{c} (m) is the mass of solvent at a given time, M_{r} (m) is the molecular weight of the solvent, and M_{i} (s) is the initial weight of the specimen.

At equilibrium swelling, Q_{t} was taken as Q_∞ the mole% uptake at infinite time.

The mechanism of penetrant transport in to the elastomer network can be analyzed in terms of the empirical relation [19]

$$\log \frac{Q_{\mathrm{t}}}{Q_\infty} = \log\ k + n \log\ t \tag{10}$$

where, Q_{t} is the mole% uptake at time t, and Q_∞ is the equilibrium mole% uptake. The factor k is a constant depending on the structural characteristics of the filler and polymer solvent interaction. The parameter n determines the mode of sorption mechanism. If the value of n is 0.5, it means that the rate of diffusion of penetrant molecules is much less than the rate of relaxation of the polymer chains. This mode of transport is termed as fickian. On the other hand, if the value of n is unity, the mode of diffusion is termed as non-fickian when the rate of diffusion of penetrant molecules is much faster than polymer relaxation. When the rates of both processes are similar, value of n will fall between 0.5 and 1, presenting anomalous behavior. The computation of n and k is done by constructing the plots of log Q_{t} vs. log t and linear regression considering only the data up to 50% sorption, which is linear.

The effective diffusivity [20], D of the elastomer-solvent system was calculated from the initial linear portion of the sorption curves using the equation given below.

$$D = \pi\left(\frac{h\theta^2}{4\,Q_\infty}\right) \tag{11}$$

where, θ, the slope of the initial linear portion of the sorption curve and Q_∞, the equilibrium mole% uptake.

If there is extensive swelling for the samples, correction to diffusion coefficients are necessary by calculating the intrinsic diffusion coefficients [21], D^* which is given by;

$$D^* = \frac{D}{\phi^{7/3}} \tag{12}$$

Another parameter called sorption coefficient [22] which is calculated from the equilibrium swelling using the relation

$$S = M_\infty/M_0 \tag{13}$$

can better describe both the initial penetration and dispersal of penetrant molecules in to the elastomer network. Here M_∞ is the mass of the penetrant sorbed at infinite time and M_0, the initial weight of the polymer sample.

The permeation coefficient which is a characteristic parameter reflecting the collective processes of diffusion and sorption is calculated using the equation;

$$P = DS \tag{14}$$

The molar equilibrium sorption constant K_s, which is defined by Hung [23] as

$$K_s = \frac{\text{No. of moles of solvent sorbed at equilibrium}}{\text{Mass of polymer sample}} \tag{15}$$

2.2.7.2. Sorption kinetics. In the case of a polymeric network, which is extensively being swollen by a penetrant, the diffusion process is characterized by linear kinetics. According to Thomas and Windle [24], a thermodynamic swelling stress is exerted by the penetrant on the polymer network, which, therefore, undergoes time dependant mechanical deformation. But in the early stages of swelling this deformation is prevented [25] to some extent by the undeformed and unswollen polymer layers below. This factor extends the stress to two dimensions. But with the progress of swelling process, the magnitude of the stress is reduced and the equilibrium swelling of the surface layer occurs. Since the rate determining step of the process is the above said time dependent mechanical deformation, it can be confirmed that rate of sorption will be proportional to the difference in osmotic pressure inside and outside the polymeric materials [26]. Consequently, since this can be related to the concentration of the penetrant in the polymer (C), the first order kinetic equations given below can be used.

$$\frac{dc}{dt} = k_1(C_\infty - C_t) \tag{16}$$

$$k_1 t = 2.303 \log \frac{C_\infty}{C_\infty - C_t} \tag{17}$$

where C_∞ is the concentration of the penetrant in the polymer at equilibrium sorption and C_t, that at any particular time. First order rate constant values (k_1) obtained from a plot of log ($C_\infty - C_t$) verses time t will be a measure of the speed with which the polymer chain segments and penetrant molecules exchange their positions.

2.2.8. Calculation of crosslink density

The extent of physical crosslinks in the elastomer vulcanizate was determined by the use of Mooney-Rivlin equation [27].

$$F = 2\,A_0(\lambda - \lambda^{-1})(C_1 + \lambda^{-2}C_2) \tag{18}$$

where F is the extension force required to stretch a piece of rubber vulcanizate of crosssection area A_0, to an extension ratio λ. A plot of $F/2A_0$ $(\lambda - \lambda^{-1})$ versus λ^{-1} gives a straight line whose 'y' intercept C_1, can be directly related to the physically effective crosslink density (ν_{phys}) by the equation,

$$C_1 = \rho_r RT\, \nu_{\text{phys}} \tag{19}$$

3. Results and discussion

3.1. Curing properties

The rheographs which characterize the crosslinking process of the rubber compounds at different temperatures (150, 160 and 170°C) are presented in Figs 2–4. Marching cure observable in the rheograph is a

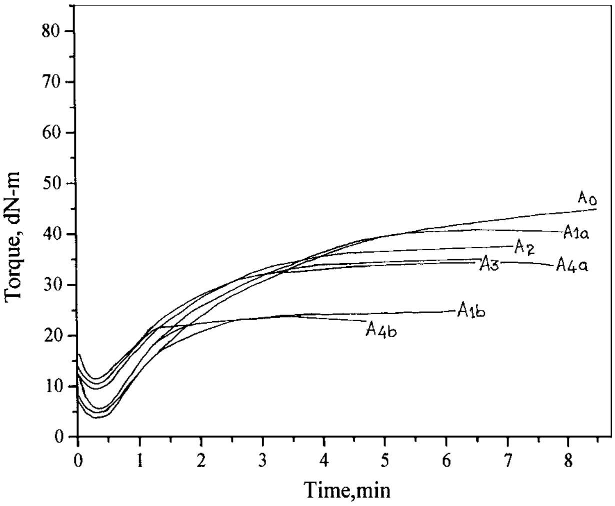

Figure 2 Rheographs of the elastomer compounds at 150°C.

