Crosslink Density and Diffusion Mechanisms in Blend Vulcanizates Loaded with Carbon Black and Paraffin Wax

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ABSTRACT: Results on blends containing different ingredients have revived the interest on the interaction parameter and crosslink density of structures that contain soft fillers. Composite blend of natural rubber and styrene butadiene rubber loaded with the percolation concentration of high abrasion furnace carbon black and different concentrations with paraffin wax were prepared. The applicability of the blends for liquid diffusion has been examined through the changes in the interaction parameter and the crosslink density at different temperatures. The transport mechanism through the vulcanized blends is governed by Fickian diffusion law at room temperatures and it becomes non-Fickian at higher temperatures. The diffusion coefficients were calculated and found to have an activated behavior with temperature from which the activation energy was calculated. The change in entropy, enthalpy, and Gibbs free energy are also studied at different temperatures. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 3232–3240, 2009

Key words: blends; crosslink density; diffusion mechanism; paraffin wax

INTRODUCTION

Blending of two or more types of polymer is a useful technique for the preparation and developing materials with properties superior to those of individual constituents. It is important especially from an industrial point of view to control the state of mixing of polymer blends.[1,2] An adequate polymer-blend process requires information and understanding of the blend behavior under production conditions. Natural rubber (NR) has been studied and reported extensively because of its superior performance in tire applications. It is well-installed that elastomers do not display all of the characteristics that are required. Elastomer blends are used for many purposes such as lowering the compound cost. The complex shaped product may be more easily fabricated during production. NR and styrene–butadiene rubber (SBR) have been blended for a long time for these reasons.[1,2] To control the effects of rubber aging, either waxes or chemical stabilizers are added. Waxes function as antiozonants by blooming to the rubber surface to form an inert protective film.[3]

The swelling process and its kinetics give an idea about the capacity of a crosslinked polymer in different liquids and vapor media. However, the interaction of polymeric materials with different solvents is a problem from both the academic and technological points of view.[4] This interaction was characterized by an interaction parameter χ and expressed as a series expansion in powers of the polymer volume fraction φ_r as[5,6]

$$\chi = \chi_1 + \chi_2\varphi_r + \chi_3\varphi_r^2 \qquad (1)$$

The coefficients χ_1, χ_2, ….. are functions of molecular characteristics and temperature.[5,6] There is a lot of work done about the interaction parameter of crosslinked networks and star polymers.[7–12] The importance of this parameter is used for the determination of the crosslink density μ_{cs} and the average molecular weight of the network chain between crosslinks M_{cs}.

Several studies applied the swelling technique in SBR compounds to estimate M_{cs} using toluene as solvent,[13–17] considering χ = constant in eq. (1). However, there is a big spread of values of χ used in these investigations.

Diffusion in polymers is an important mechanism for many applications. Diffusion in polymeric systems is passive, if the driving force is purely a Brownian molecular motion, but diffusion can also be activated by external effects, either by the influence of the release medium by swelling or by the effects of physical forces as electrical, osmotic, or convective forces.[18] The fundamental of diffusion is based on Fick's law that describes the macroscopic transport of molecules

by a concentration gradient. The first Fick's law is a pertinent modelization for a steady-state diffusional release. Fick's second law is used for the description of transient phenomena where the concentration profile of solvents in the polymer is not constant during diffusion. Fick's modelization is adapted to passive diffusional systems where the diffusion coefficient (D) may be supposed to be constant. Such systems are called Fickian systems.[19]

SBR–NBR blend loaded with carbon black and different concentrations of paraffin wax detect pressure and temperature sensors besides current voltage switching.[20] Therefore, it is of importance to search about some of their properties when they under service. In this respect, the present work aims to search the value of χ for these composites and determine its dependence on wax concentration and temperature. The crosslink density, μ_{cs}, the diffusion coefficients, D, and the diffusion mechanism of such vulcanizates at different temperatures are also studied. Some thermodynamic parameters such as the change in entropy, ΔS, enthalpy, ΔH, and Gibbs free energy, ΔG, of swollen samples at different temperatures have been studied.

EXPERIMENTAL

Materials

Commercial grades of both SBR and NR were purchased from Alexandria Trade Rubber Company (TRENCO, Alexandria, Egypt) and used with equal proportions as polymer matrix. Paraffin wax ($C_{25}H_{52}$, specific gravity of 0.9 and melting temperature 55°C) was used as a softener with different concentration. High Abrasion Furnace (HAF-N330, particle size diameter ranges from 28 to 36 nm, tensile strength 22.4 MPa) carbon black was used as reinforcement filler. Other compounding ingredients like zinc oxide and stearic acid (activators), Dibenz thiazyl disulphide (MBTS, semiultra accelerator), phenyl-naphthyl-amine (PBN, antioxidant, melting point 105°C), dioctyle phthalate (DOP, plasticizer), and sulfur (vulcanizing agent) were used. These materials were compounded according to the recipe listed in Table I. The compounds were mixed according to ASTM D 3182 in a laboratory-sized mixing mill at a friction ratio of 1 : 1.19 by careful control of the temperature, nip gap, time of mixing, and uniform cutting operation for 30 min. After mixing, the rubber compositions were molded in an electrically heated hydraulic press to the optimum cure with molding conditions that were previously determined from torque data with a Monsanto R100 rheometer (New York). Details of compounding and vulcanization process can be found elsewhere in a previous work.[21]

