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Exploring the filler-polymer interaction and solvent transport behavior of nanocomposites derived from reduced graphene oxide and polychloroprene rubber

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ABSTRACT: Aliphatic solvent resistance of polychloroprene rubber (CR) reinforced reduced graphene oxide (RGO) nanocomposites were explored in the temperature range of 30–50 °C using hexane, heptane, and octane. Microstructure-assisted solvent resistant property is evident from transmission electron microscopy images of fabricated composites. Different transport parameters such as diffusion, permeation, and sorption constants were moderate while increasing RGO content. Diffusion mechanism was explained based on the permeating molecule and is found to be close to Fickian mechanism except for heptane. Evaluation of kinetic and thermodynamic parameters shows the ability of nanoreinforcement to alter thermodynamic characteristics and rate constant values. The extent of reinforcement was also evaluated by Kraus equation. From swelling studies, molecular mass between crosslinks was evaluated using Flory–Rehner equation and compared these values with theoretical predictions such as phantom and affine models to analyze the deformation and mobility of the network during swelling. Temperature plays a significant role in the transport of organic solvent through CR/RGO nanocomposites. © 2019 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2019**, *136*, 48168.

KEYWORDS: chloroprene rubber; crosslink density; network structure; reduced graphene oxide; solvent transport; swelling coefficient; thermodynamic parameters

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INTRODUCTION

In recent years, researchers in industry and academic circles have focused their interest on polymeric nanocomposites, which stand for a radical alternative to conventional filled polymers or polymer blends. As we know that, in nanocomposites, at least one dimension is in the nanometer range. This distinctive enables the nanoreinforcement to enhance the overall material performance. Nanomaterials are more effective in reinforcements than their conventional counterparts because a smaller amount of nanomaterials causes a significant improvement of the polymer matrix properties. The field of nanoscience has blossomed over the last two decades by the discovery of graphene¹ and graphene-based polymer nanocomposites. A better enhancement in modulus, failure properties such as tensile and tear strength, barrier properties, thermal properties, and so forth was obtained by the incorporation of graphene-based filler in elastomeric matrices. Sorption and diffusion of small molecules through the polymer is a matter of the broad range of application in many industrially important phenomena. Solvent diffusion studies are vital in elastomeric composites because this method predicts the life span of the product used in the liquid atmosphere; as well, it is used to characterize the chemical structure, crosslink density, and interfacial characteristics of rubber composites. There is a rapidly increasing demand for polymer specified permeability such as selective membrane for packaging application, foaming, and plasticization. Transport properties such as diffusivity relate how rapidly molecules move through the polymer matrix.

These things are very important in many applications of polymer for films and membranes. Various factors such as nature of the polymer, nature of the solvent, crosslinking system and temperature, and so forth, were influenced the diffusion phenomenon. According to the free volume concept, chain mobility provides a

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Figure 1. Vulcanized CR/RGO sheet (a) and circular diffusion samples placed in diffusion bottles (b). [Color figure can be viewed at wileyonlinelibrary.com]

driving force for the diffusion of small molecules. In a nanocomposite, the molecular mobility is reduced in the close vicinities of the filler particles and this provides a tortuous path for the permeating molecules. The diffusion and transport in polymer nanocomposites depend on the nature of the filler and their compatibility with the polymer matrix. If the filler used is compatible with the matrix, it will take the free volume within the polymer matrix and create a tortuous path for the permeating molecule.² On the other hand, if the filler is incompatible with a polymer matrix, voids were formed at the interface which tends to increases the free volume of the system so in this manner increasing the permeability through it.³

Numerous research activities were reported in the field of diffusion and transport of solvents through a variety of polymers including elastomers. Polymeric materials that are continuously in contact with the organic liquids have absorbed these liquids as a function of time when in contact with the liquids. This absorbed liquid may significantly alter their physical and mechanical behavior. Diffusion and transport process of nitrile-butadiene rubber (NBR) nanocomposites based on TiO_2 , $Ca_3(PO_4)_2$, and layered silicates were reported by Thomas *et al.*⁴ They found that layered silicate filled nanocomposites exhibited reduced transport properties compared to the other two filled systems owing to increased polymer-filler interaction. Also, the activation energy needed for the diffusion of the permeant molecule was found to be higher for nanocomposites than that of pristine NBR. Clay intercalation and its influence on the morphology and transport properties of ethylene-vinyl acetate (EVA)/clay nanocomposites were studied by Wilson et al.⁵ They analyzed the influence of nanoclay (Cloisite 25A) loading, penetrant size, and temperature on the diffusion process. They observed the maximum solvent uptake decreases with the addition of nanoclay, due to the enhanced polymer-filler interaction.