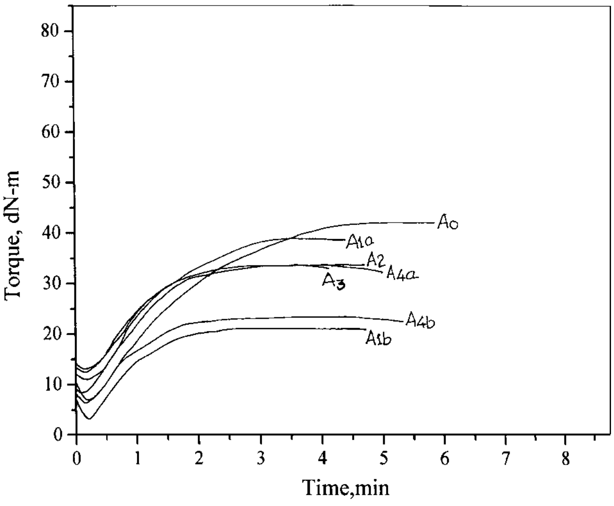

Figure 3 Rheographs of the elastomer compounds at 160°C.

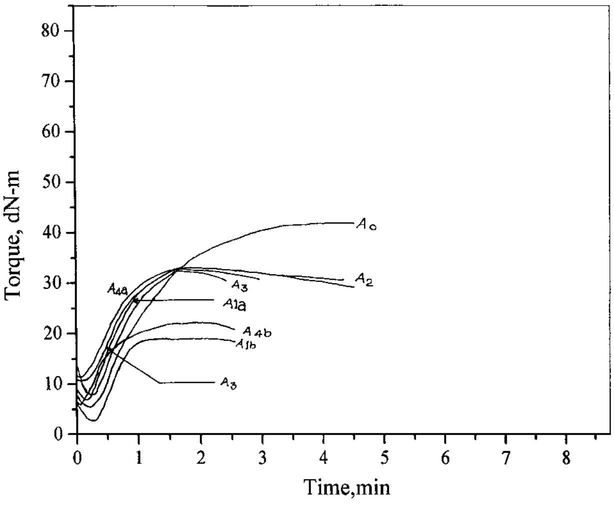

Figure 4 Rheographs of the elastomer compounds at 170°C.

TABLE III Rheometric data

Sample	Initial torque (M_i)			Minimum torque (M_n)			Maximum torque (M_h)		
	150°C	160°C	170°C	150°C	160°C	170°C	150°C	160°C	170°C
A0	7	10	12	4.5	6.5	5.5	44.5	42.5	41.5
A1a	11	10	13	6	8	6.5	40	38	32.5
A1b	9	7	6	4.5	3	3	25	21	19
A2	15	16	13	9.5	10	8	36.5	33	32
A3	17	17	15	10	12	10.5	35	33	31
A4a	17	17	15	11	12.5	11.5	35	33	32
A4b	8	11	7	4.5	6	6	23	22.5	21.5

TABLE IV Curing properties of EPDM compounds

Curing property	Sample code						
	A0	A1a	A1b	A2	A3	A4a	A4b
Optimum cure time t_{90} (min)							
150°C	29	20	12.3	18	18	18	9.5
160°C	19	11.5	11.2	10	9.5	9.5	8.5
170°C	13	6	5.8	5.8	5.3	5.5	4.8
Scorch time t_2 (min)							
150°C	3.3	3	2.5	2.75	2.75	2.75	3.5
160°C	2.3	1.8	1.9	2	1.75	2.25	2
170°C	2	1.5	1.65	1.75	1.5	1.25	1
Induction time t_1 (min)							
150°C	3	2.75	2.25	2.25	2.25	2.25	3
160°C	2	1.5	1.25	1.75	1.5	1.75	1.5
170°C	1.75	1.25	1	1.5	1.25	1	0.75

characteristic of EPDM compounds. The initial (M_i), minimum (M_n) and maximum torque or viscosity (M_h) values are presented in Table III. It can be seen from Table III that as the amount of natural rubber prophylactic in EPDM increases, the initial torque increases. This can be made clear if a comparison of the values of A0, A1a, A2, A3 and A4a is made. The initial torque values shown by EPDM samples containing prophylactic filler are found to be higher than the corresponding virgin natural rubber (ISNR-5) loaded samples (A1b and A4b). This is because of the lightly crosslinked nature of the prophylactic filler. In the case of polymer composites filled with various particulate fillers [28], the minimum torque in rheographs is considered a direct measure of the filler content. Here, as the filler also is an elastomer, such a notable increase in minimum torque cannot be expected, still a slight increase can be noted here. It is clear from the Table III that the substitution of natural rubber in the place of prophylactic filler results in a low value of minimum torque. This is true at both 10 and 40 phr loadings of the prophylactic filler in EPDM. This is again due to the lightly crosslinked nature of the prophylactic filler. The maximum torque shown by the sample is found to be decreasing with prophylactic filler loading. In this case also, lower values are also obtained for the compositions with natural rubber such as A1b and A4b compared to prophylactic filled samples (A1a and A4a).

It is interesting to check the influence of temperature on the curing properties of the samples (Table III). As the temperature increases, the initial torque or viscosity values of the EPDM sample (A0) are found to be slightly increasing. But this trend is found to be becoming less predominant with increasing loading of prophylactic filler or ISNR-5. The values show an initial slight increase followed by a decrease at higher temperatures used in the study. In the case of minimum torque values also, the same behavior is observed. A regular drop in the case of maximum viscosity is obtained with increasing temperature. The decreasing trend is due to the softening effect of temperature on the samples.

The variation of the curing properties such as optimum cure time (t_{90}), scorch time (t_2) and induction time (t_1) at 150°C are given in Table IV. These properties are calculated from the rheographs as already explained. It can be seen that, as the prophylactic filler loading increases, t_{90} values show a decrease at 10 phr loading of prophylactic (A1a) and ISNR-5 (A1b). For further loadings of prophylactic, the value increases and then levels off at 40 phr prophylactic loading. In the case of t_2 and t_1 values also, an initial slight drop in the magnitude of the values are obtained, which is followed by a slight increase.

It can be seen that both at 10 and 40 phr loading of ISNR-5 (A1b and A4b), the optimum cure time values are below that of similar compositions with prophylactic filler (A1a and A4a). The initial reduction in optimum cure time with prophylactic loading is due to presence of unreacted accelerator in the prophylactic phase. However, the reduction in t_{90} values with the addition of 10 and 40 phr of natural rubber (ISNR-5) (A1b and A4b) is found to be more than that caused by prophylactic filler.