TABLE I
Mix Formation of 40HAF/(SBR-NR) Composites Loaded with Paraffin Wax

Ingredients	Concentration (phr)
SBR	50
NR	50
HAF	40
Processing oil	10
Stearic acid	2
MBTS	2
PBN	1
Zinc oxide	5
Sulfur	2
DOP	10
Paraffin wax	0, 10, 20, 30, 40

Swelling measurements

Rubber blends were weighed and inserted into test tubes containing a solvent at constant temperature. The rubber blends were removed from the solvent and blotted with filter paper to remove excess solvent from the surface of the sample. The rubber blends were then weighed to an accuracy of 0.1 mg at a given time and at a fixed temperature. The equilibrium swelling ratio, Q, was calculated by using the gravimetric method, where Q is given by

$$Q = \frac{M_{ts} - M_r}{M_r} \times 100\%$$

where M_{ts} is the mass of the sample after swelling at time t and M_r is the mass of dry sample before swelling.

RESULTS AND DISCUSSIONS

Interaction parameter and crosslink density

From a practical point of view, it is very important to know the liability of crosslinked polymers to swelling in various liquids and vapor media. This may be assessed by determining the degree of swelling, expressed as the amount of liquid sorbed by the polymer.

One of the most important structural parameters characterizing a crosslinked polymer is its crosslink density μ_{cs}. Its magnitude is defined as the number of elastically effective chains totally included in a perfect net work per unit volume[22] and is given by

$$\mu_{cs} = \frac{\rho_r N_A}{M_{cs}} \quad (2)$$

where ρ_r is the rubber density and N_A is Avogadro's number. Equilibrium swelling is widely used to determine the average molecular weight between crosslinks M_{cs}.[7,23–25] According to the theory of Flory and Rehner,[24] for a perfect polymer,

Solvents	Formula	Molar volume (mL/mol)	δ_s $(cal/cm^3)^{1/2}$
Kerosene	$C_{10}H_{22}$ to $C_{16}H_{34}$	180	7.65
Distilled water	H_2O	18	23.2
Benzene	C_6H_6	89	9.15
Ethanol	C_2H_5OH	57.5	12.7
Methanol	CH_3OH	41	14.5
Toluene	C_6H_5OH	107	8.9
Acetone	CH_3COCH_3	74	9.9
Chloroform	$CHCl_3$	81	9.3

$$M_{cs} = -V_1 \rho_r \frac{(\varphi_r^{1/3} - \varphi_r/2)}{\ln(1-\varphi_r) + \varphi_r + \chi\varphi_r^2} \quad (3)$$

with V_1 is the molar volume of the solvent. The polymer volume fraction, φ_r can be calculated using the equilibrium swelling ratio Q and the equation,[23]

$$Q = \frac{1}{\varphi_r} = 1 + \frac{\rho_r M_s}{\rho_s M_r} \quad (4)$$

where M_r and M_s are the weights of dry rubber and absorbed solvent, respectively, and ρ_s is the solvent density. The interaction parameter χ (Flory-Hugins) is calculated from a widely used equation based on the Hildebrand solubility parameters given by[7]

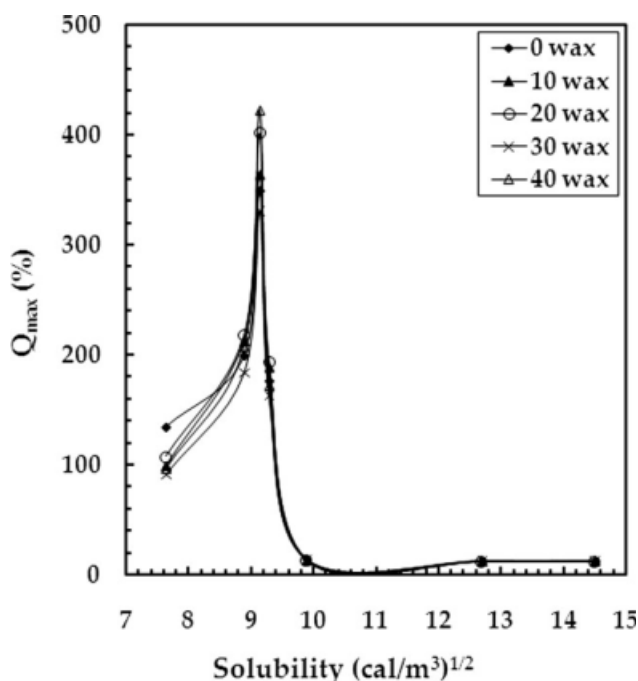$$\chi = \frac{V_1}{RT}(\delta_s - \delta_r)^2 \quad (5)$$