Thomas et al.^{6,7} reported the properties of natural rubber (NR), deoxidized NR, and NR latex reinforced with layered silicate. They also studied diffusion and permeation properties of substituted benzene through NBR/NR blends and found that the solvent uptake decreases by means of increasing NBR content. Effect of the blend ratio on the transport and dynamic mechanical properties of styrenebutadiene rubber (SBR)/NR blend was investigated at different temperatures by George et al.⁸ In recent times, in our laboratory transport properties of hybrid nanoparticle-based, crosslinked polyethylene XLPE/Al₂O₃-clay binary and ternary nanocomposites were reported by Jose and Thomas.9 They investigate the transport process follows first-order kinetics and the rate constant values confirm the superior solvent resistant characteristics of nanocomposites. Last few years, several studies were reported in solvent transport characteristics of polymer nanocomposites. Diffusion of organic solvents through a number of systems such as, SBR/carbon nanotube nanocomposites,¹⁰ SBR-poly(methyl methacrylate) interpenetrating polymer network membranes¹¹ EVA/halloysite nanotubes, fluoroelastomer/reduced graphene oxide (FKM/RGO) nanocomposites,12-14 and epoxidized NR/graphene nanocomposites¹⁵ revealed the characteristic transport properties of the nanocomposites.

The present work is mainly focused on the study of solvent transport characteristics of RGO-filled chloroprene rubber (CR) nanocomposites as a function of filler loading. As revealed from the literature hitherto, no work has been reported until now in the detailed diffusion studies of aliphatic hydrocarbons through CR

Table I. Physical Properties of the Materia

Materials	Molecular weight (g mol ⁻¹)	Molar volume	Density (g cm ⁻³)	Boiling point (°C)	Solubility parameter (Cal cm ⁻³) ^{1/2}
CR	88.53	_	0.9598	-	≈9.2
Hexane	86.17	128.61	0.659	68	7.3
Heptane	100.21	146.50	0.684	98.42	7.4
Octane	114.23	162.48	0.703	125.7	7.54



Ingredients	CGO	CG1	CG2	CG3	CG4	CG5
CR	100	100	100	100	100	100
Stearic acid	0.5	0.5	0.5	0.5	0.5	0.5
MgO	4	4	4	4	4	4
Antioxidant-(6-PPD)	1.5	1.5	1.5	1.5	1.5	1.5
RGO	0	0.3	0.6	0.9	1.5	2.5
ZnO	5	5	5	5	5	5
Ethylene thiourea (NA22)	0.5	0.5	0.5	0.5	0.5	0.5

Table II. Formulation of the mixes in phr

nanocomposites using graphene-based filler materials. For this reason, the solvent resistivity and sorption characteristics of CR nanocomposites are exposed by executing the diffusion studies by a solvent such as hexane, heptane, and octane. Transport characteristics of the prepared nanocomposites were studied in detail with respect to physicochemical properties of the solvent such as nature, molecular size, molar volume, and density. Effect of temperature on solvent diffusion process was analyzed here. Transport parameters such as diffusivity, sorptivity, and permeability at different temperatures and thermodynamic parameters were also analyzed and correlated with the polymer network structure. Besides, the mechanism of transport through the CR matrix, kinetics of diffusion, and crosslink density were determined using diffusion data.

EXPERIMENTAL

Chloroprene rubber was obtained from Du-Pond (W-grade with fast crystallization tendency, ML 1+ 4 [@100 °C] 47 \pm 1). Natural graphite powder was supplied by Sigma Aldrich RGO was prepared in our laboratory by using Hummer's method. An aliphatic solvent such as hexane, heptane, and octane of analytical grade was procured from Merck India Ltd. Physical properties of the materials are given in Table I.