This can be explained as follows. Virgin natural rubber (NR) is very fast curing than both EPDM and prophylactics due to the higher concentration of unsaturation in it. This can be made clear by comparing the general nature of rheographs of EPDM and NR (Fig. 1).

The rheographs obtained for a blend of EPDM and virgin NR or prophylactics will be a resultant plot of marching cure plot of EPDM and fast curing plot of NR. In a blend of EPDM and ISNR or prophylactics, the preference of curative will be in the order virgin NR > NR Prophylactics > EPDM. So it is clear that when the curing of NR progresses fastly, the curing of EPDM and NR prophylactics lags behind. These factors are responsible for the lower t_{90}, t_2 and t_1 of ISNR-5 containing samples of EPDM than those with NR prophylactics.

The influence of temperature on the optimum cure time of the rubber compounds is presented in Table IV. The cure activating nature of temperature can be clearly seen from here. There are two main observations connected with the influence of temperature on the crosslinking process of these systems. The primary one is that, at low temperature, an irregular drop in t_{90} is noted with the addition of prophylactic filler and ISNR-5. At higher temperatures, however, a regular drop is observed. In the present case, the NR phase (ISNR-5 or NR prophylactics) is crosslinked by both sulfur as well as peroxide. The sulfur crosslinking itself can proceed via an ionic or free radical mechanism [29]. The free radicals formed from residues of sulfur [30] or sulfenamide accelerator [31] can possibly react with the free radicals formed from peroxide. Here, it is reasonable to think that the mutual interaction between the radicals from DCP and sulfur/accelerator can enhance the rate of decomposition mutually. But at the same time, due to such an interaction, at least some of the active constituents of both DCP and sulfur/sulfenamide accelerator MBTS become unavailable for the vulcanization process. Thus the contribution of DCP and sulfur/accelerator to the vulcanization process is decreased at low temperature. This leads to abnormalities in the already seen trends with the addition of prophylactic filler. But when the temperature increases, the so-called 'high velocity crosslinking reaction' takes place. This is associated with two competing reactions such as crosslinking and desulfuration. The occurrence these two progressive reactions rules out the possibility of interaction between sulfur or accelerator fragments and DCP. DCP also undergoes complete decomposition at high temperature. This factor increases the individual contribution of sulfur or accelerator residues and DCP in the vulcanization process. So a regular decrease in the optimum cure time values can be seen with the addition of prophylactics at higher temperature. The second point to be noted is that, at low temperature, the difference in t_{90} values of EPDM—natural rubber prophylactic system and EPDM—virgin natural rubber (ISNR-5) system is higher than the corresponding difference at high temperature. This can be made clearer on comparing the t_{90} values of A1a & A1b and A4a & A4b at different temperatures. This suggests that the cure activating nature of temperature is more effective in EPDM/prophylactic systems than in EPDM/virgin ISNR-5 systems. Thus, the reduction in optimum cure time for EPDM/prophylactic systems is 69–70% with rise in temperature from 150 to 170°C, while in the case of EPDM/virgin ISNR-5 systems, the reduction is only 49–53%. This is because of the presence of unreacted accelerators in prophylactic filler. The unreacted accelerator is activated with temperature to a higher extent. As this unreacted accelerator is not available in virgin natural rubber to activate the cure with increase in temperature, systems containing virgin natural rubber are showing less reduction in optimum cure time with increasing temperature.

In Table IV, observations on the influence of temperature on scorch time are presented. As already seen in the case of t_{90}, abnormalities in t_2 arise for the plots at temperatures 150 and 160°C. The addition of prophylactic filler initially reduces the scorch time values at 150°C while at higher loadings, a leveling off is observed. At 160°C, a slight increase in scorch time can be seen at higher loadings, while at the highest temperature a more regular drop is visible as the prophylactic loading increases. This is due to the complete decomposition of DCP at higher temperature. The vulcanization system used here is a semi EV plus peroxide. The effect of peroxide will be shown predominantly at temperature 160°C or above which is the decomposition temperature of DCP. So as the temperature increases, both sulfur and peroxide crosslinking occurs progressively and so the curing results present more regular trends than at low temperatures. The addition of 10 phr ISNR-5 (A1b) instead of natural rubber prophylactic (A1a), decreased the scorch time value at 150°C while the addition of 40 phr ISNR-5 (A4b) increased it from a similar composition with prophylactic filler (A4a). On the contrary, a reverse trend could be seen at 160 and 170°C. In the case of induction time (Table IV) also, an exactly similar observation is obtained.

3.2. Kinetics of curing reaction

The cure rate index and kinetics of cure reaction are analyzed by the method already explained. The plot of ln ($M_h - M_t$) verses time 't' of the elastomer compounds at 150°C is shown in Fig. 5. The plots are found to

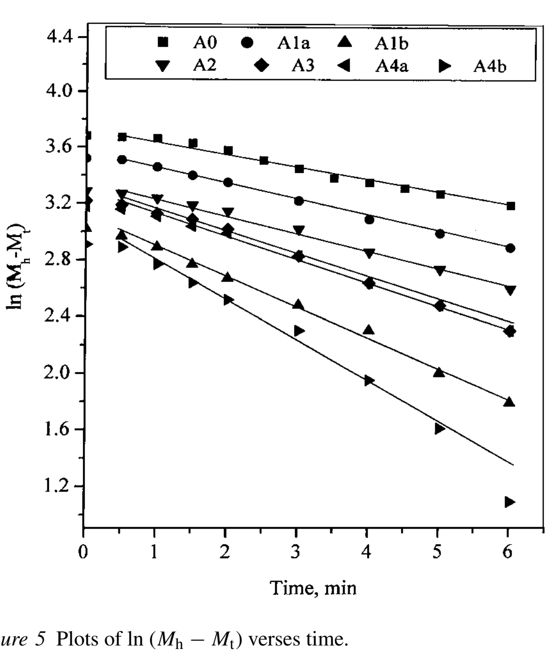

Figure 5 Plots of ln ($M_h - M_t$) verses time.