Figure 1 The equilibrium swelling ratio as a function of the solubility of different liquids for studied samples at 293 k.
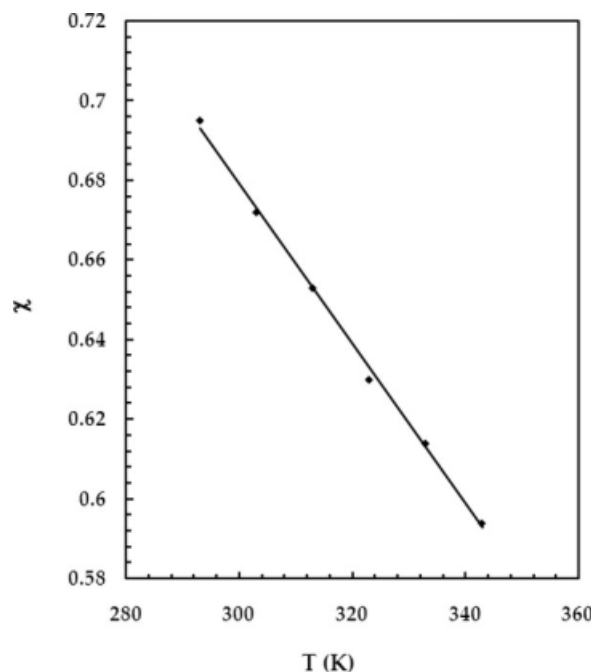
Figure 2 The dependence of the interaction parameter on temperature for studied matrix.

where δ_s and δ_r are the solubility parameters for solvent and polymer, respectively, R the molar gas constant, and T the absolute working temperature.

To know the solubility parameter of the rubber matrix, the equilibrium swelling ratio of all samples is determined experimentally in different solvents with different solubility parameters as listed in Table II. It is then plotted against δ_s. The result for all the solvents is a single master curve, (Fig. 1) having a peak value at the abscissa corresponding to the solubility parameter of the rubber matrix which was found to be around 9.15 $(cal/cm^3)^{1/2}$ and does not depend on the wax content.

The effect of temperature on the interaction parameter is studied and shown in Figure 2. This is achieved by repeating the previous work at the desired temperature and by using the solubility of the solvents at that temperature (not mentioned here to avoid repetition). The behavior of Figure 2 can be described with a linear equation of the form

$$\chi = A - BT \quad (6)$$

TABLE III
**The Calculated Crosslink Density for All Samples at
Room Temperature**

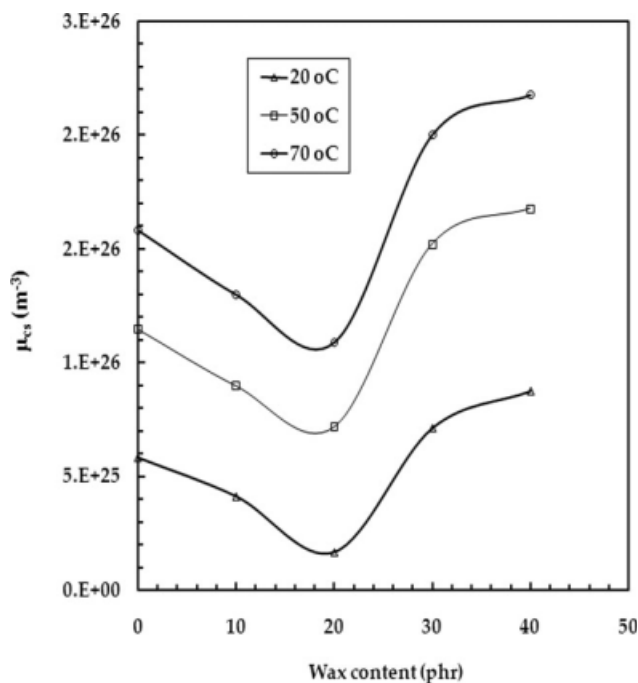| Wax content (phr)	$\mu_{sc} \times 10^{25}(m^{-3})$
0	5.81
10	4.11
20	1.66
30	7.11
40	8.73

Figure 3 The dependence of the crosslink density on wax content at different temperatures.
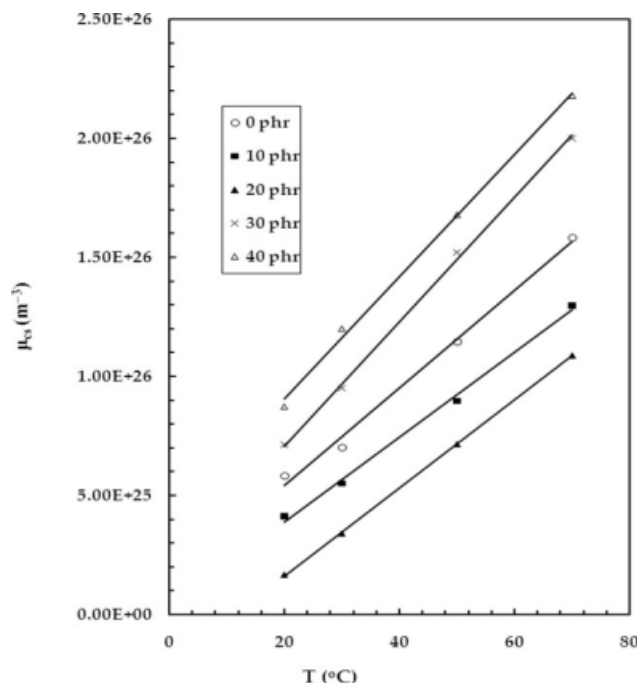