Preparation of Nanocomposites and its Characterizations

CR/RGO nanocomposites were prepared on a laboratory scale two roll mixing mill. The tailed procedure formulations of different mixes are given in Table II. CR/RGO composites were compounded according to ASTM D 3182 with the aid of a laboratory two roll mixing mill (150, 300 mm). For all the mixes, the nip gap, friction ratio, and the number of passes were kept constant. The total compounding cycle was finished within 15-18 min, and the friction ratio of the mixing mill was kept at 1:1.25 during the mixing tenures. Curing package (in phr) of CR consists of ZnO, MgO, stearic acid, and ethylene thiourea is incorporated into the matrix after admixing RGO.¹⁶ After mixing, the compounded sample thus obtained was subjected to curing study to get the optimum curing time. This study was carried out with the help of a moving die rheometer at 150 °C. The stocks were cured at their respective optimum cure time in a hydraulic press under a pressure of 120 bars at 150 °C. Samples prepared were designated as CG0, CG1, CG2, CG3, CG4, and CG5 in which the concentration of RGO varies from 0, 0.3, 0.6, 0.9, 1.5, and 2.5 phr, respectively.

Transmission Electron Microscopy. The distribution of RGO in CR matrix was explored using transmission electron microscopy (TEM). JOEL JEM TEM with an accelerating voltage of 200 keV was used to get images. An ultramicrotome fitted with a diamond knife was used to get very thin sections of the sample.

Diffusion Studies. Circular samples with a diameter of 2 cm (ASTM standard D5890) were cut from the vulcanized sheets using sharpedged steel die. The thickness of the sample was measured at numerous points using a screw gauge (2 mm). These circular samples were weighed and then dipped in 30 mL of solvent taken in diffusion bottles as shown in figure 1. Samples were taken out of the bottles at a constant time interval, and the adhering solvent was blotted off from the surface gently and then immediately weighed on highly sensitive electronic balance (0.0001 g). Weighed samples were immediately immersed into a test bottle (within 30 s). The weighing was continued until equilibrium swelling was obtained. In order to avoid the error due to the evaporation of the solvent, weighing was completed within 30 s. Transport properties were studied at three different temperatures, namely, 30, 40, and 50 $^{\circ}$ C using three different aliphatic solvents such as hexane, heptane, and octane.

Theory behind the Transport Characteristics

Diffusion Characteristics. Equation (1) is employed to get the solvent uptake at a time "t" in terms of Q_t mol %.

$$Qt \text{ mol}\% = \left(\frac{(\text{Mass of solvent sorbed}/_{\text{Molar mass of solvent}})}{\text{Mass of polymer}}\right) \times 100 \quad (1)$$

The mole percentage uptake ($Q_t \mod \%$) for the solvent was plotted against the square root of time \sqrt{t} . Transport of small molecules through polymer generally occurs through a solution-diffusion mechanism. I_e , the penetrant molecules are first sorbed by polymer followed by diffusion through the polymer. Therefore, the net diffusion through the polymer depends on the difference in the amount of penetrant molecule between the two surfaces.¹⁷

Mechanism of Transport. The sorption results were fitted in eq. (2) to get an idea about the mechanism behind solvent diffusion.

$$\log Q_t / Q_\infty = \log k + n \log t \tag{2}$$

where Q_t and Q_{∞} are the mol % of solvent uptake at time t and equilibrium, respectively, and k value specifies the degree of





Figure 2. Effect of concentration of filler on solvent uptake (octane solvent). [Color figure can be viewed at wileyonlinelibrary.com]

interaction between the solvent and polymer. Type of diffusion mechanism is obtained from the value of *n*, where n = 0.5 designates Fickian transport, n = 1 demonstrates Case II (relaxation controlled) transport, and the values of *n* between 0.5 and 1 specify an anomalous mode of diffusion. Also, there have been reports of n > 1 which is called Super-Case II.¹⁸

Transport Coefficients. *Diffusion coefficient* (D). It is a kinetic parameter, which depends on the segmental mobility of the polymer, also gives an indication of the rate at which the diffusion process takes place.¹⁹ The diffusion coefficient or the diffusivity D of a solvent molecule through a polymer membrane can be calculated using Fickian's second law.²⁰

$$D = \pi \left(\frac{h\theta}{4Q\infty}\right)^2 \tag{3}$$

where *h* is the thickness of the sample, θ is the slope of the linear portion of the sorption before attaining 50% equilibrium, (i.e., Q_t vs. $t^{1/2}$), and Q_{∞} is the equilibrium absorption.