TABLE V Cure reaction kinetics data

Sample	Cure rate index CRI			Cure reaction rate constant (k)			Energy of activation (E_{act}) (KJ/mol)
	150°C	160°C	170°C	150°C	160°C	170°C	
A0	3.88	5.97	9.09	0.09	0.17	0.19	105
A1a	5.8	10.3	22.2	0.12	017	0.41	93
A1b	10.2	13	25	0.19	0.21	0.62	91
A2	6.5	12.5	25	0.10	0.18	0.34	92
A3	6.5	12.9	26	0.14	0.19	0.38	76
A4a	6.56	13.8	23.5	0.13	0.19	0.42	89
A4b	16.6	15.4	26.6	0.24	0.25	0.54	62

be linear which proves that the cure reactions proceed according to first order kinetics. The cure rate index and cure rate constant values are presented in Table V. At 150 and 160°C, CRI values either increase or remain constant with increasing prophylactic loading. This reveals the cure activation at higher loading of prophylactic filler. However, at 170°C, lower values of CRI are observed at higher loadings compared to those at lower loading of prophylactic filler. Still, with respect to the value of gum EPDM compound, an increasing trend can be seen with the addition of prophylactic filler. Increase in temperature also fastens the cure reaction to a great extent. The CRI values obtained for natural rubber containing systems are higher than the corresponding compositions with prophylactic filler. This is true for all the temperatures studied. The cure rate constants also show a slight increase with prophylactic loading. The rate of this increase is found to increase with temperature. Also, comparatively high rate constant values are observed for compositions with virgin natural rubber (ISNR-5).

E_{act} values (Table V) are calculated from the slope of a plot of log k verses $1/T$, given in Fig. 6. Normally fast reactions (higher k) yield lower values of E_{act}. In the case of EPDM gum sample, high E_{act} value is observed. Also, as the loading of prophylactic filler increases, irregularly decreasing E_{act} values are observed. The change in cure rate constant (k) values with the substitution of virgin ISNR-5 (A1b and A4b) is well supported by the lower E_{act} values.

3.3. Technological properties

The stress-strain behavior of a rubber network is mainly influenced by the presence of crosslinks and by constraints caused by the uncrossability of the chains. The stress-strain curves of the unaged gum EPDM and prophylactic/ISNR-5 filled EPDM vulcanizates are presented in Fig. 7. The curves are slightly different from typical vulcanized low strength materials. This can be seen in the slightly rising stress value at higher strains while in the case of a low strength material such as SBR, the stress-strain plot will be parallel to the 'x' axis at higher strains. It can be seen that at 10 phr loading of prophylactic (A1a), the initial linear portion of the curve is closer to 'y' axis. With the substitution of 10 phr ISNR-5 (A1b), the curve again bends towards 'y' axis. As the prophylactic content increases further, however, the curve leans towards 'x' axis, thus showing a drop in the rigidity of the vulcanizate. The stress-strain curves after thermal aging are presented in Fig. 8. Here also similar behavior can be seen. Some samples such as EPDM with 30 phr natural rubber prophylactic (A3), however, present properties typical of vulcanized amorphous elastomers such as SBR.

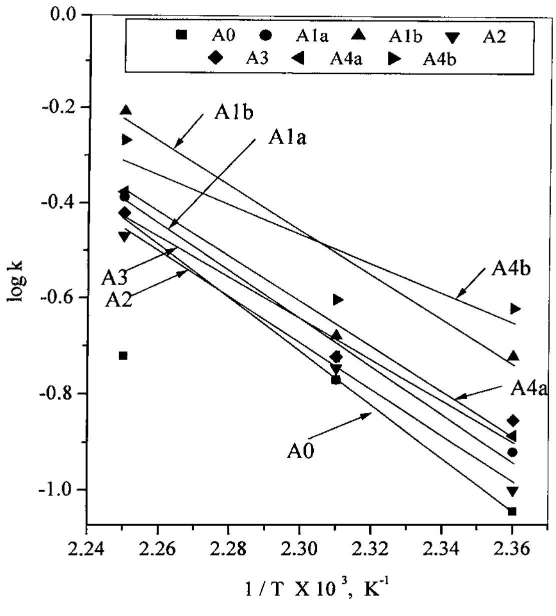

Figure 6 Plots of log k verses $1/T$ of the samples (Arrhenius plots).

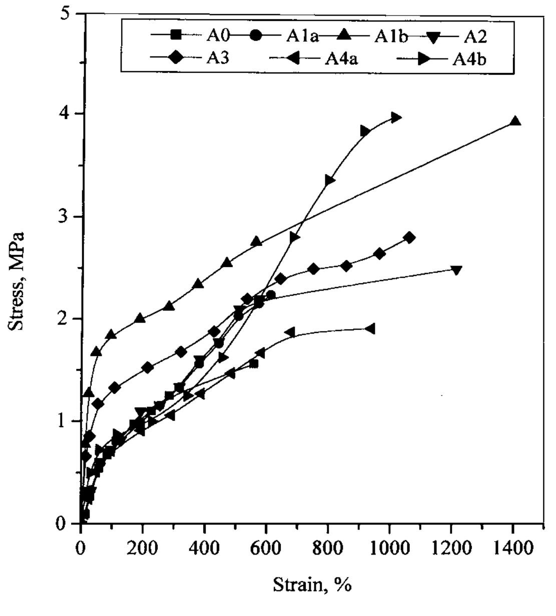

Figure 7 Stress-strain curves of the unaged vulcanizates.

TABLE VI Mechanical properties and crosslink density of EPDM vulcanizates

Mechanical property	Sample code						
	A0	A1a	A1b	A2	A3	A4a	A4b
Young's Modulus (unaged) (MPa)	0.92	1.09	7.29	4.52	4.31	1.44	1.72
Young's Modulus (aged) (MPa)	1.25	1.45	2.29	2.01	2.13	1.65	1.88
Elongation at break (unaged) (%)	556	610	1396	1215	1056	936	1006
Elongation at break (aged) (%)	416	506	883	710	583	626	630
Tensile strength (unaged) (MPa)	1.56	2.24	3.94	2.50	2.81	1.91	3.98
Tensile strength (aged) (MPa)	1.87	1.74	5.9	3.5	1.69	1.55	2.25
Tear strength (N/mm)	8.19	10.6	13.5	13.2	13.4	13.9	13
ν_{phys}, unaged ($\times 10^{-5}$)	4.7	13.1	21.5	19.6	13.1	4.77	10.7
ν_{phys}, aged ($\times 10^{-5}$)	26.2	28	31	29.8	21.5	17.9	20.9