Figure 4 The dependence of the crosslink density on temperature for all samples.

where A gives the interaction parameter at zero temperature and equal to 1.28 while B is the slope and is equal to 2.01×10^{-3} K^{-1}.

Substituting the values of χ for all samples in eq. (3) one can calculate the value of M_{cs} for each sample and hence, using eq. (2), the crosslink density, μ_{cs} is deduced and listed in Table III. Low crosslink density is observed for samples containing 20 phr of paraffin wax. This behavior of μ_{sc} is in accordance with the behavior of the dc electrical conductivity measured in a previous work for such samples.[21]
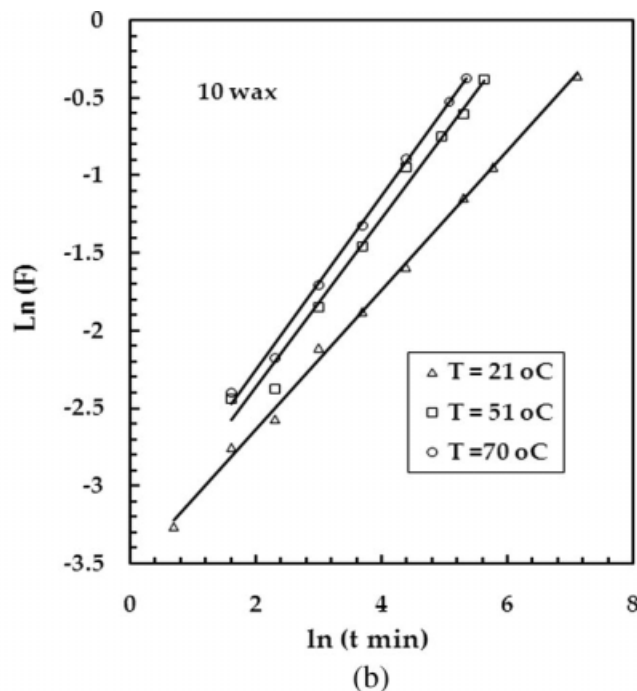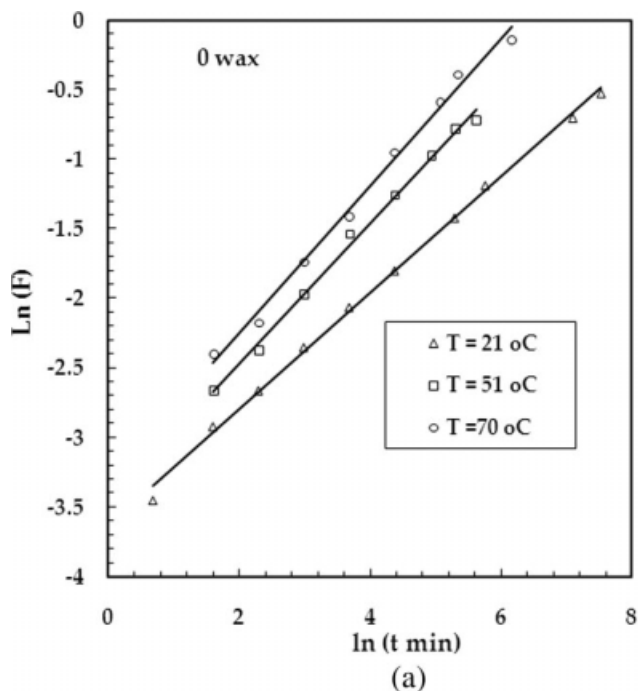

Figure 5 The dependence of ln(F) on ln(t) at different temperatures for (a) 0 phr of wax and (b) 40 phr of wax.

TABLE IV
Results of Diffusion Exponent, *n*, and the Gel Characteristic, *k*, for All Studied Vulcanizates at Different Temperatures

Wax content (phr)	20°C		50°C		70°C	
	n	*k*	*n*	*k*	*n*	*k*
0	0.418	37.7	0.504	32.5	0.503	27.4
10	0.451	34.5	0.545	31.8	0.532	26.8
20	0.470	39.7	0.599	43.8	0.512	24.8
30	0.441	30.6	0.564	32.8	0.523	22.7
40	0.493	38.1	0.554	29.1	0.492	28.8

This change in χ with temperature results in a change in the crosslink density. Figure 3 shows the dependence of the crosslink density as a function of wax content at different temperatures. It is obvious from the figure that at any temperature, μ_{cs} first decreases till the concentration of wax reaches 20 phr, which may refers to the replacement of the crosslinker (sulfur) with paraffin wax molecules and/or the excess carbon and hydrogen bonds added by wax may need more vulcanization. At concentrations of wax greater than 20 phr, μ_{cs} begins to increase gradually again owing to a new configuration that is wax acts as a softener and makes easy motion of blend chains to make additional crosslinks. Moreover, at any wax concentration the crosslink density becomes higher with increasing temperature as shown in Figure 4 . This may be due to the melting of wax at higher temperatures which transforms to the liquid state that makes the rubber chains more crosslinked with each other.