Sorption coefficient (S). Sorption coefficient is calculated by using the following equation:

$$S = \frac{M_{\infty}}{M_0} \tag{4}$$

where M_{∞} is the mass of the solvent at equilibrium swelling and M_0 is the initial polymer mass.²¹

Permeation coefficient (P). The permeability coefficient provides an idea about the quantity of solvent infused through a uniform area of the composite per second.²² The permeation coefficient (P) is calculated as follows:

$$P = D \times S \tag{5}$$

Thermodynamic Parameters. van't Hoff equation is employed to get the values of various thermodynamic functions ΔS , ΔH , and ΔG .

$$\log Ks = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT}$$
(6)

where *Ks* is the thermodynamic sorption coefficient,²³ ΔS is the entropy of sorption, and ΔH is the enthalpy of sorption. From the values of ΔS and ΔH , change in free energy (ΔG) is calculated as follows:

$$\Delta G = \Delta H - T \Delta S \tag{7}$$

From the amount of penetrant sorbed by a given mass of polymer, the thermodynamic equilibrium sorption constant *Ks* has been computed as

$$Ks = \frac{\text{Number of moles of solvent sorbed at equilibrium}}{\text{Mass of polymer}}$$
(8)

Kinetics of Diffusion. The transport kinetics of solvent through polymer nanocomposites has been evaluated using a first-order kinetic equation as given¹⁰



Figure 3. TEM images of CG1 (a) and CG5 (b) composites. [Color figure can be viewed at wileyonlinelibrary.com]





Figure 4. Influence of type of solvent on equilibrium solvent uptake. [Color figure can be viewed at wileyonlinelibrary.com]



Figure 5. Effect of temperature on octane uptake of CR-RGO nanocomposite. [Color figure can be viewed at wileyonlinelibrary.com]

$$\log (C\infty - C_t) = \log C_{\alpha} - \frac{K_1 t}{2.303}$$
(9)

where k is the first-order rate constant (min⁻¹) and C_t and C_{∞} represent the concentrations at time "t" and "infinity," respectively.

RESULTS AND DISCUSSION

Diffusion Features

Influence of Filler Loading. The incorporation of RGO into the CR matrix brings substantial changes on the solvent diffusivity (octane) in the resulting composites, and it is represented in Figure 2. It is evident from the figure that equilibrium solvent intake declines with RGO loading up to the maximum loading tested. CG0 sample shows maximum solvent intake and CG5 minimum. Low concentration of RGO induces limited tortuosity effects, and high concentration of RGO causes high tortuosity effects. Here, RGO upturns the tortuosity of the solvent transport route and lessens the quantity of solvent that can be diffuse in a given volume of the composite. Moreover, constraint in local motion and flexibility of the rubber molecules by filler incorporation tends to reduced solvent uptake.¹⁵ Even of distribution of RGO in CR resulted in decrement free volume within the matrix which further enhances its solvent resistance behavior.

The images presented in Figure 3 reveal CR containing RGO. A notable enhancement in solvent resistance behavior of CR nanocomposites is because of the increased surface area of the reinforcing phase due to their better distribution in the matrix. These images demonstrate that at lower filler loading solvent can diffuse through the rubber matrix without much hindrance [Figure 3(a)]. However, at higher concentration [Figure 3(b)], RGO becomes exfoliated and distributed very well within the polymer matrix and forming three-dimensional networks which reduce the free volume within the rubber and hence sorption.²⁴

Effect of Solvent Nature. Impact of molecular dimension on the diffusion characteristics is investigated by comparing the equilibrium solvent uptake of three solvents. Figure 4 denotes the influence of permeate dimension on the diffusion characteristics of composites with 0.9 phr RGO. As the molecular size of the penetrant increases, migration rate is diminished, so the highest solvent uptake is observed for hexane and the lowest for octane. The equilibrium solvent uptake follows the order octane < heptane < hexane.

It is detected that the equilibrium solvent intake declines as the penetrant size rises from hexane to octane. This might be due to the reduced interaction between polymer and solvent as the penetrant increases. And also, we can say that as the size of the solvent increases, it is very difficult for the penetration of the solvent through the polymer composite. The solubility parameter values of the solvent also play an important role in the equilibrium solvent uptake on the polymer nanocomposite.