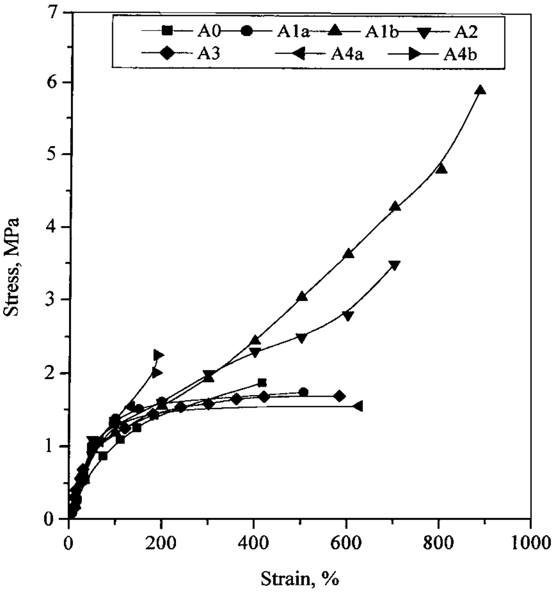

Figure 8 Stress-strain curves of the aged vulcanizates.

The slope of the initial linear region of the stress-strain curve, presented as the young's modulus is given in Table VI. It is clear from the table that for the unaged sample, the young's modulus increases with the addition of 10 and 20 phr natural rubber prophylactic filler (A0, A1a and A2). This can be expected from addition of highly strain crystallizing nature of the natural rubber prophylactic filler in the amorphous elastomeric EPDM matrix. Further addition of prophylactic filler causes a decrease in young's modulus. The values shown by virgin natural rubber filled sample at 10 and 40 phr loadings (A1b and A4b) are higher than that of the prophylactic filler. A similar observation is visible in the case of vulcanizates after thermal aging also. The young's modulus is found to be affected to a great extent by thermal aging, except for certain samples such as A0, A1a, A4a and A4b, where a slight increase is observed. It is reasonable to think that addition of natural rubber prophylactic filler and ISNR-5 can affect the thermal aging behavior of EPDM. The variation in elongation at break (e_b) is presented in Table VI. Elongation at break also is found to be increasing with the addition of 10 phr prophylactic. This is due to the ability of natural rubber prophylactic filler particles in EPDM matrix to elongate to high strains. Among the prophylactic loaded samples, the maximum value is obtained at a loading of 20 phr. Here also, the values are higher for virgin natural rubber (ISNR-5) filled samples at 10 as well as 40 phr loading. Even though thermal aging results in a decrease in the magnitude of the elongation at break values, the trend observed is the same.

The variation of unaged and aged tensile strength with the loading of prophylactic filler is depicted in Table VI. As in the case of young's modulus and elongation at break, here also the tensile strength initially increases at 10 and 20 phr prophylactic loading and then decreases. As in earlier cases, comparatively higher tensile strength values are shown by EPDM/virgin natural rubber (ISNR-5) vulcanizates. The aged tensile strength also behaves in the same way. The superior aging resistance of the EPDM vulcanizates can be understood from the either higher or comparable tensile strength values after thermal aging. This is noted for the samples A0, A1b and A2. This is due to the increase in crosslink density resulting from the influence of temperature during aging. Such results have been reported in the literature [32, 33].

The better aging resistance of the EPDM sample is clear from the increased properties after thermal aging (Table VI). The property variation observed after thermal aging varies from sample to sample. It is also important to note that the trends shown by young's modulus and tensile strength are not similar. Better aging resistance shown by the EPDM samples A0, A1a, A4a and A4b in the case of young's modulus while in the case of tensile strength A0, A1b and A2 takes that position. This can be analyzed more clearly using Table VII, where percentage change in tensile strength after thermal aging of all the samples is presented. It is a general observation that as the content of natural rubber (as

TABLE VII Thermal aging data

Sample code	Percentage change in Young's modulus	Percentage change in tensile strength
A0	35 (+)	19 (+)
A1a	33 (+)	28 (−)
A1b	68 (−)	49 (+)
A2	55 (−)	40 (+)
A3	50 (−)	66 (−)
A4a	14 (+)	23 (−)
A4b	9 (+)	77 (−)

(+), increase in property after thermal aging, (−), decrease in property after thermal aging.

natural rubber prophylactic filler or virgin natural rubber (ISNR-5)) in EPDM increases, the aging worsens the tensile strength while the trend is irregular in the case of young's modulus. Sample A2 is an exception in the case of tensile strength variation. These observations reveal that in the case of present systems, there is no necessary correlation between the stress-strain relation at low strain region (young's modulus) and that at higher strain region (tensile strength). This is contrary to the behavior shown by elastomer vulcanizates with particulate fillers where the common relation is "higher the young's modulus, higher the tensile strength." This difference arises due to the difference in the mode of filler—elastomer interactions in these cases. In the case of an elastomer vulcanizate filled with some particulates, the property improvement is due to the adhesion between rubber layers and filler surfaces resulting in the mechanical anchoring of the elastomer molecules on the porous structure of the particulate filler. This gives rise to the firm holding of a fraction of rubber molecules by the filler particles. Even the best solvent cannot dissolve this fraction of rubber. Therefore, when such a sample is allowed to swell and dissolve in its solvent, this fraction remains as 'bound rubber'. In the present case, the property enhancement is due to the strain crystallizing nature of the natural rubber prophylactic filler or ISNR-5 phase in the amorphous EPDM matrix. Thus any correlation between young's modulus and tensile strength cannot be expected in this case. Even though the interpenetration of prophylactic filler or virgin NR phase and EPDM phase occurs to some extent, this is totally different from the 'bound rubber' phenomenon shown by particulate filled EPDM rubber compound. When the interpenetrated prophylactic phase undergoes crosslinking in itself and co-crosslinking with EPDM phase, the 'bound rubber' is not involved in the crosslinking process of the rest of the matrix.

As far as tear strength is concerned, the behavior is different from earlier discussions (Table VI). On increasing the loading of natural rubber prophylactic filler, tear strength increases sharply and levels off at higher loadings. Also, better values are shown by the substitution of prophylactic filler with ISNR-5 only at 10 phr. At 40 phr, the tear strength for the EPDM/ISNR-5 system is lower than that for EPDM/prophylactic filler. The higher tear strength results from the ability of natural rubber prophylactic and ISNR-5 phases in EPDM to elongate to high strains and obstruct the advancing tear front.