Diffusion studies in kerosene

In polymeric systems, absorption of liquids from the environment changes the dimensions and physicomechanical properties of the system. A model based on the work of Alfery et al.[26] describes the swelling membrane, which consists of three zones. Adjacent to the bulk liquid is a layer of completely swollen gel. Then, there is a thin layer in which the polymer chains are slowly hydrating and relaxing. The third zone is a matrix of unswollen, completely dried, rigid polymer. The diffusion of liquids through polymers is classified

into three different types based on the relative rates of diffusion and polymer relaxation.[26] The first one is the simple Fickian diffusion at which the rate of diffusion is much less than that of relaxation. Second is the relaxation-controlled transport, which occurs when diffusion is very rapid compared with the relaxation of polymer chains. The third type of diffusion is called Non-Fickian anomalous diffusion. It takes place when the diffusion and relaxation rates are comparable. The weight gain of solvent, M_s, is described by an equation of the form

$$M_s = k\,t^n \tag{7}$$

where *k* and *n* are constants. Normal Fickian diffusion is characterized by $n = 0.5$ or less, while relaxation-controlled transport diffusion is characterized by $n = 1.0$. Values of *n* between 0.5 and 1.0 indicate a mixture of the last two types, which is usually called non-Fickian or anomalous diffusion.[26] eq. (7) could be used to evaluate a quantitative understanding of the nature of the sorption kinetics in the polymeric system. Ritger et al.[27] wrote eq. (7) as

$$F = \frac{M_t}{M_\infty} = kt^n \tag{8}$$

where *F* is the fractional uptake, M_t is the amount of diffusant sorbed at time *t* and M_∞ is the maximum amount absorbed, *k* is a constant incorporating characteristics of macromolecular network system and penetrant that is sometimes named gel characteristic constant and *n* as defined above. When a plot is drawn between $\ln(\frac{M_t}{M_\infty})$ and $\ln(t)$, the slope of the plot gives the value of *n* and the intercept will inform about value of *k*. This equation applies until 60% of the normalized solvent uptake. Figure 5 a,b) shows the dependence of $\ln(\frac{M_t}{M_\infty})$ on $\ln(t)$ at different concentrations of paraffin wax and at different temperatures. The behaviors are similar for either different wax concentrations or temperatures. So, some arbitrary concentrations and temperatures are presented in Figure 5 to avoid repetition. All the figures predict a straight-line dependence and obey eq. (8). The slopes, *n*, and the intercept, *k*, of these lines are listed in Table IV. The diffusion mechanism of

TABLE V
Results of the Calculated Diffusion Coefficients for the Different Studied Samples at Different Temperatures