Table III. Value of n and k for Various CR Nanocomposites

	n					$k \times 10^2 \text{ (min}^{-1}\text{)}$						
Solvent	CG0	CG1	CG2	CG3	CG4	CG5	CGO	CG1	CG2	CG3	CG4	CG5
Hexane	0.48	0.43	0.39	0.41	0.42	0.43	1.34	1.31	1.12	1.17	1.21	1.20
Heptane	0.62	0.66	0.64	0.63	0.54	0.56	2.07	2.02	1.88	1.96	1.61	1.14
Octane	0.37	0.47	0.35	0.66	0.40	0.58	1.96	1.55	1.23	1.19	1.42	1.90





Figure 6. Schematic representation of the expansion of polymer chains during swelling. [Color figure can be viewed at wileyonlinelibrary.com]

Influence of Temperature. Solvent transport studies were performed at 30, 40, and 50 °C to analyze the temperature effects on solvent transport and it is displayed in Figure 5. Equilibrium solvent uptake improved with rising in temperature. Enhanced mobility of solvent molecules, as well as the quickening of the relaxation processes in the host polymer at high temperature, is the reasons behind increased solvent uptake at high temperature. This tends to a decline in tortuosity effect and thus more solvent molecules can accommodate in the polymer matrix.

Mechanism of Transport

The mechanism of transport is interpreted from the values of n and k for different samples which were determined by using eq. (2) and from these values, one can identify solvent transport mechanism.

 Table IV. Values of Transport Coefficients for Various CR Nanocomposites in Different Solvents

Solvent	Sample	$D \times 10^4$ cm ² s ⁻¹	S	$P \times 10^4$ cm ² s ⁻¹
Octane	CGO	1.31	1.16	1.52
	CG1	1.28	1.10	1.41
	CG2	1.26	0.98	1.23
	CG3	1.25	0.94	1.17
	CG4	1.17	0.86	1.01
	CG5	1.13	0.70	0.791
Heptane	CGO	2.79	1.20	3.34
	CG1	2.62	1.16	3.04
	CG2	2.35	1.14	2.68
	CG3	2.21	1.12	2.47
	CG4	2.96	1.09	3.22
	CG5	1.88	1.07	2.01
Hexane	CGO	5.73	1.89	10.82
	CG1	3.84	1.63	6.25
	CG2	3.28	1.46	4.78
	CG3	3.02	1.23	3.71
	CG4	2.92	1.18	3.44
	CG5	2.85	1.12	4.54

Values of *n* and *k* are listed in Table III, and it is found that there are deviations from the Fickian dynamics. Values of n for hexane and octane are less than 0.5. This type of transport is termed as "quasi-Fickian" or "less Fickian." Here, solvent diffuses gradually through the swollen polymer matrix and the free spaces in the nanocomposites.^{10,25} However, for heptane value of n > 0.5 and this mode of transport are described as anomalous. Coupling of Fickian and non-Fickian diffusion transport is the reason behind anomalous transport. Here, penetrant mobility and the rubber segmental relaxation rates are almost similar. Deviation from Fickian sorption is related to the time taken by the rubber parts to respond to the swelling stress and reorganize them to accommodate the solvent.¹⁴ The reinforcement of RGO resulted in greater constraint to the reorganization of rubber molecules. k value depends on the solvent-polymer interaction and structural significance of polymer. Among various samples, k value is maximum for a neat sample in all solvents, and the k values decreased for increasing the RGO concentration representing limited diffusion.

Transport Coefficient

Solubility is usually considered as the amount of solute that dissolves in a unit volume of a solvent to form a saturated solution under specified conditions of temperature and pressure. Solubility is expressed usually as moles of solute per 100 g of solvent. The solubility of a gas depends on the pressure as Henry's law. Here, the solvent sorption of rubber sample taking place in a solvent medium. Thereby swelling of the rubber sample took place as a result of the incoming solvent molecules. By the incoming solvent molecules, expansion of polymer chains occurs and thereby swelling occurs (see Figure 6). Initially, the rate of swelling is very high as the free volume available is getting occupied by solvent molecules quickly and later it leads to equilibrium. By weighing the initial weight of the polymer (M0) and the final weight of swollen polymer, we can calculate the sorption coefficient "S" by eq. (4).