The idea that one can obtain from the above results is that the mechanical properties will be better if the inclusion also is allowed to vulcanize in the same cure cycle as the matrix. The difference between the properties of prophylactic and ISNR-5 filled EPDM systems occurs because vulcanization of ISNR-5 takes place together with the vulcanization of the EPDM matrix while the natural rubber prophylactics were already in a lightly crosslinked state during the maxing. Virgin natural rubber (ISNR-5) might have been efficiently mixed with EPDM due to its low viscosity resulting from uncrosslinked state. However, the lightly crosslinked nature of the prophylactic filler and the resulting viscosity difference with respect to EPDM matrix might give rise to secondary reasons for its inferior performance. Still, considering the economic aspects of the EPDM/NR systems, better performing combinations of EPDM/Prophylactic/ISNR-5 with comparatively larger proportion of virgin NR (than prophylactics) reinforced with particulate fillers can be tried. If a masterbatch technique can be used for the incorporation of particulates, such a system will be more successful in achieving efficient covulcanisation and better mechanical properties. However, this is the subject of another publication in a near future.

3.4. Solvent diffusion studies

The sorption curves of EPDM gum and prophylactic/virgin NR filled vulcanizates at room temperature and 40°C are presented in Figs 9 and 10 respectively.

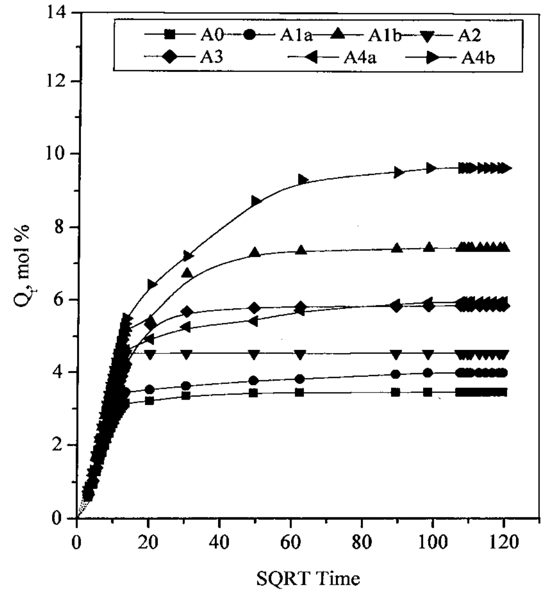

Figure 9 Sorption curves of the EPDM vulcanizates at room temperature (28°C).

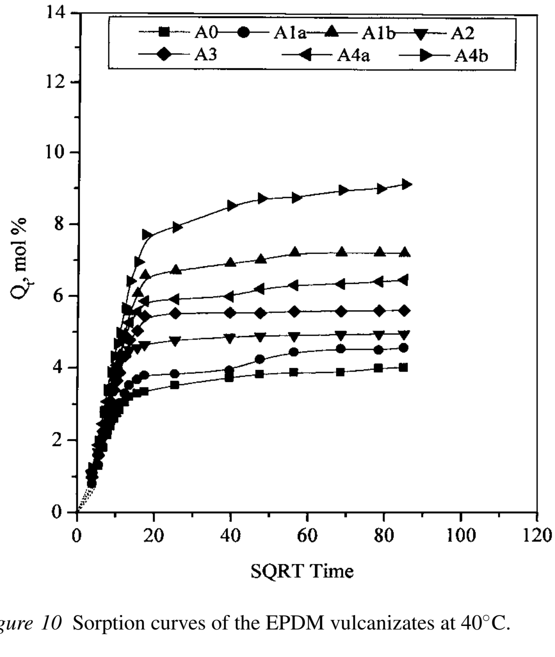

Figure 10 Sorption curves of the EPDM vulcanizates at 40°C.

TABLE VIIIA Sorption data at 28°C

Sample code	Q_∞ (mol%)	n	k (gg^{-1} min^n $\times$ 10^{-2})	K_s (min^{-1} $\times$ 10^{-2})	k_1 (min^{-1} $\times$ 10^{-3})	D ($\times$10^{-5} cm^2 s^{-1})	D^* ($\times$10^{-4} cm^2 s^{-1})	ϕ	S (gg^{-1})	P ($\times$10^{-4} cm^2 s^{-1})
A0	3.4597	0.6616	0.0378	0.0346	0.0056	5.70	16.7	0.2369	16.44	9.37
A1a	3.9895	0.6690	0.0335	0.0399	0.0047	4.82	18.0	0.2121	3.68	1.78
A1b	7.4491	0.7001	0.0214	0.0745	0.0028	2.17	27.0	0.1260	6.86	1.49
A2	4.5421	0.6711	0.0285	0.0421	0.0037	4.15	21.6	0.1824	5.24	1.73
A3	5.8616	0.6887	0.0229	0.0586	0.0029	3.10	24.1	0.1549	5.40	1.68
A4a	5.9587	0.6825	0.0262	0.0596	0.0035	3.22	25.8	0.1527	5.49	1.77
A4b	9.6554	0.6860	0.0178	0.0966	0.0019	1.78	38.2	0.1001	8.89	1.58

TABLE VIIIB Sorption data at 40°C

Sample code	Q_∞ (mol%)	n	k (gg^{-1} min^n $\times$10^{-2})	K_s (min^{-1} $\times$ 10^{-2})	k_1 (min^{-1} $\times$ 10^{-3})	D ($\times$10^{-5} cm^2 s^{-1})	D^* ($\times$10^{-4} cm^2 s^{-1})	ϕ	S (gg^{-1})	P ($\times$10^{-4} cm^2 s^{-1})
A0	4.0109	0.5907	0.0438	0.0401	0.0024	5.08	19.1	0.2112	3.69	1.88
A1a	4.5608	0.6209	0.0354	0.0456	0.0024	4.89	23.4	0.1906	4.20	2.06
A1b	7.2187	0.6926	0.0222	0.0722	0.0034	3.35	39.5	0.1295	6.65	2.23
A2	4.9543	0.6299	0.0356	0.0459	0.0031	5.11	29.1	0.1875	4.82	2.34
A3	5.6197	0.6456	0.0323	0.0562	0.0046	5.01	35.7	0.1605	5.18	2.59
A4a	6.4822	0.6241	0.0346	0.0648	0.0033	3.86	36.7	0.1421	5.97	2.31
A4b	9.1388	0.7223	0.0190	0.0914	0.0026	2.89	55.4	0.1052	8.42	2.43