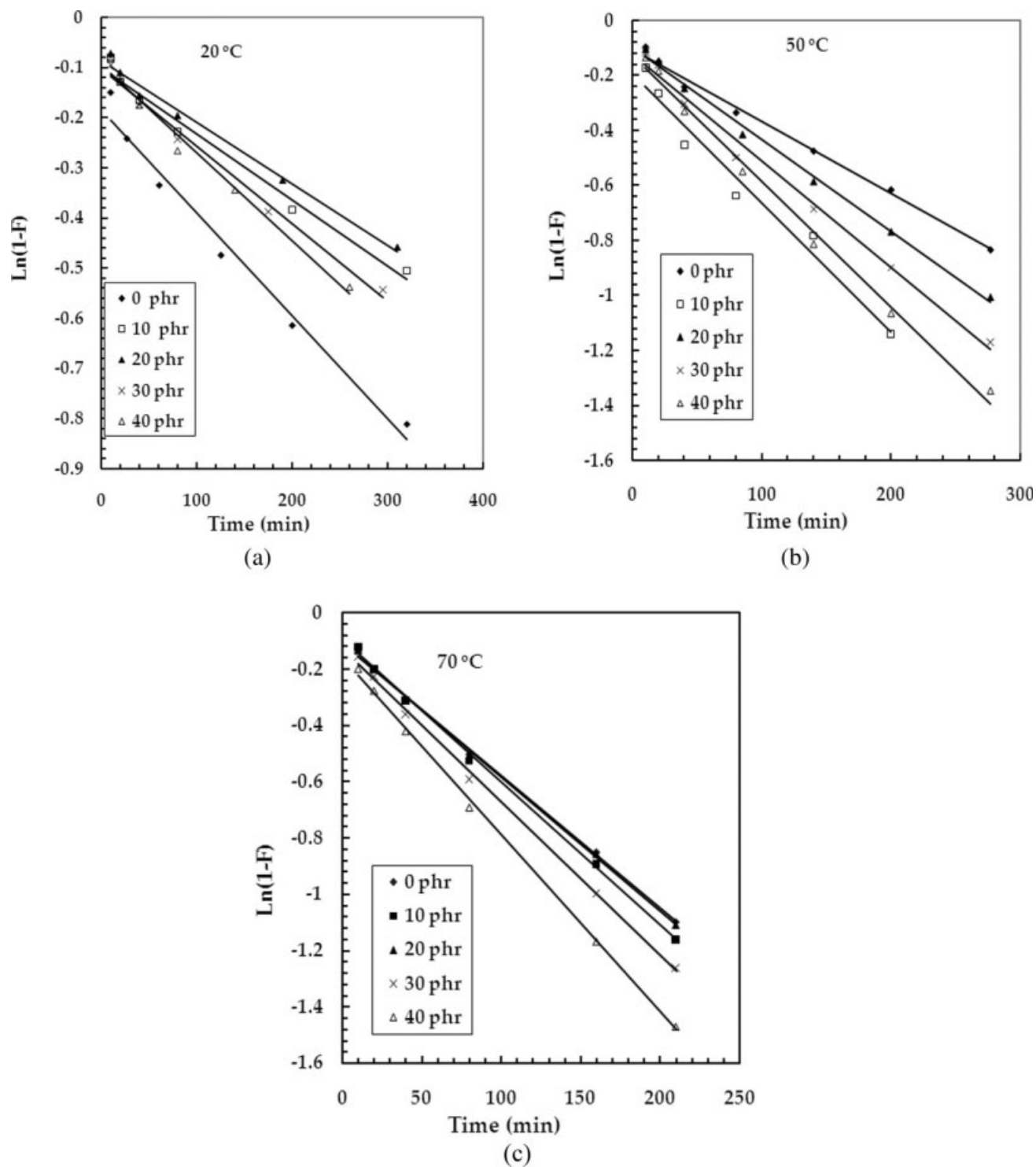| Wax content (phr)	$D_i \times 10^{-11}$ (m²/sec)			$D_A \times 10^{-11}$ (m²/sec)			$D_L \times 10^{-11}$ (m²/sec)		
	20°C	50°C	70°C	20°C	50°C	70°C	20°C	50°C	70°C
0	1.43	1.36	2.63	1.28	1.36	2.70	85.0	105	190
10	0.68	1.96	2.77	0.57	2.09	2.96	52.7	190	207
20	0.57	1.77	2.66	0.58	1.93	2.85	48.6	134	194
30	0.79	2.74	3.19	0.74	2.27	3.27	60.7	158	223
40	0.85	2.27	3.85	0.82	2.8	4.03	72.9	186	255

Figure 6 The dependence of ln(1 − F) on time for different paraffin wax loadings at (a) 20°C, (b) 50°C, and 70°C.

kerosene is Fickian for all vulcanizates at 20°C. This mechanism becomes anomalous one (non-Fickian) at higher temperatures (n is greater than 0.5) except for sample containing 40 phr of wax at 70°C. On the other hand, samples containing 20 phr of wax have a maximum diffusion exponent of 0.599 at 50°C while at 70°C, 10 phr waxed samples have maxi-

mum n (0.532) but still less than that of 20 phr at 50°C. The gel characteristic is found to have a decreasing behavior with temperature for samples containing 0, 10, and 40 phr of wax. For samples containing 20 and 30 phr of wax, k found to increase slightly at 50°C followed by a decrease at 70°C. This decrease in k can be attributed to effects of the blend

composition on the dissipation of solvent swelling tension.[28]

The diffusion coefficient, D, is an important kinetic parameter of the swelling process that indicates the transport abilities of solvent molecules in the blend and depends on the polymer segmental mobility. Fick's laws of diffusion adequately describe the most diffusion processes. For cylindrical shaped samples the initial diffusion is given in simple form by

$$F = 4\left(\frac{D_i t}{\pi \ell^2}\right)^{1/2} \quad (9)$$

where l is the sample thickness. Slopes of linear plots between F and $t^{1/2}$ are calculated and, subsequently, the initial diffusion coefficient D_i is calculated at different wax concentrations and different temperatures and presented in Table V.

The average diffusion coefficient D_A can be calculated for 50% of the total release by putting the fractional uptake $F = 0.5$ in eq. (9), which finally yields

$$D_A = \frac{0.049\ell^2}{(\sqrt{t})^2} \quad (10)$$

where $t^{1/2}$ is the square root of time for 50% of solvent uptake.