The transport coefficient (*D*), sorption coefficient (*S*), and permeation coefficient (*P*) were calculated and are presented in Table IV. Superior solvent resistance of nanocomposites is evident from the low transport coefficients of composites as compared with neat one.^{17,26} The suppression in transport coefficients values with



Figure 7. Schematic representation of diffusion of a solvent through a tortuous pathway in CR–RGO nanocomposites. [Color figure can be viewed at wileyonlinelibrary.com]



		$D \times 10^4$ (cr	(cm ² s ⁻¹) S $P \times 10^4$ (cm ² s ⁻¹)			S		m ² s ⁻¹)		
Solvent	Material	30 °C	40 °C	50 °C	30 °C	40 °C	50 °C	30 °C	40 °C	50 °C
Octane	CGO	1.31	1.832	2.314	1.16	1.45	1.643	1.51	2.656	3.801
	CG1	1.28	1.754	2.212	1.10	1.469	1.805	1.41	2.576	3.992
	CG2	1.26	1.706	2.136	0.98	1.328	1.491	1.23	2.543	3.184
	CG3	1.25	1.565	2.041	0.94	1.151	1.287	1.17	2.014	2.626
	CG4	1.17	1.482	1.989	0.86	1.097	1.319	1.01	1.954	2.623
	CG5	1.13	1.477	1.883	0.70	1.081	1.262	0.791	1.863	2.376

Table V. The Values of Various Transport Coefficients for CR-RGO Nanocomposites At Diverse Temperatures

RGO content can be described based on two factors, the role of nanofillers with the high aspect ratio as an effective barrier towards solvent transport and also the restriction in the intermolecular movement of rubber chains by nanoreinforcement. Among all the solvents tested here, octane has the lowest transport coefficient values because if its larger size in comparison with the other two solvents.

Diffusion coefficient declined with increase in penetrant size. Here, the D values of CR-RGO composites follow the order of hexane > heptane > octane. The decrease in D, S, and P values can also be attributed to the decreased response of the rubber filler aggregate with an increase in the size of the solvent molecule. According to the free volume theory for the polymer diffusion process, the diffusion rate of the polymer depends on the rate at which the polymer chain segments exchange their position with penetrant molecules. Due to the nanosized dispersion of the polymer matrix, the available free volume decreases and the presence of nanofillers resulted in an increase in tortuosity of the path which leads to the reduced diffusivity. Figure 7 shows the schematic representation of tortuous pathway in CR-RGO nanocomposites. Table V gives the influence of temperature on octane transport CR-RGO nanocomposite. Table V displays the increment in all the transport coefficients with temperature. At high temperature, the polymer chains become more flexible thereby enable the solvent permeability.



Figure 8. Plot of V_{r0}/V_{rf} versus (f/1-f) of CR nanocomposites. [Color figure can be viewed at wileyonlinelibrary.com]

The incorporation of nanosized fillers in polymer creates a good interface between macromolecular chains and RGO which leads to reduced swelling. The reduction in solvent uptake can be interrelated with better reinforcement explained by Kraus plot. Kraus equation²⁷ conveys the idea about the degree of strengthening of filler in the polymer matrix. As per the Kraus equation

$$V_{r_0}/V_{r_f} = 1 - m\left(\frac{f}{1-f}\right)$$
 (10)

Here, V_{r0} represents the volume fraction of rubber in the fully swollen unfilled sample V_{rf} represents volume fraction of rubber in the fully swollen filled sample and f is the volume fraction of the filler. For an unfilled system f = 0, and the slope m indicates reinforcing the capacity of the filler in the polymer matrix. A linear relationship is obtained on plotting V_{r0}/V_{rf} versus f/(1-f) and it is in good agreement with the mathematical relation given by Kraus. A decreasing trend for V_{r0}/V_{rf} with RGO loading is observed. The ratio of V_{r0}/V_{rf} constitutes the degree of restriction on the swelling of elastomer by the occurrence of filler. Negative slope designates the superior reinforcing capability of RGO.^{14,17} In the present study (Figure 8), a negative slope is obtained from the Kraus plot, which indicates the improved interaction between RGO and CR.