The mole% uptake, Q_t of the solvent toluene is plotted vs. square root of time, t. At equilibrium swelling, Q_t was taken as Q_∞ the mol% uptake at infinite time. It is clear from the figure that all the plots are sigmoidal. The sigmoidal shape is associated with the time taken by the polymer chains to respond to the swelling stress and rearrange to accommodate the penetrant molecules [34]. It can be seen from the sorption curves of the samples that the initial swelling rate is very high owing to the large concentration gradient. This keeps the polymer sample under intense solvent stress. As the concentration gradient decreases with advancing swelling, the swelling rate decreases and the concentration difference becomes negligible at equilibrium swelling. The equilibrium mol% uptake value Q_∞ (Table VIIIa) of the samples at room temperature increases with increasing the content of second elastomer component, with very high values for the EPDM vulcanizates filled with 10 and 40 phr ISNR-5. From this result, we may be able to understand the inability of the prophylactic filler and ISNR-5 to restrict the solvent uptake just as particulate fillers do. But the analysis of other diffusion parameters such as k, K_s, D and D^* shows uncomparable and abnormal trends.

The mechanism of penetrant transport in to the elastomer network can be analyzed by the method already given. The values of n and k also are presented in Table VIIIa. Since the value of n obtained here falls in the range 0.5 to 1, the process can be considered to be anomalous. From the lower value of n for EPDM gum vulcanizate, it is reasonable to think that in this sample, the diffusion of the penetrant might have slowed down compared to that in filled vulcanizates.

The values of effective diffusivity (D) and intrinsic diffusion coefficient (D^*) are given in Table VIIIa. It can be seen that D values of the prophylactic or ISNR-5 filled vulcanizates show a decreasing trend even though it is not in a regular manner. This trend shown by D values does not correlate with the swelling phenomena observed here from Q_∞ results. Meanwhile the corrected D values (D^*) are in agreement with the increased solvent uptake. When the higher Q_∞ value of ISNR-5 filled samples with respect to prophylactic filled samples is unsupported by D values, this also is supported by D^* values. The importance of correction to diffusion coefficient can be understood from these results on diffusion of extensively swelling elastomer vulcanizates.

The values of sorption coefficient 'S' of the samples at room temperature also are presented in Table VIIIa and b are found to be not in good agreement with the mol% uptake values in the same table. The permeation coefficient values (P) given in the same table, also depicts similar abnormality as earlier denoted for D. Similar behavior to D^* is shown by the molar equilibrium sorption constant K_s (Table VIIIa). Thus, in the present work, only D^* and K_s are in agreement with observed increasing solvent uptake behavior of the EPDM vulcanizates with increasing loading of prophylactic filler.

Sorption data at 40°C is given in Table VIIIb. The Q_∞ values also register an increase with prophylactic loading. It is also seen that at lower loadings of natural rubber prophylactic, increase in swelling temperature causes an increase in Q_∞ while at higher loadings, a decrease is obtained. In the case of D, an increase is observed in all the systems except the gum EPDM sample. The same is the case for D^*, but all the samples behave in the same way without any exception. Another difference which observed for the diffusion behavior at 40°C is the similar value of S for the EPDM gum sample to that of filled EPDM samples. On the other hand, for the experiment at 28°C, an abnormally high value of S was obtained for the gum EPDM sample. This is different to that noted earlier for the diffusion at 28°C. Here D^*, K_s and in addition S and P also are found to be in agreement with the trend in Q_∞ with increasing prophylactic loading. Earlier in the case of curing parameters also, similar influencs of higher temperature in clearing the abnormalities of the results was discussed. The observations here also support this fact.

3.5. Sorption kinetics

Figs 11 and 12 represent the plots of log ($C_\infty - C_t$) verses time t, for the experiments at room temperature and 40°C respectively. It can be clearly understood from the linearity of the plots in Fig. 11 that the kinetics of diffusion of gum EPDM and natural rubber prophylactic/ISNR-5 filled samples follow first order kinetics at room temperature while at 40°C, some deviation from linearity is observed (Fig. 11). The values of k_1 are a measure of the speed with which the polymer chain segments and penetrant molecules exchange their positions. The k_1 values are presented in Table VIIIa and b. The first order rate constant k_1 values decrease until 30 phr (Table VIIIa) loading of prophylactic waste while a higher value is obtained at 40 phr loading. The initial decreasing trend in the k_1 values points out that the addition of natural rubber prophylactic slows down the initial rate of uptake of the solvent by the vulcanisate. Again, it is interesting to note how the present system behaves differently from other particulate filled vulcanizates. In the case of elastomer vulcanizates filled with particulate fillers, both the initial rate and equilibrium solvent uptake values vary in the same manner with increasing loading of the filler. But for the present case, such a correlation cannot be seen as equilibrium uptake value increases while rate of initial uptake decreases with prophylactic loading. The drop in the initial rate of uptake reflected in first order rate constant values is due to the heterogeneous nature of the composite samples. As these prophylactic filler particles also start absorbing solvent at later stages of the diffusion process, the final uptake value increases with prophylactic loading.

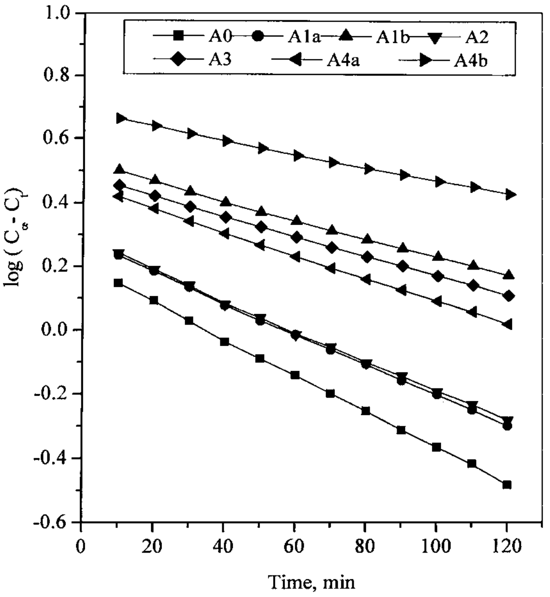

Figure 11 Plots of log ($C_\infty - C_t$) verses time of the samples at room temperature (28°C).