Late diffusion coefficients, D_L, can be calculated using the late time approximation equation[26]

$$F = 1 - \left(\frac{8}{\pi}\right)\exp\left(\frac{-\pi^2 D_L t}{\ell^2}\right) \quad (11)$$

The slopes of the plots between $\ln(1 - F)$ and t (Fig. 6) are used for the evaluation of D_L which presented in Table V.
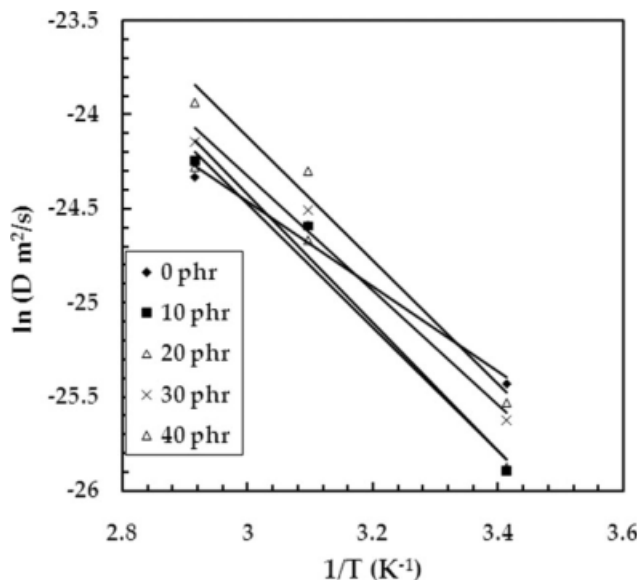
TABLE VI
The Calculated Values of the Activation Energy for All Vulcanizates

Wax content (phr)	E_a (eV)
0	0.195
10	0.295
20	0.283
30	0.263
40	0.284

$$D_L = -\frac{1}{\pi^2}[(slope)\ell^2] \quad (12)$$

As could be expected, there is an increase in the diffusion coefficients with increasing temperature. At high temperatures, the polymeric chains are more flexible and the process of diffusion becomes easier. As the temperature decreases, the free volume decreases, and the exchange of polymer chain segments becomes less, which leads to a decrease in the values of the diffusion coefficients. It can also be analyzed as the blend at relatively small temperatures that offers resistance to the uptake of solvent molecules, and it is more difficult to accommodate larger molecules in the polymer matrix.

Figure 7 shows the temperature dependence of $\ln(D_A)$ for all samples. This dependence is found to obey the well-known Arrhenius relation

$$D_A = D_o \exp\left(\frac{-E_a}{kT}\right) \quad (13)$$

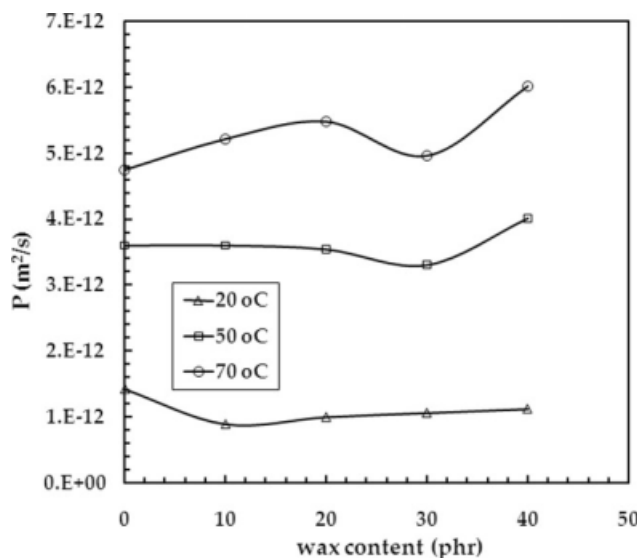where D_o is the average diffusion coefficient at certain temperature T_o, k is the Boltzmann constant and

Figure 7 Temperature dependence of ln(D) for different paraffin wax loadings.

Figure 8 Dependence of the permeability coefficient on wax content at different temperatures.
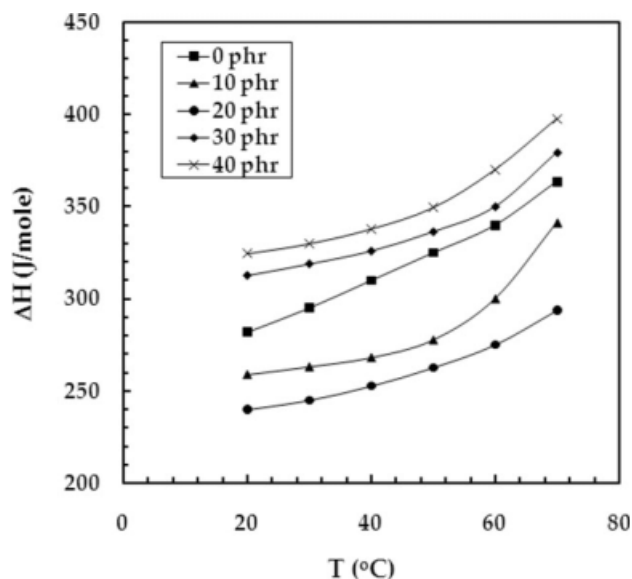
Figure 9 Temperature dependence of ΔH for different samples.