Thermodynamic Parameters

Thermodynamic parameters of the diffusion through CR/RGO nanocomposites are represented in Table VI. van't Hoff's relation [eq. (6)] is used for finding the thermodynamic parameters such as ΔH and ΔS . The values of ΔH and ΔS are found by the

 Table VI. Thermodynamic Parameters of CR-RGO Composites with Hexane as Solvent

Sample	ΔH (kJ mol ⁻¹)	ΔS (kJ mol ⁻¹)	(–) ΔG (kJ mol ⁻¹)
CG0	3.77	0.0029	5.89
CG1	4.16	0.0028	3.97
CG2	4.75	0.0028	3.77
CG3	5.44	0.0035	3.80
CG4	9.79	0.0022	3.73
CG5	9.01	0.0043	7.71





Figure 9. Plot of log $(C_{\infty}$ - $C_{t})$ versus time for different CR nanocomposites in octane at room temperature. [Color figure can be viewed at wileyonlinelibrary.com]

regression analysis of the graphs of log Ks versus 1/T. Log Ks was calculated using eq. (9).

From Table VI, the heat of enthalpy (ΔH) values are greater for the CR/RGO nanocomposites; it indicates that a higher amount of energy is required for the diffusion process. Also, ΔH values are positive, which shows the endothermic nature of solvent transport process. Here, diffusion process is controlled by Henry's law, that is, development of empty locations and the incorporation of these locations by solvent molecules.^{28,29} The enhanced number of crosslinks is responsible for the positive values for entropy change and the rise in entropy value with RGO concentration. Thus, ΔS values favor the spontaneity of the process because all the ΔS values obtained are positive. This is a clear indication of the stability of the system against solvent penetration through it. In our composites, the change in free energy values rises with the filler content, that is, the stability of the composite against solvent penetration increases with increases in filler loading.

Kinetics of Diffusion

Kinetics of polymer is important when barrier applications are considered. The first order kinetics can be applied to the diffusion-controlled swelling. The efforts have been made to investigate the kinetics of sorption in terms of first-order kinetic equation. The transport kinetics of solvent through CR/RGO composites has been evaluated using the first-order kinetic equation given in eq. (9). Figure 9 represents the plot of log (C_{∞} - C_t) versus t for different filler loadings and nature of the plot indicates first-order kinetics. From the slope of the plot, rate constant of the diffusion process was calculated. Table VII represents the rate constant values of CR nanocomposites using octane solvent. As the filler loading increases the rate of swelling decreases and this is due to increased RGO rubber interaction at higher filler loading. Here, the rate constant kdecreased as the filler loading increases due to increased RGO-rubber interaction at higher loading.

Crosslink Density and Network Structure

Molecular mass (M_c) between consecutive crosslinks and can be found out by Flory–Rehner equation.^{30,31}

$$M_{c} = -\frac{(\rho_{r} V_{s} \varphi)^{1/3}}{\ln(1-\varphi) + \varphi + \chi \varphi^{2}}$$
(11)

where ρ_r is the density of rubber, V_s is the molar volume of the solvent, and φ is the volume of the rubber in the swollen state. χ is polymer–solvent interaction parameter and φ is given by eq. (12) of Ellis and Welding.³²

$$\varphi = \frac{\left(\frac{d-fw}{\rho_p}\right)}{\left(\frac{d-fw}{\rho_p}\right) + \frac{A_s}{\rho_s}}$$
(12)

where *d* is the deswollen weight of the polymer, *f* is the volume fraction of the filler, *w* is the initial weight of the polymer, and A_s is the amount of solvent absorbed. Polymer–solvent interaction parameter χ is determined using Hildebrand equation.³³

$$\chi = \beta + \frac{V_s \left(\delta_s - \delta_p\right)^2}{RT}$$
(13)

where β is the lattice constant, V_s is the molar volume, R is the universal gas constant, T is the absolute temperature, and δ_s and δ_p are the solubility parameter of the solvent and the polymer, respectively. The calculated values of molecular mass are given in Table VIII.