The rate constant values of the diffusion at 40°C can be seen from Table VIIIb. A similar behavior can be observed here also. As the temperature increases, the magnitude of the rate constant values decreases for the EPDM samples with 10 and 20 phr prophylactic loading. After this loading, for the samples A3 and A4b, the values are found to be higher at higher temperature. Slightly lower values of k_1 at both temperatures are shown by the sample A4a.

3.6. Calculation of crosslink density

The crosslink density values (ν_{phys}) calculated from the stress-strain data using Mooney-Rivlin plots (Figs 13 and 14) are given in Table VI. ν_{phys} values are calculated from the respective trend lines in Mooney-Rivlin plots. The ν_{phys} values increase at 10 phr loading of prophylactic filler and then decrease for further loadings. Thus, the maximum extent of physically effective crosslinks ν_{phys} can be seen for EPDM sample filled with 10 and 15 phr prophylactic filler. It can be seen

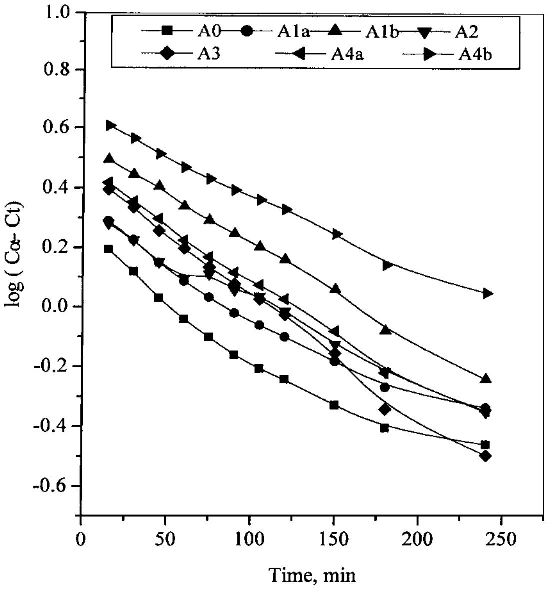

Figure 12 Plots of log ($C_\infty - C_t$) verses time of the samples at 40°C.

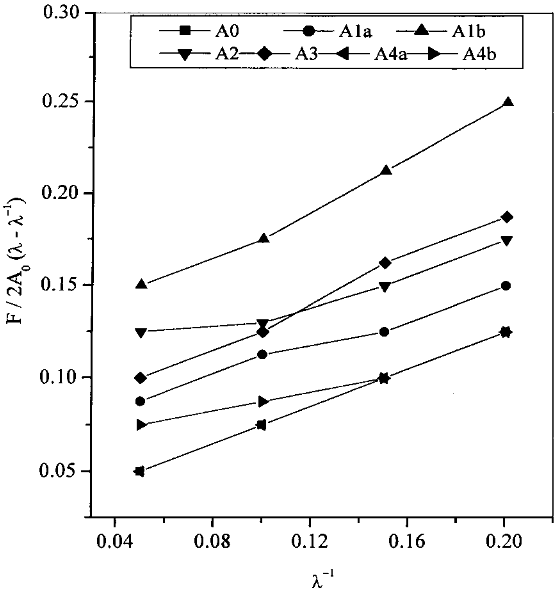

Figure 13 Plots of $F/2A_0$ ($\lambda - \lambda^{-1}$) verses λ^{-1} of the unaged samples.

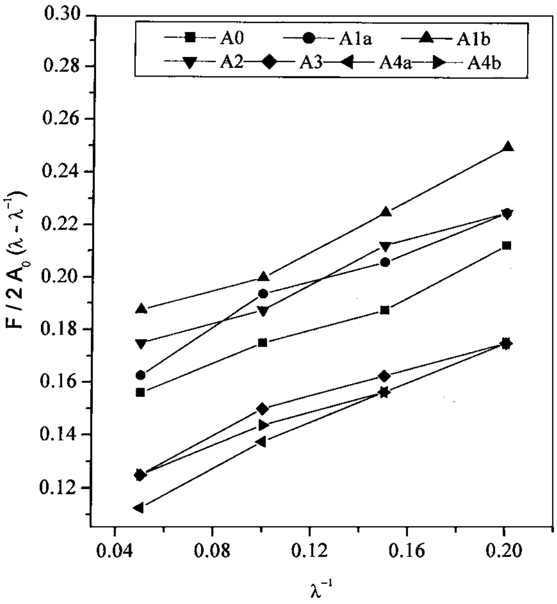

Figure 14 Plots of $F/2A_0(\lambda - \lambda^{-1})$ verses λ^{-1} of the aged samples.

from a comparison of values in Table VI that ν_{phys} gives good agreement with the observed tensile strength data.

4. Conclusions

The present investigation discusses the role of recycled natural rubber prophylactic waste compared to virgin natural rubber in the development of novel ethylene propylene diene rubber composites. The mixing of the components was carried out in an open mill. A mixed vulcanization recipe consisting of sulfur and dicumyl peroxide was used to effect the co-vulcanization. The processing characteristics were evaluated using a Monsanto rheometer at three different temperatures 150, 160 and 170°C. It was found that the curing properties such as optimum cure time, scorch time and induction time at 150°C decreased with the addition of natural rubber prophylactic filler. The cure activating nature of the inclusion in ethylene propylene diene rubber was found to be greater at higher temperature. The curing properties of the samples with virgin natural rubber were found to be lower compared to those with natural rubber prophylactic filler. The stress-strain behavior and physical property measurements of the unaged and aged vulcanizates indicates the better performance of the mixed samples compared to gum ethylene propylene rubber sample. The unaged tensile strength was found to be highest at 30 phr loading of prophylactic filler. The aged tensile strength, and elongation at break were found to be maximum at a natural rubber prophylactic loading of 20 phr, while tear strength showed a maximum at 40 phr. The values were found to be higher for virgin natural rubber filled samples in the case of unaged and aged tensile strength, elongation at break and tear strength, except at 40 phr loading. The network density calculated using Mooney-Rivlin equation was found to be giving a better agreement with the observed trend in the variation of tensile strength of the systems with prophylactic loading.

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