E_a is the activation energy. The calculated values of E_a are listed in Table VI for all vulcanizates. Only E_a for zero wax (= 0.159 eV) is far from those containing wax. These values are within the range expected for rubbery polymers, well-above their glass transition temperature.[29]

The permeation coefficient, P, is a collective process of diffusion and sorption, and so the permeability of liquid molecules into a blend sample depends on both the diffusion and solubility, S. P has been calculated from the equation[30]

$$P = DS \qquad (14)$$

and S is given by

$$S = M_\infty / M_p \qquad (15)$$

where M_p is the polymer sample.

Figure 8 depicts the calculated values of P as a function of paraffin wax concentration. At 20°C P decreased at 10 phr of wax and seems to be independent on the wax content. At a temperature of 50°C, P slightly decreases with wax concentration up to 30 phr, which means that the presence of wax up to a certain value hinders the movement of kerosene between the polymer segments. At this temperature, further increase of P is observed at 40 phr of wax. At 70°C, wax becomes in the liquid state that it becomes easier to penetrate. This results in a general increase in P values.

Thermodynamic parameters

The change in entropy, ΔS, enthalpy, ΔH, and Gibbs free energy, ΔG, values of the composite blend provide information about their thermal shielding appli-

cations. These thermodynamic parameters are calculated using the equations,[31,32]

$$\Delta S = -R[\text{In}(1 - \varphi_r) + \varphi_r - \frac{\rho_r V_1 \varphi_r}{M_{cs}}] \qquad (16)$$

$$\Delta G = RT[\text{In}(1 - \varphi_r) + \varphi_r + \chi\varphi_r^2] \qquad (17)$$

$$\Delta H = \Delta G + T\Delta S \qquad (18)$$

The calculated values of ΔH and ΔG as a function of temperature for the different wax concentrations are plotted in Figures 9 and 10. ΔH for all wax concentrations increases with increasing temperature. This can attributed to the fact that, with increasing temperature, the number of elastically effective chains and the interfacial adhesion of the vulcanizate blend increases. That ΔH is positive suggests that the liquid solvent have to make room for themselves in the blend matrix and the sorption mechanism is an endothermic one. This may be also the reason behind the increase of ΔH for samples containing 30 and 40 phr of paraffin wax. The ΔG values of all the samples are negative. This suggests that there is retention of the liquid structure in the sorbed state within the polymer matrix. These values of ΔG was found to decrease linearly with temperature according to an empirical equation of the form

$$\Delta G = \Delta G_o - A_o KT \qquad (19)$$

where ΔG_0 is the change in the Gibbs free energy at zero Kelvin and A_0 is a constant with a value equal slope/k.
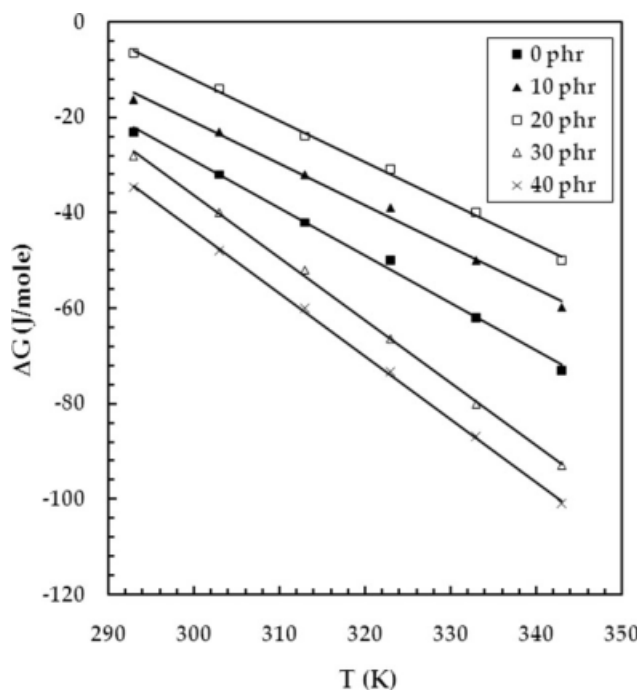

Figure 10 Temperature dependence of ΔG for different samples.

CONCLUSIONS

From the foregone swelling kinetics study, the following results could be concluded:

1. The interaction parameter does not depend on paraffin wax, but it depends on both polymer matrix and temperature. It decreased with increasing temperature.
2. The crosslink density was found to have a minimum value at 20 phr of wax in accordance with the dc electrical conductivity measured in a previous work. It also increased with increasing temperature.
3. The diffusion mechanism of kerosene was Fickian at 20°C and became anomalous at higher temperatures.
4. The late time diffusion coefficient was more than the initial one, especially at high temperatures. The average diffusion coefficient was found to be thermally activated. Samples containing 10 phr of wax have maximum activation energy of 0.295 eV.
5. The change in enthalpy was found to have a minimum value at 20 phr of wax content but it increased with increasing temperature. The values of DH indicated that the sorption mechanism is an endothermic one. The Gibbs free energy decreased linearly with temperature.

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