From Table VIII, it is clear that the M_c value is maximum for CG0 which indicates that maximum solvent uptake is for CG0. Then, the values slowly decrease in all solvents from CG0 to CG5. As expected, the filler content increases M_c values decreases. It means the filler–polymer interaction increases upon filler addition, and hence the maximum solvent uptake gradually decreases. The highest M_c value of CG0 indicates that the crosslinks are far away from each other, as a result, it shows maximum solvent uptake. To compare with the theory, molecular weight between the crosslinks were compared with the affine limit of the model M_c (aff) and phantom network model M_c (ph) proposed by James and Guth using eqs. (14) and (15), respectively.

 Table VII. Rate Constants for CR/RGO Nanocomposite Using Octane as a Solvent

Samples	CGO	CG1	CG2	CG3	CG4	CG5
Rate constant ($k \times 10^2 \text{ min}^{-1}$)	4.77	4.46	4.39	4.17	3.18	3.01



 Table VIII. Values of the Molecular Mass of Different Samples

Samples	<i>M_c</i> (Exp)	<i>M_c</i> (phantom)	M_c (affine)
Hexane			
CGO	341.22	497.6	21.52
CG1	336.49	495.6	20.02
CG2	340.26	496.25	21.45
CG3	334.9	458.59	18.75
CG4	325.05	442.37	17.5
CG5	316.48	427.88	15.92
Heptane			
CGO	74.96	108.73	0.719
CG1	33.43	48.26	0.319
CG2	30.64	44.19	0.292
CG3	31.76	45.77	0.303
CG4	31.40	45.18	0.299
CG5	27.48	39.41	0.261
Octane			
CGO	75.14	97.58	0.580
CG1	68.45	86.79	0.425
CG2	70.44	85.73	0.537
CG3	69.28	109.81	0.660
CG4	67.83	107.52	0.401
CG5	52.32	72.55	0.151

$$M_{c} (aff) = \frac{\rho_{p} V_{s} v_{2c}^{2/3} v_{2m}^{1/3} \left(1 - \frac{\mu}{v} v_{2m}^{1/3}\right)}{-\left[\ln\left(1 - v_{2m}\right) + v_{2m} + \chi v_{2m}^{2}\right]}$$
(14)

where μ and υ are the number of effective chains and junctions, is the polymer volume fraction at equilibrium swelling, is the polymer volume fraction during crosslinking. According to the



Figure 10. Filler loading against molar mass for hexane solvent using data from Table VIII. (Comparison of network models with experimental results.) [Color figure can be viewed at wileyonlinelibrary.com]

phantom network model, the molecular weight between the crosslinks for the phantom limit of model M_c (ph) was calculated by the following equation:

$$M_{c}(\mathrm{ph}) = \frac{\rho_{p} V_{s} v_{2c}^{2/3} v_{2m}^{1/3} \left(1 - \frac{2}{\varphi}\right)}{-\left[\ln\left(1 - v_{2m}\right) + v_{2m} + \chi v_{2m}^{2}\right]}$$
(15)

where χ is the junction functionality. Calculated M_c values along with experimental values are given in Table VIII. For a better understanding to compare the network models with experimental results, Figure 10 shows the filler loading against molar mass for hexane solvent.

It was found that the M_c values of phantom network model showed moderate agreement with experimental values rather than the affine model (Figure 10). This is because here the chains can move freely through one another, that is, the junction points fluctuate over time around their mean position without any hindrance from the neighboring molecules.

CONCLUSIONS

Effect of RGO concentration on the transport behavior of CR is investigated. From the observed data, it was found that RGO had a prominent role in the diffusion process. The temperature has a positive effect on the equilibrium solvent uptake. Transport mechanism suggests that the process is less Fickian or quasi Fickian for hexane and octane because all the values of n lie below 0.5. However, for heptane, the mode of transport is anomalous (n > 0.5). The negative slope of the Kraus plot indicated the enhanced interaction between CR and RGO nanoparticles, which was the reason for the improvement in the characteristic properties of the nanocomposites. The thermodynamic parameters for diffusion such as ΔH and ΔS were calculated and these parameters suggest that the sorption process is endothermic. Diffusion of solvent through CR/RGO nanocomposite followed first-order kinetics. In addition to this, the phantom and affine models were used to analyze the deformation of the network during swelling. It is found that phantom models agree well with the experimental values. The transport parameters presented in this study give an insight into the characteristic features of RGO-filled CR nanocomposites, which could be of importance to problem solving while designing a barrier material for transporting liquids.

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